MASARYKOVA UNIVERZITA

PŘÍRODOVĚDECKÁ FAKULTA

CENTRUM PRO VÝZKUM TOXICKÝCH LÁTEK

V PROSTŘEDÍ

Vývoj metód pasívneho vzorkovania znečisťujúcich látok vo vodnom prostredí

Habilitační práce

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Poďakovanie

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1 Obsah

2 Zoznam skratiek a symbolov

A	plocha vzorkovača, cez ktorú difunduje analyt
APV	Adsorpčný pasívny vzorkovač
BAF	bioakumulačný faktor
BCF	biokoncentračný faktor
BMF	biomagnifikačný faktor
C_{free}	koncentrácia voľne rozpustenej látky
ChA	chemická aktivita látky
D	difúzny koeficient
ENK	environmentálna norma kvality
j_i	difúzny tok látky i-tou fázou
k_i	koeficient prestupu látky i-tou fázou
k_e	eliminačná rýchlostná konštanta prvého poriadku
K_{mw}	rozdeľovací koeficient membrána-voda
K_{ow}	rozdeľovací koeficient oktanol-voda
K_{sw}	rozdeľovací koeficient vzorkovač-voda,; polymér-voda
K_s	vysoľovacia konštanta Setchenowovej rovnice
LDPE	polyetylén s nízkou hustotou
PA	polyakrylát
PAH	polycyklické aromatické uhľovodíky
POM	polyoxymetylén
PCB	polychlórované bifenyly
PDMS	polydimetylsiloxán
PRC	performančné referenčné látky (performance reference compounds)
Q	prietok vody v systéme; objem vody vymenený za jednotku času
R	univerzálna plynová konštanta

Re	Reynoldsovo číslo
RPV	rozdeľovací pasívny vzorkovač
R_S	vzorkovacia rýchlosť látky
RSV	Rámcová smernica o vode 2000/60/ES
RSV	Rámcová smernica o vode 2000/60/ES
Sc	Schmidtovo číslo
SPE	extrakcia na tuhej fáze
SPME	mikroextrakcia na tuhej fáze
Sh	Sherwoodovo číslo
S_w	rozpustnosť látky vo vode
TMF	faktor trofickej magnifikácie
TWA	time-weighted average; časovo vážený priemer koncentrácie
V_S	objem sorpčnej fázy vzorkovača
WBL	medzná difúzna vrstva vody (water boundary layer)

3 Introduction

The quality of the environment is recognised as a high priority across the world, and measures towards its improvement have a positive effect on the quality of human life. Anthoropgenic pollutants in the aquatic environment may have a negative effect not only on the ecosystems, but, ultimately, also on the human health. In areas where water bodies cross national boundaries, there is a need to establish international monitoring networks that enable to obtain comparable, representative data on pollutant concentrations and trends. In order to succeed, it is necessary to obtain reliable information that is comparable between laboratories, is representative of environmental quality and underpins risk assessments and decisions on remedial actions. Much emphasis has been placed on the analytical chemical aspects of measuring pollutant levels in discrete samples but less attention has been paid to the underpinning sampling procedures despite the very much larger uncertainties associated with this crucial phase of the monitoring process. Passive samplers present an innovative monitoring tool for the time-integrated measurement of bioavailable contaminants in the aquatic environment. Passive sampling is based on the deployment *in-situ*, or use in the laboratory, of non-mechanical devices of simple construction capable of accumulating contaminants dissolved in water or sediment pore water. Such accumulation occurs via diffusion, typically over periods of days to weeks. This technology has great potential because of the simplicity of the principles underlying its function, and structure. In contrast to active samplers, passive samplers have no moving parts, they do not require a power source for their operation, and are relatively inexpensive. In addition, these devices can be deployed in almost any environmental condition, thus making them ideal for pollutant monitoring even in remote areas with minimal infrastructure.

The presented habilitation thesis gives a brief introduction to passive sampling of pollutants in the aquatic environment. The development of selected methods is illustrated on my own scientific publications, or the reader is referred to available reviews.

The thesis discusses functional principles of passive samplers and problems associated with the effects of environmental variables (temperature, water turbulence and sampler fouling) on their performance. Further, it gives a reference to the established or expected/potential performance of passive samplers for monitoring of the most discussed groups of aquatic pollutants and availability of calibration data that enable to obtain quantitative monitoring data. The document also explains the applicability of the passive sampling concept in the assessment of exposure of aquatic organisms in the process of risk assessment of pollutants.

Finally, the thesis discusses the state of the art and future research needs in development of method validation, quality assurance/quality control schemes and standardisation of the passive sampling technology. The thesis refers to studies that demonstrate the performance of passive samplers alongside conventional sampling schemes, and inter-laboratory studies that demonstrate reproducibility of data produced by different designs of passive samplers. These issues present the prerequisite for the future use of the passive sampling technology in scientific research as well as in regulatory monitoring.

4 Úvod

Kvalita životného prostredia je prioritou v mnohých krajinách sveta, a opatrenia v tejto oblasti majú pozitívny vplyv na zlepšenie kvality ľudského života. Antropogénne znečisťujúce látky vo vodnom prostredí môžu mať negatívny vplyv nielen na ekosystémy, ale v konečnom dôsledku i na zdravie človeka. V oblastiach, kde vodné toky prekračujú hranice štátov, je potrebné etablovať medzinárodné monitorovacie siete, ktoré umožnia získať reprezentatívne a navzájom porovnateľné údaje o koncentráciách a trendoch znečisťujúcich látok. Pre úspešnosť týchto aktivít je potrebné získavať údaje, ktoré sú porovnateľné medzi laboratóriami, reprezentujú stav životného prostredia a sú vhodné na hodnotenie rizík i na rozhodovanie o opatreniach na zabránenie ďalšiemu znečisteniu. Hoci sa veľa dôrazu kladie na chemickú analýzu znečisťujúcich látok v diskrétnych vzorkách životného prostredia, menej pozornosti sa venuje aspektom vzorkovania, hoci táto kľúčová fáza procesu monitorovania je zvyčajne spojená s najväčšou neistotou. Pasívne vzorkovanie je inovatívny monitorovací nástroj na časovo integračné meranie biodostupných kontaminantov v životnom prostredí. Pasívne vzorkovanie je založené na *in situ* alebo *ex situ* použití nemechanických vzorkovačov jednoduchej konštrukcie, ktoré akumulujú rozpustené kontaminanty z vody alebo z pórovej vody v sedimentoch. Akumulácia látok do vzorkovačov prebieha samovoľne (difúziou) počas niekoľkých dní alebo týždňov expozície. Táto technológia má veľký potenciál využitia, hlavne vďaka jednoduchosti princípov, na ktorých je založená ich funkcia a konštrukcia. Na rozdiel od aktívnych vzorkovačov pasívne vzorkovače nemajú žiadne mechanické časti, väčšinou nevyžadujú na svoju prevádzku vonkajší zdroj energie, a navyše sú pomerne lacné. Tieto zariadenia môžu byť použité v takmer ľubovoľných podmienkach prostredia, čo umožňuje monitorovanie znečisťujúcich látok aj v odľahlých oblastiach bez infraštruktúry.

Predložená habilitačná práca podáva stručný úvod do problematiky pasívneho vzorkovania znečisťujúcich látok vo vodnom prostredí. Vývoj a využitie vybraných metód sú ilustruované na vlastných vedeckých publikáciách autora, alebo je čitateľ odkázaný na dostupné prehľadové štúdie.

Práca diskutuje funkčné princípy pasívneho vzorkovania a problémy spojené s vplyvmi premenlivých podmienok vzorkovaného prostredia (napr. teplota, turbulencia vody a znečistenie vzorkovačov) na ich funkciu. Ďalej odkazuje na etablovaný alebo očakávaný potenciál pasívnych vzorkovačov na monitorovanie najdiskutovanejších skupín znečisťujúcich látok a tiež na kalibračné údaje, ktoré umožňujú získať kvantitatívne údaje

z monitorovania. Dokument tiež vysvetľuje použiteľnosť konceptu pasívneho vzorkovania v monitorovaní expozície vodných organizmov, potrebnom v procese hodnotenia rizík znečisťujúcich látok. Práca posktuje prehľad o súčasnom stave a potrebe ďalšieho výskumu v oblasti validácie metód, zabezpečovania a kontroly kvality a štandardizácie technológie pasívneho vzorkovania. Práca sa pritom odvoláva na štúdie, ktoré porovnávajú pasívne vzorkovače s konvenčnými metódami odberu vzoriek, a tiež na medzilaboratórne štúdie, ktoré demonštrujú reprodukovateľnosť dát získaných rôznymi typmi pasívnych vzorkovačov. Tieto témy tvoria predpoklad pre budúce využitie technológie pasívneho vzorkovania vo výskume i v regulačnom monitorovaní životného prostredia.

5 Koncept pasívneho vzorkovania

Pasívne vzorkovanie je založené na použití *in situ* zariadenia, ktoré akumuluje kontaminanty z vody, alebo z iného média životného prostredia. Prestup kontaminantu z prostredia do vzorkovača je samovoľný difúzny proces, ktorý je hnaný rozdielom chemických aktivít monitorovanej látky medzi vzorkovaným médiom a sorpčnou fázou vzorkovača (Obrázok 3). Akumulácia látky vo vzorkovači prebieha až do ustálenia termodynamickej rovnováhy (resp. ustáleného stavu v dynamických systémoch, akými sú napr. rieky) medzi vzorkovačom a vodou, alebo až kým sa proces vzorkovania nepreruší. Doba expozície vzorkovačov je zvyčajne niekoľko dní až týždňov. Akumulované kontaminanty sa následne extrahujú a v extrakte sa stanovia ich koncentrácie. Ak sú vzorkovače kalibrované, je možné z množstva látky vo vzorkovači vypočítať koncentráciu látky rozpustenej vo vzorkovanom médiu. Pasívne vzorkovanie je často integračné, t.j. získaná vzorka reprezentuje koncentráciu látky vo vzorkovanom médiu za určité časové obdobie. Veľmi dôležitým aspektom pasívneho vzorkovania je možnosť vyjadriť množstvo látky vo vzorkovači v rovnováhe so vzorkovaným médiom formou chemickej aktivity (Mayer et al., 2003, viď kapitola 6.), ktorá je mierou hnacej sily pre samovoľný prestup látky medzi rôznymi zložkami životného prostredia.

Vďaka vysokej sorpčnej kapacite a integračnému charakteru pasívnych vzorkovačov je možné monitorovať látky, ktoré sa nachádzajú rozpustené vo vode v extrémne nízkych koncentráciách (rádovo až pg/L). Konvenčné metódy vzorkovania vody, založené na bodových odberoch, neumožňujú stanovenie takýchto nízkych koncentrácií, hoci napr. environmentálne normy kvality, určené Rámcovou smernicou o vode(EU, 2013, 2008, 2000) vyžadujú monitorovať niektoré znečisťujúce látky vo vode metódami, ktoré majú medzu stanovenia na úrovni ng/L i nižšie.

V odbornej literatúre je dostupných niekoľko prehľadových prác, ktoré opisujú dizajn, kalibračné postupy, pracovné charakteristiky a príklady aplikácie rôznych pasívnych vzorkovčov na monitorovanie znečisťujúcich látok vo vodnom prostredí (Esteve-Turrillas et al., 2007; Kot-Wasik et al., 2007; Lobpreis et al., 2009; Lohmann et al., 2012; Lydy et al., 2014; Mills et al., 2007; Namieśnik et al., 2005; Ouyang and Pawliszyn, 2007; Söderström et al., 2009; Stuer-Lauridsen, 2005; Branislav Vrana et al., 2005; Vrana et al., 2010). (Booij, 2009)) v správe pre ICES Marine Chemistry Working Group sumarizoval potenciál využitia rôznych pasívnych vzorkovačov na monitorovanie látok regulovaných v Rámcovej Smernici o vode (EU, 2000) a v iných smerniciach a dohovoroch. (Vrana et al., 2010) vypracovali pre asociáciu laboratórií NORMAN pozičný dokument, ktorý uvádza prehľad použiteľnosti pasívneho vzorkovania pre monitorovanie emergentných (dosiaľ neregulovaných) znečisťujúcich látok vo vodnom prostredí. Ďalší aktuálny pozičný dokument asociácie NORMAN o pasívnom vzorkovaní bol aktuálne publikovaný medzinárodnou skupinou expertov, ktorú som v rokoch 2009-2014 koordinoval, na základe diskusií na špecializovanom workshope, ktorý sa konal v novembri 2014 v Lyone (Miège et al., 2015). Dokument identifikuje konkrétne aktivity, ktoré sú potrebné, aby pasívne vzorkovanie mohlo byť v budúcnosti využívané v rutinnom monitoringu vodného prostredia za účelom hodnotenia rizík a manažmentu kontaminantov. Užitočným zdrojom informácií o princípoch a aplikáciách pasívneho vzorkovania vo vodnom prostredí je i špecializovaná monografia, venovaná jednej z najznámejších vzorkovacích techník, tzv. semipermeabilným membránam (SPMD) (Huckins et al., 2006), a tiež prehľadová monografia pasívnych vzorkovacích technikách pre monitorovanie životného prostredia (Greenwood et al., 2007). V ďalšom texte je uvedené všeobecné rozdelenie metód pasívneho vzorkovania a tiež princípy ich funkcie.

5.1 Rozdeľovacie pasívne vzorkovače

Rozdeľovacie pasívne vzorkovače (RPV) sú konštruované z hydrofóbnych polymérnych materiálov s vysokou permeabilitou pre nepolárne zlúčeniny. RPV absorbujú nepolárne látky z vody, pretože v porovnaní s vodou je rozpustnosť látok vo vzorkovači je oveľa vyššia ako vo vode. Hydrofóbne látky s nízkou rozpustnosťou vo vode sa dobre akumulujú v RPV, zatiaľ čo hydrofilné látky sa koncentrujú v oveľa menšej miere. Po dostatočne dlhej expozícii koncentrácia látky v RPV dosiahne dynamickú rovnováhu s koncentráciou vo vzorkovanom prostredí, napr. vo vode. Z rovnovážej koncentrácie látky v RPV je možné vypočítať koncetráciu vo vode pomocou rozdeľovacieho koeficienta vzorkovač-voda (K_{sw}). Táto koncentrácia vyjadruje koncentráciu voľne rozpustenej látky (C_{free}), ktorá ale nie je totožná

s celkovou koncentráciou látky vo vzorke vody. Celková koncentrácia nepolárnych látok vo vode závisí i od koncentrácie látky viazanej na rozpustené koloidy alebo dispergované častice organickej hmoty vo vode. Voľne rozpustná koncentrácia C_{free} je priamo úmerná chemickej aktivite látky vo vode, a preto je vhodným parametrom, ktorý opisuje proces akumulácie chemických látok do vodných organizmov a tiež ich distribúciu medzi rôznymi zložkami životného prostredia.

Pre použitie RPV sa predpokladá termodynamická rovnováha látky medzi vzorkovačom a vodou, ale pri praktickom použití vzorkovačov vo vode sa zvyčajne dosiahne rovnováha len pre látky s log K_{sw} < 5.5. Pre hydrofóbnejšie látky je prestup látky príliš pomalý (alebo sorpčná kapacita vzorkovača je príliš veľká) na rýchle dosiahnutie rovnováhy za typickú dobu expozície (2-8 týždňov). V takýchto prípadoch sa odhad C_{free} opiera o meranie objemu vody, z ktorého vzorkovač *in situ* extrahuje sledovanú látku počas expozície.

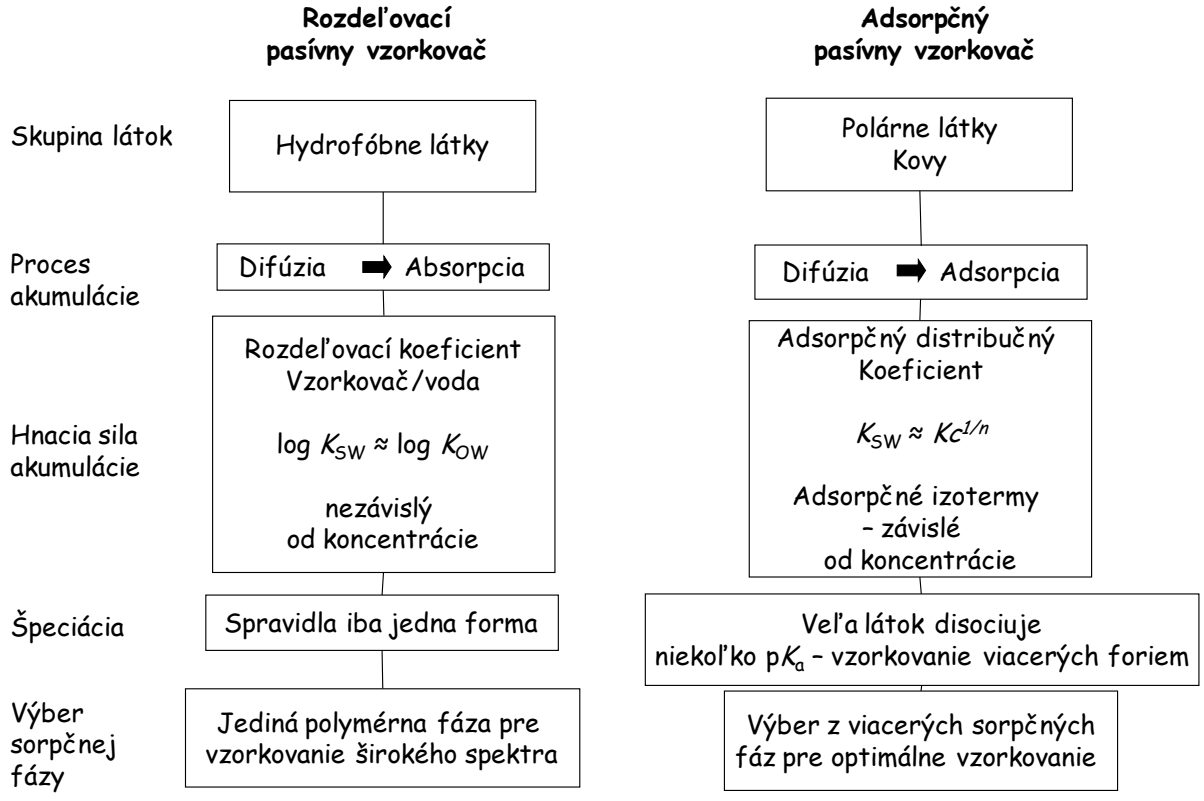
Extrahovaný objem vody (alebo vzorkovacia rýchlosť, ak je objem vyjadrený za jednotku času) sa dá odvodiť z rýchlosti uvoľňovania vybraných značených látok pridaných do vzorkovača pred expozíciou. V princípe ide o stanovenie rýchlosti uvoľňovania týchto látok, ktorá je kontrolovaná difúziou. Rýchlostná konštanta eliminácie prvého poriadku, meraná *in situ* je pre určitú látku rovnaká, ako je jej rýchlostná konštanta akumulácie, a preto môže byť použitá na výpočet C_{free} i v situáciách, keď vzorkovač nie je v rovnováhe s okolitým prostredím. Boli vyvinuté modely a metódy pre odhad vzorkovacích rýchlostí látok (Booij and Smedes, 2010; Tatsiana P Rusina et al., 2010; Branislav Vrana et al., 2006) ako aj pre meranie rozdeľovacích koeficientov K_{sw} (Difilippo and Eganhouse, 2010; Hale et al., 2010; Smedes et al., 2009), čo umožnuje výpočet C_{free} z koncentrácie látky vo vzorkovači.

5.2 Adsorpčné pasívne vzorkovače

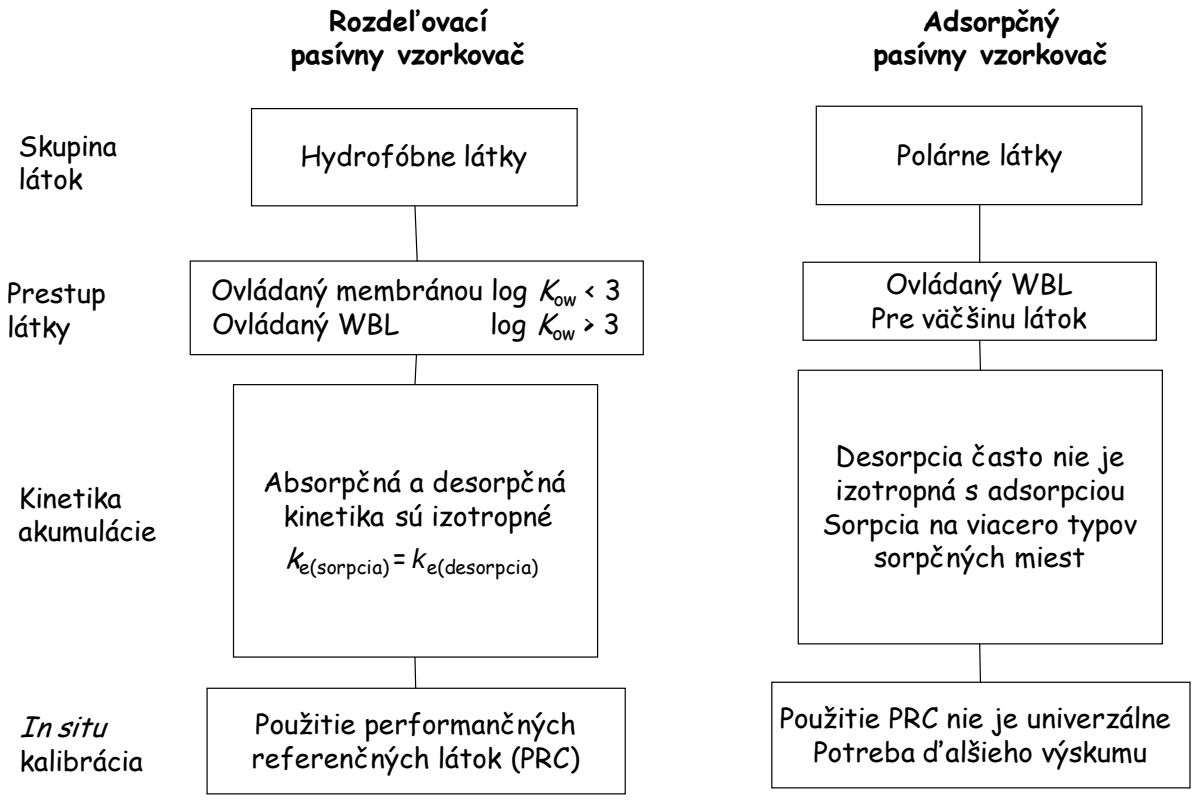
*Adsorpčné pasívne vzorkovače(*APV*)*, obsahujú adsorbenty, ktoré sa tiež bežne používajú pri extrakcii na tuhej fáze (SPE) pri stanovení hydrofilných látok vo vode. V APV sa používa tenká vrstva takéhoto materiálu a od vodnej fázy ju zvyčajne oddeľuje filter alebo vhodná polopriepustná membrána.

Podobne ako v prípade RPV látky difundujú cez hraničnú vrstvu vody a cez membránu alebo filter, ale akumulácia v sorpčnom materiáli prebieha adsorpciou na povrchu častíc sorbentu, a nie rozpúšťaním v objeme sorbentu. Adsorpcia hydrofilných látok je možná, pretože tieto látky sa môžu viazať rôznymi interakciami medzi povrchom sorbentu a funkčnými skupinami sledovaných látok, napr. van der Waals interakciami, π-π interakciami, vodíkovými väzbami

alebo elektrostatickými interakciami (Bäuerlein et al., 2012). Po dlhšej dobe expozície sa vzorkovacia rýchlosť v APV môže postupne znižovať nielen s dosiahnutím rovnovážneho stavu, ale môže byť obmedzená aj saturáciou adsorpčných miest sorbentu. Sorpcia iných ako sledovaných látok, napr. rušivých látok, prirodzene sa vyskytujúcich látok v prostredí, môže prispievať k zahlteniu sorpčných miest, alebo ku vzájomne kompetitívnej sorpcii sledovaných a interferujúcich látok. Aby sa týmto javom predišlo, alebo aby sa znížil účinok týchto javov na funkčnosť vzorkovača, sú APV zvyčajne exponované kratšie ako RPV. Krátka expozícia (niekoľko dní) je postačujúca, lebo polárne látky sa vo vodnom prostredí vyskytujú spravidla v rádovo vyšších koncentráciách ako hydrofóbne látky. Hoci pre APV bolo publikovaných veľa kalibračných štúdií, variabilita publikovaných vzorkovacích rýchlostí je vysoká (Harman et al., 2012, 2011) a proces akumulácie látok do APV dosiaľ nie je detailne pochopený, takže i použitie laboratórnych kalibračných dát v terénnych aplikáciách je doposiaľ iba empirické.



Obrázok 1 Rozdiely v pasívnom vzorkovaní rozdeľovacími a adsorpčnými vzorkovačmi.



Obrázok 2 Rozdiely v mechanizme prestupu látok do rozdeľovacích a adsorpčných pasívnych vzorkovačov.

Napriek týmto nedostatkom poskytujú APV cenné výsledky v skríningu polárnych znečisťujúcich látok vo vodách, pretože často umožňujú detegovať stopové množstvá látok v situáciách, kde klasické metódy vzorkovania, založené na nízkofrekvenčných bodových odberoch, zlyhávajú. Rozdiely medzi oboma typmi vzorkovačov sú ilustrované na obrázkoch 1 a 2.

6 Koncept chemickej aktivity a rovnovážnej distribúcie látky v prostredí

Výsledkom pasívneho vzorkovania je odhad voľne rozpustenej koncentrácie (C_{free}), ktorá sa považuje za najvhodnejší parameter expozície vodných živočíchov (Cornelissen et al., 2008). Dôvodom nie je, že by všetky látky, ktoré sa akumulujú v biote, pochádzali z vodného roztoku voľne rozpustených látok, ale fakt, že C_{free} je priamo úmerná chemickej aktivite (*ChA*) látky v sledovanej zložke životného prostredia, a dá sa vyjadriť ako pomer medzi koncentráciou a kapacitou pre akumuláciu látky v sledovanom médiu (C_{free}/S_w), danom rozpustnosťou látky (vo stave podchladenej kvapaliny) (S_w)(Reichenberg and Mayer, 2006), teda ako podiel medzi koncentráciou látky v sledovanej fáze a kapacitou tejto fázy. Ak je

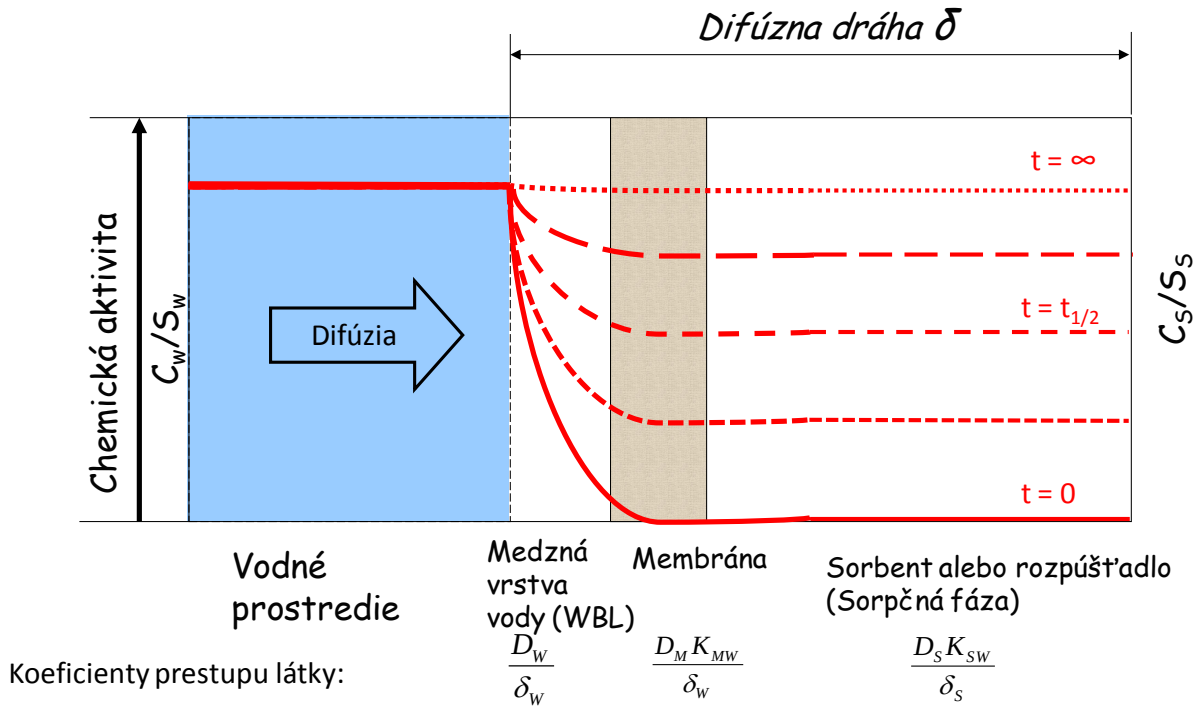
známa chemická aktivita *ChA* látky vo vode, látka má podľa teórie rovnovážneho rozdelenia tú istú chemickú aktivitu aj vo všetkých okolitých matriciach (zložkách životného prostredia), ktoré sa nachádzajú v rovnováhe s vodou.

$$\mathrm{ChA} = \frac{C_{\mathrm{free}}}{S_{\mathrm{w}}} = \frac{C_{\mathrm{sed}}}{U_{\mathrm{sed}}} = \frac{C_{\mathrm{biota}}}{U_{\mathrm{biota}}} = \frac{C_{\mathrm{lipid}}}{U_{\mathrm{lipid}}} \text{ , ale tiež} = \frac{C_{\text{pasívny vzorkova č}}}{U_{\text{pasívny vzorkova č}}} \qquad (1)$$

kde C_x a U_x predstavujú koncentrácie a sorpčné kapacity matrice x (napr. sediment, vodný živočích, tukové tkanivo vodného živočícha, častice plaveniny a pod.).

V systéme, ktorý je v stave termodynamickej rovnováhy, chemická aktivita je rovnaká vo všetkých zložkách prostredia. Naopak, rozdiel v chemickej aktivite medzi zložkami/matricami vo vodnom prostredí je hnacou silou pre pasívny/difúzny transport látok medzi nimi (Di Toro et al., 1991). Chemická aktivita látky v prostredí je teda vhodným parametrom na hodnotenie kvality životného prostredia.

Táto teória je aplikovateľná napr. i pre akumuláciu látok z vody do vodných organizmov, dokonca i v prípade, že organizmy prijímajú tieto látky potravou, ak táto potrava je v termodynamickej rovnováhe s vodnou fázou (látka má v tejto fáze rovnakú *ChA*). V procese trávenia potravy jej akumulačná kapacita (*U*) klesá, čo spôsobuje zvýšenie *ChA* zložky oproti okolitému prostrediu. To urýchli ustálenie dynamickej rovnováhy, pri ktorej rýchlosť disipácie látky z vodného živočícha do vody je rovnaká ako opačný proces akumulácie. Nerovnovážny pomer chemickej aktivity látky medzi predátorom a jeho korisťou v zmysle tejto teórie vysvetľuje jav biomagnifikácie látok.



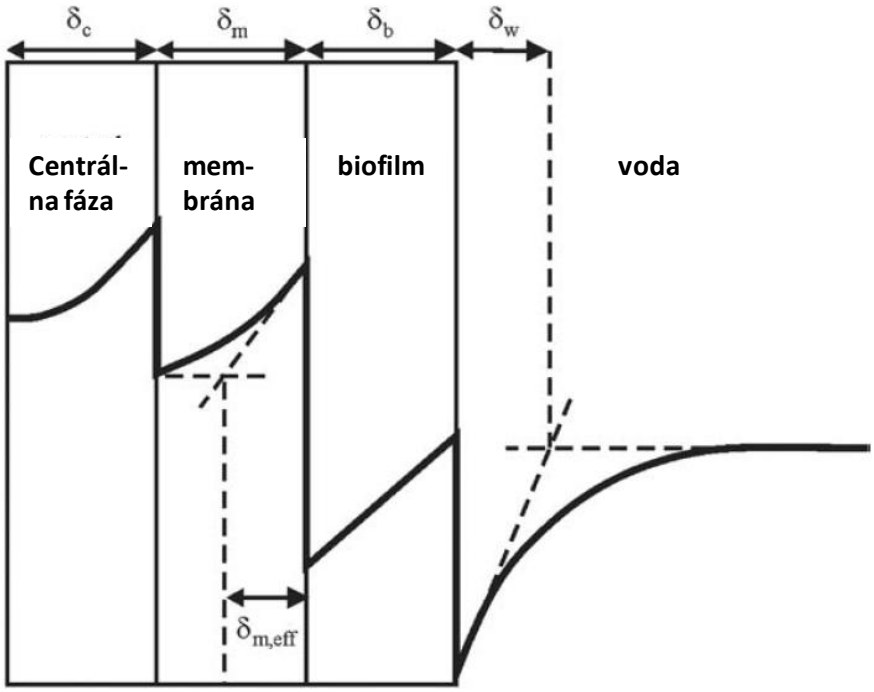
Obrázok 3 Funkčný princíp pasívneho vzorkovača, ktorý ukazuje koncentračný profil látky počas difúzie a akumulácie z vodného prostredia (alebo iného vzorkovaného média, ľavá strana obrázka) do sorbentu (sorpčná fáza) cez permeabilnú (pórovitú alebo nepórovitú) membránu v čase *t*. Vysoká afinita látky k sorpčnej fáze je hnacou silou difúzie molekúl sledovanej látky do vzorkovača, až kým nedôjde k vyrovnaniu chemickej aktivity látky v oboch médiách, t.j. k ustáleniu termodynamickej rovnováhy.

7 Teória, modelovanie a kalibrácia pasívnych vzorkovačov

Akumulácia kontaminantov do pasívneho vzorkovača je viacstupňový transportný proces. Na ilustráciu základných krokov tohoto procesu uvádzam najprv príklad akumulácie kontaminantu do vzorkovača, ktorý pozostáva z centrálnej sorpčnej fázy, obklopenej membránou. Ďalej sa predpokladá, že na povrchu vzorkovača sa nachádza vrstva biofilmu (biofouling), a že vzorkovač je umiestnený v ochrannej klietke (Obrázok 4).

Analyt rozpustený vo vode najprv vstupuje konvekciou z okolitých vôd do ochrannej klietky, kde pohyb vody môže byť pomalší ako v prúde vody v okolí klietky. V blízkosti vrstvy biofilmu sa transport molekúl analytu konvekciou stále viac znižuje, až napokon celý prestup látky prebieha molekulárnou difúziou cez medznú vrstvu vody (water boundary layer, WBL). Po difúzii cez membránu sa analyt sorbuje do sorpčnej fázy. Tento všeobecný náčrt má rôzne modifikácie a dá sa aplikovať na rôzne typy vzorkovačov. Napr. niektoré vzorkovače nepoužívajú ochrannú klietku, vrstva biofilmu nemusí byť prítomná a membrána môže

zároveň plniť úlohu sorpčnej fázy (napr. v rôznych zariadeniach využívajúcich mikroextrakciu na tuhej fáze (SPME) (Ouyang et al., 2007), pásky z polyetylénu s nízkou hustotou (LDPE) (Estoppey et al., 2015), alebo z polydimetylsiloxánu (PDMS) (Smedes and Booij, 2012)), alebo vzorkovače môžu byť vybavené ďalšími fázami, ktoré sú umiestnené medzi membránou a centrálnou fázou (napr. membrane-enclosed sorptive coating (MESCO) (Vrana et al., 2001) alebo Chemcatcher (Kingston et al., 2000).



Obrázok 4 Schematické znázornenie koncentračných profilov v dvojfázovom rozdeľovacom pasívnom vzorkovači, na ktorom sa nachádza vonkajšia vrstv biofilmu. Vzorkovač je vizualizovaný ako pravá strana symetrického vzorkovača, alebo ako celkový prierez vzorkovačom, ktorý obsahuje nepriepustnú stenu naľavo od centrálnej fázy. Čiarkované línie indikujú, ako je možné odhadnúť účinnú hrúbku jednotlivých vrstiev vzorkovača. Prevzaté z (K Booij et al., 2007)**.**

Za posledných dvadsať rokov bolo vyvinutých a je používaných niekoľko modelov, ktoré umožňujú lepšie pochopiť kinetiku prestupu kontaminantu do pasívneho vzorkovača. Tieto modely sú potrebné, aby bolo možné porozumieť, ako súvisí množstvo látky sorbované do vzorkovača s jej koncentráciou vo vonkajšom prostredí (vo vode), ako aj pre navrhovanie a vyhodnocovanie kalibračných experimentov. Modely sa líšia v počte uvažovaných fáz, ako aj v zjednodušujúcich predpokladoch, ktoré sa berú do úvahy, ako je napr. existencia pseudo-ustáleného stavu (steady-state), prítomnosť alebo absencia lineárnych koncentračných gradientov pozdĺž priečneho profilu fáz, a ďalej spôsob, akým sa modeluje prestup látky

medznou vrstvou vody (WBL), a či je koncentrácia látky počas expozície vzorkovača konštantná.

V nasledujúcom texte sú predstavené základné koncepty a modely používané v literatúre o pasívnom vzorkovaní. Ďalej je diskutovaný prestup látok cez rôzne fázy, z ktorých vzorkovače pozostávajú. Napokon sú diskutované dôsledky týcho modelov pre dizajn a evaluáciu kalibračných experimentov.

7.1 Základné koncepty a modely pre rozdeľovacie pasívne vzorkovače

Koeficienty prestupu látky (k_i) sa často používajú na prepojenie toku látky (j_i) s koncentračným rozdielom ΔC_i látky medzi okrajovými bodmi tejto fázy

$$j_i = k_i \, \Delta C_i \tag{2}$$

Rovnica 2 vyjadruje predstavu, že tok látky (j_i) je priamo úmerný hnacej sile ΔC_i. Koeficient prestupu látky sa dá interpretovať ako vodivostný člen, s rozmerom rýchlosti (napr. m s^{-1}). Tento postup bol použitý na modelovanie akumulácie látok do niekoľkých typov pasívnych vzorkovačov (Chen and Pawliszyn, 2004; Flynn and Yalkowsky, 1972; Huckins et al., 2006, 1993; Tcaciuc et al., 2015; B Vrana et al., 2005; Vrana et al., 2001; Wennrich et al., 2003). Diferenciálna rovnica, ktorá opisuje akumuláciu látky do vzorkovača, sa dá zapísať:

$$\frac{\mathrm{d}C_\mathrm{s}}{\mathrm{d}t} = \frac{Ak_\mathrm{o}}{V_\mathrm{s}}\left(C_\mathrm{w} - \frac{C_\mathrm{s}}{K_\mathrm{sw}}\right) \tag{3}$$

kde C_s a C_w sú objemové koncentrácie kontaminantu vo vzorkovači a v povrchovej vode, V_s je objem vzorkovača, A je plocha vzorkovača, cez ktorú difundujú do vzorkovača molekuly analytu a K_sw je rozdeľovací koeficient látky v systéme vzorkovač-voda. Celkový koeficient prestupu látky do vzorkovača k_o je daný:

$$\frac{1}{k_o} = \frac{1}{k_w} + \frac{1}{k_b K_{bw}} + \frac{1}{k_m K_{mw}} \tag{4}$$

kde k_w, k_b, k_m sú koeficienty prestupu látky cez WBL, biofilm a membránu a K_bw a K_mw sú rozdeľovacie koeficienty látky v systéme biofilm-voda a membrána-voda. Rovnica (4) vyjadruje, že celkový odpor k prestupu látky ($1/k_\mathrm{o}$) je rovný súčtu odporov k prestupu látky v jednotlivých fázach vzorkovača. Ak uvážime, že koeficient prestupu látky je daný podielom difúzneho koeficienta a účinnej hrúbky difúznej vrstvy (δ), rovnica (4) sa dá napísať aj

$$\frac{1}{k_o} = \frac{\delta_w}{D_w} + \frac{\delta_m}{D_m K_{mw}} + \frac{\delta_b}{D_b K_{bw}} \quad (5)$$

(Bartkow et al., 2005) počítali aj s odporom k prestupu látky, spôsobeným ochrannou klietkou, ktorá je okolo vzorkovača a pridali v rovnici do súčtu člen A/Q_v, kde Q_v je prietok vody cez klietku a A je plocha vzorkovača. Tento čiastkový odpor sa však väčšinou môže zanedbať, okrem niektorých extrémnych dizajnov klietok, ktoré obmedzujú prietok vody vzorkovacím zariadením.

Po krátkej dobe expozície vzorkovača je koncentrácia sledovanej látky vo vzorkovači oveľa nižšia ako je jej rovnovážna koncentrácia, t.j. $C_s << K_{sw}C_w$ a rovnica sa zjednoduší

$$dC_s \approx \frac{Ak_o}{V_s} C_w dt \quad (6)$$

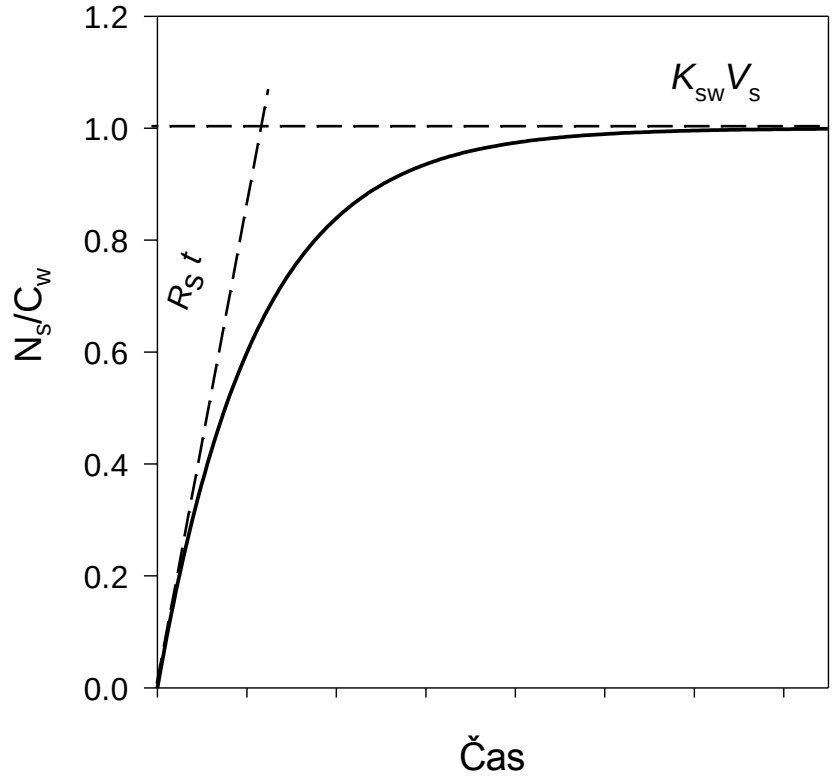
a po integrácii v čase dostávame

$$\int C_s \approx \frac{Ak_o}{V_s} C_w dt = \frac{Ak_o}{V_s} C_{w,TWA} t \quad (7)$$

kde $C_{w,TWA}$ je časovo vážený priemer (TWA) koncentrácie vo vodnej fáze. Na označenie prvej fázy vzorkovacieho procesu používajú tri pojmy. Keď je C_w konštantná v čase, koncentrácia akumulovaných kontaminantov lineárne narastá v čase. Tento časový úsek vzorkovania sa preto nazýva *lineárna fáza* akumulácie. Pre scenáre, keď vodné koncentrácie kolíšu v čase, koncentrácia vo vzorkovači je priamoúmerná TWA koncentrácii a vzorkovanie sa nazýva *časovo integračné*. Napokon, pretože rýchlosť zmeny koncentrácie vo vzorkovači je priamo úmerná koncentrácii vo vode, táto raná fáza vzorkovania sa nazýva *kinetickým vzorkovaním*. Zaujímavým aspektom rovnice (7) je, že produkt k_oA je ekvivalentný zdanlivému objemu vody, z ktorého vzorkovač vyextrahuje analyt za dobu expozície t. Na tento produkt ($k_o \times A$) nahliadame ako na vzorkovaciu rýchlosť (R_s):

$$R_s = k_o A \quad (8)$$

Pretože R_s reprezentuje objem vody extrahovaný za jednotku času, vytvára konceptuálne prepojenie medzi tradičnými vsádzkovými extrakčnými metódami a metódami založenými na pasívnom vzorkovaní. Rovnica (**(8)** vyjadruje, že vzorkovacia rýchlosť je priamo úmerná ploche vzorkovača. Preto porovnanie vzorkovacích rýchlostí medzi rôznymi dizajnmi vzorkovačov poskytuje relevantné výsledky iba v prípade, že sa berú do úvahy i rozdiely v ploche A.



Obrázok 5 Efektívny objem vody ektrahovaný vzorkovačom (N_s/C_w) ako funkcia času. Pre dlhé expozičné doby je extrahovaný objem obmedzený sorpčnou kapacitou vzorkovača ($K_{sw}\times V_s$) a pre krátke expozičné časy súčinom vzorkovacej rýchlosti a doby expozície. Približné modely, ktoré platia pre lineárnu časť akumulácie (krátka doba expozície) a rovnovážne vzorkovanie (dlhá doba expozície) sú znázornené čiarkovanými čiarami. Upravené podľa (K Booij et al., 2007).

Pre veľmi dlhé expozičné časy a pri konštantnej hodnote C_w sa koncentrácia vo vzorkovači nemení v čase a riešením rovnice (3) je:

$$C_w - \frac{C_s}{K_{sw}} = 0 \qquad (9)$$

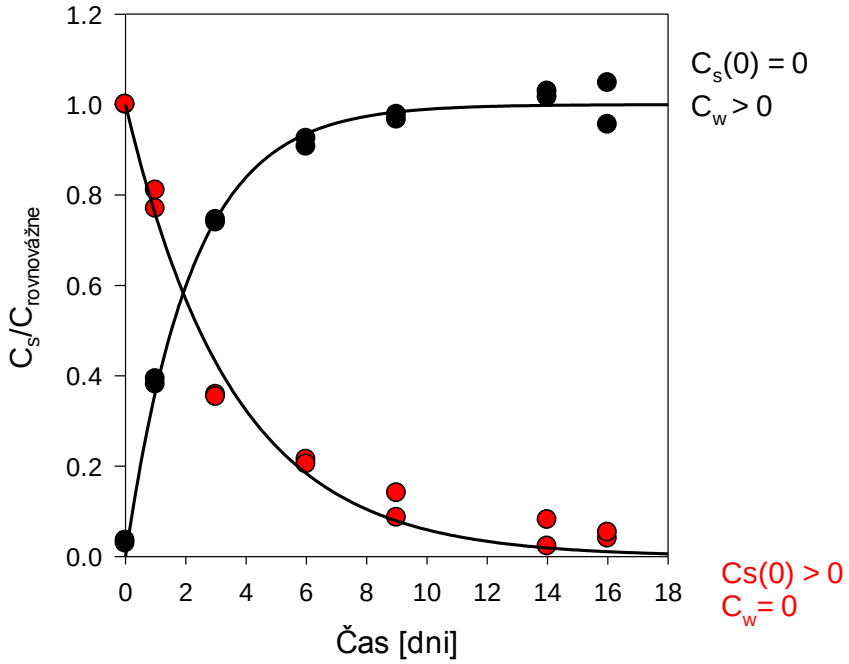
čo je vyjadrením, že koncentrácia látky vo vzorkovači dosahuje rovnovážnu hodnotu ($C_s = K_{sw}\times C_w$). Príslušný vzorkovací režim sa nazýva *rovnovážne vzorkovanie*.

Všeobecné riešenie rovnice rovnice (3) pre konštantnú koncentráciu C_w je dané (Vrana et al., 2001):

$$C_s = K_{sw}\,C_w\,[1-\exp(-k_e t)] + C_0\exp(-k_e\,t) \qquad (10)$$

kde C_0 je koncentrácia vo vzorkovači v čase $t = 0$ a eliminačná rýchlostná konštanta (k_e) je daná:

$$k_e = \frac{k_o A}{K_{sw} V_s} = \frac{R_s}{K_{sw} V_s} \qquad (11)$$



Obrázok 6. Príklad izokinetickej výmeny látky medzi rozdeľovacím pasívnym vzorkovačom a vodou. Graf ukazuje kinetiku akumulácie fluoranténu do pasívneho vzorkovača (Gerstel Twister, 2×0,5 cm) z vody s konštantnou koncentráciou C_w (čierne body) a kintetiku disipácie perdeuterovaného fluoranténu, ktorý bol pred experimentom pridaný do vzorkovača, a ktorého koncentrácia vo vode je počas experimentu udržiavaná pod medzou detekcie ($C_w = 0$). Plné čiary predstavujú fit experimentálnych dát modelom podľa rovnice (10). Akumulácia i disipácia látky je charakterizovaná tou istou hodnotou eliminačnej rýchlostnej konštanty k_e, čo je princíp *in situ* kalibrácie – stanovenia vzorkovacích rýchlostí priamo v teréne. (Vrana, nepublikované).

Rovnica (10) ukazuje, že akumulácia z prostredia a eliminácia počiatočného množstva látky vo vzorkovači (stanovuje sa analýzou tzv. fabrikačných blankov) sú aditívne. Odčítanie týchto koncentrácií môže byť problematické, keď pôvodná koncentrácia je vyššia alebo rovná rovnovážnej koncentrácii. V takom prípade koncentrácia v exponovanom vzorkovači môže byť menšia ako v kontrolných neexponovaných vzorkách (fabrikačné blanky) a odčítanie koncentrácie v kontrole by malo za následok negatívnu vypočítanú hodnotu v exponovanom vzorkovači. Preto sa v prípade rovnovážneho vzorkovania neodporúča odčítanie hodnoty fabrikačného blanku od výsledku merania v exponovanom vzorkovači. Rovnica (10) tiež ukazuje, že v rozdeľovacích pasívnych vzorkovačoch je akumulácia i eliminácia jednej a tej istej látky charakterizovaná rovnakou hodnotou k_e (Obrázok 6). Tento poznatok tvorí základ

odhadu *in situ* vzorkovacích rýchlostí z rýchlostí disipácie tzv. performančných referenčných látok (PRCs) (Huckins et al., 2002)

Keď je počiatočná koncentrácii vo vzorkovači rovná nule, rovnica (10) sa dá integrovať:

$$C_s = K_{sw} C_w \left[1 - exp\left(- \frac{R_s t}{K_{sw} V_s} \right) \right] \quad (12)$$

a pre krátke časy expozície je možné ju zjednodušiť na lineárnu rovnicu:

$$C_s = \frac{C_w R_s t}{V_s} \quad (13)$$

Pre disipáciu látok, ktoré sa nenachádzajú v prostredí (C_w = 0), ale sú pridávané do vzorkovača pred expozíciou (napr. PRC), rovnica (10) sa dá zjednodušiť:

$$C_s = C_0 \exp(-k_e t) \quad (14)$$

Koncentrácie vo vode sa dajú vypočítať z množstva látky sorbovaného vo vzorkovači (N_s), in situ vzorkovacej rýchlosti látky R_S a jej rozdeľovacieho koeficienta v systéme vzorkovač-voda K_{sw}, použitím preusporiadanej rovnice (12):

$$C_w = \frac{N_s}{K_{sw} V_s \left[1 - exp\left(- \frac{R_s t}{K_{sw} V_s} \right) \right]} \quad (15)$$

Pre rovnovážne vzorkovače je člen v hranatých zátvorkách rovný 1 a vodné koncentrácie sa vypočítajú pomocou rovnice:

$$C_w \approx \frac{N_s}{K_{sw} V_s} \quad (16)$$

Pre kinetické vzorkovače, ktoré pracujú v lineárnom akumulačnom móde je člen v hranatej zátvorke približne rovný $(R_s t)/(K_{sw} V_s)$, a koncentrácia vo vode sa dá vypočítať:

$$C_w \approx \frac{N_s}{R_s t} \quad (17)$$

Menovatele v rovniciach (*15*(17) sa dajú interpretovať ako zdanlivý objem vody, z ktorého vzorkovač odstráni analyt počas expozície (Obrázok 5). V prípade rovnovážneho vzorkovania je tento objem obmedzený sorpčnou kapacitou vzorkovača ($K_{sw} \times V_s$). Pri

kinetickom vzorkovaní je zdanlivý exktrahovaný objem vody obmedzený vzorkovacou rýchlosťou a expozičným časom (Rs×t).

7.2 Zovšeobecnený model pasívneho vzorkovača

Diskusia v predchádzajúcej časti sa dá rozšíriť na iné pasívne vzorkovače, ktoré obsahujú ľubovoľný počet sub-fáz (bariér), za predpokladu, že sorpčná rovnováha je ustálená na rozhraniach medzi nimi, a že sú ustálené (steady-state) toky látky vo vnútri jednotlivých bariér medzi vodou a sorpčnou fázou (t.j. rozdiel medzi tokom látky dovnútra a von z každej čiastkovej bariéry je relatívne malý). Rovnica (5) sa dá zovšeobecniť (Vrana et al., 2001):

$$\frac{1}{k_{\mathrm{o}}} = \sum \frac{\delta_{\mathrm{i}}}{D_{\mathrm{i}} K_{\mathrm{iw}}} \tag{18}$$

kde súčet platí pre všetky fázy i, z ktorých vzorkovač pozostáva. Vývoj množstva analytu akumulovanom v sorpčnej fáze vzorkovača (t.j. v tej časti vzorkovača, ktorá sa extrahuje a následne analyzuje) je daný rovnicou (12), kde celková hodnota K_{sw} je vyjadrená zovšeobecneným vzorcom

$$K_{\mathrm{sw}} = \frac{\sum V_{\mathrm{i}} K_{\mathrm{iw}}}{\sum V_{\mathrm{i}}} \tag{19}$$

a objem vzorkovača V_{s} je rovný súčtu objemov všetkých sub-fáz, ktoré sa analyzujú.

V literatúre venovanej SPME sa používa podobný empirický model, ktorý opisuje výmenu látky medzi vzorkovačom a vodou (Chen and Pawliszyn, 2003; H. J. Vaes et al., 1996):

$$\frac{\mathrm{d}C_{\mathrm{s}}}{\mathrm{d}t} = k_1 C_{\mathrm{w}} - k_2 C_{\mathrm{s}} \tag{20}$$

Tento model je matematicky ekvivalentný s rovnicou (2), kde $k_2 = (A\ k_{\mathrm{o}})/(K_{\mathrm{sw}}\ V_{\mathrm{s}})$ and $k_1 = K_{\mathrm{sw}} k_2$.

7.3 Platnosť podmienok modelu

Pre vyššie opísané modely sa predpokladá, že v membráne a v centrálnej fáze existujú lineárne koncentračné gradienty, že na rozhraní medzi fázami sa okamžite ustaľuje termodynamická rovnováha, a že molekulárna difúzia je hlavným transportným mechanizmom látok v membráne, nezávisle od času a koncentrácie.

V počiatočnej fáze expozície vzorkovača analyty musia penetrovať cez membránu, aby sa dostali do centrálnej sorpčnej fázy, čo spôsobuje tzv. lag fázu. Teoretický model toku látky cez plochú dosku s konštantnou koncentráciou látky na oboch stranách predpovedá dobu oneskorenia (lag time) (Crank, 1975):

$$t = \frac{\delta_{\mathrm{m}}^2}{6 D_m} \tag{21}$$

Difúzne koeficienty organických látok v polyméroch sú veľmi rozličné. Hodnoty difúzneho koeficienta polycyklických aromatických uhľovodíkov a polychlórovaných bifenylov pre polymér PDMS sa pohybujú v rozmedzí od 10^{-11} do 10^{-10} m^2 s^{-1} (T. Rusina et al., 2010), pre polymér LDPE v rozmedzí hodnôt od 10^{-14} do 10^{-12} m^2 s^{-1} (T. Rusina et al., 2010). Hodnoty difúzneho koeficienta benzénu v poly(metylmetakryláte) sú rádovo 10^{-16} m^2 s^{-1} a v poly(vinylalkohole) 10^{-19} m^2 s^{-1} (George and Thomas, 2001). Rovnica (21) predikuje pre membránu s hrúbkou 100 μm dobu zdržania analytu vo vrstve PDMS 17-167 sekúnd, 30 minút až 46 hodín vo vrstve LDPE, cca. niekoľko mesiacov vo vrstve poly(metylmetakrylát)u a niekoľko storočí vo vrstve poly(vinylalkohol)u. Je zrejmé, že v prípade, ak akumulácia látok do vzorkovača je kontrolovaná difúziou cez WBL, distribúcia analytu v materiáli, z ktorého sú zhotovené membrány vzorkovača, neovplyvňuje vzorkovacie rýchlosti. Ak uvažujeme difúzny koeficient látky vo vode cca. 5×10^{-10} m^2 s^{-1} a účinnú hrúbku hraničnej vrstvy vody 30 až 300 μm, pre akumuláciu kontrolovanú difúziou vo WBL sú očakávané doby zdržania látky vo vrstve medzi 0.3 a 30 s. V prípade, že membrána sa pri spracovaní vzorky vyhadzuje a analyzuje sa iba centrálna fáza (napr. vo vzorkovači POCIS), musí sa počítať s dobou zdržania analytu počas difúzie membránou aj v prípade, že rýchlosť určujúcim krokom je WBL.

Lineárne koncentračné gradienty nemôžu existovať v membráne, ktorá akumuluje analyty, pretože v takom prípade tok látky do membrány musí byť väčší ako tok látky von z membrány na opačnej strane. Podľa tej istej argumentácie nemôže existovať lineárny gradient ani v centrálnej sorpčnej fáze vzorkovača. Koncentračný gradient v strede sorpčnej fázy (napr. pre SPMD, MESCO s PDMS tyčkou) alebo v blízkosti nepriepustnej steny (napr. Chemcatcher alebo SPME) by mal byť nulový (ináč by vznikala diskontinuita toku látky). Koncentračný gradient na vonkajšej strane centrálnej fázy by mal byť nenulový (inak by centrálna fáza nič neakumulovala). V prípade, že akumulácia látky je kontrolovaná WBL, existencia nelineárnych gradientov v membráne alebo v centrálnej fáze nespôsobuje

neplatnosť modelu, ale v prípade, že je akumulácia kontrolovaná difúziou v membráne, je potrebné tento jav zobrať do úvahy. Nelinearita koncentračných gradientov sa dá hodnotiť použití tzv. účinnej hrúbky vrstvy ($\delta_{i,eff}$), ako je zobrazené na Obrázok 4. (Louch et al., 1992) ukázali, že účinná hrúbka membrány sa od skutočnej hrúbky líši len menej ako 20% pre expozičné časy, ktoré sú vyššie ako doba zdržania látky v membráne.

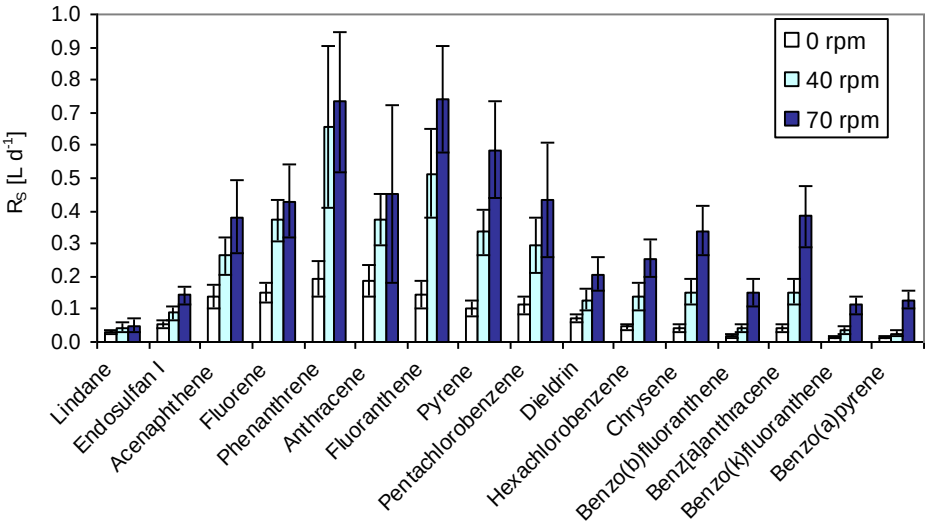
Predpoklad, že na rozhraní fáz je okamžite ustálená termodynamická rovnováha, je pravdepodobne splnená pre nízke hodnoty rýchlostí prestupu látky, aké sú typické pre metódy pasívneho vzorkovania, hlavne pre pryžové polyméry, ktoré majú krátku dobu relaxácie (George and Thomas, 2001). Hoci difúzne koeficienty látok v polyméroch závisia na koncentrácii difundujúcej látky, bolo ukázané, že táto závislosť je slabá (George and Thomas, 2001) a môže sa zanedbať, lebo pri pasívnom vzorkovaní sú nízke koncentrácie.

7.4 Odpor k prestupu látky vo vodnej difúznej vrstve (WBL)

Exaktné modely prestupu látky cez WBL sú k dispozícii len pre niektoré jednoduché usporiadania toku vody, ako napr. pre tok v potrubí a paralelný tok pozdĺž absorbujúcej plochej dosky (Bird et al., 2007; Kader and Yaglom, 1972; Schlichting et al., 2000). V tesnej blízkosti platne sa moment vodného toku postupne od okraja znižuje vplyvom povrchového trenia. Keď sa voda pohybuje pozdĺž platne, táto spomalená vrstva atenuuje moment vodných vrstiev, ktoré sa nachádzajú vo väčšej vzdialenosti od povrchu, čo spôsobuje vznik viskóznej vrstvy, ktorej hrúbka postupne narastá so rastúcou vzdialenosťou od okraja platne v smere toku vody. Analogicky, analyty sa odstraňujú z vrstvy, ktorej hrúbka narastá v smere toku, čo spôsobuje vznik tzv. medznej koncentračnej vrstvy (WBL). S narastajúcou hrúbkou tejto vrstvy je významnejší prestup látky turbuletnou difúziou, pretože turbulentné difúzne koeficienty narastajú s rastúcou vzdialenosťou od povrchu (Kader and Yaglom, 1972; Son and Hanratty, 1967). Vo veľkej vzdialenosti od okrajovej hrany sa ustáli koncentračný profil, ktorý už nezávisí na vzdialenosti pozdĺž platne. Rovnice pre extrémne situácie – krátka platňa s rastúcimi koncentračnými hraničnými vrstvami a dlhá platňa (koncentračné medzné vrstvy sú nezávislé od vzdialenosti od hrany) boli odvodené pre laminárne toky (Opdyke et al., 1987). Koeficienty prestupu látky pre krátku platňu (spriemerované pre celý povrch) sú odvodené v (Opdyke et al., 1987). Vo všeobecnosti je však takmer nemožné odvodiť rovnicu, ktorá by umožnila presne odhadnúť koeficient prestupu látky vo WBL pre komplexnejšie geometrie vzorkovača umiestnené v prirodzenom toku, ktorého rýchlosť a turbulencia sa

menia v čase a priestore. (K Booij et al., 2007) však uvádzajú niekoľko zovšeobecnení, ktoré je možné uplatniť pri opise prestupu látky cez WBL do vzorkovača:

1. Počet premenných v modelových experimentoch prestupu látky cez WBL sa dá zmenšiť korelovaním bezrozmenrých kritérií používaných v chemickom inžinierstve (Sherwoodovo číslo (Sh), Reynoldsovo číslo (Re) a Schmidtovo číslo (Sc)), charakteristických pre zvolenú geometriu vzorkovača.
2. Pre širokú škálu takýchto empirických korelácií chemicko-inžinierska literatúra uvádza, že koeficient prestupu látky medznou vrstvou vody k_w je priamoúmerný molekulovému difúznemu koeficientu vo vode D podľa vzťahu $k_w \sim D^{2/3}$ (Bird et al., 2007; Worch, 1993). To v dôsledku značí, že hrúbka účinnej medznej vrstvy klesá s hodnotou rastúceho difúzneho koeficienta podľa $\delta_w \sim D^{-1/3}$.
3. Účinná vodná medzná difúzna vrstva WBL, hoci je užitočná ako model pre vizualizáciu, kam až zasahuje koncentračný gradient sledovanej látky do vodného toku, by nemala byť dezinterpretovaná ako hrúbka fyzicky nereálnych objektov ako je napr. stagnantný film alebo nepremiešavaná hraničná vrstva vody.
4. Pre danú geometriu vzorkovača a prúdenie by mali byť hodnoty k_w pre malé vzorkovače vyššie ako pre veľké vzorkovače.
5. k_w narastá s rýchlosťou toku pre danú geometriu pasívneho vzorkovača (Obrázok 7Obrázok 7 Vplyv hydrodynamiky na vzorkovacie rýchlosti (R_s) látok do vzorkovača Chemcatcher s LDPE membránou. Experiment bol uskutočnený pri troch rýchlostiach prúdenia vody, dosiahnutými v laboratórnych podmienkach rôznymi frekvenciami otáčania karuselu s vzorkovačmi v prietokovom systéme. Prevzaté z (B Vrana et al., 2006).), ale predikcia jeho absolútnej hodnoty modelovaním je veľmi obtiažna. Navyše, porovnanie odhadutých a experimentálnych vzorkovacích rýchlostí je komplikované tým, že rýchlosti prúdenia vody v okolí vzorkovača sú väčšinou odhadované/vypočítané a nie fyzicky merané.



Obrázok 7 Vplyv hydrodynamiky na vzorkovacie rýchlosti (R_s) látok do vzorkovača Chemcatcher s LDPE membránou. Experiment bol uskutočnený pri troch rýchlostiach prúdenia vody, dosiahnutými v laboratórnych podmienkach rôznymi frekvenciami otáčania karuselu s vzorkovačmi v prietokovom systéme. Prevzaté z (B Vrana et al., 2006)**.**

7.5 Odpor k prestupu látky v membráne

V pasívnych vzorkovačoch sa používajú dva typy polymérnych membrán. Často používanými neporóznymi membránami sú najmä LDPE (Huckins et al., 1993, 1990; Kingston et al., 2000; B Vrana et al., 2005; Wennrich et al., 2003), PDMS (Tatsiana P Rusina et al., 2010; Smedes and Booij, 2012; van Pinxteren et al., 2010), polyakrylát (Leslie et al., 2002; Paschke and Popp, 2003) a iné nepolárne polyméry. Mikroporózne membrány môžu byť zhotovené z regenerovaného acetátu celulózy (CA) (Sabaliunas and Södergren, 1996; Södergren, 1990; Vrana et al., 2001), polyétersulfónu (Alvarez et al., 2007, 2004), polysulfónu (Kingston et al., 2000), polyakrylamidového (Zhang and Davison, 1995) či agarózového (Chen et al., 2012) hydrogélu. V niektorých aplikáciách membrána je zároveň aj primárnou sorpčnou fázou vzorkovača, napr. PDMS v Gerstel-Twister (Assoumani et al., 2015), pre LDPE pásky (Adams et al., 2007a), SPME vlákna (Ouyang et al., 2005), či pláty PDMS (Smedes and Booij, 2012). V iných aplikáciách je membrána určená na separáciu sorpčnej fázy od vody, napr. vo vzorkovači Chemcatcher (Greenwood et al., 2007), MESCO (Vrana et al., 2001), SPMD (Huckins et al., 1993), a tiež na zníženie difúzneho toku látky do sorpčnej fázy. Konduktivita membrány pre prestup látky je daná rovnicou:

$$k_m K_{mw} = \frac{D_m K_{mw}}{\delta_m} \quad (22)$$

kde δ_m je hrúbka membrány (rovnica (5)). Hodnoty D_m i K_{mw} sú špecifické pre každú látku. Úloha K_{mw} v rovnici (22) je zrejmá, ak uvážime, že látky s vysokou hodnotou rozdeľovacieho koeficienta membrána-voda majú i vysoké koncentrácie v membráne v blízkosti rozhrania membrána-voda, ak predpokladáme okamžité ustálenie sorpčných rovnováh na fázových rozhraniach. Dôsledkom toho je zvýšený koncentračný gradient naprieč membránou v porovnaní s látkami, ktoré majú nízke hodnoty K_{mw}. Strmší koncentračný gradient spôsobuje vyšší tok látky cez membránu. Naopak, výber membrány, voči ktorej majú analyty nízku afinitu (napr. hydrofilné membrány pri vzorkovaní hydrofóbnych látok) spôsobuje zvýšený odpor voči prestupu látky, čo vedie k zníženiu vzorkovacích rýchlostí. Je dokumentovaných niekoľko prípadov takéhoto efektu. Vzorkovacie rýchlosti chlórovaných pesticídov vo vzorkovačoch, ktoré obsahovali LDPE membránu, boli až stonásobne vyššie ako v prípade, keď bolo použité organické rozpúšťadlo naplnené do membrány z acetátu celulózy (Sabaliunas and Södergren, 1996). Náhrada hydrofilnej membrány vo vzorkovačoch MESCO a Chemcatcher polyetylénom viedla k výraznému zvýšeniu vzorkovacích rýchlostí (B Vrana et al., 2005; Wennrich et al., 2003) a vzorkovacie rýchlosti polárnych látok do pasívneho vzorkovača POCIS boli oveľa vyššie v prípade použitia polárnej polyétersulfónovej membrány, ako v prípade, keď sa použili nepolárne polyetylénové alebo nylonové membrány (Alvarez et al., 2007).

Výber materiálu membrány má vplyv nielen na vzorkovaciu rýchlosť, ale aj na citlivosť vzorkovača na zmeny prúdenia vody. Keď sa zníži odpor membrány, rýchlosť vzorkovania je kontrolovaná medznou vrstvou vody (WBL), ktorá je silne závislá od hydrodynamických podmienok na rozhraní membrána-voda. Z toho vyplýva, že pokusy znížiť citlivosť pasívneho vzorkovania na prúdenie vody pridaním membrány, ktorá má nízke hodnoty rozdeľovacieho koeficienta pre sledované látky, spôsobia automaticky zníženie vzorkovacích rýchlostí. Naopak, pridanie membrán s vysokými hodnotami K_{mw} zvýši vzorkovacie rýchlosti, ale aj ich citlivosť na zmeny rýchlosti prúdenia vody (B Vrana et al., 2005). Zníženie vzorkovacej rýchlosti nemusí vždy znamenať problém. Závisí to od viacerých faktorov, napr. od koncentrácie látky vo vode, expozičnej doby a citlivosti analytického prístroja. Záverom predchádzajúcej diskusie je, že nie je možné vyvinúť pasívny vzorkovač, ktorý by mal dostatočne vysoké vzorkovacie rýchlosti vo všetkých prostrediach.

V prípade akumulácie kontrolovanej membránou sa predpokladá, že smernica závislosti log R_S voči log K_{mw} je približne jednotková, pretože $R_s \sim k_o \sim D_m \times K_{mw}$. V praxi sa dosahujú mierne nižšie smernice, pretože hodnota D_m mierne klesá s rastúcou veľkosťou molekuly (Booij et al., 2003; H. J. Vaes et al., 1996; Verbruggen et al., 2000). Akumulácia kontrolovaná membránou sa dá identifikovať, ak smernica závislosti log k_e od log K_{mw} je približne 0, alebo mierne nižšia, pretože podľa rovnice (**11**) platí $k_e \sim K_{mw}^{-1}$. Tieto podmienky sa typicky pozorujú pre látky s hodnotami log K_{mw} values < 3.5 pre SPME vlákna s polyakrylátovou fázou (H. J. Vaes et al., 1996; Verbruggen et al., 2000) a pre látky z log K_{ow} hodnotami <4.5 pre SPMD vzorkovače (Vrana and Schüürmann, 2002) (Obrázok 8).

Je potrebné pripomenúť, že hranica medzi akumuláciou kontrolovanou WBL a membránou nezávisí iba od vlastností analytov, ale aj od hydrodynamických podmienok na rozhraní membrána-voda (5). Preto v stagnantnej vode môže byť kritická hodnota K_{mw} rozhrania medzi WBL a membránovou kontrolou posunutá smerom k nižším, v turbulentnej vode zase k vyšším hodnotám.

7.5.1 Difúzny koeficient látky v membráne D_m

Odhad vzorkovacích rýchlostí pre transport kontrolovaný difúziou v membráne je možný na základe nameraných hodnôt difúznych koeficientov D_m sledovaných látok v materiáli, z ktorého sú membrány zhotovené. Difúzne koeficienty D_m je možné pomerne ľahko stanoviť pomocou metódy navrstvených filmov (Sjöberg et al., 1996), ktorá spočíva v jednorozmernej difúzii (kolmo na povrch filmu) látky cez na seba navrstvené filmy polyméru. Po vhodnom čase sa jednotlivé vrstvy analyzujú na obsah látky a zo získaného koncentračného profilu sa vypočíta difúzny koeficient z parciálneho riešenia druhého Fickovho zákona (Crank, 1975). (T. Rusina et al., 2010) použila túto metódu na stanovenie D_m pre polychlórované bifenyly a polyaromatické uhľovodíky v LDPE a PDMS. Odhadnuté hodnoty D_m boli 2-2.5 rádu nižšie v LDPE ako v polyméroch na báze PDMS. Log D hodnoty ($m^2\ s^{-1}$) pre PCB sú v rozsahu -10.1 do -10.9 v PDMS a -11.9 do -13.7 v LDPE. Difúzne koeficienty v polyoxymetyléne, ktorý sa tiež používa v konštrukcii niektorých pasívnych vzorkovačov (Hawthorne et al., 2011), boli publikované iba pre fenantrén a pyrén, a ich log D hodnoty ($m^2\ s^{-1}$) sa pohybujú okolo -14 (Ahn et al., 2005). Vo všeobecnosti hodnoty D_m klesajú s rastúcou mólovou hmotnosťou látky a tiež s rastúcim povrchom molekuly (T. Rusina et al., 2010), čo umožňuje extrapolovať hodnoty difúznych koeficientov aj pre ďalšie látky.

7.5.2 Rozdeľovací koeficient látky v systéme membrána-voda K_{mw} (alebo K_{sw})

K_{mw} (alebo K_{sw}) hodnoty niektorých, hlavne perzistentných organických látok sa dajú nájsť v literatúre pre polyméry na báze PDMS (DiFilippo and Eganhouse, 2010; Mayer et al., 2000; Paschke and Popp, 2003; Smedes et al., 2009; H. J. Vaes et al., 1996; Yates et al., 2007), LDPE (Adams et al., 2007b; Fernandez et al., 2009; Hale et al., 2010; Lohmann, 2012; Smedes et al., 2009) a polyoxymetylén (POM) (Endo et al., 2011).

Podľa termodynamických zákonov rozdelenie organickej látky z vody do organickej fázy (alebo do polyméru) narastá s poklesom teploty a nárastom salinity (Schwarzenbach et al., 1993). V oboch prípadoch sa znižuje rozpustnosť organickej látky vo vode, čoho dôsledkom je nárast hydrofóbnosti organickej látky, a tým aj afinita k hydrofóbnemu materiálu polyméru.

Hodnoty K_{sw} je možné upraviť podľa lokálnych podmienok experimentu, použitím Van`t Hoffovej rovnice na korekciu vplyvu teploty (Lohmann, 2012; Schwarzenbach et al., 1993):

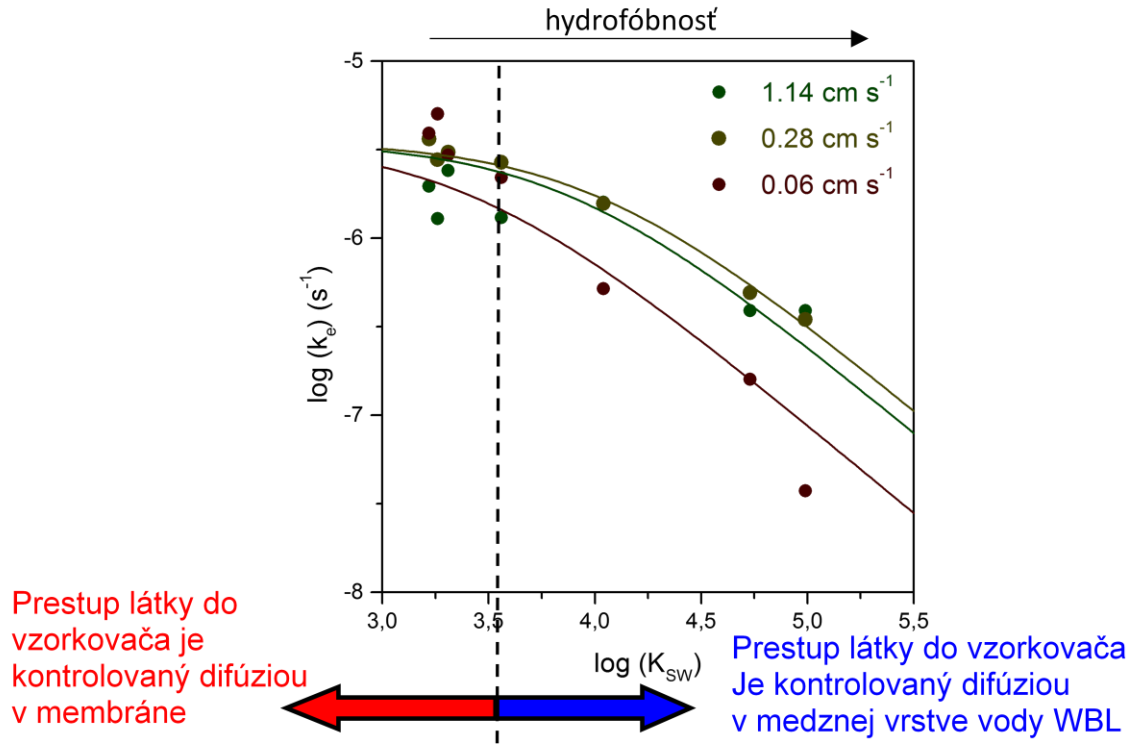
$$K_{SW}(T) = K_{SW}(298)e^{(\Delta H_{SW}/R)\left(\frac{1}{298}-\frac{1}{T}\right)} \quad (23)$$

kde K_{sw} (T) a K_{sw} (298) sú hodnoty rozdeľovacieho koeficienta pri termodynamickej teplote T a pri 298 K, ΔH_{sw} je entalpia distribúcie medzi polymér a vodu (kJ/mol) a R je univerzálna plynová konštanta (8.3143 J/mol/K).

Podobne možno korigovať vplyv salinity (iónovej sily) na K_{sw} použitím empirickej Setchenowovej rovnice (Perron et al., 2013), ktorá vyjadruje závislosť rozpustnosti látky vo vode C_w^{sol} od molárnej iónovej sily roztoku [sol] a takzvanej vysoľovacej konštanty K_S:

$$C_w^{sol} = C_w 10^{-K_s[sol]} \quad (24)$$

Iónová sila neovplyvňuje rozpustnosť analytov v hydrofóbnych polyméroch, preto hodnoty K_{sw} narastajú nepriamo úmerne s klesajúcou rozpustnosťou látky vo vode (Adams et al., 2007b). Pre polyméry na báze silikónovej gumy (PDMS) boli publikované i tieto závislosti K_{sw} hodnôt od teploty a salinity (Jonker et al., 2015). Pre ďalšie polyméry je potrebné uskutočniť ďalšie merania.



Obrázok 8 Závislosť eliminačných rýchlostí chlórovaných pesticídov z RPV vzorkovača SPMD v závislosti od rozdeľovacieho koeficienta K_{sw} pri rôznych lineárnych rýchlostiach prúdenia vody. Upravené z (Vrana and Schüürmann, 2002).

7.6 Kalibrácia pasívnych vzorkovačov

7.6.1 Statický expozičný dizajn

V experimentálne jednoduchom statickom expozičnom scenári sa pasívne vzorkovače exponujú v obmedzenom objeme kontaminovanej vody vo vhodnej nádobe. Táto metóda sa používala v minulosti pre stanovenie bioakumulačných faktorov a rýchlostí akumulácie kontaminantov do rýb alebo mäkkýšov. Časový vývoj koncentrácie látky vo vode počas expozície pasívneho vzorkovača (Banerjee et al., 1984; W. H. J. Vaes et al., 1996; Y. Xu et al., 2005) je:

$$C_w = \frac{C_{w0}\left\{1+\frac{K_{sw}V_s}{V_w}exp\left[-\left(1+\frac{K_{sw}V_s}{V_w}\right)\frac{R_s t}{K_{sw}V_s}\right]\right\}}{1+\frac{K_{sw}V_s}{V_w}} \qquad (25)$$

kde C_{w0} je koncentrácia látky vo vode v čase t = 0. Koncentráciu vo vzorkovači je možné vyhodnotiť z hmotnostnej bilancie ($V_s \times C_s = V_w \times [C_{0w} - C_w]$):

$$C_s = \frac{C_{w0} K_{sw} \left\{ 1 - exp\left[-\left(1 + \frac{K_{sw} V_s}{V_w} \right) \frac{R_s t}{K_{sw} V_s} \right] \right\}}{1 + \frac{K_{sw} V_s}{V_w}} \quad (26)$$

Táto rovnica sa dá zjednodušiť na rovnicu (*12*) v limitnej situácii pre nekonečne veľký objem vzorkovanej vody $V_w \to \infty$. V rovniciach ((25)(**26**) sa uvažuje, že v expozičnom systéme okrem vzorkovača nie je prítomná žiadna konkurujúca sorpčná fáza (napr. steny zariadenia alebo rozpustená organická hmota). Pre krátke doby expozície je možné rovnicu ((25) zjednodušiť nasledovne:

$$C_w = C_{w0} \left(1 - \frac{R_s t}{V_w} + ... \right) \quad (27)$$

a koncentrácia vo vzorkovači sa dá aproximovať vzťahom:

$$C_s = \frac{C_{w0} R_s t}{V_s} \left(1 - \frac{1}{2} \frac{R_s t}{V_w} - \frac{1}{2} \frac{R_s t}{K_{sw} V_s} . + ... \right) \quad (28)$$

Ak je koncentrácia vo vzorkovači oveľa nižšia ako rovnovážna hodnota (t.j. ak $R_s \times t << K_{sw} \times V_s$), tretí člen súčtu v zátvorkách v rovnici (28) sa dá zanedbať a rovnica (28) sa zjednoduší na:

$$C_s = \frac{C_{w,TWA} R_s t}{V_s} \quad (29)$$

kde $C_{w,TWA}$ je TWA koncentrácia počas expozície.

Statické expozície sa v minulosti používali na kalibráciu SPMD a iných vzorkovačov (Kurt E. Gustafson and Dickhut, 1997; Huckins et al., 2002, 1999; Vrana and Schüürmann, 2002; Y. P. Xu et al., 2005) a najčastejštie na kalibráciu SPME vláken (Ouyang and Pawliszyn, 2006). Doby ustálenia rovnováhy dosiahnuté pomocou statických expozícií sa občas mylne považujú za platné aj v terénnych expozíciách (K E Gustafson and Dickhut, 1997; Y. Xu et al., 2005). Rovnica (25) ukazuje, že vývoj koncetrácií analytov vo vzorkovači sa správa podľa kinetiky prvého poriadku, s rýchlostnou konštantou, ktorá je závislá (okrem ďalších faktorov) od objemu vody v systéme. Vysoké rýchlostné konštanty sa dajú dosiahnuť v prípade, ak objem vody v systéme je malý v porovnaní so sorpčnou kapacitou vzorkovača ($V_w << K_{sw} \times V_s$). V takom prípade je rýchlostná konštanta približne rovná R_s/V_w. Naopak, v teréne je

objem vzorkovanej vody v podstate nekonečne veľký ($V_w >> K_{sw} \times V_s$) a rýchlostná konštanta je v takom prípade rovná $R_s/(K_{sw} \times V_s)$. Intuitívne vysvetlenie kratších časov ustálenia rovnováhy v statických pokusoch je také, že akumulácia látky do vzorkovača i pokles koncentrácie vo vode spolu pôsobia na rýchlejšie dosiahnutie rovnováhy (Prest et al., 1998). Naopak, v teréne v otvorenom vodnom toku pokles koncentrácie vo vode vplyvom extrakcie látky z vody do vzorkovača je prakticky zanedbateľný.

7.6.2 Statický obnovovací dizajn

V statickom obnovovacom dizajne sa expozičná voda vymieňa za čerstvú v pravidelných dávkach (Alvarez et al., 2004; Richardson et al., 2002). Tento dizajn sa môže používať v prípadoch, keď statický alebo prietokový expozičný dizajn nie sú vhodné. Táto situácia môže nastať napr., keď pri statickej expozícii dochádza k príliš veľkému poklesu koncentrácie látky vo vodnej fáze počas expozície, alebo ak nastávajú problémy s udržiavaním stabilných koncentrácií látok vo vode počas prietokových expozícií. Koncentrácie vo vode by mali byť merané aspoň na začiatku a na konci každého intervalu obnovenia vzorky, aby sa mohla odhadnúť priemerná hodnota počas expozície. Akumulačné krivky je možné vytvoriť, keď sa dá predpokladať, že množstvo látky odstránené z vody je zároveň sorbované do vzorkovača (t.j. že je možné zanedbať straty látky procesmi ako sú prchanie, sorpcia na steny kalibračného zariadenia, sorpcia na rozpustnú organickú hmotu alebo na častice) a tiež, že priemerná koncentrácia látky sa veľmi nemení medzi jednotlivými výmenami roztoku. Ani v takom prípade však matematické modelovanie nie je jednoduché, snáď s výnimkou kinetického vzorkovania počas celej expozičnej doby – viď rovnica ((**29**).

7.6.3 Prietokový dizajn

Prietokový dizajn má cieľ udržať konštantnú koncentráciu sledovanej látky vo vodnej fáze počas expozície a zabrániť jej poklesu vplyvom sorpcie do vzorkovačov. Robí sa to zabezpečením konštantného prítoku čerstvo kontaminovanej vody s konštantnou koncentráciou látok do expozičnej komory. Podobne ako v statickom a statickom obnovovacom dizajne by mala byť zabezpečená zanedbateľná sorpcia látok na na rozpustnú organickú hmotu alebo na častice, aby sa pri analýze vzoriek vody z aparatúry zabránilo nadhodnoteniu voľne rozpustenej koncentrácie C_w. Naproti tomu sorpcia na zariadenia v expozičnom systéme nemá vplyv na výsledky kalibrácie, ak je zariadenie vopred ekvilibrované s expozičnou vodou. Stabilné koncentrácie je možné udržiavať počas celej expozície, ak je rýchlosť prietoku (Q, objem vody za jednotku času) v expozičnej komore

oveľa väčší ako celková sumárna vzorkovacia rýchlosť všetkých vzorkovačov (Booij et al., 2003):

$$Q >> n \times R_s \quad (30)$$

kde R_s je vzorkovacia rýchlosť jedného vzorkovača, a n je celkový počet vzorkovačov v expozičnom systéme. Napríklad expozičný systém, ktorý obsahuje päť pasívnych vzorkovačov, ktoré majú vzorkovaciu rýchlosť pre sledovanú látku 4 L d^{-1} by potreboval rýchlosť prietoku oveľa vyššiu ako 20 L d^{-1}. Takáto zostava by vyžadovala prietokovú rýchlosť vody Q minimálne 100 L d^{-1} s hladinou rozpusteného organického uhlíka (DOC), ktorá je dostatočne nízka, aby bolo zabezpečené, že sorpcia kontaminantov na DOC je zanedbateľná. Pri postupnom odstraňovaním vzorkovačov počas experimentu sa prietoková rýchlosť môže postupne znižovať, za predpokladu, že hydrodynamické podmienky v expozičnej komore sa udržujú konštantné, napr. dodatočným miešaním vody, alebo recirkulačným čerpaním (B Vrana et al., 2006). Pretože vzorkovacie rýchlosti sú priamo úmerné povrchu vzorkovača, použitie menších vzorkovačov môže pomôcť znížiť spotrebu vody. V tomto prípade je ale potrebné uvážiť, že pre akumuláciu kontrolovanú WBL vzorkovacia rýchlosť môže byť slabou funkciou dĺžky vzorkovača (Kees Booij et al., 2007).

Zmiešavanie zásobných roztokov analytov v metanole alebo v acetóne s vodou vo vhodnom pomere je najčastejšie používanou metódou prípravy kontaminovanej vody (Greenwood et al., 2006; Huckins et al., 1993; Vrana and Schüürmann, 2002; B Vrana et al., 2006), ale používa sa tiež technika generátorovej kolóny, založená na desorpcii analytov zo sorbentu na báze C_{18}-silika (Booij et al., 2003), alebo permeácie cez dialyzačnú membránu (Ouyang et al., 2006).

Keď je možné udržiavať konštantné koncentrácie analytov v roztoku počas celého experimentu, je možné získať vzorkovacie rýchlosti a rozdeľovacie koeficienty látok fitovaním dát pomocou nelineárnej regresie podľa rovnice (12). V prípade, že počas expozície koncentrácia vo vzorkovači je dostatočne vzdialená od rovnovážnej hodnoty, je možné použiť lineárnu regresiu podľa rovnice (13). Metódy, ktoré umožňujú rozhodnúť sa pre vhodný model sú diskutované v literatúre (Booij et al., 1998; Vrana and Schüürmann, 2002).

Trochu komplikovanejšie modely je potrebné použiť v prípade, ak koncentrácia vo vode nie je konštantná počas expozície. Predpokladajme, že koncentrácia vo vode sa dá opísať polynómom druhého stupňa:

$$C_w(t) = C_0 + C_1 t + C_2 t^2 \quad (31)$$

Explicitné riešenie diferenciálnej rovnice (3) je v tomto prípade (Weast, 1983):

$$\frac{C_s}{K_{sw}} = \left(C_0 - \frac{C_1}{k_e} + \frac{2C_2}{k_e^2}\right)\left[1 - exp(-k_e t)\right] + \left(C_1 - \frac{2C_2}{k_e}\right)t + C_2 t^2 \qquad (32)$$

kde k_e je dané rovnicou (11). Riešenie rovnice pre konštantnú koncentráciu (rovnica (12) a pre koncentráciu vo vode, ktorá sa lineárne mení s časom (Booij et al., 2003) sú špeciálnymi riešeniami tejto rovnice.

7.6.4 Pasívne dávkovanie

Prietokový dizajn má nevýhodu, že vzhľadom na potrebný prietok vody Q pri dlhých expozíciách neúnosne narastá objem spotrebovanej vody, zásobného roztoku analytov, a navyše vzniká i problém dekontaminácie odpadovej vody zo systému. Ďalším problémom je možná nestabilita koncentrácie v dôsledku premenlivého výkonu čerpadiel, ktoré sa používajú na prísun vody a zásobného roztoku analytov. Konštantnú koncentráciu v roztoku možno, najmä pre hydrofóbne látky, udržiavať i v uzavretom systéme s obmedzeným objemom vody použitím metódy tzv. *pasívneho dávkovania* (Tatsiana P. Rusina et al., 2010). Princíp metódy spočíva v použití tenkých plátov vhodného polyméru (napr. silikónovej gumy) s veľkou sorpčnou kapacitou ($K_{sw}\times V_s$) s veľkou permeabilitou ($D_s\times K_{sw}$) a s veľkým povrchom, do ktorého sa homogénne nadávkuje potrebná koncentrácia sledovaných látok. Dávkovanie látky do plátov pred expozíciou je možné napr. metódou na princípe rozdeľovacej rovnováhy látok do polyméru z metanolického roztoku, v ktorom sa postupne zvyšuje percento vody (Booij et al., 2002). Takýto materiál sa umiestni v expozičnej komore spolu so známym objemom vody a následne sa do systému pridajú i vzorkovače, ktoré je potrebné kalibrovať. Celkové množstvo dávkovacích plátov musí mať minimálne 10-násobne vyššiu sorpčnú kapacitu a tiež oveľa vyššiu „dávkovaciu“ rýchlosť ako majú kalibrované vzorkovače, aby koncentrácia analytov vo vode počas expozície významne neklesala vplyvom distribúcie látky do kalibrovaných vzorkovačov. Ak je známa hodnota rozdeľovacieho koeficienta látky v systéme dávkovací polymér-voda K_{sw}, je možné dávkovanú koncentráciu odhadnúť pomocou rovnice (16). V prípade, že kalibrované vzorkovače sú z rovnakého materiálu, ako dávkovacie pláty, je navyše rovnovážna koncentrácia sledovanej látky v oboch materiáloch rovnaká, čo uľahčuje interpretáciu nameraných dát; napr. rozhodovanie, či pre sledovanú látku skutočne bola dosiahnutá rovnováha v systéme. Interpretácia dát navyše nie je zaťažená neistotou v meraní C_w.

7.6.5 *In situ* kalibrácia

Evaluácia rýchlostných konštánt disipácie PRC sa používa ako metóda kalibrácie rýchlostí akumulácie látok do pasívnych vzorkovačov *in situ* (Booij et al., 1998; Huckins et al., 2002; Vrana and Schüürmann, 2002). Keď sa vhodne vyberú PRC látky, ktoré sa nevyskytujú vo vzorkovanom prostredí v merateľných koncentráciách (napr. ^{13}C značené kongenéry PCB, alebo perdeuterované polycyklické aromatické uhľovodíky), ich rýchlostné konštanty disipácie sa dajú odhadnúť z rovnice (14):

$$k_e = -\frac{ln(C/C_0)}{t} \tag{33}$$

kde C_0 je koncentrácia PRC vo vzorkovači v čase t=0. Následne sa dá vzorkovacia rýchlosť tejto PRC látky vypočítať z rovnice (11):

$$R_S = k_e \times K_{sw} \times V_S \tag{34}$$

PRC látky sa dajú použiť v prípade, ak ich rýchlosť disipácie je dosť veľká, aby sa dal kvantifikovať rozdiel v koncentrácii na začiatku a na konci expozície. V tomto prípade je určujúcim faktorom precíznosť analytického stanovenia PRC. Pre látky, ktoré majú veľké rýchlosti disipácie, možnosť stanoviť látku po určitom čase je daná medzou stanovenia. Dôsledkom je, že signifikantné vzorkovacie rýchlosti pre PRC sa dajú získať len pre látky v intervale cca. 1.5 log jednotiek na škále hydrofóbnosti (log K_{ow}). Pracovný interval hodnôt log K_{ow} PRC látok závisí od kapacity vzorkovača a od použitého materiálu.

Extrapolácia vzorkovacích rýchlostí, založených na PRC látkach, pre látky s oveľa nižšou hodnotou log K_{ow} nepredstavuje principiálny problém, pretože tieto látky sa počas expozície zvyčajne rýchlo blížia k rovnováhe alebo dosahujú rovnováhu a C_w vypočítaná z rovnice (15) pre tieto látky nie je citlivá voči neistotám vzorkovacej rýchlosti. Naopak, pre látky, ktoré majú vysokú hodnotu log K_{ow} (alebo K_{sw}), je neistota R_s vysoká a vzniká otázka, ako majú byť vzorkovacie rýchlosti PRC extrapolované pre veľmi hydrofóbne látky.

Hodnota vzorkovacej rýchlosti R_s môže byť kontrolovaná transportom látky medznou vodnou difúznou vrstvou (WBL) alebo tiež transportom v polyméri (membránou kontrolovaná akumulácia). Odhad vzorkovacích rýchlostí pre veľmi hydrofóbne látky sa zakladá na predpoklade, že koeficient prestupu látky vo WBL je priamo úmerná difúznemu koeficientu vo vode ($k_w \sim D^{2/3}$) (Kader and Yaglom, 1972; Opdyke et al., 1987). (Rusina et al., 2007; Tatsiana P Rusina et al., 2010) po prvýkrát aj experimentálne dokázali pre polymér na báze

silikónovej gumy, ktorý sa vyznačuje vysokou permeabilitou ($D_m \times K_{mw}$) pre malé molekuly nepolárnych látok, že R_S pre PAH a PCB sú úplne kontrolované difúziou vo WBL a hodnoty R_S mierne klesajú s rastúcou mólovou hmotnosťou látkok (M):

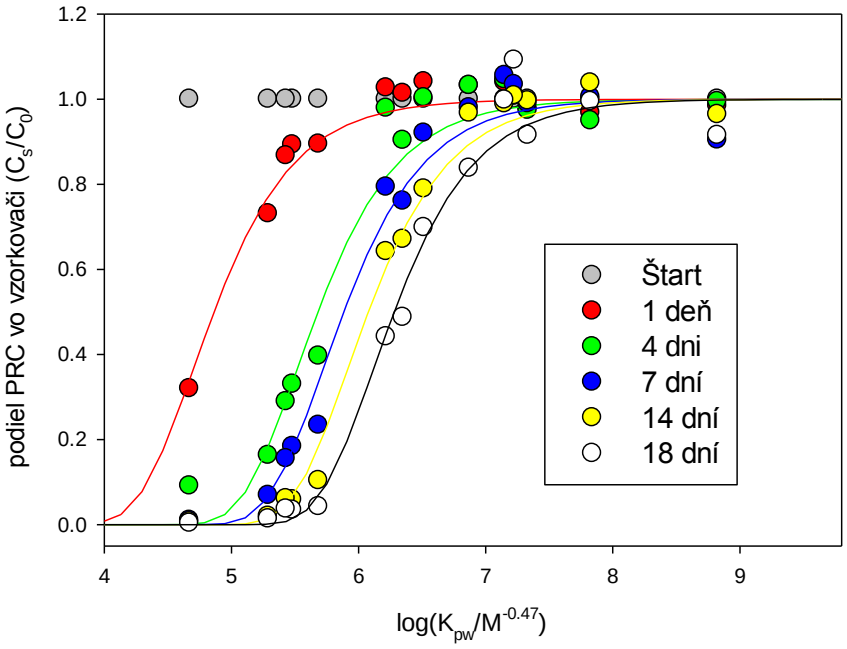
$$R_S = \frac{B}{M^{0.47}} \tag{35}$$

kde parameter B závisí od lokálnych hydrodynamických podmienok a je priamo úmerný ploche vzorkovača. Kombináciou rovníc (11),(14),(35) sa dá vyjadriť vzťah medzi percentom PRC zostávajúcim vo vzorkovači a časom (Booij and Smedes, 2010):

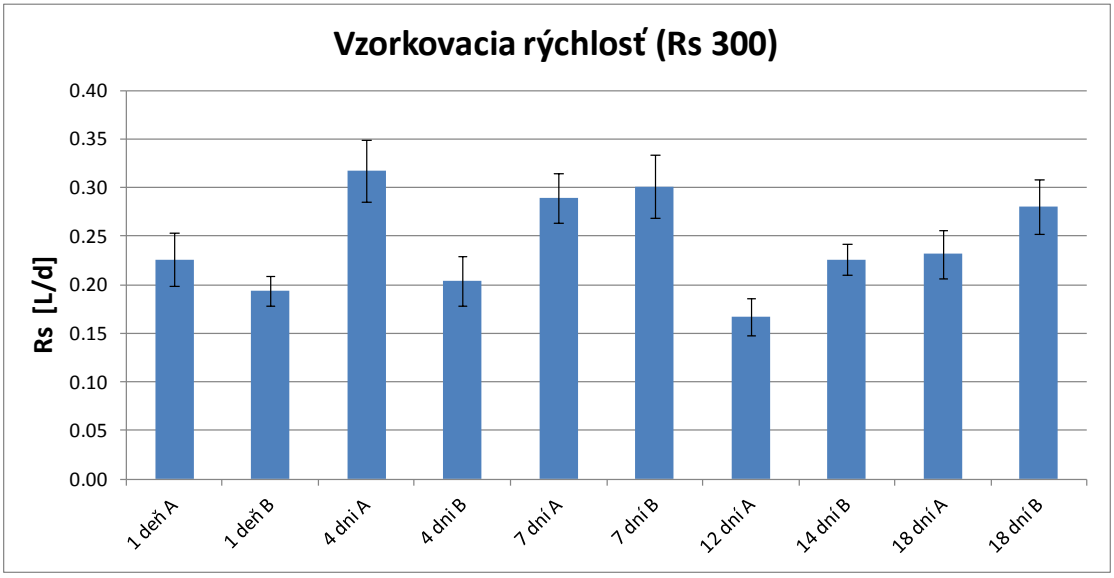
$$\frac{C_S}{C_0} = exp\left(\frac{B\,t}{K_{sw} M^{0.47} V_s}\right) \tag{36}$$

Adjustovateľný parameter B je možné získať fitovaním $f=(C_s/C_0)$ ako funkcie nezávisle premennej $K_{sw} \times M^{0.47}$ použitím neváženej nelineárnej regresie metódou najmenších štvorcov (Booij and Smedes, 2010). Táto metóda využíva pre výpočet vzorkovacích rýchlostí Rs hodnoty všetkých dát z disipácie PRC, ktoré sú k dispozícii, vrátane PRC látok, u ktorýc dochádza k úplnému, alebo naopak k žiadnemu, vyplaveniu zo vzorkovača. Táto metóda je málo citlivá k odľahlým hodnotám. Na obrázku 9 je uvedený príklad použitia metódy pre stanovenie vzorkovacích rýchlostí vzorkovača na báze komerčne dostupného zariadenia Gerstel Twister, ktorého sorpčná fáza pozostáva z polydimetylsiloxánu. Pretože konštanta B sa dá ťažko interpretovať, je konvenciou vypočítať pre ilustráciu vzorkovaciu rýchlosť látky s mólovou hmotnosťou (M) rovnou 300 g/mol použitím rovnice (35) (Obrázok 10).

V mnohých prípadoch sa stáva, že akumulácia polárnych látok do adsorpčných (APV) vzorkovačov je ovládaná difúziou látok vo WBL vrstve, a preto je tiež citlivá na zmeny prúdenia vody. Vyššie uvedený PRC koncept sa vša nedá všeobecne použiť na *in situ* kalibráciu, lebo pri APV vzorkovačoch kinetika desorpcie látok nemusí byť izotropná s kinetikou sorpcie (Shaw et al., 2009). Hoci použitie PRC v niektorých expozičných scenároch bolo demonštrované (Mazzella et al., 2010), tento koncept nie je doposiaľ dostatočne preskúmaný a overený. V prípadoch, keď disipácia PRC nie je izotropná s akumuláciou sledovaných látok, možným riešením je použitie paralelne uložených APV a RPV vzorkovačov. V prípade, že v oboch typoch vzorkovačov je akumulácia kontrolovaná difúziiou vo WBL, z kinetiky eliminácie PRC z RPV vzorkovača je možné odhadnúť i vzorkovaciu rýchlosť pre APV vzorkovač.



Obrázok 9 Percento PRC zostávajúce vo vzorkovači (Gerstel Twister, 2×0.5 cm) ako funkcia $K_{sw}\times M^{0.47}$. Ako PRC boli použité PCB kongenéry, ktoré sa bežne nevyskytujú v technických zmesiach PCB. Fity modelovou funkciou (36) **sú zobrazené ako plné čiary. (Vrana, nepublikované).**



Obrázok 10 Vzorkovacie rýchlosti látky s mólovou hmotnosťou 300 g/mol (*R*s 300) vo vzorkovačoch Gerstel Twister (2×0.5 cm) po rôznej dobe expozície v kalibračnom systéme opísanom v časti 7.6.4., odhadnuté z PRC dát modelom podľa rovnice (36). **(Vrana, nepublikované).**

In situ kalibračná technika, ktorá využíva PDMS disky (s pridanými PRC látkami) v paralelnej expozícii s APV vzorkovačmi na báze Empore diskov, bola po prvýkrát demonštrovaná v práci (Shaw et al., 2009) a následne použitá napr. v Dunajskej expedícii JDS3 (Vrana et al., 2015b). Alternatívnou metódou merania prestupu látky *in situ* je tzv. „pasívny monitor toku“, ktorý je založený na rýchlosti rozpúšťania sadrového bloku s určitým povrchom v závislosti od rýchlosti prúdenia vody (Sara O'Brien et al., 2009).

8 Zabezpečenie a kontrola kvality a štandardizácia

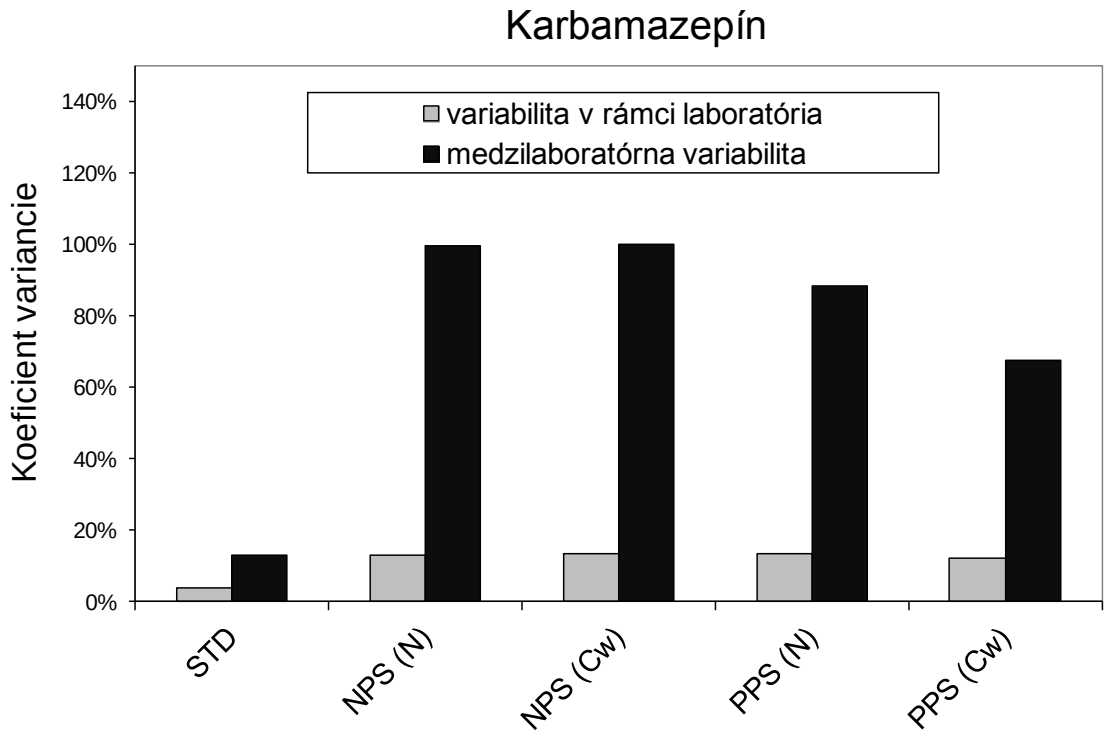
Aby sa pasívne vzorkovanie stalo akceptovanou metódou, použiteľnou na regulačné monitorovanie kvality vôd v Európe a vo svete, je potrebné vyvinúť pre túto technológiu validačné schémy a tiež postupy zabezpečenia a kontroly kvality. Podobne ako pre etablované metódy analýzy rôznych znečisťujúcich látok v rôznych environmentálnych matriciach, je potrebný celý rad validačných aktivít, zahŕňajúci napr. vývoj certifikovaných referenčných materiálov, organizáciu medzilaboratórnych porovnávacích testov zameraných na odber vzoriek a ich analýzu, a tiež publikácia štandardizovaných metód a noriem.

8.1 Medzilaboratórne testy

Prvé pokusy porovnať rôzne metódy monitorovania znečisťujúcich látok vo vodách, ktoré by mohli potenciálne byť použité v regulačnom monitorovaní podľa RSV boli uskutočnené v rámci FP6 EU projektu SWIFT-WFD (Gonzalez et al., 2009). V rámci projektu bolo uskutočnených i niekoľko terénnych porovnaní pasívnych vzorkovačov, s dôrazom na vzorkovanie hydrofóbnych látok (Allan et al., 2010, 2009). Tieto prvé pokusy ukázali, že napriek rôznorodosti použitých vzorkovačov, metód analýzy a vyhodnotenia dát, výsledky merania koncentrácie vo vode boli konzistentné a boli navrhnuté opatrenia, ktoré by mali znížiť variabilitu metódy. Následne organizovalo francúzske referenčné laboratórium pre oblasť vôd AQUAREF medzilaboratórnu štúdiu, ktorá hodnotila meranie vybraných polárnych pesticídov, polycyklických aromatických uhľovodíkov a kovov rôznymi pasívnymi vzorkovačmi v povrchovej a morskej vode (Miège et al., 2012). Hoci táto štúdia ukázala súčasnú variabilitu technológie pasívneho vzorkovania, použitý dizajn štúdie neumožnil hodnotiť príspevok rôznych krokov v procese (t.j. vzorkovanie, analýza vzoriek, výpočet koncentrácie vo vode) k celkovej pozorovanej variabilite.

Ďalšia medzilaboratórna štúdia bola organizovaná v roku 2011 pod mojím vedením v rámci aktivít asociácie NORMAN (Sieť referenčných laboratórií pre monitorovanie emergentných

látok v životnom prostredí; www.norman-network.net) spoločne s Európskym DG Joint Research Centre. Štúdia bola naplánovaná ako tzv. „learning“ aktivita, ktorej cieľom bolo tiež zhodnotiť variabilitu metódy, ale na rozdiel od štúdie AQUAREF hodnotila tiež rôzne zdroje neistoty pasívneho vzorkovania. Cieľom ešte nebola validácia metódy, ale najmä snaha identifikovať slabé miesta technológie, kde je potrebný ďalší vývoj. Na rozdiel od predchádzajúcich štúdií boli testované najmä polárne látky (napr. farmaceutiká, polárne pesticídy, steroidné hormóny, pefluorované látky) pomocou APV vzorkovačov, ale tiež extrémne hydrofóbne brómované spomaľovače horenia (Vrana et al., 2015a, n.d.). Štúdie sa zúčastnilo 30 laboratórií, a každé z nich mohlo použiť v porovnávacej štúdii svoj vlastný dizajn vzorkovačov. Všetky vzorkovače sa exponovali na jednom odberovom mieste vo vyčistenej odpadovej vode z komunálnej čistiarne odpadových vôd v Brne-Modřiciach. Navyše, pre každú skupinu analytov organizátor exponoval veľký počet (cca 400) vzorkovačov jedného typu, ktoré boli následne rozoslané spolu s testovanými vzorkovančmi na analýzu účastníkom štúdie. Tento postup umožnil vyhodnotiť príspeky rôznych analytických a interpretačných prístupov k celkovej variabilite dát.



Obrázok 11 Variabilita výsledkov medzilaboratórneho porovnania pasívnych vzorkovačov na rôznych úrovniach analytického postupu: príklad pre látku karbamazepín. STD – roztok štandardu; NPS – pasívny vzorkovač poskytnutý organizátorom; PPS – pasívne vzorkovače účastníkov. (N) – množstvo; (Cw) – koncentrácia vo vode. (Vrana a kol., nepublikované.)

Štúdia priniesla niekoľko na prvý pohľad prekvapivých zistení. Vo väčšine prípadov bola pozorovaná medzilaboratórna variabilita asi päťkrát vyššia ako vnútrolaboratórna precíznosť (Obrázok 11). Podobné výsledky merania, získané jednotlivými laboratóriami pre rôzne typy vzorkovačov, a tiež nízka variabilita výsledkov v rámci jednotlivých laboratórií naznačujú, že proces vzorkovania prispieva k celkovej variabilite merania menej ako následná laboratórna analýza. Zúčastnené laboratóriá mali problém s presným stanovením množstva sledovaných látok vo vzorkovači, ako aj s výpočtom koncentrácie látky vo vode z množstva látky sorbovaného vo vzorkovači. Výsledky meraní kompozitných vzoriek vody sa nachádzali v intervale hodnôt pasívneho vzorkovania. V budúcnosti bude potrebné výrazne zlepšiť presnosť pasívneho vzorkovania, najmä pre APV vzorkovače. Celkový záver tejto medzilaboratórnej štúdie je, že proces pasívneho vzorkovania prebieha podľa očakávania s dobrou reprodukovateľnosťou, ale laboratóriá, ktoré vzorky analyzovali, mali vo všeobecnosti problém s laboratórnou analýzou a interpretáciou dát. Závery štúdie boli zaslané na publikáciu v časopise TrAC (Vrana et al., n.d.), stav august 2015).

8.2 Normalizácia pasívneho vzorkovania

V posledných rokoch bol urobený značný pokrok v normalizácii vzorkovacích metod. Jedným z výstupov projektu STAMPS financovaného európskou úniou v rámci 5. rámcového programu bol vývoj britskej národnej normy o pasívnom vzorkovaní (*BSI, Publicly Available Specification: Determination of priority pollutants in surface water using passive sampling (PAS-61), May 2006.*, n.d.). Tento dokument sa stal podkladom pre prípravu medzinárodnej normy ISO 5667-23:2011 (ISO, 2011), ktorá predstavuje praktickú príručku pre pasívne vzorkovanie znečisťujúcich látok v povrchových vodách.

9 Využitie pasívneho vzorkovania v regulačnom monitorovaní

9.1 Rámcová smernica o vode

Prijatím Rámcovej smernice o vode (RSV) 2000/60/ES (EU, 2000), ktorá nadobudla účinnosť v decembri 2000, sa mení pohľad na ochranu vodných zdrojov. Orientuje sa na vytváranie podmienok pre trvalo udržateľné využívanie vodných zdrojov. Kladie sa dôraz na zachovanie hydroekologických potrieb krajiny. Tento meniaci sa vzťah človeka k vode vyžaduje zo strany štátnych orgánov a inštitúcií zavedenie nových prístupov v chápaní a zabezpečovaní jej ochrany, ktoré vychádzajú z požiadavky zabezpečenia potrebného množstva vody

v zodpovedajúcej kvalite pre hospodárske využitie, za podmienky zachovania prírodných funkcií tokov a prírodného ekosystému a krajiny.

V Rámcovej smernici o vode boli formulované nasledujúce hlavné ciele:

- rozšíriť ochranu vôd na všetky vody – tak povrchové ako aj podzemné,
- dosiahnuť „dobrý stav“ všetkých vôd do roku 2015, špecifikovaný v smernici ako environmentálny cieľ,
- aplikovať reálny integrovaný manažment ľudských aktivít na báze riečnych povodí,
- uplatňovať kombinovaný prístup pri ochrane vôd, t. j. súbežnú aplikáciu limitných hodnôt emisií a environentálnych noriem kvality (ENK) životného prostredia, vrátane vylúčenia prísunu rizikových prioritných látok do vodného prostredia a znižovaniu obsahu prioritných látok vo vodnom prostredí.,
- dosiahnuť aplikáciu cien za užívanie vôd, zodpovedajúcich „správnym cenám“, stimulujúcich trvalo udržateľný rozvoj,
- dosiahnuť zapojenie celej spoločnosti do implementácie RSV,
- vypracovať a prijať efektívnu legislatívu.

9.2 Európska stratégia boja proti znečisťovaniu vôd chemickými látkami

Znečistenie povrchových vôd chemickými látkami môže narúšať vodné ekosystémy a spôsobovať úbytok biotopov a zníženie biodiverzity. Znečisťujúce látky sa môžu hromadiť v potravnom reťazci a škodiť dravcom, ktoré konzumujú kontaminované ryby. Ľudia sú vystavení znečisťujúcim látkam konzumáciou rýb, pitnej vody a prípadne aj rekreačnými aktivitami. Znečisťujúce látky sa môžu nachádzať v prostredí mnoho rokov potom, ako boli zakázané. Niektoré sa môžu transportovať na veľké vzdialenosti a možno ich nájsť i v odľahlých oblastiach. Znečisťujúce látky môžu prenikať do životného prostredia z rôznych zdrojov, napríklad z poľnohospodárstva, priemyslu, spaľovaním, ako produkty alebo ako neúmyselne vypúšťané vedľajšie produkty. Mohli byť vypúšťané v minulosti, alebo sa aj naďalej uvoľňujú z výrobkov používaných v každodennom živote.

Stratégia boja proti znečisťovaniu vôd chemickými látkami je vytýčená v článku 16 Rámcovej smernice o vode 2000/60/ES (RSV) (EU, 2000). Ako prvý krok tejto stratégie bol prijatý zoznam prioritných látok (EU, 2001), ktorý identifikoval 33 látok alebo skupín látok prioritného záujmu v povrchových vodách v celej Európskej únii kvôli ich rozšírenému používaniu a ich vysokým koncentráciám v riekach, jazerá, brakických a pobrežných vodách.

Tento zoznam je revidovaný každé štyri roky a podľa potreby aktualizovaný. Aktuálny zoznam zahŕňa hlavne organické zlúčeniny vrátane rôznych pesticídov, niektoré polycyklické aromatické uhľovodíky (PAU), benzén, halogénované rozpúšťadlá, spomaľovače horenia, zmäkčovadlá, povrchovo aktívne látky, antivegetatívne prípravky a aj niektoré ťažké kovy.

9.3 Hodnotenie stavu znečistenia povrchových vôd prioritnými látkami

Európska komisia prijala Smernicu 2008/105/ES o environmentálnych normách kvality v oblasti vodnej politiky (EU, 2008). Táto smernica stanovuje limity na koncentrácie v povrchových vodách pre 41 nebezpečných chemických látok vrátane 33 prioritných látok a 8 ďalších znečisťujúcich látok, ktoré predstavujú významné riziko pre zdravie zvierat a rastlín vo vodnom prostredí a pre ľudské zdravie. Má za cieľ zabezpečiť vysokú úroveň ochrany proti rizikám pochádzajúcim z týchto 41 látok a stanovuje pre ne environmentálne normy kvality (ENK) na európskej úrovni. Okrem toho členské štáty EU ustanovujú ENK pre ďalšie syntetické a nesyntetické špecifické znečisťujúce látky relevantné pre jednotlivé povodia, ktoré môžu mať škodlivý účinok na biologickú kvalitu, a ktoré sú vypúšťané do povrchových vôd vo významných množstvách. Podľa RSV dodržiavanie ENKs pre prioritné látky je súčasťou hodnotenia chemického stavu útvarov povrchových vôd. Dodržiavanie ENK pre špecifické znečisťujúce látky je súčasťou hodnotenia ekologického stavu. Pre dodržiavanie predpisov na hodnotenie stavu vôd boli prijaté ENK pre vnútrozemské povrchové vody (rieky a jazerá) a ďalšie povrchové vôd (prechodné, pobrežné a teritoriálne vody). Boli stanovené dva druhy ENK: ročná priemerná koncentrácia (RP-ENK) pre ochranu proti dlhodobým a chronickým účinkom, a maximálne prípustná koncentrácia (NPK-ENK), aby sa predišlo nezvratným vážnym dôsledkom pre ekosystémy v dôsledku akútnej krátkodobej expozície. Vzhľadom na nedostatočný rozsah spoľahlivých informácií o koncentráciách prioritných látok v živých organizmoch a v sedimentoch na úrovni Spoločenstva, ako aj na skutočnosť, že informácie o povrchových vodách poskytujú dostatočný základ pre zabezpečenie komplexnej ochrany a účinnej kontroly znečistenia, hodnoty ENK boli v tomto štádiu pre väčšinu látok odvodené pre povrchové vody. V prípade troch prioritných látok (ortuť, hexachlórbenzén a hexachlórbutadién) boli ENK odvodené pre koncentrácie v organizmoch (biote). S výnimkou kadmia, olova, ortuti a niklu ENK sú vyjadrené ako celková koncentrácia stanovená vo vzorke vody. V prípade kovov ENK odkazujú na koncentráciu rozpustených látok, t.j. koncentráciu v kvapalnej fáze vzorky vody získanej filtráciou cez 0.45 μm filter.

Sediment a vodné organizmy (biota) sú tiež dôležitými matricami pre monitorovanie niektorých prioritných látok a iných znečisťujúcich látok, ktoré majú tendenciu hromadiť sa v nich, s cieľom posúdiť dlhodobé vplyvy ľudskej činnosti a časové trendy. Cieľom monitorovania je zabezpečiť, aby sa existujúce úrovne kontaminácie v živých organizmoch a v sedimentoch nezvyšovali. V tejto súvislosti je relevantné monitorovať v sedimente a biote látky s akumulačným potenciálom ako sú polybrómované difenylétery (PBDE), C_{10}-C_{13} chlóralkány, bis(2-etylhexyl)ftalát, hexachlórbenzén, hexachlórbutadién, hexachlór-cyklohexán, pentachlórbenzén, polycyklické aromatické uhľovodíky, tributylciničitý katión a kovy kadmium, olovo a ortuť.

V roku 2013 bola prijatá Smernica Európskeho parlamentu a Rady 2013/39/EU, ktorou sa menia smernice 2000/60/EC a 2008/105/EC, pokiaľ ide o prioritné látky v oblasti vodnej politiky (EU, 2013). Obsahom tejto smernice je rozšírenie zoznamu prioritných látok o 12 nových látok a aktualizácia hodnôt ENK pre prioritné láty v povrchových vodách. Berúc do úvahy tendenciu niektorých látok bioakumulovať sa, pre 8 prioritných látok boli zavedené ENK hodnoty ako maximálne prípustné koncentrácie v biote (v mäkkýšoch alebo v rybách). Na základe smernice musia členské štáty postupne zaviesť program na monitorovanie koncentrácie týchto látok látok v živých organizmoch alebo vo vode, a hodnotiť, či stav povrchových vôd vyhovuje novo zavedeným ENK.

ENK pre matricu „biota“ sú odvodené ako koncentrácie v rybách, s výnimkou pre polycyklické aromatické uhľovodíy, kde sa uvádza odkaz na ryby, kôrovce a mäkkýše (v súlade s právnymi predpismi o bezpečnosti potravín). Členské štáty EÚ sa môžu rozhodnúť, používať pri hodnotení stavu povrchových vôd ENK v inej matrici, ako je špecifikovaná v smernici 2013/39/EU, prípade pre iné druhy živočíchov, ako sú uvedené v smernici. V prípadoch, kde je ENK nastavená pre živé organizmy, je dovolené, aby príslušné normy bolo možno odvodiť ako ekvivalentné koncentrácie vo vodnom stĺpci (pomocou biokoncentračného faktora (BCF)/biomagnifikačného faktora (BMF) alebo bioakumulačného faktora (BAF)). Jednotlivé členské štáty EÚ sa môžu rozhodnúť, v ktorej matrici budú monitorovať prioritné látky za účelom hodnotenia stavu vôd, ale musia pritom zvážiť rad praktických a etických otázok, ako je napríklad nutnosť merať extrémne nízke koncentrácie látok vo vodách, alebo potreba odlovu veľkého množstva rýb na účel monitorovania.

9.4 Požiadavky na analytické metódy vo vzťahu k hodnoteniu povrchových vôd podľa Rámcovej Smernice o vode

Pri kontrole kvality a stavu vôd je nevyhnutné, aby boli zabezpečené vyhovujúce analytické nástroje, umožňujúce stanovovať hladiny znečisťujúcich látok sledovaných na medzinárodnej úrovni (napr. monitoring hraničných tokov), ako aj na vnútroštátnej úrovni (potreby dané špecifickými zdrojmi znečistenia).

Všetky analytické metódy, ktoré sa použijú na účely programov chemického monitorovania stavu vôd, musia spĺňať určité minimálne pracovné kritériá vrátane pravidiel neistoty meraní a limitov kvantifikácie metód (EU, 2009). Všetky metódy analýzy vrátane laboratórnych, terénnych a on-line testov používaných na účely programov sledovania chemických látok, uskutočňovaných v súlade s RSV, majú byť validované a dokumentované v súlade s normou EN ISO/IEC-17025 alebo inými zodpovedajúcimi normami uznanými na medzinárodnej úrovni. Všetky používané analytické metódy stanovenia sa musia opierať o hodnotu neistoty merania 50 % alebo nižšiu (k = 2) odhadnutú na koncentračnej úrovni príslušnej ENK a limit kvantifikácie rovný alebo nižší ako 30 % príslušnej ENK. Ak v prípade niektorého parametra neexistuje príslušná ENK, alebo ak neexistuje analytická metóda spĺňajúca vyššie uvedené minimálne pracovné kritériá, príslušná smernica vyžaduje, aby sa monitorovanie uskutočňovalo s použitím najlepších dostupných techník, ktoré nespôsobujú prílišné zvyšovanie nákladov.

Laboratóriá musia preukázať svoju spôsobilosť na analyzovanie príslušných látok účasťou na programoch testovania odbornosti, ktoré zahŕňajú analytické metódy na úrovni koncentrácií, ktoré sú reprezentatívne pre programy monitorovania chemických látok uskutočňované podľa RSV a analýzou dostupných referenčných materiálov, ktoré reprezentujú odoberané vzorky obsahujúce primerané koncentrácie vzhľadom na príslušné ENK (EU, 2009).

9.5 Použiteľnosť pasívneho vzorkovania na monitorovanie prioritných látok podľa RSV

Aktualizovaná smernica o environmentálnych normách kvality odporúča členským štátom aktívne postupovať pri implementácii inovatívnych monitorovacích nástrojov na hodnotenie koncentrácií a trendov prioritných látok v povrchových vodách: „Nové metódy monitorovania, ako napríklad ***pasívne odbery vzoriek*** a iné nástroje, sa z hľadiska budúceho uplatňovania javia ako sľubné a mali by sa preto ďalej rozvíjať“ (EU, 2013).

Podobne, ako je akumulácia hydrofóbnych/lipofilných látok do tkanív vodných živočíchov hnaná lepšou rozpustnosťou týchto látok v lipidoch ako vo vode, je aj prestup týchto látok z vody do pasívneho vzorkovača založený na lepšej rozpustnosti organických látok v materiáli, z ktorého sú vzorkovače zhotovené. Tieto vlastnosti pasívnych vzorkovačov určujú ich potenciálne využitie v regulačnom monitoringu, najmä pre hydrofóbne látky.

Potenciál pasívneho vzorkovania na podporu monitorovania znečisťujúcich látok pri implementácii RSV bola prvýkrát diskutovaný na ad hoc expertnom stretnutí, organizovanom v roku 2009 asociáciiou NORMAN ("NORMAN Expert Group Meeting: Passive Sampling of Emerging Pollutants: state of the art and perspectives 27 May 2009 - Prague, The Czech Republic," 2009) a v pozičnom dokumente, ktorý bol spracovaný na základe tejto diskusie (Vrana et al., 2010). Ďalšími iniciatívami, kde bola riešená problematika využitia pasívnych vzorkovačov v regulačnom monitoringu bol „Utrechtský seminár" ("Include passive sampling in WFD-monitoring? Passive Sampling Workshop, Utrecht, The Netherlands 9-10 November 2011," 2011), workshop organizovaný SETAC o metódach pasívneho vzorkovania v sedimentoc h (Parkerton et al., 2012), ICES workshop o pasívnom vzorkovaní a pasívnom dávkovaní (International Council for the Exploration of the Sea, 2013), workshop organizovaný RECETOXom a asociáciou NORMAN ("Linking Environmental Quality Standards and Passive Sampling," 2013) a napokon workshop organizovaný asociáciou NORMAN v spolupráci s francúzskym referenčným laboratóriom pre oblasť vôd AQUAREF (Miège et al., 2015, 2014).

Pasívne vzorkovanie je považované za monitorovací nástroj – rovnovážnu (alebo nerovnovážnu) extrakčnú techniku, ktorá umožňuje stanoviť koncentrácie voľne rozpustených prioritných látok vo vode. Alternatívne sa na vzorkovač môže nahliadať ako na referenčnú matricu (zložku životného prostredia), ktorá je homogénna a má dobre definované vlastnosti, ktoré sú málo ovplyvnené okolitým prostredím. Výsledky meraní látok pasívnym vzorkovaním sa môžu prepočítať (konvertovať) v súlade s teóriou rovnovážnej distribúcie na ekvivalentné koncentrácie látky v iných zložkách životného prostredia. Najčastejšie ide o prepočet koncentrácie látky vo vzorkovači na koncentráciu látky voľne rozpustenej vo vode, v princípe je ale možné urobiť i prepočet na rovnovážnu koncentráciu látky v lipide vodných živočíchov (Jahnke et al., 2008).

Tabulka 1. **Výhody (+) a nevýhody (-) priameho a pasívneho odberu vzoriek vody a možné riešenia**

	Priamy odber vzoriek vody	Pasívne vzorkovanie
Analytická porovnateľnosť výsledkov meraní	+ tradičný prístup s dlhodobou históriou vývoja metód, dostupnosť validovaných metód a interkalibračných štúdií	+/- tréning laboratórií a ďalšia kalibrácia vzorkovačov umožní výrazne zlepšiť vzájomnú porovnateľnosť meraní
Vzájomná porovnateľnosť výsledkov meraní z rôznych vodných útvarov	- vzorky vody z rôznych útvarov, v rôznych režimoch toku a v rôznych obdobiach roka majú odlišné zloženie matrice; celková koncentrácia nedostatočne reflektuje riziko, ktoré znečisťujúce látky predstavujú pre vodné živočíchy	+/- pasívny vzorkovač pozostáva z materiálu (matrice) s dobre definovaným zložením v rôznych podmienkach prostredia; výsledky meraní sú navzájom priamo porovnateľné a umožňujú identifikáciu priestorových a časových trendov znečisťujúcich látok vo vodách
Meranie veľmi nízkych koncentrácií	- bežne používaný odber malého objemu vody (niekoľko litrov na účel analýzy) nie je vhodný na meranie ultrastopových koncentrácií látok vo vodách	+ pasívna akumulácia znečisťujúcich látok do vzorkovača z veľkého objemu vody (až niekoľko tisíc litrov) umožňuje dosiahnuť extrémne nízke medze stanovenia látok vo vode
Reprezentatívnosť vzoriek	- výsledok merania z bodového odberu vody reprezentuje iba koncentráciu za veľmi krátky časový úsek	+ pasívne vzorkovanie poskytuje integratívnu vzorku, ktorá je menej citlivá na krátkodobé zmeny vo vzorkovanom vodnom útvare

Z koncentrácie látky v pasívnom vzorkovači je možné odhadnúť voľne rozpustenú koncentráciu látky rozpustenej látky, ktorá predstavuje hnaciu silu pre biokoncentráciu látok

do tkanív vodných živočíchov. Pasívne vzorkovače teda umožňujú stanoviť koncentráciu, v ktorej sú exponované vodné živočíchy na najnižších trofických úrovniach. Výsledky z rovnovážneho pasívneho vzorkovania je možné kovertovať na koncentrácie v lipide organizmu, ktorý je v rovnováhe s prostredím, v ktorom žije. Tento prístup je podobný, ako keď sa koncentrácie organických látok v sedimente normalizujú na obsah organického uhlíka a následne konvertujú na koncentrácie v iných environmentálnych matriciach. Na rozdiel od sedimentov v prípade pasívnych vzorkovačov nie je potrebné brať do úvahy variabilnú povahu organického uhlíka, pretože polymérne sorbenty používané na konštrukciu pasívnych vzorkovačov majú dobre definované a konštantné vlastnosti.

Aplikácia pasívnych vzorkovačov môže pomôcť zefektívniť monitorovanie a následné hodnotenie a kvality vody, znížiť náklady spojené s monitorovaním, najmä pre látky s extrémne nízkymi koncentráciami vo vodnej fáze a pre látky, ktorých koncentrácie kolíšu v čase. Integratívne pasívne vzorkovanie má oproti bodovým odberom vzoriek výhodu, pretože poskytuje priemernú koncentráciu analytu vo vzorkovanej matrici za dlhšie časové obdobie. Nižšie sú uvedené niektoré požiadavky na monitorovanie vôd a porovnanie pre priamy a pasívny spôsob odberu vzoriek.

9.5.1 Hodnotenie súladu s ENK pre matricu voda

Na hodnotenie chemického stavu vodného útvaru podľa Rámcovej smernice o vode sú určené ENK (EU, 2008)(EU, 2013). Tie sa zvyčajne vyjadrujú ako ako AA-ENK (ročný priemer) a MAC-NEK (maximálna prípustná koncentrácia). Ten je zvyčajne vyjadrená ako vysoko percentil, napr 90%(Hanke et al., 2009).

Chemické monitorovanie diskrétnych environmentálnych vzoriek väčšinou spĺňa legislatívne požiadavky na analytické metódy (EU, 2009), ale existujú situácie, kedy pasívne vzorkovanie môže byť veľmi užitočné a doplniť chýbajúce informácie. Je zrejmé, že keď medza stanovenia vo vzorkách vody odobraných klasickým spôsobom je vyššia ako 30% príslušnej ENK (a preto nie je možné hodnotenie stavu vodného útvaru v súlade s vyššie uvedenými legislatívnymi normami) použitie metódy pasívneho vzorkovania, ktorá má vyhovujúcu medzu stanoveni, predstavuje logickú alternatívu.

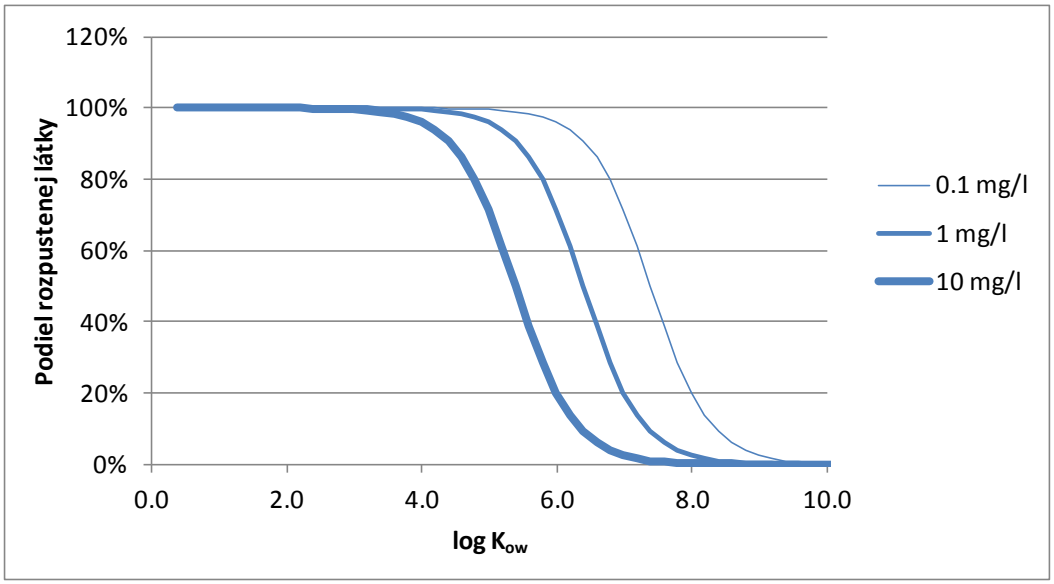
V prípade, že medza stanovenia metódy pasívneho vzorkovania + príslušná neistota neprekračuje príslušnú hodnotu ENK, je možné vykonať hodnotenie chemického stavu útvaru vôd pre danú látku i v prípade, že rozšírená neistota merania pri koncentrácii rovnej ENK

nespĺňa súčasné právu požiadavky, t.j. aby neistota stanovenia bola nižšia ako 50% (k=2)(EU, 2009).

Ďalším prípadom, keď môže byť výhodné použiť pasívne vzorkovanie, je ak koncentrácie kolíšu v čase, čo nastáva najmä u prípravkov na ochranu rastlín v malých vodných útvaroch. V takom prípade je relevantné kontrolovať dodržanie MAC-ENK. Pasívne vzorkovanie síce poskytuje informáciu iba o časovo váženom priemere koncentrácie počas expozície (alebo počas polčasu ustálenia rovnováhy, ak je polčas kratší ako doba expozície), ale integratívny charakter vzorkovania umožňuje „zbadať" krátkodobý pulzný nárast koncentrácie. Faktom je, že intenzita ani trvanie takéhoto pulzného nárastu koncentrácie sa nedá odvodiť z jedného odberu pasívneho vzorkovača. Napriek tomu pasívne vzorkovanie umožňuje výrazne znížiť pravdepodobnosť, že takáto udalosť ostane nepovšimnutá, ako to často býva v prípade použitia konvenčného bodového odberu vzoriek s mesačnou frekvenciou odberu. Na odberových profiloch, kde pasívne vzorkovače namerajú najvyššie priemerné koncentrácie, je následne možné naplánovať intenzívnejšie vzorkovanie (napr. pomocou automatického vzorkovača), ktoré potvrdí alebo vyvráti prekročenie príslušnej ENK.

Organické znečisťujúce látky vo vodách sa môžu vyskytovať, v závislosti od charakteru ich vypúšťania, s variabilnými alebo relatívne konštantnými koncentráciami. Na základe fyzikálnochemických vlastností sa môžu látky rozdeliť na hydrofilné (log K_{ow} < 4) a hydrofóbne (logK_{ow} >4), a pre tieto dve skupiny je nutné použiť dva rôzne typy pasívnych vzorkovačov. Tabulka 2 poskytuje prehľad použiteľnosti pasívnych vzorkovačov pri monitorovaní látok vo vodách. V prípadoch, keď koncentrácie látok v prostredí kolíšu iba málo, pasívne vzorkovanie je preferovanou technikou odberu, a ich hlavná výhoda je v možnosti dosiahnuť veľmi nízke hodnoty medze stanovenia. Prípadné výkyvy koncentrácií sú vo vzorke integrované, preto získaná vzorka dobre reprezentuje priemerné zloženie vody vo vodnom útvare za dlhšie časové obdobie.

Ďalšiu komplikáciu v hodnotení stavu poďla RSV predstvuje fakt, že podľa smerníc, ktoré v súčasnosti platia (EU, 2008)(EU, 2013), hodnotenie súladu s ENK sa má vykonávať porovnaním „celkovej" koncentrácie látky vo vodnom stĺpci, zatiaľ čo pasívne vzorkovanie poskytuje iba informáciu o rozpustnej koncentrácii C_{free}. V prípade, že koncentrácia celkového organického uhlíka (TOC) vo vodnom stĺpci neprekročí hodnotu 10 mg/l, vyskytujú sa látky, ktorých log K_{ow} < 5 vo vode prevažne v rozpustenej forme (teda nenaviazané na častice) (Obrázok 12). Pre takéto látky je meranie pomocou pasívneho vzorkovania možné použiť na priame porovnanie s hodnotou ENK.



Obrázok 12 Odhad podielu rozpustenej látky (C_{free}) vo vode v závislosti od jej hydrofóbnosti (log K_{ow}) pre tri rôzne koncentrácie celkového organického uhlíka [TOC] vo vodnom stĺpci. Na odhad bol použitý vzťah $K_{oc} = 0.41 \times K_{ow}$ (Karickhoff, 1981) a model $C_{free}/C_{total} = 1/(1+[TOC] \times K_{oc})$.

Iná situácia vzniká pre hydrofóbnejšie látky, pre ktoré sa voľne rozpustený podiel vo vode prudko znižuje s rastúcou hodnotou log K_{ow}. V takom prípade je riešením odvodiť z legislatívne ukotvenej ENK pre celkovú koncentráciu „odvodenú" hodnotu normy kvality, ktorá poskytuje rovnakú úroveň ochrany vodných živočíchov ako pôvodná ENK, ale vzťahuje sa na rozpustenú koncentráciu látky vo vode $ENK_{voda,c\ free}$ (Whitehouse and Paya-Perez, 2011). Hodnoty C_{free}, získané pasívnym vzorkovaním, je v takomto prípade možné porovnať s odvodenou hodnotou $ENK_{voda,c\ free}$ i pre hydrofóbnejšie látky.

Tabulka 2. Použiteľnosť pasívneho vzorkovania na hodnotenie stavu znečistenia vôd

logK_{OW}	Konštantná koncentrácia	Fluktuujúca koncentrácia
< 4	Výhody pasívneho vzorkovania oproti štandardnému postupu vzorkovania vôd bodovými odbermi sú obmedzené	Adsorpčné pasívne vzorkovanie má rolu skríningového nástroja, ale môže byť preferovanou metódou v prípade, že neistota vzorkovania je menšia ako variabilita koncentrácie vo vode
> 4	Rozdeľovacie pasívne vzorkovače umožňujú stanovenie voľne rozpustenej koncentrácie hydrofóbnych látok vo vode, hlavne v prípadoch extrémne nízkych hodnôt environmentálnych noriem kvality	Rozdeľovacie pasívne vzorkovače poskytujú informáciu o priemernej hodnote koncentrácie, ale neumožňujú stanoviť maximálnu koncentráciu látky počas krátkodobého výkyvu koncentrácie

9.5.2 Hodnotenie súladu s ENK pre matricu biota

Smernica 2013/39/EÚ (EU, 2013) umožňuje pre látky s bioakumulačným potenciálom použiť na hodnotenie chemického stavu vôd koncentrácie namerané v tkanivách vodných živočíchov. Pre skupinu 8 látok určuje i príslušné ENK pre biotu na úrovni Spoločenstva. Výhodou použitia bioty (napr. rýb) pri monitorovaní chemických látok je, že mnohé z týchto látok sa vo vode vyskytujú len vo veľmi nízkych koncentráciách, ale v dôsledku bioakumulácie sú ich koncentrácie dobre merateľné v tkanivách vodných živočíchov použitím dostupných analytických metód. Ďalšou výhodou tohto prístupu je, že meranie koncentrácií v tkanive živočíchov umožňuje priamo hodnotiť ich expozíciu, ak tieto látky nie sú aktívne metabolizované. Použitie organizmov na monitorovanie chemických látok však prináša niekoĺko problémov:

- neistota spôsobená variabilitou vzorkovaných druhov, veľkosti, veku, pohlavia, fyziologického stavu a trofickej úrovne organizmov, môže zaniesť do procesu hodnotenia stavu vôd významné skreslenie. Ďalším problémom je výsledná variabilita, ktorá komplikuje hodnotenie časových alebo priestorových trendov sledovaných látok, čo môže obmedziť možnosť porovnať výsledky meraní pre rovnakú látku medzi regiónmi
- druhy rýb alebo iných vodných živočíchov, potrebné pre monitorovanie chemických látok, nemusia byť k dispozícii na všetkých odberových miestach
- monitorovanie bioty je ekonomicky (a prakticky) uskutočniteľné iba s nižšou frekvenciou odberov, ako je frekvencia odberov vzoriek vody
- je potrebné deštrukčné vzorkovanie (nutnosť zabitia živočíchov odobraných na účel monitoringu), ktoré v prípade intenzívneho odlovu rýb za účelom chemického monitorovania môže dokonca ohroziť miestne populácie rýb

Hoci je dostupná technická príručka Európskej komisie na monitorovanie chemických látok v biote v povrchových vodách (Deutsch et al., 2014), dáta získané týmto spôsobom budú veľmi pravdepodobne zaťažené značnou variabilitou, a v dôsledku toho i hodnotenie vôd bude zaťažené zvýšenou neistotou. To bude komplikovať následné rozhodnutia vodohospodárov pri nastavení opatrení na zlepšenie kvality vôd.

Potenciálnym riešením problémov spojených s chemickým monitorovaním v živých organizmoch je aplikovať abiotické metódy monitorovania, napr. pomocou pasívnych vzorkovačov, ktoré poskytnú "biomimetické" meranie znečisťujúcich látok, t.j. budú

simulovať proces biokoncentrácie znečisťujúcich látok z vody do vodných organizmov s nízkou inherentnou variabilitou.

Rozdeľovacie koeficienty vzorkovač-voda (K_{sw}) sú v prvom priblížení rovné hodnote rozdeľovacieho koeficienta v systéme oktanol-voda (K_{ow}). Vzhľadom na to, že parameter K_{ow} sa používa ako surogát lipidov, ktorý sa používa na opis biokoncentrácie látok do organizmov, existuje i vzťah medzi akumuláciou látok do pasívnych vzorkovačov a do organizmov. Za predpokladu, že kvantitatívne vzťahy sú dostatočne charakterizované (Rovnica (37), výsledky meraní z RPV umožňujú predikovať koncentrácie znečisťujúcich látok v biote a môžu sa potenciálne použiť ako náhrada monitorovania chemických látok pomocou bioty:

$$K_{s,lipid} = \frac{C_{PS}}{C_{lipid}} = \frac{C_{PS} f_{lipid}}{C_{biota}} = \frac{ENK_{PS}}{ENK_{lipid}} = \frac{ENK_{PS} f_{lipid}}{ENK_{biota}} \quad (37)$$

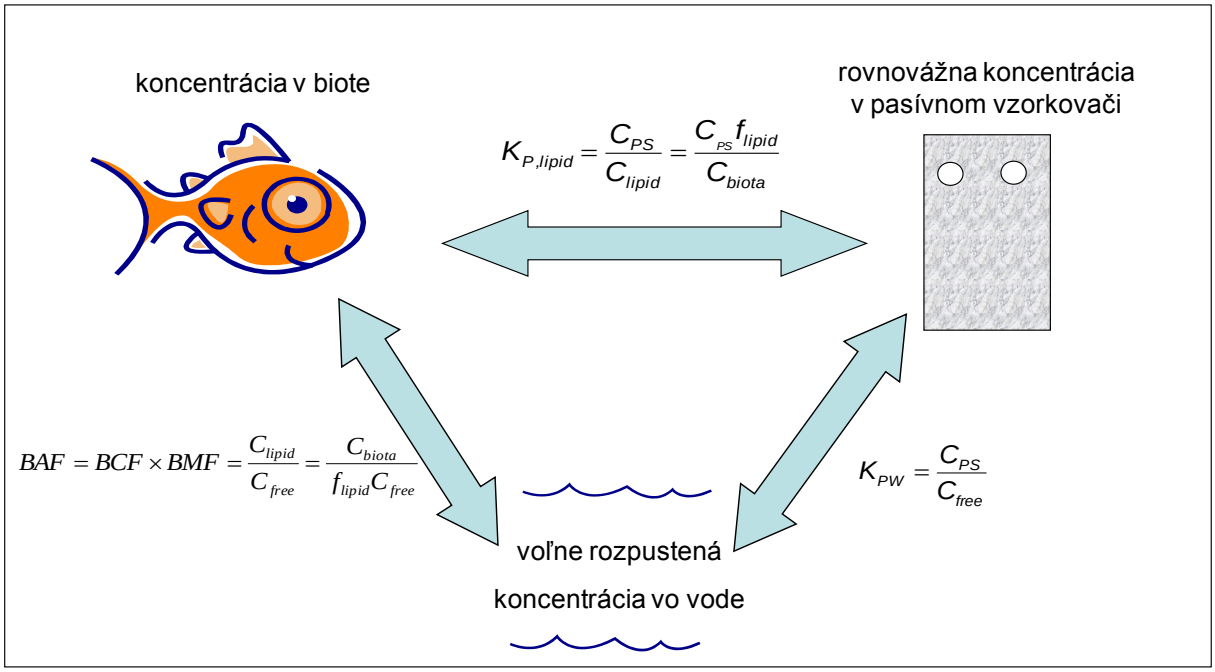
kde $K_{s,lipid}$ je rozdeľovací koeficient látky medzi vzorkovačom a lipidom, C_{lipid} je koncentrácia látky v biote, vztiahnutá na koncentráciu v lipide, f_{lipid} je podiel lipidu v tkanive organizmu a ENK_{lipid} je hodnota ENK_{biota} vyjadrená na základe koncentrácie v lipide.

Návrh, aby sa konverzia výsledkov meraní pasívnym vzorkovaním prepočítala pomocou vyššie uvedenej rovnice na ekvivalentnú koncentráciu v modelovom lipide (napr. trioleíne), a aby aj príslušná hodnota ENK bola vyjadrená ako koncentrácia v lipide (Jahnke et al., 2008), žiaľ nenachádza v súčasnosti podporu u expertov, ktorí sú zodpovední za prípravu technickej dokumentácie na podporu implementácie RSV. Jedným z dôvodov je, že tento prístup vnáša do procesu hodnotenia stavu vôd ďalšiu neistotu, a tiež preto, že ciele ochrany takouto ENK by boli ťažko komunikovateľné vo vzťahu k verejnosti. Výhodami takéhoto prístupu je, že ENK_{lipid} má vzťah ku koncentrácii látok vo vodných organizmoch, a tiež, že pre veľmi hydrofóbne látky hodnota ENK nepredstavuje extrémne nízku koncentráciu, ako je to často v prípade ENK_{voda}. V súčasnosti je pomerne ťažké vysvetliť neodborníkovi v tejto oblasti a presvedčiť verejnosť, že koncentrácie látok vo vode, ktoré sa pohybujú rádovo v pikogramoch na liter, môžu spôsobovať poškodenie ekosystému a sú škodlivé.

Vzhľadom na to, že biomimetická extrakcia je založená na jednoduchom fyzikálnom procese rozďeľovacej rovnováhy, nemôže dokonale opísať proces bioakumulácie, ktorý zahŕňa i akumuláciu v potravnom reťazci, a tiež metabolizmus. Preto pasívne vzorkovanie simuluje iba proces biokoncentrácie v organizmoch, ktoré sledované látky nemetabolizujú (Verbruggen et al., 2000, 1999). Vo všeobecnosti nie je ani možné priamo porovnávať koncentráciu

získanú pasívnym vzorkovaním s hodnotou ENK_{biota}. Hoci pre niektoré druhy živočíchov sa našla veľmi dobrá korelácia medzi koncentráciami látok v pasívnych vzorkovačoch a v biote (Smedes, 2007), pre iné druhy bola táto korelácia slabá (Ashton et al., 2012).

V princípe je možné nepriame hodnotenie súladu s ENK pre matricu biota pomocou pasívneho vzorkovania. RPV poskytujú spoľahlivé meranie (so známou neistotou) voľne rozpustenej koncentrácie C_{free} väčšiny látok, ktoré majú tendenciu akumulovať sa v biote. Vychádzajúc z vyššie uvedenej tézy, že C_{free} je najrelevantnejší parameter expozície vodných organizmov účinkom znečisťujúcich látok, koncentrácie látok vo vzorkovači i v biote sú priamo úmerné hodnote C_{free} (Obrázok 13), a tento vzťah je možné použiť ako spoločný menovateľ pri hodnotení súladu s ENK.



Obrázok 13 Distribúcia organických látok medzi vodou (voľne rozpustná koncentrácia), vodnou biotou a rozdeľovacím pasívnym vzorkovačom.

Zatiaľ čo vzťah koncentrácie C_{PS} ku C_{free} je pomerne jednoduchý a dá sa charakterizovať známou neistotou (Lohmann et al., 2012), v prípade bioty je vzťah medzi C_{biota} a C_{free} oveľa komplexnejší a zahŕňa nielen biokoncentráciu (charakterizovanú BCF), ale aj akumuláciu látky potravou v trofickom reťazci, charakterizovanú bioakumuláciou (BAF) a biomagnifikáciou (BMF).

Aby bola možná kontrola súladu s ENK_{biota}, založenom na monitorovaní C_{free} pomocou pasívneho vzorkovania, je potrebné najprv odvodiť potrebné kritérium hodnotenia súladu; t.j. prepočítať hodnotu ENK_{biota} na $ENK_{voda,cfree}$, ktorá poskytne ekvivalentnú ochranu vodných

organizmov pred negatívnymi účinkami sledovaných látok. Problém tkvie v tom, že sa pritom musia použiť hodnoty BAF, BMF a TMF, ktoré sú zaťažené veľkou variabilitou a môžu potenciálne vnášať veľkú neistotu do takejto konverzie (Moermond and Verbruggen, 2013). Konverzia je zmysluplná len v prípade, ak je možné variabilitu udržať v rozumných medziach. Je to možné urobiť niekoľkými prístupmi:

- aplikáciou konzervatívnych (maximálnych) hodnôty BAF
- aplikáciou BAF hodnôt, ktoré úzko súvisia s lokálnym ekosystémom v monitorovanom vodnom útvare, aby bola zabezpečená dostatočná ochrana lokálnych vodných živočíchov
- starostlivým výberom druhov monitorovaných organizmov z rôznych trofických úrovní, vo vzťahu k cieľom ochrany (t.j. ochrana ľudského zdravia, vodného vtáctva, vodných cicavcov), receptorov, ktoré sú ohrozené, ako aj expozičných ciest

Tento spôsob hodnotenia chemického stavu, i spôsob založený na monitorovaní bioty sú oba založené na porovnaní nameraných koncentrácií s ENK_{biota}, ale použitie pasívneho vzorkovania poskytuje výhodu oproti monitorovaniu bioty, pretože umožňuje vyhnúť sa neistotám, ktoré do procesu hodnotenia vnáša vzorkovanie bioty. Pri zvažovaní, ktorý spôsob je vhodnejší, treba brať do úvahy i neistotu prepočtu hodnoty ENK_{biota} na $ENK_{voda,cfree}$, ako aj neistotu vzorkovania pomocou pasívnych vzorkovačov.

Pokiaľ sa v budúcnosti podarí vymedziť dobre definované kritérium $ENK_{voda,cfree}$, pasívne vzorkovače môžu zohrať významnú úlohu v regulačnom monitorovaní znečisťujúcich látok, ako súčasť tzv. viacstupňového procesu hodnotenia stavu vôd.

9.5.3 Úloha pasívneho vzorkovania vo viacstupňovom procese hodnotenia stavu vôd

Pasívne vzorkovače je možné použiť v prvom stupni tzv. viacstupňového procesu (tiered approach) hodnotenia stavu chemického znečistenia vôd a sedimentov (Deutsch et al., 2014). Viacstupňový postup nastavenia monitorovacích programov sa používa, pretože monitorovanie prioritných látok vo vodných organizmoch (v prípade hodnotenia chemického stavu na základe ENK pre matricu biota) si vyžaduje veľké nasadenie vzorkovacích, logistických a analytických kapacít. Preto je potrebné monitorovanie sústrediť na oblasti a vodné útvary, kde je zvýšené riziko prekročenia príslušných ENK. V takýchto oblastiach môže nastať situácia, že požadované druhy živočíchov nie sú k dispozícii, alebo sú

k dispozícii v nedostatočnom počte, veľkosti alebo vekovom rozmedzí. Existuje reálne riziko, že práve v oblastiach, kde sú prekročené ENK, sa biota vôbec nemusí vyskytovať.

Viacstupňový skríningový prístup umožňuje v niekoľkých krokoch identifikovať problematické oblasti alebo hlavné zdroje rizík pre vodné živočíchy. Týmto postupom sa najprv rôzne geografické oblasti zoradia podľa informácie z dostupných monitorovacích dát alebo z modelovania, a následne sa identifikujú a prioritizujú oblasti/vodné útvary, kde sa očakávajú najvyššie koncentrácie znečisťujúcich látok. V prioritizovaných oblastiach sa následne uskutoční monitorovanie koncentrácií znečisťujúcich látok vo vodných živočíchoch. Prvostupňové hodnotenie môže byť založené na meraniach vo vode, plavenine, dnových sedimentoch, ale najmä meranie pomocou pasívneho vzorkovania môže výrazne spresniť prvotné hodnotenie chemického znečistenia.

V prvom stupni sa monitorovanie látok uskutoční iba pomocou pasívnych vzorkovačov a aplikuje sa konzervatívne (najhorší možný scenár znečistenia) hodnotiace kritérium (ENK). Na miestach, kde pasívne vzorkovanie jasne ukazuje na dodržanie príslušných noriem kvality, ďalší intenzívny monitoring nebude potrebný. Len vo vodných útvaroch, kde pasívne vzorkovanie ukazuje prekročenie ENK, je potrebné v druhom kroku uskutočniť detailnejší monitoring, napr. pomocou bioty. Takýto postup by umožnil znížiť závislosť monitoringu na analýze tkanív vodných živočíchov, ale stále by zachoval využitie ENK_{biota} ako regulačnej normy pre hodnotenie stavu vôd, na základe ktorého sa uskutočňujú vodohospodárske opatrenia.

10 Závery

Všeobecným úvodom do problematiky pasívneho vzorkovania, ktorý je v prílohách doplnený súborom mojich vlastných publikácií a prác, ktoré s témou habilitačnej práce úzko súvisia, som sa pokúsil ukázať, že pasívne vzorkovanie je sľubnou metódou, ktorá má veľký potenciál vo výskume osudu znečisťujúcich látok v životnom prostredí. Naznačil som aj možnosti praktického využitia pasívneho vzorkovania v regulačnom monitorovaní znečisťujúcich látok v povrchových vodách a smery budúceho výskumu, ktoré povedú k splneniu tohoto cieľa.

V posledných rokoch bol dosiahnutý výrazný pokrok v porozumení faktorov, ktoré ovládajú akumuláciu kontaminantov do rozdeľovacích pasívnych vzorkovačov. Rovnovážne pasívne vzorkovanie umožňuje priamo porovnať úroveň znečistenia rôznych zložiek životného prostredia chemickými látkami, a preto je táto metóda veľmi vhodná pre štúdium distribúcie a transportu chemických látok v životnom prostredí. Pri vzorkovaní hydrofóbnych látok však ustálenie rovnováhy medzi vzorkovačovm a vodou trvá často veľmi dlho, preto sa na meranie koncentrácií týchto látok vo vode používajú kinetické parametre, ktoré charakterizujú rýchlosť prestupu látky z vody do vzorkovača.

Prestup látky cez medznú vrstvu vody je vo všeobecnosti limitujúcim krokom pre akumuláciu hydrofóbnych látok do vzorkovača. Dôsledkom toho je závislosť vzorkovacích rýchlostí R_S od hydrodynamických podmienok na mieste expozície. Žiaľ, vzorkovacie rýchlosti nie je možné presne odhadnúť z lokálnych hydrodynamických podmienok (t.j. z rýchlosti prúdenia a z intenzity turbulencie toku), takže je potrebné použiť *in situ* kalibračné techniky, ktoré sú založené na použití performančných referenčných látok (PRC).

Difúzia cez membránu je limitujúcim krokom akumulácie pre látky s nízkymi hodnotami permeability. Permeabilita je produktom a difúzneho a rozdeľovacieho koeficienta látky v membráne ($D \times K_{sw}$). Vzorkovacie rýchlosti týchto látok závisia iba na teplote a vzorkovacie rýchlosti získané v laboratóriu sa dajú priamo aplikovať v teréne.

Vplyv závislosti vzorkovacích rýchlostí od rýchlosti prúdenia vody je možné eliminovať pridaním ďalších transportných bariér do vzorkovača, a tiež použitím polárnych membrán. Dôsledkom takéhoto snaženia je ale zvyčajne dramatický pokles vzorkovacích rýchlostí, čo napokon spôsobuje problémy s detegovateľnosťou sledovaných látok v pasívnom vzorkovači. Odhad vzorkovacích rýchlostí *in situ* je možný z rýchlosti disipácie PRC látok zo vzorkovača. Tento prístup je obmedzený malým intervalom hydrofóbnosti látok, pre ktoré sú disipačné rýchlostné konštanty stanoviteľné. Preto je nutné použiť modely, ktoré extrapolujú

vzorkovacie rýchlosti, založené na PRC, pre hydrofóbnejšie látky. Pre spoľahlivý odhad týchto parametrov je potrebné poznať presné experimentálne hodnoty rozdeľovacích koeficientov látok K_{sw}, a tiež hodnoty difúznych koeficientov týchto látok v polymérnych materiáloch, z ktorých sú vzorkovače zhotovené.

Oveľa menej je známe o procesoch, ktoré ovládajú akumuláciu hydrofilných látok do adsorpčných pasívnych vzorkovačov (APV). Modely, ktoré boli odvodené pre rozdeľovacie pasívne vzorkovače (RPV), sú užitočné aj pre pochopenie funkcie vzorkovačov polárnych látok, ale je potrebné spomenúť niektoré významné rozdiely medzi vzorkovačmi APV a RPV. V literatúre je pomerne málo publikovaných hodnôt sorpčných distribučných koeficientov hydrofilných látok pre sorbenty, ktoré sa používajú v APV (Bäuerlein et al., 2012). Vzhľadom na komplexnosť interakcií medzi sorpčnou fázou a analytom je potrebné vyvíjať nové modely, ktoré by boli schopné odhadnúť tieto parametre zo štruktúry molekúl sledovaných látok i zo štruktúry sorpčných miest adsorbentov. Sorpcia hydrofilných látok do membrán a sorpčnej fázy zahŕňa sorpciu na povrchy, a teda sorpčné izotermy sú vo všeobecnosti nelineárne. Tento jav spôsobuje anizotropnú výmenu látok medzi sorbentom a vodou a tiež kompetíciu o sorpčné miesta na povrchu sorbentu. Vzorkovacie rýchlosti pre vzorkovače hydrofilných látok sú vo všeobecnosti nižšie ako pre hydrofóbne látky, čo má za dôsledok vyššie medze detekcie.

Pasívne vzorkovanie má potenciál využitia v regulačnom monitorovaní, pretože umožňuje meranie extrémne nízkych (ale z hľadiska rizík pre životné prostredie a človeka veľmi relevantných!) koncentrácií znečisťujúcich látok vo vodách, poskytuje reprezentatívny obraz o kontaminácii a reflektuje expozíciu vodných organizmov. Rozdeľovacie pasívne vzorkovače už v súčasnosti umožňujú meranie kontaminantov v prostredí s neistotou, ktorá spĺňa požiadavky kladené na metódy, ktoré sa v Európskej únii môžu používať na účel regulačného monitorovania chemických látok vo vodách. Adsorpčné pasívne vzorkovače sú zatiaľ využiteľné hlavne ako nástroj pre skríning znečistenia a pre identifikáciu vodných útvarov so zvýšeným rizikom prekročenia environmentálnych noriem kvality.

Ďalši výskum a vývoj pasívnych vzorkovačov pre monitorovanie chemického znečistenia vodného prostredia by mal mať hlavný cieľ zabezpečiť presnosť meraní získaných touto metódou. Čiastkovými úlohami tohoto výskumu bude a) pochopenie a kvantitatívny opis funkcie adsorpčných pasívnych vzorkovačov, b) vývoj a validácia robustných metód stanovenia znečisťujúcich látok v extraktoch pasívnych vzorkovačov, c) stanovenie kalibračných parametrov pasívnych vzorkovačov a vývoj modelov, ktoré umožnia

nevychýlený odhad koncentrácie sledovaných látok vo vode alebo v inej relevantnej zložke životného prostredia.

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12 Zoznam publikovaných prác k téme habilitačnej práce

Habilitačná práca obsahuje v prílohe niektoré vybrané publikácie, ktoré sa priamo vzťahujú k téme práce, t.j. k vývoju metód pasívneho vzorkovania znečisťujúcich látok vo vodnom prostredí. Sú uvedené publikácie, v ktorých som bol prvým autorom, korešpondujúcim autorom alebo spoluautorom. Tieto práce boli publikované od roku 2001 a sú uvedené v chronologickom poradí. Ďalšie rozdelenie prác je na pôvodné vedecké články v časopisoch, kapitoly v odborných knihách a ďalšie práce.

12.1 Pôvodný vedecký článok v časopise

1. **Vrana B.**, Paschke A., Popp P., and Schüürmann G., Use of semipermeable membrane devices (SPMDs): Determination of bioavailable, organic, waterborne contaminants in the industrial region of Bitterfeld, Saxony-Anhalt, Germany, *Environ. Sci. Pollut. Res*., 2001, 8, 27–34.
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12.2 Kapitoly v odbornej knihe

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12.3 Ďalšie práce

33. **Vrana B**., Vermeirssen E. L. M., Allan I., Kohoutek J., Kennedy K., Mills G., and Greenwood R., Passive sampling of emerging compounds in the environment: state of the art and perspectives, 2010. [Online]. Available: http://www.norman-

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Príloha 1

Vrana B., Paschke A., Popp P., and Schüürmann G., Use of semipermeable membrane devices (SPMDs): Determination of bioavailable, organic, waterborne contaminants in the industrial region of Bitterfeld, Saxony-Anhalt, Germany, ***Environ. Sci. Pollut. Res*.., 2001, 8, 27–34.**

Research Articles

Use of Semipermeable Membrane Devices (SPMDs)

Determination of Bioavailable, Organic, Waterborne Contaminants in the Industrial Region of Bitterfeld, Saxony-Anhalt, Germany

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Abstract. Triolein-containing semipermeable membrane devices (SPMDs) were employed as passive samplers to provide data on the bioavailable fraction of organic, waterborne, organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PAHs) in streams flowing through a highly polluted industrial area of Bitterfeld in Saxony-Anhalt, Germany. The contamination of the region with organic pollutants originates in wastewater effluents from the chemical industry, from over one-hundred years of lignite exploitation, and from chemical waste dumps. The main objective was to characterise time-integrated levels of dissolved contaminants, to use them for identification of spatial trends of contamination, and their relationship to potential pollution sources. SPMDs were deployed for 43 days in the summer of 1998 at four sampling sites. The total concentration of pollutants at sampling sites was found to range from a low of 0.8 µg/SPMD to 25 µg/SPMD for PAHs, and from 0.4 µg/SPMD to 22 µg/SPMD for OCPs, respectively. None of the selected PCB congeners was present at quantifiable levels at any sampling site. A point source of water pollution with OCPs and PAHs was identified in the river system considering the total contaminant concentrations and the distribution of individual compounds accumulated by SPMDs at different sampling sites. SPMD-data was also used to estimate average ambient water concentrations of the contaminants at each field site and compared with concentrations measured in bulk water extracts. The truly dissolved or bioavailable portion of contaminants at different sampling sites ranged from 4% to 86% for the PAHs, and from 8% to 18% for the OCPs included in the estimation. The fraction of individual compounds found in the freely dissolved form can be attributed to the range of their hydrophobicity. In comparison with liquid/liquid extraction of water samples, the SPMD method is more suitable for an assessment of the background concentrations of hydrophobic organic contaminants because of substantially lower method quantification limits. Moreover, contaminant residues sequestered by the SPMDs represent an estimation of the dissolved or readily bioavailable concentration of hydrophobic contaminants in water, which is not provided by most analytical approaches.

Keywords: Bioavailability; monitoring; organochlorine pesticides; passive sampling; persistent organic pollutants; priority pollutants; polyaromatic hydrocarbons; polychlorinated biphenyls; semipermeable membrane devices (SPMDs); water contamination

Introduction

Qualitative and quantitative assessment of pollution of aquatic ecosystems by hydrophobic organic contaminants is a continuing challenge to environmental scientists. The fate and transport of these compounds depends on their physicochemical phase distribution. In aquatic systems, it is important to identify the freely dissolved concentration of a compound. The amount of substance freely dissolved in water also yields an approximate characterisation of the bioavailable fraction [1].

Concentrations of truly dissolved or bioavailable contaminants cannot be determined by most water sampling methods. Instead, total quantities of analytes are measured, including those molecules that are not readily bioavailable because they are bound to dissolved colloids present in water. Moreover, grab water samples provide information only about contaminant concentrations at the moment of sampling and may fail to account for episodic contamination events. Because of the low aqueous solubility of hydrophobic contaminants, it is often impossible to excise sufficiently large water samples to achieve instrumental detection limits. For these reasons, integrative sampling devices are needed which sequester truly dissolved contaminants over a longer time period and provide information about the time-averaged water concentration of contaminants.

Huckins et al. [2,3] described the development of a semipermeable membrane device (SPMD) for passive and integrative *in situ* monitoring of waterborne contaminants. The SPMD sampler consists of layflat, polyethylene tubing containing a thin film of triolein, a high molecular-weight neutral lipid. The polyethylene used in SPMDs is commonly referred to as nonporous, even though transient cavities with diameters approaching about 1 nm are formed by random thermal motions of the polymer chains [3]. The thermally mediated transport corridors of the polyethylene exclude larger molecules, as well as those that are adsorbed on sediments or humic acids. Only truly dissolved (but generally nonionized) contaminants are sequestered. The process mimics the transfer of organic contaminants through biomembranes. The utility of the SPMD has been shown for monitoring aqueous residues of polychlorinated biphenyls, various organochlorine pesticides, polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and polycyclic aromatic compounds.

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Results are reported here from a study where SPMDs were used to obtain information on spatial trends in bioavailable contaminants in a long-term polluted river system of the Mulde River, a major branch of the Elbe River flowing through a highly polluted industrial area of Bitterfeld in Saxony-Anhalt, Germany (**Fig. 1**). The contamination of the region with organic pollutants originates in wastewater effluents from the chemical industry, from over one-hundred years of lignite exploitation, and from chemical waste dumps. During the production of organochlorine insecticides like DDT (dichlorodiphenyl-trichloroethane) and lindane (γ-hexachlorocyclohexane, γ-HCH) in the past decades, the toxic by-product HCH isomers (84% of the produced quantity of HCH isomers) was obtained and deposited on dumps. Most of these dumps located in former lignite pits are not sealed and waste HCH and DDT is washed out by the drainage water before entering the groundwater [4]. About 76 000 tons of HCH isomers, 3000 tons of DDT and its metabolites (DDX), and 13 000 tons of distillation residues containing chlorinated benzenes were deposited during the time period from 1960 to 1982 in the abandoned Antonie lignite pit, located in the centre of the industrial zone near Bitterfeld. The main stream in this area, called the Spittelwasser, served as a wastewater channel for several decades. As a consequence of flood events, the soils of the wetland area along the Spittelwasser also became highly polluted with organic contaminants when the contaminated water covered the wetlands [5,6].

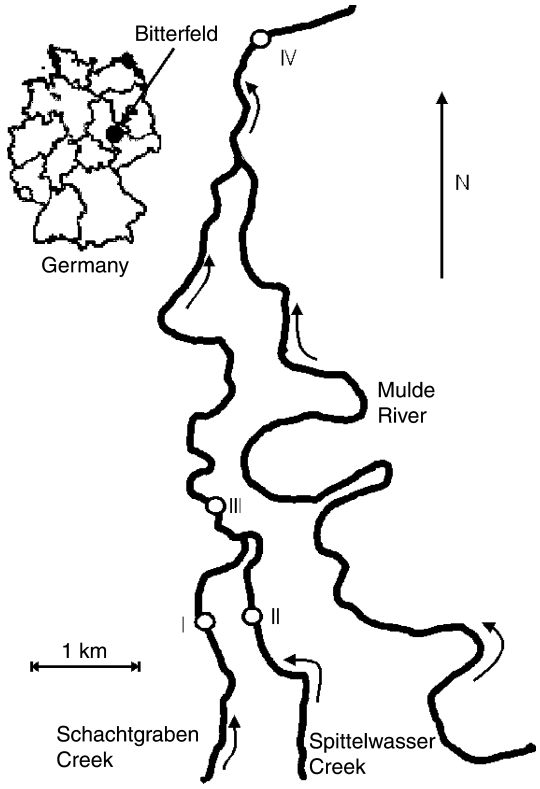

Fig. 1: Map of the streams in the area of Bitterfeld in Saxony-Anhalt, Germany. Hollow circles indicate SPMD deployment sites. The chemical plants in Bitterfeld, and the spring of the Schachtgraben Creek are located 6 km upstream from sampling site I. Arrows show the direction of flow in the streams

The aim of the present study was to characterise spatial variations in the concentrations and relative proportions of the persistent organic pollutants at the various sites, and gradients in river water contamination were identified. In addition, average ambient water concentrations of the organic contaminants were estimated at each field site and compared with concentrations determined in bulk water samples.

1 Experimental Section

1.1 Materials and chemicals

The solvents acetone, dichloromethane, hexane, isopropanol, and toluene in LiChrosolv quality were obtained from Merck. Acetonitrile (HPLC, Ultra Gradient Grade) and HPLC water were purchased from Baker. Hexachlorobenzene (HCB), HCH and DDX reference materials were obtained from Supelco, PAH standard materials from Supelco and PCB reference materials from Promochem.

1.2 Sampling devices

SPMDs with standard configuration, designed by Huckins et al. [2] at the USGS in Columbia, MO, USA, consisting of a thin film of 1 mL of triolein (95% pure) sealed in a low-density, polyethylene, layflat tube (2.54×91.4 cm, 75-90 μm wall thickness), were purchased from Origo Hb, Tavelsjö, Sweden. They were stored in original, gas-tight, metal paint cans until just before field deployment.

1.3 SPMD deployment

The SPMDs were placed at 4 sites in the streams of the Schachtgraben (**Site I**), the Spittelwasser (**Sites II** and **III**; above and below its confluence with the Schachtgraben, respectively), and the Mulde River (**Site IV**; below the tributary of the Spittelwasser), flowing through a highly polluted industrial area of Bitterfeld in Saxony-Anhalt, Germany (**Fig. 1**). The centre of the industrial area of Bitterfeld, including chemical plants and waste dumps, is located 6 km upstream from sampling Site I. The Schachtgraben Creek collects drainage water from this area. The SPMDs were deployed for 43 days during summer 1998 (29th July to 9th September). During the exposure, the water temperature varied from 17.5 to 21.5°C at all sampling sites. On the day of deployment and retrieval of the samples, water temperatures were equal (±1°C) at each sampling site.

Two SPMDs were deployed at each of the four sampling sites. At each deployment site, SPMDs were removed from the metal can and placed into a stainless steel 1 cm mesh frame (20×100 cm) which protected the SPMDs from both sides. SPMDs were secured by fastening their ends to the frame using flat, stainless steel belts which were screwed to opposite ends of the frame. The frame was deployed in the horizontal orientation above the bottom of the stream and held by tent pegs. The depth below the water surface at which SPMDs were deployed at sampling sites ranged from 40 to 70 cm. On day 43, the SPMDs were removed from their frames and immediately sealed in individual amber glass jars.

The jars were transported to the laboratory in a cooler (on ice and in darkness) and were kept in a freezer at -20°C until processing. Exposed SPMDs were analysed for selected PAHs, PCBs and OCPs.

1.4 Sediment and soil samples

A top soil sample from the site located in the floodplain of the Spittelwasser stream near sampling site III and a sediment sample from sampling site III were taken for PAH, PCB and OCP determination. Samples were extracted with toluene using accelerated solvent extraction technique and analysed for PAH, PCB and OCP content as described by Popp et al. (1997) [7].

1.5 Water samples

Water samples were taken from each sampling site at the end of the exposure period. Water samples were sealed in amber glass jars at 4°C until processing. One litre from each water sample was extracted three times with 30 mL toluene. Combined toluene extracts were filtered through anhydrous Na_2SO_4, concentrated by rotary evaporation and by nitrogen blow-down, redissolved in 500 µL acetonitrile and analysed for PCBs, PAHs and OCPs.

1.6 Sample processing and residue enrichment

Biofouling removal. The devices were subjected to an exterior cleanup for biofouling removal. SPMDs were shaken with 50 mL hexane for 20-30 s, rinsed with running deionized water, and scrubbed with soft toothbrushes. After that, they were submerged in 1 M HCl for 30 s, then rinsed with running deionized water, rinsed with acetone and then with isopropanol. SPMDs were then allowed to dry in a glass column in a stream of high-purity nitrogen.

Dialytic recovery of analytes. SPMDs were dialysed three times with 250 mL hexane per SPMD at 18°C for 24 hours. The dialysate volume was reduced to approximately 10 mL by rotary evaporation, and further reduced in volume with streams of high-purity nitrogen to dryness. The residue was redissolved in 5 mL dichloromethane and cleaned up by size exclusion chromatography (SEC).

Size exclusion chromatography. The concentrated dialysate was cleaned up using a high performance SEC column (22.5 mm ID×250 mm, 10 µm particles) Lichrogel® PS 20 (Merck, Germany). The mobile phase for the SEC was dichloromethane (5 mL/min). The collected fraction containing the compounds of interest extended from 85-195 mL. The eluate from SEC was concentrated to approximately 10 mL by rotary evaporation. The volume of concentrated eluate was adjusted to 10 mL. Nonane (100 µL) was added as a keeper. From the eluate, 1 mL was taken and solvent exchanged to 1 mL acetonitrile for HPLC analysis of priority pollutant PAHs. In the remaining 9 mL of eluate, dichloromethane was evaporated using high-purity nitrogen. The residue was redissolved in hexane to 1 mL final volume, and was used for GC analysis of PCBs and OCPs.

1.7 Analysis

The qualitative analysis of the PCBs and OCPs of interest was made by a mass spectrometric detector after separation of the contaminants by GC (HP 5890) using a capillary column (30 m×0.25 mm ID) with a non-polar stationary phase HP5MS (thickness 0.25 µm). Temperature conditions: Injector 250°C, column 80°C (6 min)- 6°C/min- 250°C (8.67 min). For quantitation of the PCBs and OCPs, sample extracts in hexane were analysed by GC (HP 5890) using an electron capture detector (300°C) and a capillary column (25 m×0.32 mm ID) with a non-polar stationary phase Ultra 2 (thickness 0.17 µm). Temperature conditions: Injector 300°C, column 80°C (6 min)- 6°C/min- 250°C (8.67 min). Quantitation of the residues was accomplished using a ten-point, external standard curve.

The extract in acetonitrile was analysed for EPA priority pollutant PAHs by HPLC (HP 1050) using a programmable fluorescence detector and C18 Vydac201TP54 (250×4.6 mm ID) column. The mobile phase was acetonitrile/water pumped at 1 mL/min at 23°C with gradient elution. The composition gradient started with 60% water and 40% acetonitrile (3 min), then the acetonitrile content was increased to 100% in 24 min with a linear gradient. The contents were held constant for 13 min until the end of the analysis. Quantification of the PAH residues was accomplished using a 7-point, external standard curve. Acenaphthylene was not included in the analytical procedure because the substance shows no fluorescence.

1.8 Quality control

Because SPMDs have a propensity to sequester vapour-phase contaminants [8], additional two trip blank SPMDs were exposed to air at each site while the water sampling SPMDs were being deployed and collected. Trip blanks were processed exactly as deployed samples and were used to define contamination of the SPMDs during transportation and handling. In addition, fresh SPMDs were taken through the entire dialytic and cleanup procedure (procedural blanks). Samples containing contaminant residues exceeding the procedural blank values were considered positive for contaminants.

Spiked SPMDs were also analysed by fortifying fresh membranes and then processing them as a sample. The PCBs and OCPs were spiked at 500 ng per SPMD and PAHs at 80 ng per SPMD for each single component. Recovery rate values of the fortified PAHs from SPMDs were good and reproducible, with the exception of naphthalene. Average percent recoveries of the remaining PAHs varied from 56% for indeno[1,2,3] pyrene to 137% for phenanthrene, and the relative standard deviation of three spiked samples did not exceed 11% for any compound. Average percent recoveries for the organochlorine compounds varied from 68% for β-HCH to 125% for PCB 153, and the relative standard deviation of three spiked samples did not exceed 11% for any compound.

Method quantification limits (MQL) for PAHs in SPMDs ranged from 4 ng/SPMD for anthracene to 50 ng/SPMD for chrysene. In bulk water samples, the MQL ranged from 0.2 ng/L for anthracene to 2.5 ng/L for chrysene. MQL for PCBs and OCPs in SPMDs ranged from 0.5 to 2 ng/SPMD.

In water samples, MQL for PCBs and OCPs ranged from 0.25 to 1 ng/L.

2 Results and Discussion

2.1 Occurrence of contaminants

Concentrations of compounds of interest found in the SPMDs exposed for 43 days at different sampling sites are presented in **Table 1**. The concentrations of compounds are adjusted according to their recoveries from fortified SPMDs.

The trip-blank SPMDs were devoid of quantifiable residues of OCPs, PCBs and PAHs, except for naphthalene and phenanthrene; the phenanthrene concentration in the trip blank was much lower (more than 3 times) than its concentration in the SPMDs at sampling sites. Because of high trip-blank values, high differences in results from duplicate samples, and bad recovery from SPMDs, naphthalene was ignored in the further discussion.

Duplicate SPMDs sequestered similar amounts of PAHs and OCPs of interest. In general, the relative percent differences between two SPMDs deployed at the same sampling site did not exceed 29% for PAHs, except for acenaphthene at sampling site III (44%). Relative percent differences for OCPs were not greater than 24%, except for p,p'-DDD at sampling site III (40%).

Prest and Jacobson [9] have shown that the ratio of contaminant concentrations sequestered by two SPMDs at two sampling sites under similar conditions is equal to the ratio of time-averaged aqueous concentrations at the two sampling sites. When using SPMDs with a standard configuration, designed by Huckins et al. [2], mainly temperature and biofouling can effect the sampling rate. We assumed that the hydrodynamic conditions did not effect the uptake kinetics dramatically, although it has been reported that aqueous diffusion boundary layer at the membrane surface controls contaminant uptake for compounds with log

Table 1: Mean concentrations of PAHs and OCPs found in SPMDs (ng SPMD, n=2) (a) and in sediment and top soil samples (ng/g: dry weight based), at sampling sites in the Bitterfeld region

ampling site	Trip blank	Site I	Site II	Site III	Site IV	Sediment at site III	Top soil at site III
AHs							
Naphthalene (b)	86	711	117	378	205	729	1795
Acenaphthene	<10	514	50	168	31	38	25
Fluorene	<50	603	110	246	90	218	132
Phenanthrene	59	1163	290	387	227	2461	1863
Anthracene	<4	775	26	224	16	377	259
Fluoranthene	<30	7420	365	2293	155	1002	1168
Pyrene	7	8420	304	2214	92	2106	1768
Benzo[a]anthracene	<20	1198	41	410	<20	231	231
Chrysene	<50	2918	124	1041	<50	714	1035
Benzo[b]flouranthene	<20	747	36	335	<20	162	NQ (c)
Benzo[k]fluoranthene	<5	343	16	155	<5	114	115
Benzo[a]pyrene	<5	470	14	204	<5	207	122
Dibenz[a,h]anthracene	<15	21	<15	<15	<15	39	40
Benzo[g,h,i]perylene	<15	165	<15	83	<15	212	151
Indeno[1,2,3]pyrene	<25	153	<25	106	<25	210	188
Σ PAHs	152	25621	1493	8243	815	8820	8892
OCPs							
α-HCH	2	4597	21	3283	90	266	5330
β-HCH	1	944	34	1073	42	NQ	5329
γ-HCH	1	1835	11	1551	43	NQ	274
δ-HCH	2	2935	8	2330	32	NQ	660
HCB	3	3955	42	1482	66	402	3276
4,4'-DDD	1	3877	23	1397	106	NQ	842
4,4'-DDE	1	1286	22	318	29	NQ	14
4,4'-DDT	1	2934	15	545	39	NQ	NQ
Σ OCPs	12	22362	176	11979	446	668	15725
Σ PCBs (d)	<6	<6	<6	<6	<6	<6	<6

) Concentrations are recovery-rate-corrected
) Concentrations of naphtalene are not recovery-rate-corrected
) NQ - not quantifiable (presence of interfering peaks)
) PCBs quantified include congeners IUPAC No. 28, 52, 101, 138, 153 and 180

K_{ow}>4.4 at water flow velocities of 30 cm/s and lower [10]. To correct the sampling rate values for the effects of biofouling and the flow velocity, Huckins et al. [3] suggested the use of a permeability reference compound (PRC). PRC is a non-interfering compound with moderate SPMD fugacity added to SPMD lipid prior to exposure. However, the data on this application in practice is still very limited. In this study, water temperatures were comparable (±1°C) at each sampling site. When assuming a similar biofouling at each sampling site, uptake rates were expected to be the same, and the ratio of contaminant concentrations found in SPMD samplers at two sampling sites was considered to be equal to the ratio of average water concentrations at these sites, a finding which must be taken into consideration for further discussion.

2.1.1 PAHs: Absolute concentrations in SPMDs

The sites can be ranked from lowest to highest concentrations of total PAHs as follows: Mulde (site IV), Spittelwasser above its confluence with the Schachtgraben (site II), Spittelwasser below its confluence with the Schachtgraben (site III), and the Schachtgraben (site I). Concentrations of individual PAHs at the sampling sites generally followed the same pattern as the totals (**Table 1**). The PAHs found at the highest level at all four sampling sites (fluoranthene, pyrene, and phenanthrene) are ubiquitous contaminants found in the runoff from urban and industrialised areas, and their origin can be ascribed to combustion and industrial activity [11]. The highest total levels of PAHs sequestered by SPMDs in this study were comparable on the order of magnitude of the amounts found in SPMDs in other studies conducted under similar conditions [10,12,13]. Fluoranthene (the PAH found at the highest level in most samples) concentrations ranged from a low of 155 ng/sample at site IV to a high of 7.4 µg/sample at site I.

The highest total concentration of PAHs, found in SPMDs from the Schachtgraben Creek (site I), is not surprising considering that the Schachtgraben drains away the water from the centre of the industrial area in Bitterfeld. Elevated concentrations of PAHs could also be found in the Spittelwasser River above its confluence with the Schachtgraben (site II). However, the total PAH concentration at the sampling site II was more than one order of magnitude lower than the concentration at the sampling site I. The PAHs found at sampling site II are likely to originate from air deposition and the passage of contaminated groundwater.

Below the confluence of the Schachtgraben, the PAH concentration in the Spittelwasser River (site III) rises more than 10 times in comparison with that at site II. It is likely that this extreme concentration rise originates from the contribution of the Schachtgraben water. At the sampling site in the Mulde River (site IV) about 4 km downstream from sampling site III, near the confluence of the Mulde and the Spittelwasser, the concentration of several PAHs (acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene) was still measurable. It is likely that the water quality in the Mulde River at site IV is negatively influenced by the nearby tributary of the Spittelwasser.

2.1.2 PAH patterns in SPMDs

To examine the relative concentrations of PAHs detected in SPMD samples among sites, the concentrations of individual PAHs were normalised by proportioning to fluoranthene's concentration for each site (**Fig. 2**). No major differences in relative concentrations were determined between site I and site III. In comparison with these sites, samples from sites II and site IV contain relatively higher normalised concentrations for compounds such as acenaphthene, fluorene, and phenanthrene. Among other PAHs, these compounds demonstrate a relatively good aqueous solubility and a low hydrophobicity. These properties allow for transport to longer distances from the pollution source in the dissolved phase. Therefore, we conclude that sampling sites II and IV are more distant from a point source of pollution than sites I and III. This hypothesis is supported by a second observation that sites II and IV contain lower or negligible normalised concentrations for more hydrophobic compounds (log K_{ow}>5.5) in comparison with sites I and III.

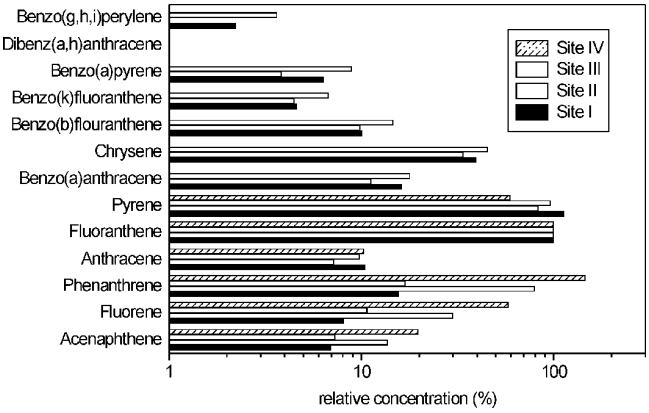

Fig. 2: Patterns of polyaromatic hydrocarbons found in SPMDs exposed for 43 days at four deployment sites presented as fluoranthene normalized concentrations

On the basis of total OCP residues, the sites can be ranked from lowest to highest as follows: Site II, site IV, site III, and site I. The sequestered amounts of OCPs (HCHs, HCB and DDX) were up to several orders of magnitude higher than observed in other studies [14-16]. None of the selected PCBs was present at quantifiable levels at any sampling site.

Below the confluence of the Schachtgraben, the concentration of total OCPs of interest in the Spittelwasser stream (site III) rises almost two orders of magnitude. The OCP concentration in the Mulde River (site IV) was low; nevertheless, it was almost three times higher than that found at site II.

HCB (the organochlorine compound found at the highest level in all samples) concentrations ranged from 42 ng/sample at site II to 4.0 µg/sample at site I. As concluded for PAHs, the most probably contamination source of the water in the Spittelwasser is the Schachtgraben tributary.

The spatial trends in the HCH (summed-up) concentrations were similar as determined for total OCPs, ranging from 74 ng/sample at site II to 10.3 µg/sample at site I.

The DDX components found in the samples were 4,4'-DDD (from 23 ng/sample to 3.9 µg/sample), 4,4'-DDE (from 22 ng/sample to 1.3 µg/sample), and 4,4'-DDT (from 15 ng/sample to 2.9 µg/sample), with the spatial trends similar to total OCPs.

2.1.3 OCPs in SPMDs

On the basis of the comparison of total contaminant concentrations sequestered by SPMDs at different sampling sites, but also after considering the distribution of individual compounds sampled by SPMDs at the sampling sites, we conclude that there is a point source of water pollution upstream to sampling site I in the Schachtgraben Creek. The concentration of PAHs and OCPs at sampling site III might be additionally elevated due to contaminant mobilization from historically contaminated sediments and soils of the wetland area along the Spittelwasser, which are likely to cause additional diffuse entries (**Table 1**). A simple, quantitative, intersite comparison between water and sediment or soil from a specific site cannot be made since the sampled contaminants in the water column were sampled using SPMDs during a relatively short exposure period, whereas the contaminants in sediment were deposited during long time periods (months to years). Moreover, processes having control over the accumulation of contaminants from water to sediment, soil and SPMDs are of a different character. However, the PAH patterns of the three matrices sampled at this site (i.e. SPMD, sediment and top soil) have similar profiles, which suggests that the sources of the contamination might be the same between the past and present.

2.2 Water concentration estimation

Using models previously developed [3] and applied [15-18], the time-averaged, bioavailable, waterborne concentrations of OCPs and PAHs at the sampling sites were estimated from concentrations in the SPMDs exposed in this study. The details of the model development are available [3,19] and will not be presented here. Equation 1 was used to calculate the dissolved (i.e. readily available), waterborne concentrations of compounds.

$$C_w = \frac{C_{SPMD} V_{SPMD}}{R_{sc} t} \quad (1)$$

As applied here, C_w is the concentration of the analyte in water, C_{SPMD} is the concentration of the analyte in the SPMD (lipid+membrane), t is the exposure time in days, V_{SPMD} is the volume of the SPMD (lipid+membrane), and R_{sc} is the SPMD sampling rate which is given by

$$R_{sc} = R_s F_i \quad (2)$$

where F_i is 1 – the fractional reduction in uptake flux or sampling rate due to fouling impedance. Sampling rates for the PAHs at 18°C have been reported [19], and were utilised for water concentration estimation in this study. Sampling rate (R_s) data for the OCPs at 26°C reported by Huckins et al. [20] is based on the analyte concentrations determined only in lipid.

$$C_w = \frac{C_l V_l}{R_{sc} t} \quad (3)$$

To utilise this data for an estimation of the water concentration of OCPs, the concentration of analytes in the lipid phase C_l was calculated from the total analyte mass in a SPMD dialysate (M_d: averaged value from two parallel SPMDs) as described by the relationship [3].

$$C_l = M_d / \left(M_l + K_{ml} M_m\right) \quad (4)$$

where M_l and M_m are the weights of the lipid and the membrane. For a first approximation, a substance-unspecific, membrane/lipid, partition coefficient (K_{ml}) of 0.1 was used as shown by Huckins et al. [3]. This results in an analyte distribution of 73% in the lipid and 27% in the membrane [18] for the linear uptake phase.

An average fouling resistance of 20% (F_i = 0.8) was employed for biofouled SPMDs to correct for reduction in SPMD uptake [16,18] SPMD sampling rates for PAHs and OCPs are given in **Table 2**.

The estimation of time-averaged water concentration using equations (1) and (3) has one limitation, it is applicable only for highly hydrophobic substances with log K_{ow} values higher than 4. Gale [21] showed that the linear uptake model cannot be applied for compounds with lower hydrophobicity, because SPMDs do not sample these chemicals integratively during exposure periods longer than several weeks. Therefore, the estimation was not applied for acenaphthene, fluorene, and HCH isomers.

The estimated ambient concentrations of selected contaminants are presented in **Table 2**. Note that the water concentration estimated with the SPMDs is an average concentration over a 43 d interval, not the maximum concentration during that interval.

When method quantification limits in SPMDs for contaminants selected for an estimation of aqueous concentrations were substituted into the linear model equations (1) and (3), the resulting MQL values for PAHs in water were lowered to between 0.04 ng/L for anthracene and 0.39 ng/L for chrysene. For OCPs, the MQL in water were even lower, ranging between 1 pg/L for HCB and 10 pg/L for 4,4'-DDT. The SPMD MQL values are substantially lower than the MQL determined with the water extraction method, on average by a factor of 5 for PAHs and by a factor of 150 for OCPs, respectively. The MQL of the direct water analysis could be lowered by extracting larger volumes of water, although quality control and physical difficulties are often encountered when collecting and extracting large water volumes needed for the quantitation of trace organic contaminants. Therefore, in comparison with direct water analysis, the SPMD method is more suitable for the assessment of background concentrations of hydrophobic organic contaminants.

The estimated water concentrations (C_w) are comparable to or lower than concentrations measured in bulk water extracts (C_b). The discrepancy between C_w and C_b can be explained by the fact that C_w represents only the truly dissolved (readily bioavailable) fraction of contaminants in

Table 2: Estimates of truly dissolved aqueous concentrations from SPMDs C_w at sampling sites, and concentrations measured in bulk water samples C_b. Concentrations reported are in ng/L. Published sampling rates (R_s) for individual PAHs [19] and for OCPs [20] were used to estimate the C_w values

	Rs	Site I		Site II		Site III		Site IV	
Compound	**(L/d)**	C_w	C_b	C_w	C_b	C_w	C_b	C_w	C_b
PAHs									
Phenanthrene	3.8	8.9	85.8	2.2	29.3	3.0	52.6	1.7	57.1
Anthracene	2.9	7.8	8.2	0.3	3.7	2.2	7.1	0.2	5.0
Fluoranthene	3.6	59.9	38.8	2.9	6.0	18.5	31.1	1.3	12.7
Pyrene	4.5	54.4	50.8	2.0	9.1	14.3	30.8	0.6	12.7
Benzo[a]anthracene	3.2	10.9	3.9	0.4	<1.0	3.7	2.6	NR	2.1
Chrysene	3.7	22.9	NQ	1.0	NQ	8.2	NQ	NR	<2.5
Benzo[b]flouranthene	2.8	7.8	3.4	0.4	<1.0	3.5	3.3	NR	<1.0
Benzo[k]fluoranthene	2.9	3.4	3.5	0.2	0.4	1.6	1.4	NR	0.9
Benzo[a]pyrene	3.2	4.3	8.4	0.1	1.8	1.9	4.3	NR	3.6
Dibenz[a,h]anthracene	2.0	0.3	1.2	NR	<0.8	NR	<0.8	NR	<0.8
Benzo[g,h,i]perylene	1.8	2.7	7.9	NR	2.2	1.3	4.1	NR	4.1
Indeno[1,2,3]pyrene	3.0	1.5	4.3	NR	<1.3	1.0	1.8	NR	<1.3
Σ PAHs		184.7	216.1	9.4	53.4	59.2	139.8	3.7	98.2
OCPs									
HCB	8.2	10.2	NQ	0.1	NQ	3.8	NQ	0.2	NQ
4,4'-DDD	5.0	16.5	86.0	0.1	<0.5	5.9	75.0	0.5	5.0
4,4'-DDE	7.6	3.7	7.0	0.1	<0.4	0.9	5.0	0.1	<0.4
4,4'-DDT	4.4	14.1	221.0	0.1	<1	2.6	80.0	0.2	<1
Σ OCPs		44.6	314.0	0.3	NQ	13.3	160.0	0.9	5.0

NQ - not quantifiable (presence of interfering peaks)
NR - no residue was found in SPMD sampler

water, whereas C_b includes both contaminants dissolved and bound to the dissolved organic matter. The ratio C_w/C_b shows that the bioavailability of hydrophobic compounds is strongly affected by the dissolved organic carbon (DOC) content of the water, which ranged from 4.5 to 11.2 mg/L in water samples taken at the four sampling sites. The truly dissolved or bioavailable portion of contaminants at different sampling sites ranges from 4% to 86% for the PAHs, and from 8% to 18% for the OCPs included in the estimation. For individual compounds, differences in the percentages found in the freely dissolved form can be attributed to the range of their hydrophobicity. For PAHs with moderate hydrophobicity, the portion bound to DOC seems to be low or even negligible (with the exception of phenanthrene), whereas the PAHs with high log K_{ow} values, and the DDX will be partitioned to DOC to a greater extent.

3 Conclusions

This study is the first field application of SPMDs reported in Germany and it confirms that this sampling method is convenient for the continuous monitoring of hydrophobic organic contaminants in a watercourse. The SPMD technique has several important advantages over conventional episodic analytic measurements. The devices can be used in the field with only little technical support, which is particularly useful for monitoring programmes in remote regions. Due to the principally great flexibility in selecting sampling sites, this technique enables a pseudo-continuous monitoring of hydrophobic pollutants along potentially relevant emission and transfer pathways, thus allowing one to unravel pollution sources in cases of both episodic contamination events as well as long-term, low-dose contamination. The integrative approach allows one to reduce the costs of monitoring campaigns by a substantial reduction of the required sampling frequency. An estimate of average water concentrations over an extended period of time can be obtained in contrast to conventional direct water sampling and liquid/liquid extraction unless a water sample is continually collected, composited and analysed over the time period. Moreover, the SPMD MQL values for estimation of the water concentration have been shown to be up to two orders of magnitude lower than MQL determined with the conventional water extraction method. However, more substance-specific, sampling rate data is needed to allow for the estimation of average ambient water concentrations of a broader range of contaminants. Also, more research is necessary to examine the effect of different milieu conditions on the sampling function (pH, salinity, hydrodynamics, temperature, dissolved organic matter), which is important for the purpose of deriving reliable quantitative results under in situ conditions. To make the technique more suitable for routine monitoring, a less expensive and less time consuming sample processing would be required. A simplified sample extraction and cleanup with reduced solvent consumption would also reduce the risk of sample contamination during handling in the laboratory.

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Polyaromatic hydrocarbon concentrations and patterns in sediments and surface water of the Mansfeld region, Saxony-Anhalt, Germany†

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The composition and spatial distribution of polyaromatic hydrocarbons (PAHs) and their relation to potential pollution sources were investigated in the Böse Sieben Creek, Saxony-Anhalt, Germany, using two techniques: semipermeable membrane devices (SPMDs) and sediment analysis. SPMD is an integrative device that passively samples hydrophobic chemicals of low to moderate molecular weight (<600 Da) in water. SPMDs were placed in water for 34 days at three sites where sediments were also sampled. Fifteen PAHs were determined in SPMDs and in sediment samples to evaluate the concentration levels and specific PAH patterns. Time-weighted average aqueous PAH concentrations were estimated from the PAH amount accumulated in SPMDs during the deployment period using previously reported sampling rates. Sediment–water partition coefficients were used to estimate PAH concentrations in pore water from sediments. Calculated pore water concentrations were, on average, almost three orders of magnitude higher than those calculated from SPMDs. Thus, in addition to contamination from other sources, the water concentration at the sampling sites might be elevated due to contaminant mobilization from historically contaminated sediments. Relative PAH patterns from SPMDs and sediment were compared using principal component analysis, and were correlated with the PAH patterns from different potential contamination sources, including Theisen sludge, one of the by-products of the smelting process for copper production in the region in the past, which is likely to be the main contamination source of PAHs. Moreover, three origin indices (concentration ratios of PAH isomer pairs) were used to evaluate the suitability of these compounds as tracers to distinguish between the contamination arising from different sources. The evaluation of contaminant patterns permits the conclusion that the PAHs are of pyrolytic, industrial origin, possibly including contamination by Theisen sludge, and rules out a petrogenic source for the hydrocarbons.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) form a widespread class of environmental chemical pollutants. They arise from the incomplete combustion of recent and fossil organic matter in flames, engines and industrial processes (pyrolytic origin), from emissions of non-combustion-derived matter (petrogenic origin) and from the post-depositional transformation of biogenic precursors (diagenetic origin).[1,2] PAHs enter surface waters mainly *via* atmospheric fallout, urban run-off, municipal effluents and oil spillage or leakage. After entering the aquatic environment, their behaviour and fate depend on their physicochemical properties.[3,4] Volatilization, dissolution, adsorption onto suspended solids and subsequent sedimentation, biotic and abiotic degradation, uptake by aquatic organisms and accumulation are all major processes to which PAHs in water are subjected. Due to their low aqueous solubilities and hydrophobic nature (log K_{ow} = 3–8), the concentrations of dissolved PAHs in water are very low. Otherwise, PAHs associate easily with particulate matter and are finally deposited in the sediment.[3,5]

In the Mansfeld region of Saxony-Anhalt, Germany, one of the potential emission sources of PAHs originates from the traditional mining and processing of Kupferschiefer, a metalliferous Permian black marine shale. For more than 800 years, this bituminous shale was mined for copper and smelted in a coke-fired blast furnace to produce copper. One of the by-products of the smelting process, originating from the washing procedure of the flue dust from the furnace, is the 'Theisen sludge'. By 1990, when mining and copper production were stopped, a total of approximately 220 000 tons of this slurry had been deposited at several sites. These deposits were neither sealed from the ground nor covered, and were therefore a major source of contamination to surface water, groundwater and soil. In addition to the large quantity of heavy metals and metalloids, the Theisen sludge material contains substantial amounts of PAHs, dioxins and furans.[6] Although the majority of the hydrocarbons involve a mixture of polyaromatic hydrocarbons with a high boiling point, additional alkylated homologues and partially hydrogenated aromatics have also been detected. The extremely fine-grained nature of the material facilitates emissions into the environment, in particular into surface water and groundwater adjacent to the present deposit. Therefore, Theisen sludge can cause major environmental problems. No reliable information is available on the aqueous concentrations of PAHs in the streams of the region of Mansfeld. However, a few measurements have detected elevated PAH levels in the region. In addition, studies have been conducted to assess the leaching behaviour of Theisen sludge, which indicated the elevated remobilization potential of the PAHs from this material.[7]

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The main objective of this study was to assess the level of contamination by PAHs in the stream of the Böse Sieben due to industrial historical activities in the study area and, in particular, to identify the PAH composition, spatial distribution and potential pollution sources. The small river collects surface water from the Mansfeld region. Surficial sediment samples and passive samplers (semipermeable membrane devices, SPMDs) from three sampling locations were analysed for PAHs to obtain information on the concentrations of PAHs in the sediment and aqueous phase. SPMDs are innovative devices suitable for the passive and integrative *in situ* monitoring of dissolved water-borne contaminants.[8,9] The SPMD sampler consists of lay-flat polyethylene tubing containing a thin film of triolein, a high molecular weight neutral lipid. The utility of SPMDs has been shown in monitoring aqueous residues of polychlorinated biphenyls (PCBs),[10] various organochlorine pesticides,[11] polychlorinated dibenzofurans and dibenzo-*p*-dioxins[12] and polycyclic aromatic compounds.[13]

Experimental section

Materials and chemicals

The 15 PAHs analysed in the samples are listed in Table 1. The solvents acetone, dichloromethane, hexane, isopropanol and toluene (LiChrosolv quality) were obtained from Merck (Darmstadt, Germany). Acetonitrile (HPLC, Ultra Gradient Grade) and HPLC water were purchased from Baker (Deventer, The Netherlands). A standard solution of a PAH mixture in methanol was purchased from Supelco (Deisenhofen, Germany).

Sampling devices

SPMDs with a standard configuration (2.54 cm × 91.4 cm; 75–90 μm membrane thickness; total mass, 4.3 g each), designed by Huckins *et al.*[8] at the USGS in Columbia, MO, USA, were assembled from low density polyethylene lay-flat tubing containing a thin film of 95% pure triolein (1 mL). They were purchased from Exposmeter, Tavelsjö, Sweden, and were stored in original, gas-tight, metal paint cans until just before field deployment.

SPMD deployment

The SPMDs were placed at three sites in the stream of the Böse Sieben [near Wimmelburg (Site I), the Böse Sieben near Unterrißdorf (Site II) and the Süßer See lake (Site III), near the mouth of the Böse Sieben], in the Mansfeld region in Saxony-Anhalt, Germany (Fig. 1). The river basin of the Böse Sieben comprises almost the whole area affected by copper mining and processing.

The SPMDs were deployed for 34 days during the autumn of 1998 (18th September to 22nd October). During exposure, the average water temperature varied from 12 to 14 °C at all sampling sites. Two SPMDs were deployed at each of the three sampling sites. At each deployment site, SPMDs were removed from the metal can and placed into a stainless steel 1 cm mesh frame (20 cm × 100 cm) which protected the SPMDs from both sides. SPMDs were secured by fastening their ends to the frame using flat, stainless steel belts screwed to opposite ends of the frame. The frame was deployed in a horizontal orientation above the bottom of the stream and held by tent pegs. The depth below the water surface at which SPMDs were deployed at the sampling sites ranged from 15 to 90 cm. On day 34, the SPMDs were removed from their frames and immediately sealed in individual amber glass jars. The jars were transported to the laboratory in a cooler (on ice and in darkness) and were kept in a freezer at −20 °C until processing. Exposed SPMDs were analysed for selected PAHs.

Sediment samples

Sediment samples from the sampling sites were collected using an Ekman–Birge grab (Hydro-Bios Apparatebau GmbH, Kiel, Germany), which penetrated about 15 cm and collected about 0.1 m^2 of surface sediments. Samples were air dried and the coarse material (>2.5 mm) was removed. Duplicate sediment samples were extracted with toluene using the optimized accelerated solvent extraction technique, as described by Popp *et al.*[14] Solvent exchange to acetonitrile was performed prior to HPLC analysis of PAHs. The organic carbon content of the sediment sample was measured with a total organic carbon (TOC) analyser (Leco) using sample combustion at 1000 °C.

SPMD processing

SPMD processing has been described previously.[15] Briefly, the devices were subjected to exterior clean-up for biofouling removal. SPMDs were then dialysed three times with 250 mL of hexane per SPMD at 18 °C for 24 h and cleaned up by size exclusion chromatography (SEC). The SEC fraction containing the PAHs was collected, and solvent exchange from dichloromethane to acetonitrile was performed prior to HPLC analysis of PAHs.

Table 1 Mean concentrations of PAHs in SPMDs (ng per SPMD; $n = 2$; mass of SPMD, 4.28 g) and in sediment samples (ng g^{-1}, dry weight based) at sampling sites in the Mansfeld region

PAH	No.	Sediment, Site I	Sediment, Site II	Sediment, Site III	SPMD[a], trip blank	SPMD, Site I	SPMD, Site II	SPMD, Site III
Naphthalene[b]		<5	28	205	168	292	235	286
Acenaphthene	1	11	23	59	<10	24	36	51
Fluorene	2	52	33	216	<50	122	160	217
Phenanthrene	3	1024	546	2208	20	513	762	710
Anthracene	4	196	81	371	<4	52	62	91
Fluoranthene	5	1670	801	2393	<30	715	821	1048
Pyrene	6	1272	659	1624	8	933	956	1073
Benzo[*a*]anthracene	7	702	338	723	<20	105	89	97
Chrysene	8	682	667	798	<50	170	189	168
Benzo[*b*]fluoranthene	9	679	407	569	<20	74	57	80
Benzo[*k*]fluoranthene	10	274	210	215	<5	31	26	31
Benzo[*a*]pyrene	11	546	441	425	<5	31	26	33
Dibenz[*a*,*h*]anthracene	12	103	79	78	<15	<15	15	<15
Benzo[*g*,*h*,*i*]perylene	13	389	359	283	<15	14	31	25
Indeno[1,2,3]pyrene	14	329	417	206	<25	<25	27	<25
Sum of PAHs		7929	5089	10373	197	3077	3491	3910

[a]Concentrations found in SPMDs are recovery rate corrected. [b]Concentrations of naphthalene are not recovery rate corrected.

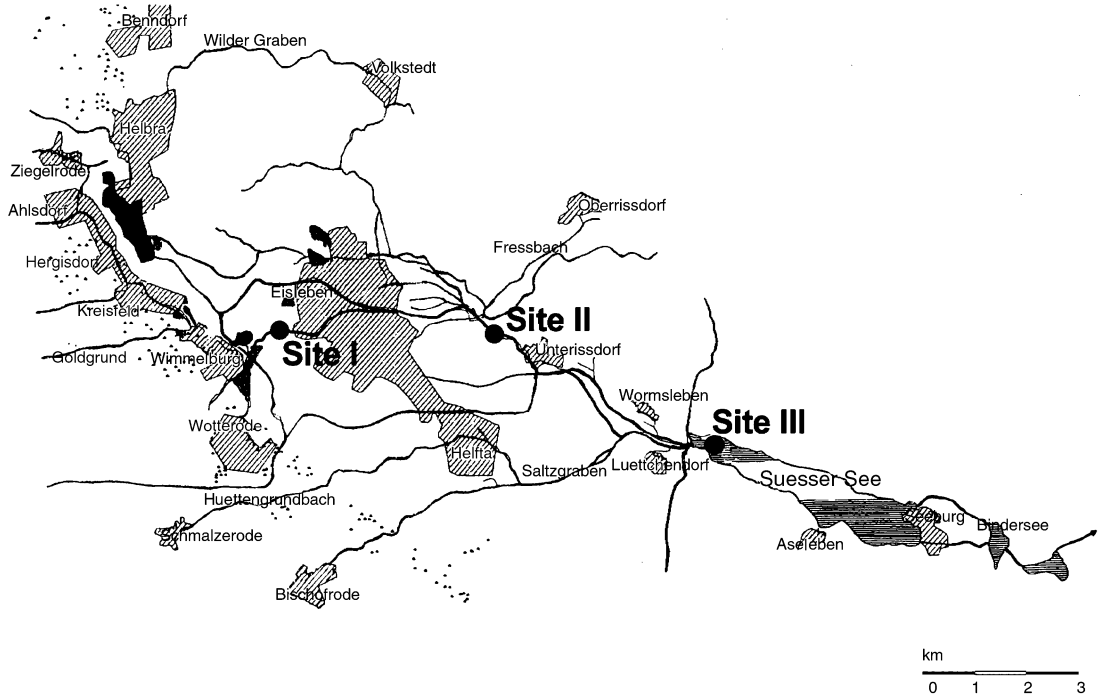

Fig. 1 Map of the sampling sites (filled circles) in the stream Böse Sieben in the Mansfeld region in Saxony-Anhalt, Germany. The black areas on the left of the map represent the heaps and ponds from copper mining and processing.

Quality control

Because SPMDs have a propensity to sequester vapour phase contaminants,[16] additional two trip blank SPMDs were exposed to air at each site while the water sampling SPMDs were being deployed and collected. Trip blanks were processed exactly as deployed samples and were used to define the contamination of the SPMDs during transportation and handling. In addition, fresh SPMDs were taken through the entire dialysis and clean-up procedure (procedural blanks). Spiked SPMDs were also analysed by fortifying fresh membranes and then processing them as samples. PAHs were spiked at 80 ng per SPMD for each individual component. Recovery rate values of the fortified PAHs from SPMDs were good and reproducible, with the exception of naphthalene. The average percentage recoveries of the remaining PAHs varied from 56% for indeno[1,2,3]pyrene to 117% for phenanthrene, and the relative standard deviation of three spiked samples did not exceed 11% for any compound.

Analysis

PAHs in sediment and SPMD extracts were analysed by HPLC (HP 1050) using a C18 Vydac201TP54 (250 mm × 4.6 mm id) column and a programmable fluorescence detector (FD). The mobile phase was acetonitrile–water pumped at 1 mL min^{-1} at 23 °C with gradient elution. The gradient elution started with 60% water and 40% acetonitrile (3 min); then, the acetonitrile content was increased with a linear gradient to 100% in 24 min, and was maintained in this condition for 13 min. Quantification of the PAH residues was accomplished using a seven-point, external standard curve. The standard curves were linear, with correlation coefficients for the investigated PAHs ranging between 0.996 and 0.999. No internal standards were employed for quantification using HPLC with FD; nevertheless, quantification using an external standard only is also permitted in the standard EPA 610 method. Method quantification limits (MQLs) for PAHs in sample extracts calculated from procedural blanks were determined as the average concentration plus ten times the standard deviation of the procedure blanks, ranging from 4 ng mL^{-1} for anthracene to 50 ng mL^{-1} for chrysene. Acenaphthylene was not included in the analytical procedure because the compound shows no fluorescence.

Distribution of PAHs using principal component analysis

Principal component analysis (PCA) was used to compare the PAH distribution in different matrices (sediment, SPMD and aqueous phase) at the sampling sites. This was performed on data standardized to the total PAH concentration of each sample, focusing on relative patterns. The PCA represents the patterns by arranging the PAHs (variables) and sites along axes (principal components), which are assumed to represent basic factors or relationships. The first principal component (PC1) describes the maximum amount of variation of the data. Subsequent calculated principal components (PC2, PC3, *etc.*) describe the remaining variation of the data in decreasing order of importance. Each PC is orthogonal (uncorrelated) to the previous one. The results are depicted in plots of samples and variables, with the variables represented by lines running from the origin of the plot to the position of the variable loadings. The lines point in the direction of increasing variable relative concentrations, and the length of the line represents the extent of the increase. Data were modelled by PCA with KyPlot software.[17]

Results and discussion

Absolute concentrations of PAHs in sediments and SPMDs

The concentrations of the compounds of interest found in the sediments and the SPMDs exposed for 34 days at different sampling sites are presented in Table 1. Quantifiable amounts of all PAHs were found in sediments from all sampling sites. On average, the total PAH concentrations in the sediments were approximately ten times those found in the SPMDs on a μg g^{-1} basis. On the basis of total PAH residues, the sites can be ranked from lowest to highest as follows: Site II < Site I < Site III. The PAH concentrations in sediments ranged from 5.1 μg g^{-1} at Site II to 10.4 μg g^{-1} at Site III. The average relative percentage difference between duplicate sediment

samples from the same sampling site was 10%, and never exceeded 40%. The pollution levels can be assigned as elevated, although below the maximum admissible concentration of 20 μg g^{-1} set by the Directive on the Disposal of Dredged Materials of Saxony-Anhalt.[18]

Apart from dibenz(*a*,*h*)anthracene and indeno(1,2,3)pyrene at sampling sites I and III, all PAHs were also quantified in the SPMD samples. The concentrations of compounds in SPMDs (Table 1) were adjusted according to their recoveries from fortified SPMDs. The trip blank SPMDs were devoid of quantifiable residues of PAHs, except for naphthalene, phenanthrene and pyrene. Only naphthalene was ignored in further discussions because of high trip blank values, large differences in results from duplicate samples and poor recovery from SPMDs; the phenanthrene and pyrene concentrations in the trip blanks were much lower (more than 20 and 100 times, respectively) than their concentrations in the SPMDs at the sampling sites. The average relative percentage difference between two SPMDs deployed at the same sampling site was 23%, and never exceeded 40%.

The sites can be ranked from the lowest to the highest concentrations of total PAHs in SPMD samples as follows: Site I < Site II < Site III. The PAH concentrations increase downstream towards the mouth of Böse Sieben to the Süßer See lake. The concentrations of individual PAHs at the sampling sites generally followed the same pattern as the totals (Table 1). The highest total levels of PAHs sequestered by SPMDs in this study were of a comparable order of magnitude to the amounts found in SPMDs in other studies conducted under similar conditions.[19–21] The PAH concentrations ranged from a low of 3.1 μg per SPMD at Site I to a high of 3.9 μg per SPMD at Site III.

SPMD and sediment samples provide complementary information. PAH concentrations in sediments reflect long periods of time, because sediments are sinks for hydrophobic contaminants, while SPMDs only integrate water concentrations during the sampling period. Moreover, PAHs present in sediments are bound to particles, whereas SPMDs sample only PAHs truly dissolved in the water column.

Water concentration estimation

Sediment-based PAH concentrations in water (pore water) (C_{WS}) were estimated from the concentrations found in sediment (C_S) using the equilibrium partitioning approach discussed by Di Toro *et al.*[22]

$$C_{WS} = C_S/(f_{oc}\rho K_{oc}) \quad (1)$$

where f_{oc} is the fraction of sediment organic carbon, ρ is the sediment bulk density and K_{oc} is the sediment organic carbon–water partition coefficient. K_{oc} was calculated using Karickoff's approximation,[23] *i.e.* $K_{oc} = 0.41 \times K_{ow}$. The octanol–water partition coefficient values (K_{ow}) of the PAHs utilized for the calculation are given in Table 2. f_{oc} measured in sediments was 3.92% at Site I, 1.56% at Site II and 4.86% at Site III. The substitution of Karickoff's equation by alternative correlations recently proposed to estimate K_{oc} from K_{ow}[25,26] yields PAH concentrations in pore water comparable (of the same order of magnitude) to the estimation results given in Table 2.

The time-averaged water-borne concentrations of PAHs at the sampling sites can also be estimated from concentrations in exposed SPMDs. The details of the model development are available elsewhere,[9,27,28] and are not presented here. In general, ambient water concentrations can be calculated using

$$C_{WM} = C_M/K_M[1 - \exp(-k_e t)] \quad (2)$$

As applied here, C_{WM} is the concentration of the analyte in water derived from SPMD (estimate of average value over the exposure period), C_M is the concentration of the analyte in the SPMD (lipid + membrane), t is the exposure time in days, k_e is the exchange rate constant for both overall uptake and elimination and K_M is the equilibrium partition coefficient between SPMD and water.

The selection of the most appropriate approach to estimate aqueous concentrations from concentrations in exposed SPMDs depends on whether the overall uptake is linear, curvilinear or equilibrium is attained between the SPMD and the aqueous phase during exposure.[11] The time an analyte remains in the linear uptake phase (first-order uptake half-time, $t_{1/2}$) can be estimated from the reported equilibrium partitioning coefficient (K_M) and actual sampling rate (R_{SC}) for a specific average temperature value at each sampling site using

$$t_{1/2} = (\ln 2)K_M V_M/R_{SC} \quad (3)$$

where V_M is the volume of the SPMD (lipid + membrane) and R_{SC} is the SPMD sampling rate given by

$$R_{SC} = R_S F_i \quad (4)$$

where F_i is 1 − the fractional reduction in uptake flux or sampling rate R_S determined under defined conditions due to fouling impedance.

R_{SC} is related to k_e by

$$R_{SC} = k_e K_M V_M \quad (5)$$

The chemical uptake into SPMD remains linear and integrative in the initial period of the exposure until the concentration factor (ratio C_M/C_{WM}) in the SPMD reaches approximately half-saturation ($k_e t < \ln 2$) and eqn. (2) can be reduced to

$$C_{WM} = (C_M V_M)/(R_{SC} t) \quad (6)$$

Among environmental variables, mainly temperature and biofouling can affect the sampling rate. We assumed that the hydrodynamic conditions at the sampling sites did not affect the uptake kinetics dramatically, although it has been reported that the aqueous diffusion boundary layer at the membrane surface affects contaminant uptake for compounds with log $K_{ow} > 4.5$.[15,29] In general, elevated sampling rates are expected in turbulent environments, and the application of laboratory-derived sampling rates may cause overestimation of the aqueous concentrations. Sampling rates for the PAHs at different temperatures have been reported,[27] and were utilized for water concentration estimation in this study. The sampling

Table 2 Estimates of dissolved pore water concentrations from sediments, C_{WS}, at the sampling sites. Concentrations reported are in ng L^{-1}. Recommended octanol–water partition coefficients for individual PAHs[24] were used to estimate the C_{WS} values using eqn. (1)

PAH	log K_{ow}	Site I, C_{WS}	Site II, C_{WS}	Site III, C_{WS}
Acenaphthene	4.0	68.5	920.6	758.8
Fluorene	4.2	523.3	833.4	1752.8
Phenanthrene	4.5	5164.5	6910.7	8979.8
Anthracene	4.6	785.2	814.4	1198.5
Fluoranthene	5.1	2115.6	2546.6	2444.6
Pyrene	5.1	1611.4	2095.2	1659.0
Benzo[*a*]anthracene	5.9	140.9	170.3	117.1
Chrysene	5.7	217.0	532.7	204.8
Benzo[*b*]fluoranthene	5.8	171.6	258.2	116.0
Benzo[*k*]fluoranthene	6.0	43.7	84.1	27.7
Benzo[*a*]pyrene	6.2	54.9	111.4	34.5
Dibenz[*a*,*h*]anthracene	6.8	2.9	5.6	1.8
Benzo[*g*,*h*,*i*]perylene	6.9	7.8	18.1	4.6
Indeno[1,2,3]pyrene	6.8	8.3	26.5	4.2
Σ PAHs		10915.8	15327.6	17304.0

Table 3 Estimates of dissolved aqueous concentrations from SPMDs, C_{WM}, at sampling sites. Concentrations reported are in ng L^{-1}. Published sampling rates (R_S) and equilibrium SPMD–water partition coefficients (K_M) for individual PAHs[27] were utilized to estimate the C_{WM} values using eqn. (2) (curvilinear model) and eqn. (6) (linear model), respectively

PAH	MW	log K_M	R_S @ 10 °C/L d^{-1}	R_S @ 18 °C/L d^{-1}	Site I, C_{WM}	Site II, C_{WM}	Site III, C_{WM}	Model used
Acenaphthene	154.2	4.05	2.7	2.3	0.7	1.0	1.4	Curvilinear
Fluorene	166.2	4.21	3.0	1.7	2.7	3.7	5.3	Curvilinear
Phenanthrene	178.2	4.47	3.8	3.6	3.4	5.1	4.8	Linear
Anthracene	178.2	4.67	2.9	3.6	0.4	0.5	0.7	Linear
Fluoranthene	202.3	4.68	3.6	4.5	4.6	5.2	6.4	Linear
Pyrene	202.3	4.79	4.5	5.2	4.9	5.0	5.5	Linear
Benzo[*a*]anthracene	228.3	5.32	3.2	3.2	0.8	0.7	0.7	Linear
Chrysene	228.3	5.32	3.7	4.8	1.1	1.1	1.0	Linear
Benzo[*b*]fluoranthene	252.3	5.55	2.8	3.0	0.6	0.5	0.7	Linear
Benzo[*k*]fluoranthene	252.3	5.44	2.9	3.9	0.2	0.2	0.2	Linear
Benzo[*a*]pyrene	252.3	5.11	3.2	3.7	0.2	0.2	0.2	Linear
Dibenz[*a*,*h*]anthracene	278.4	4.83	3.0	3.8	NR[a]	0.1	NR	Linear
Benzo[*g*,*h*,*i*]perylene	276.3	4.51	2.0	3.0	0.2	0.3	0.2	Linear
Indeno[1,2,3]pyrene	267.0	4.04	1.8	1.9	NR	0.4	NR	Linear
Σ PAHs					22.6	27.9	30.6	

[a]NR, no residue found in SPMD sampler.

rates at individual sampling sites were interpolated from these values for an average temperature at each sampling site. An average fouling resistance of 20% ($F_i = 0.8$) was employed for biofouled SPMDs to correct for reduction in SPMD uptake.[30] Laboratory-derived SPMD sampling rates R_S for PAHs utilized for calculation are given in Table 3.

Except for acenaphthene and fluorene, the estimated first-order uptake half-time was longer than the exposure period, and the linear model [eqn. (6)] was used to calculate the dissolved water-borne concentrations of the compounds. For acenaphthene and fluorene, the curvilinear model [eqn. (2)] was used. It should be noted that the water concentration estimated with the SPMDs is an average concentration over a 34 day interval, not the maximum concentration during that interval.

The estimated ambient concentrations of the selected contaminants by the two techniques are presented in Tables 2 and 3.

Water–sediment equilibrium issues

Absolute water PAH concentrations, estimated from sediment concentrations, were on average almost three orders of magnitude higher than those calculated from SPMDs, although the SPMDs were exposed close to the bottom sediment. To assess the net flux of PAHs between water and sediment at the sampling sites, fugacity quotients (ratio of the fugacity in the sediment f_S to the fugacity in the water f_W) can be calculated using the SPMD and the sediment concentration data. It can be shown that the fugacity quotient can be calculated using the ratio of the aqueous concentrations in equilibrium with individual compartments[31]

$$f_S/f_W = C_{WS}/C_{WM} \quad (7)$$

The fugacity quotient can be cautiously interpreted as an indication of sediment–water equilibrium status. A ratio of unity indicates equilibrium, a ratio of less than unity indicates net movement from water to sediment and a ratio of more than unity indicates net movement from sediment to water.

Fig. 2 shows the sediment/water fugacity quotients calculated using the approach outlined above. For PAHs in this study, movement is predicted to be from sediment to water, *i.e.* the sediment has a tendency to release these compounds. The low actual aqueous concentrations of PAHs in surface water can promote the dissolution of sediment-bound PAH residues. Thus, in addition to contamination from other sources, the water concentration at sampling sites might be elevated due to contaminant mobilization from historically contaminated sediments. Of the PAHs, anthracene and phenanthrene show the highest remobilization potential. The fugacity quotients have the highest values at Site II.

PAH patterns

In order to determine the nature of PAH pollution, we compared the PAH patterns of sediment, SPMD and the dissolved phase at different sampling sites. For this purpose, the relative concentrations of PAHs in samples were analysed by PCA.

From an inspection of the PCA pattern analysis for the matrices, the score plot [PC1 *vs.* PC2, Fig. 3(a)] shows the separation of the samples along the principal components. As can be seen in the loading plot [Fig. 3(b)], the compounds (PAHs) are separated on the principal component plane (PC1 × PC2) according to their molecular weight or lipophilicity. Four main groups can be distinguished. The first group represents the di-aromatics, acenaphthene and fluorene. The second group contains the tri-aromatics, phenanthrene and anthracene. These two groups represent the most water-soluble PAHs. The third group comprises the tetra-aromatics, fluoranthene and pyrene. Finally, the fourth group consists of the remaining tetra-, penta- and hexa-aromatics, *i.e.* the least water-soluble and most hydrophobic of the compounds studied.

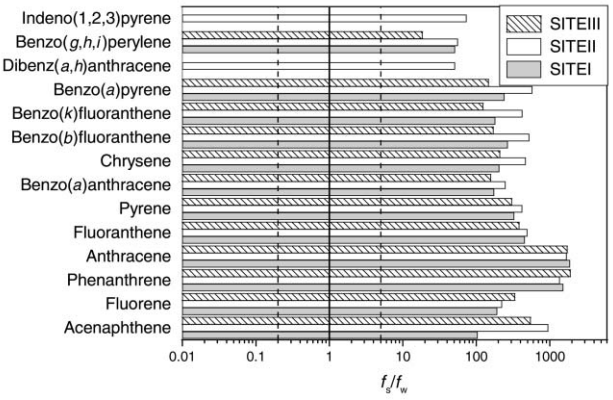

Fig. 2 Sediment/water fugacity quotients of the PAHs at the sampling sites, calculated as described in the text. The broken lines show the quotient range where the sediment is predicted to be close to equilibrium with the aqueous phase. (Fugacity quotients could not be calculated for Site I and Site III for indeno(1,2,3)pyrene and dibenz(*a*,*h*)anthracene due to concentrations below the limit of detection in SPMDs at these sites.)

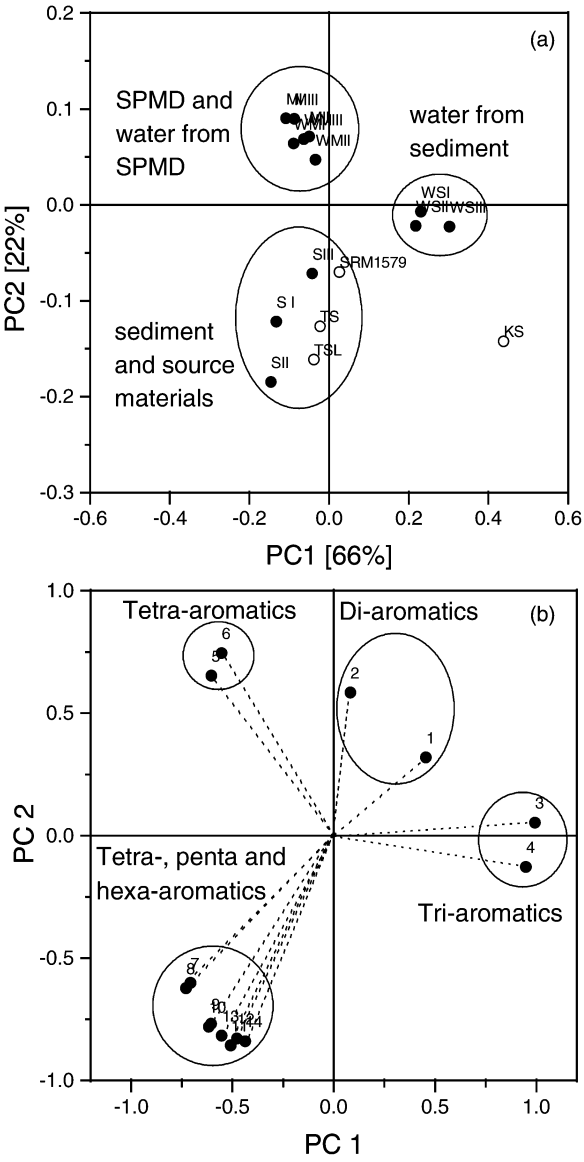

Fig. 3 Principal component plot (PC1 *vs.* PC2) for comparison of the PAH profiles of all matrices from all sites. (a) Scores of samples. Open circles represent calculated scores of potential pollution source materials, which were not included in the analysis. (b) Loadings for the individual PAHs. Sample site numbers and analyte numbers correspond to site numbers in Fig. 1 and analyte numbers in Table 1. S, sediment; M, SPMD; WM, calculated water from SPMD; WS, estimated water pattern from sediment; TS, Theisen sludge; TSL, Theisen sludge leachate; KS, Kupferschiefer; SRM 1579, coal tar.

The most important trend (PC1) accounts for 66% of the total variance. The separation of the PC1 sample scores correlates with the molecular weight or the lipophilicity of the PAHs. The low hydrophobic PAHs (log $K_{ow} < 4.6$) co-vary positively with each other, but they co-vary negatively with the very hydrophobic PAHs (log $K_{ow} > 5.1$). Along PC1, sediment, SPMD samples and water patterns estimated from SPMDs have negative scores, whereas water patterns estimated from sediments have positive scores.

The second most important trend (PC2) explains 22% of the variance in the data. Samples with a positive score on the PC2 axis are characterized by higher relative concentrations of the di- and tetra-aromatics, whereas samples with negative scores have higher relative concentrations of penta- and hexa-aromatics. Along this principal component, the sediment samples have negative scores, whereas the SPMD samples and water patterns derived from SPMDs have positive scores. This is because higher molecular PAHs with high K_{ow} values are more likely to be associated with dissolved, particulate and sediment organic carbon than dissolved in the water, and thus available to be sampled by SPMDs.

Sediment scores from different sampling sites have a much greater spread within their cluster than the PAH profiles within the SPMD matrix. The sediment sample from Site II contains higher relative concentrations of very hydrophobic PAHs (log $K_{ow} > 5.5$) in comparison with sites I and III, which could indicate a contribution from an additional source of PAH pollution at this site. Sediment from Site III contains higher relative concentrations of fluorene, phenanthrene and anthracene and lower relative concentrations of more hydrophobic compounds (log $K_{ow} > 5.5$) in comparison with sites I and II.

The estimated water patterns for SPMD are very similar to the SPMD patterns, whereas the calculated water patterns from sediment vary considerably from the sediment PAH patterns. Water patterns calculated from SPMD and sediment do not cluster together on the PCA plot. The pore water at equilibrium with sediment contains higher relative concentrations of di- and tri-aromatics (especially anthracene and phenanthrene, respectively) than the water column. In surface water, these compounds can be reduced due to their elevated volatility and by different degradation processes (*i.e.* biodegradation and/or photodegradation).

Sources of PAH contamination

No dramatic rise in absolute PAH concentration was observed for any of the sampling sites, for any matrix, which indicates that the PAHs are likely to originate from diffusive sources rather than from a small number of discrete point sources. To identify a similarity in contamination pattern with some of the possible pollution sources (Table 4), principal component scores were calculated for potential source materials, including the Theisen sludge and its aqueous leachate, the Kupferschiefer and the coal tar SRM 1579, using eigenvectors (scoring coefficients) of the data covariance matrix obtained in the PCA [Fig. 3(a)]. Along PC1, Kupferschiefer has a very positive score, which clearly sets it apart from the remaining data. Theisen sludge patterns and the coal tar pattern are not separated well from each other on the PC1 axis and their scores are slightly more positive in comparison with SPMD and sediment samples, respectively. Along PC2, Theisen sludge and coal tar have negative scores. This demonstrates a similarity in the composition of this sediment to that of these two materials.

Another method to determine the PAH source is to calculate specific PAH/PAH ratios.[33–35] These ratios can be compared with the fingerprints of PAHs from pyrolytic or petrogenic origin to identify the most likely contamination source material. The usual index of combustion and/or anthropogenic input is an increase in the proportion of the thermodynamically less stable parent PAH isomers relative to the stable isomers (*e.g.* anthracene relative to phenanthrene , fluoranthene relative to pyrene, benzo[*a*]anthracene relative to chrysene, *etc.*). One difficulty in identifying PAH origins is the possible coexistence of many contamination sources, and the transformation processes that PAHs can undergo in matrices from diverse environmental compartments. The good correlation observed between PAH pairs with similar physicochemical properties indicates their similar behaviour irrespective of the sampling sites and matrices.

On the principal component plane (PC1 × PC2) [Fig. 3(b)], good correlation was observed, especially between relative concentrations of phenanthrene and anthracene ($r = 0.94$), fluoranthene and pyrene ($r = 0.87$) and benzo[*a*]anthracene and chrysene ($r = 0.84$). The ratios of phenanthrene/anthracene (Phe/Ant), fluoranthene/pyrene (Flt/Py) and chrysene/benzo-[*a*]anthracene (Chry/BaA) were examined as origin indices. The Phe/Ant ratio can be seen to be very high in petrogenic pollution by PAHs (*i.e.* Phe/Ant > 10), but lower in pyrolytic

Table 4 PAH contents of some potential pollution source materials (d.w., dry weight)

PAH	Theisen sludge[a]/μg g^{-1} d.w.	Theisen sludge aqueous leachate[b]/μg L^{-1}	Coal tar SRM 1579[c]/μg g^{-1} d.w.	Kupferschiefer/ μg g^{-1} d.w.
Acenaphthene	1.5	1.3	NR[d]	NR
Fluorene	23.6	4.8	140.0	0.05
Phenanthrene	209.1	14.6	462.0	4.40
Anthracene	38.8	2.5	101.0	0.01
Fluoranthene	76.1	3.3	322.0	0.14
Pyrene	120.2	5.9	235.0	0.46
Benzo[*a*]anthracene	38.7	1.1	98.6	0.07
Chrysene	75.5	2.6	71.7	0.73
Benzo[*b*]fluoranthene	26.7	1.8	66.0	0.22
Benzo[*k*]fluoranthene	9.8	0.4	43.0	NR
Benzo[*a*]pyrene	23.9	1.5	95.8	NR
Dibenz[*a*,*h*]anthracene	1.2	NR	NR	NR
Benzo[*g*,*h*,*i*]perylene	14.5	0.4	53.7	0.37
Indeno[1,2,3]pyrene	9.0	0.7	60.2	NR
Σ PAHs	668.6	40.9	1749.0	6.47

[a]Taken from Popp *et al.*[14] [b]Taken from Paschke *et al.*[7] [c]Taken from ref. 32. [d]NR, no residue found.

contamination cases. In the case of pyrogenic pollution, the Flt/Py ratio ought to be >1, and the Chry/BaA ratio ought to be <1.[35,36]

The origin indices of the sediment and SPMD samples and those derived from the estimated dissolved aqueous phase composition at the sampling sites were compared with origin indices of potential pollution source materials, including the Theisen sludge, the Kupferschiefer and the reference material coal tar SRM 1579[32] (Table 5).

Coal tar SRM 1579 is characterized by origin indices typical of a material generated by pyrolytic processes, as indicated by the low Phe/Ant ratio of 4.57, the elevated Flt/Py ratio (1.37) and the low value of Chry/BaA (0.73). On the other hand, the criteria for a petrogenic PAH origin are confirmed very clearly when inspecting the origin indices calculated for the black shale Kupferschiefer. The characteristic extremely high Phe/Ant ratio of 344, low Flt/Py ratio (0.31) and high Chry/BaA ratio (10.37) allow for the clear differentiation of this petrogenic PAH source from other sources.

Theisen sludge exhibits characteristic indices distinct from those of petrogenic origin. The Phe/Ant ratio is 10 in Theisen sludge samples. In contrast to typical material of pyrolytic origin, Theisen sludge is characterized by Flt/Py values $\leqslant 1$ and Chry/BaA values >1.

The sediment, SPMD samples and calculated water patterns at the sampling sites are characterized by Phe/Ant values <10. One exception is the SPMD sample at Site II and the water pattern derived from this sample (Phe/Ant = 12.36 and 10.49, respectively). However, this ratio might be additionally elevated because of selective photo-oxidation of anthracene during transport in the dissolved phase.[37] This hypothesis is supported by the fact that the Phe/Ant values in the SPMD samples, which reflect the composition of the dissolved PAHs in water, are higher than those in sediment samples.

The results of the Flt/Py ratios examined are ambiguous. Flt/Py ratios >1 are observed in sediment samples and pore water patterns derived from sediment data, whereas ratios between 0.77 and 1.17 characterize the SPMD samples and water patterns from SPMD data. Except for the sediment sample at site I, Chry/BaA ratios >1were observed in all samples.

Table 5 Selected PAH ratios (origin indices) for SPMDs, sediment samples, estimated water compositions and potential source samples in the Mansfeld region

Sample	Phe/Ant	Flt/Py	Chry/BaA
Sediment at Site I	5.22	1.31	0.97
Sediment at Site II	6.74	1.22	1.97
Sediment at Site III	5.95	1.47	1.10
SPMD at Site I	9.91	0.77	1.62
SPMD at Site II	12.36	0.86	2.13
SPMD at Site III	7.79	0.98	1.74
Water from SPMD at Site I	8.13	0.94	1.30
Water from SPMD at Site II	10.49	1.04	1.66
Water from SPMD at Site III	6.84	1.17	1.31
Pore water from sediment at Site I	6.58	1.31	1.54
Pore water from sediment at Site II	8.49	1.22	3.13
Pore water from sediment at Site III	7.49	1.47	1.75
SRM 1579 (coal tar)	4.57	1.37	0.73
Theisen sludge	10.44	0.95	2.94
Kupferschiefer	344.05	0.31	10.37

[a]NR, no residue found.

Conclusions

SPMD and sediment samples provide complementary information. The use of sediments to predict water concentrations and patterns may not be representative of the concentrations and patterns in the upper levels of the water column. PAH concentrations and patterns in sediment are changed by weathering and ageing, and reflect longer periods of time because sediments are sinks for hydrophobic contaminants, while SPMDs integrate water concentrations only during the sampling period. Moreover, PAHs present in sediment are bound to particles, whereas SPMD samples only PAHs truly dissolved in the water column. The comparison of data obtained by PAH analysis in sediment samples and SPMDs allows the specific distribution of PAHs to be determined in individual environmental compartments and the mobilization potential of these compounds to be assessed. Moreover, the evaluation of contaminant patterns in sediment and SPMD samples permits the assessment of the possible pyrolytic, industrial origin of the PAHs in the region. Although it was not possible to clearly identify one definite contamination source in the region, the results indicate that Theisen sludge cannot be ruled out as a possible source of PAH pollution. However, a conclusive statement about the origin of pollution will entail additional sampling with a higher density of sampling sites. In addition, studies currently being conducted on the assessment of the leaching behaviour of the Theisen sludge will produce more information on the potential contribution of this industrial waste to the pollution situation in the region of Mansfeld.

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Príloha 3

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Membrane-Enclosed Sorptive Coating. An Integrative Passive Sampler for Monitoring Organic Contaminants in Water

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An integrative sampler that consists of a bar coated with poly(dimethylsiloxane) (PDMS) enclosed in a dialysis membrane bag has been developed combining the advantages of the passive sampling approach with solventless preconcentration of organic solutes from aqueous matrixes and subsequent desorption of the sequestered analytes on-line with a capillary GC/MS system. The performance of the sampler was tested for integrative sampling of hydrophobic persistent organic pollutants including γ-hexachlorocyclohexane, hexachlorobenzene, 2,2′-bis(4-chlorophenyl)-1,1′-dichloroethylene, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls in the laboratory in a continuous-flow system. Linear uptake of all test analytes during exposure periods up to one week has been observed, and concentration proportionality of response of the sampler has been demonstrated. Over the range of controlled laboratory conditions, the magnitude of sampling rate values varied from 47 to 700 μL h^{-1} per sampler. The uptake rate of chemicals was dependent on their molecular mass, as well as on the partition coefficient between the PDMS and water. A decrease in sampling rates with decreasing water temperature was observed. The sampling device has the potential to detect low aqueous concentrations (ng to pg L^{-1}) of test substances.

Qualitative and quantitative assessment of pollution of ecosystems by persistent organic pollutants (POPs) is a continuing challenge to environmental scientists. In aquatic systems, it is important to obtain information on the time-weighted average (TWA) concentrations of pollutants, which is a fundamental part of an ecological risk assessment process for chemical stressors. Moreover, the quantification of freely dissolved concentrations of pollutants in water is needed for approximate characterization of the bioavailable fraction.

Concentrations of truly dissolved contaminants cannot be determined by most water sampling methods. Instead, total quantities of analytes are measured, including those molecules that are not readily bioavailable because they are bound to dissolved colloids present in water. Grab water samples provide information only about contaminant concentration at the moment of sampling and may fail to account for episodic contamination events. Because of the low aqueous solubility of many contaminants, it is often impossible to excise sufficiently large water samples to achieve instrumental detection limits. For these reasons, an integrative approach is needed, which would provide information about truly dissolved TWA contaminant concentrations over a long time period.

Passive sampling devices allow convenient measurement of an average concentration over a long time period, on the order of several weeks. In contrast to active sampling, they require no mechanical devices to collect sample or a series of samples; this makes the method inexpensive, suitable to use at remote sites, and perhaps less prone to vandalism. The successful use of passive monitors in the industrial hygiene field for monitoring exposure of workers to chemicals in the air has contributed to the application of the same principle to dissolved organic contaminants in aquatic environments.[1,2] Despite numerous shortcomings of the earlier developed devices, their use in field studies[3,4] demonstrated that the in situ passive sampling approach had considerable potential.

Most passive sampling devices typically consist of a receiving phase, with a high affinity for organic pollutants, separated from the aquatic environment by a diffusion-limiting membrane.[5−8] They can be calibrated in the laboratory so that TWA concentrations of organic pollutants can be determined in field studies.[9]

Södergren[2] developed a sampler design consisting of a dialysis membrane filled with organic solvents. The disadvantage of this design was the successive loss of the organic solvent from the device by diffusion through the membrane during exposure.

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Huckins et al.[10,11] described the development of a semipermeable membrane device (SPMD) for passive and integrative in situ monitoring of waterborne contaminants. The SPMD sampler consists of lay-flat polyethylene tubing containing a thin film of triolein, a high molecular weight neutral lipid. The utility of the SPMD has been shown for monitoring aqueous residues of polychlorinated biphenyls (PCBs),[12] various organochlorine pesticides,[13] polychlorinated dibenzofurans and dibenzo-*p*-dioxins,[14] and polycyclic aromatic compounds (PAHs).[15] The application of the device is limited to nonionized contaminants.

Zhang et al.[16] described a direct solid-phase microextraction (SPME) of complex aqueous samples with hollow fiber membrane protection. In this approach, the fiber of an SPME device was placed inside a cellulose hollow membrane, which allows target analytes to diffuse through while excluding high molecular weight interfering compounds. This arrangement can be used for determination of truly dissolved contaminants in aqueous samples; however, it is not suitable for passive sampling over a long time period. Recently, Alvarez et al.[17] and Kingston et al.[18] described development of passive samplers that enable to widen the application to a broader range of contaminants including low-hydrophobic substances (log K_{ow} < 4) such as atrazine,[17,18] diazinon,[17] 17α-ethynylestradiol,[17] or diuron.[18] These samplers consist of a hydrophilic membrane material enveloping immobilized solid-phase materials as an alternative to a liquid receiving phase.

The common disadvantage of the above-mentioned passive sampling techniques is a laborious recovery of analytes from samplers after exposure by solvent extraction or dialysis[19] and a need for additional cleanup of the samples before gas chromatographic analysis.[15,20,21] To make the passive sampling technology more suitable for routine monitoring, low-cost and less time-consuming sample processing is required. Sample processing with reduced solvent consumption would also minimize the risk of sample contamination during handling in the laboratory and enable to improve the quality control measures.

Recently, a novel solventless and simple technique for preconcentration of organic solutes from aqueous matrixes, the stir bar sorptive extraction (SBSE), was developed by Baltussen et al.[22] In SBSE, a stir bar coated with poly(dimethylsiloxane) (PDMS) is placed in the sample and stirred for a predetermined time. The stir bar is then thermally desorbed on-line with a capillary GC/MS system. The use of PDMS as a receiving organic phase in extraction and thermodesorption has several advantages over other sorbents including inertness, negligible permanent sorption and reactions of analytes on it, and good blanks in GC analyses.[23] Absorptive partitioning is the predominant mechanism of extraction of analytes into PDMS.[24] The applicability of SBSE was demonstrated for the analysis of volatile and semivolatile micropollutants from aqueous samples.[22] In this work, we describe an adaptation of this novel technique to integrative passive sampling for hydrophobic persistent organic pollutants in aqueous environment.

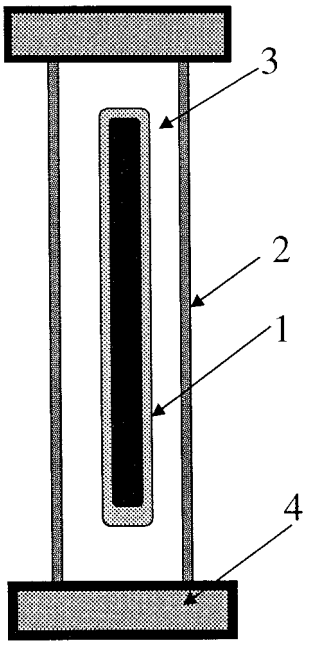

Figure 1. Schematic diagram of the MESCO passive sampling device. A Gerstel-Twister bar used for SBSE (component 1) is enclosed in a dialysis membrane bag made from regenerated cellulose (component 2). The dialysis membrane bag is filled with 3 mL of bidistilled water (component 3) and sealed at each end with Spectra Por enclosures (component 4).

THEORY

Previously, models have been developed describing the uptake kinetics of organic contaminants in water by passive samplers constructed as a solvent-filled dialysis membrane[25] or triolein-filled polyethylene membrane.[11]

The passive sampling device described in this study consists of a hydrophobic solid receiving phase enclosed in a water-filled hydrophilic semipermeable membrane (Figure 1). The passive sampler lowered in aqueous solution can be divided into several compartments including the bulk aqueous phase with constant solute concentration, the stagnant aqueous boundary layer, possible biofilm layer, the membrane, the inner aqueous phase, and

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the receiving organic phase. Under steady-state conditions, the flux of the solute is assumed to be constant and equal in each of the individual compartments. The overall mass transfer from the bulk aqueous phase to the receiving organic phase includes several diffusion and interfacial transport steps across all barriers. The resistances of each barrier to the mass transfer of analytes are assumed to be additive and independent,[26] and the interfacial resistances are assumed to be negligible compared with diffusional resistances.[27] Also, negligible accumulation of analyte in the diffusion-limiting membrane is assumed. Then, the rate of transport can be described by the overall mass-transfer coefficient k_{ov} (m s^{-1}), relating the net diffusive steady-state flux of the solute J (kg s^{-1}) to its concentrations in the bulk aqueous phase C_W (kg m^{-3}) and the receiving organic phase C_S (kg m^{-3})

$$J = \mathrm{d}M_S/\mathrm{d}t = V_S\,\mathrm{d}C_S/\mathrm{d}t = k_{ov}A\alpha(C_W - C_S/K_{SW}) \quad (1)$$

where M_S (kg) is the mass of analyte in the receiving organic phase, A is the membrane surface area (m^2), α is the pore area of the membrane as fraction of total membrane area (membrane porosity), K_{SW} is the receiving organic phase/water partitioning coefficient, and t (s) equals time. Equation 1 can be integrated

$$C_S(t) = C_{S0} + (C_W K_{SW} - C_{S0})\left[1 - \exp\left(-\frac{k_{ov}A\alpha}{K_{SW}V_S}\right)t\right] \quad (2)$$

where C_{S0} is the concentration of analyte in the organic phase at $t = 0$.

In the initial uptake phase, when the exponential term is very small (≪1) or $C_S/C_W \ll K_{SW}$, chemical uptake is linear or integrative. Thus, in the linear region, eq 2 can be reduced

$$C_S(t) = C_{S0} + C_W k_{ov}(A\alpha/V_S)t \quad (3)$$

For practical application, eq 3 can be rewritten

$$M_S(t) = M_0 + C_W R_S t \quad (4)$$

where M_0 (kg) is the amount of analyte in the organic phase at $s = 0$. R_S (m^3 s^{-1}) is the sampling rate of the system

$$R_S = k_{ov}A\alpha \quad (5)$$

When fitting the eq 4 to experimental data, a negative intercept can be interpreted as a lag phase between initial deployment and penetration of analyte through the diffusion-limiting membrane. Sampling rate can be determined experimentally under fixed conditions at constant analyte concentration. Under environmental conditions, when the water concentration is changing during the exposure, the term C_W represents a TWA concentration during the deployment period. The TWA aqueous concentration can be then estimated from the amount of analyte accumulated in the sampler during the exposure

$$C_W = (M_S - M_0)/R_S t \quad (6)$$

The chemical uptake into passive sampler remains linear and integrative approximately until the passive sampler concentration factor (ratio $C_S(t)/C_W$) reaches half-saturation.[9] When calibration data, i.e., R_S and K_{SW}, are available, the following equation can be used to estimate maximal exposure time in which the passive sampling system accumulates integratively under field conditions

$$t_{50} \approx \ln 2\, K_{SW}V_S/R_S \quad (7)$$

where the term t_{50} is the first-order half-time of the uptake curve.

Under these conditions the concentration of a chemical in the organic phase is directly proportional to the product of the concentration in the surrounding aqueous medium and the exposure time.

EXPERIMENTAL SECTION

Materials and Chemicals. Test chemicals (Table 1) included several groups of persistent organic pollutants: γ-hexachlorocyclohexane (lindane, γ-HCH), hexachlorobenzene (HCB), 2,2′-bis-(4-chlorophenyl)-1,1′-dichloroethylene (DDE), PAHs, and PCBs. γ-HCH reference material was obtained from Riedel-de Haen. HCB, DDE, and PAH reference materials were obtained from Dr. Ehrenstorfer. PCB reference material and test chemicals in high purity (>99%; γ-HCH, HCB, DDE, PAHs, and PCBs) were purchased from Promochem. Dialysis membrane Spectra/Por 6 (molecular weight cutoff 1000) was obtained from Spectrum Laboratories. The Gerstel-Twister stir bar for sorptive extraction was obtained from Gerstel. Lichrolut (R) (diameter of particles 40−63 μm) was purchased from Merck. The solvents methanol and hexane were used in LiChrosolv quality from Merck.

Sampler Design. The passive sampling device, referred to as the *m*embrane-*e*nclosed *s*orptive *co*ating sampler (MESCO), consists in the actual investigation of a Twister bar used for SBSE (component 1, Figure 1) enclosed in a dialysis membrane bag made from regenerated cellulose (Spectra/Por 6, molecular weight cutoff 1000, 18-mm flat width, 30-mm length; component 2, Figure 1). Twister is a stir bar (15 mm length) consisting of a magnetic core sealed inside a glass coated with 22 mg of PDMS. The PDMS sorptive layer (receiving phase) is 500 μm thick and its volume is 24 μL. Prior to first use, the stir bar was placed into a vial containing 1 mL of a 1:1 mixture of methylene chloride and methanol, and the mixture treated for 5 min with sonication. Then the solvent mixture was rejected and the procedure repeated three times. The stir bar was dried in a desiccator at room temperature. Prior to each use, the stir bar was conditioned by heating for 180 min at 280 °C with a nitrogen stream of ∼100 mL min^{-1}. The dialysis membrane bag with Twister inside is filled with 3 mL of bidistilled water (component 3, Figure 1) and sealed at each end with 35-mm Spectra Por enclosures (component 4, Figure 1). The stir bar was allowed to freely move inside the membrane. As a relationship is likely to exist between the surface area and the rate of uptake, the area of the membrane was held constant at 1100 mm^2. To enable a simultaneous exposure of a series of samplers, they were connected to a string, which was then exposed to organic analytes in a continuous-flow system.

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Table 1. Selected Physicochemical Properties of Test Analytes at 25 °C

no.	compound	MW[a]	log K_{ow}[b]	S[c] (g m^{-3})	ΔG_S(w)[d] (kJ mol^{-1})	ΔG_S(o)[e] (kJ mol^{-1})
1	HCB	284.8	5.5	0.005	−6.9	−38.2
2	γ-HCH	290.8	3.7	7.3	−9.5	−30.6
3	*p,p′*-DDE	318.0	5.7	0.04	−9.4	−41.8
4	PCB28	257.5	5.6	0.16	−8.7	−40.6
5	PCB52	292.0	6.1	0.03	−10.3	−45.0
6	PCB101	326.4	6.8	0.01	−10.1	−48.8
7	PCB138	360.9	7.6	0.0015	−11.0	−54.3
8	PCB153	360.9	7.8	0.001	−10.0	−54.4
9	PCB180	395.3	8.3	0.0003	−10.0	−57.3
10	acenaphthylene	152.2	4.0	16.1	−13.9	−36.7
11	acenaphthene	154.2	4.0	3.8	−8.6	−31.4
12	fluorene	166.2	4.2	1.9	−9.3	−33.2
13	anthracene	178.2	4.6	0.045	−10.9	−37.1
14	phenanthrene	178.2	4.5	1.10	−11.6	−37.2
15	fluoranthene	202.3	5.1	0.26	−17.1	−46.2
16	pyrene	202.3	5.1	0.132	−16.5	−45.6
17	benzo[*a*]anthracene	228.3	5.9	0.011	−15.0	−48.6
18	chrysene	228.3	5.7	0.0019	−15.5	−48.0
19	benzo[*b*]fluoranthene	252.3	5.8	0.0015	−19.9	−53.0
20	benzo[*k*]fluoranthene	252.3	6.0	0.0008	−19.8	−54.0
21	benzo[*a*]pyrene	252.3	6.2	0.0038	−19.7	−55.0
22	indeno[1,2,3-*cd*]pyrene	276.3	6.8	0.0005	−24.5	−63.2
23	benzo[*ghi*]perylene	276.3	6.9	0.0003	−24.5	−63.8

[a] Molecular weight. [b] Octanol−water partition coefficient.[41,42] [c] Aqueous solubility.[41,42] [d] Calculated free energy of aqueous solvation. [e] Calculated free energy of solvation in octanol.

Laboratory Exposures. *Batch Exposures.* Twister bars designed for later use in flow-through exposures were individualized (by attributing a number to each bar) and the extraction efficiency and repeatability was tested in a batch system, at first. Conditioned Twister bars (without the membrane) were separately lowered to 20 mL of aqueous solution in a 25-mL closed amber glass vessel containing test solution of analytes. The test solution was prepared by spiking double-distilled water with a test substance mixture dissolved in methanol to give nominal concentration of individual analytes of 125 ng L^{-1}. The flask content was stirred at 1000 min^{-1} for 60 min at room temperature. After this, the Twister bars were removed from the sample, washed with a small amount of bidistilled water, and dried with a paper cloth. The accumulated analyte content was analyzed by GC/MS as described below. Detection of outliers was performed using the Mahalanobis distance technique ($p = 0.05$).[28] The normal distribution of the errors for individual analytes in the sample set was tested by the Kolmogorov−Smirnov test ($p = 0.05$).

Flow-Through Exposures. MESCO samplers were exposed to test chemicals at nominal concentration of 20 and 50 ng L^{-1} in a flow-through exposure system. Exposures were conducted at 14 and 19 °C. The experimental conditions of individual exposures are given in Table 2. The experimental setup of the flow-through exposure system has been described.[29] Exposures were conducted at a linear flow velocity of 0.6 cm s^{-1}. The exposures lasted between 4 and 7 days, during which the samplers were sampled at time intervals and their contents analyzed to determine accumulated concentrations of test chemicals as described below. Water samples from the exposure column (5 L) were taken at each time when samplers were sampled and analyte concentration in water was determined.

Table 2. Summary of Passive Sampler Flow-Through Exposure Experimental Conditions

expt no.	nominal concn (ng L^{-1})	temp (°C)	exposure period (h)	no. of MESCOs sampled
1	20[a]	19	0−166	16
2	20	14	0−165	12
3	50	19	0−96	6

[a] The nominal concentration of PCB180 was 40 ng L^{-1}.

Sampler Processing. Following exposure, MESCOs were dismantled, Twister bars were washed with bidistilled water, dried with a paper cloth, checked visually for possible damage of the sorptive layer, and analyzed for accumulated analyte content (test substances only) by thermodesorption-GC/MS.

Processing of Water Samples. The residues in the water samples were extracted using solid-phase extraction (SPE) using Lichrolut (R) sorbent. The quantification of acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, and HCB in water was carried out using SPME technique (Supelco 65-μm poly(dimethylsiloxane)−divinylbenzene (PDMS−DVB) solid-phase microextraction fiber assembly) in combination with a gas chromatographic system. The detailed description of the procedures is given in the Supporting Information section.

Instrumental Analysis. The quantitation and qualitative control of the compounds accumulated during exposures in Twister bars was performed by thermodesorption-GC/MS. For thermodesorption, the Twister bar was positioned in the middle of the heated zone of a desorption tube (178-mm-length, 6-mm-o.d, 4-mm-i.d. glass tube) in a thermal desorption device. Thermodesorption-GC/MS was performed on an Agilent Technologies (Palo Alto, CA) system equipped with a Gerstel (Mülheim/Ruhr, Germany) thermodesorption device TDS A. A cold injection

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system from Gerstel (CIS-4) with an empty liner was used for cryofocusing of the analytes prior to the transfer onto the analytical column. The cold injection system was cooled with liquid nitrogen to −150 °C during thermal desorption. The following conditions were chosen for the thermodesorption of the compounds from the stir bars: desorption temperature, 250 °C; helium flow rate, 100 mL min^{-1}; desorption time, 10 min. The transfer line both from the thermodesorption device to the CIS and from the GC to the MSD ion source was set to 250 °C. After stir bar desorption, the CIS was heated to 250 °C with a rate of 12 °C s^{-1}, the injector was used in the splitless mode with a splitless time of 1.5 min. A HP-5 MS column (30-m length, 0.25-μm i.d., 0.25-μm film thickness) was used with the following temperature program: 50 °C, 3 min isothermal, 15 °C min^{-1} to 160 °C, then at 3 °C min^{-1} to the final temperature of 280 °C, and held for 9 min. Helium was used as carrier gas at a linear velocity of 39 cm s^{-1}. The single ion monitoring (SIM) mode applying one or two characteristic ions per compound was chosen for the detection.

For the external calibration, a small bunch of glass wool was positioned to an empty desorption tube. The desorption tube was then connected to a cool injector of a GC and flushed with 20 mL min^{-1} nitrogen. The desorption tube with glass wool was then spiked with 2 μL of a calibration standard solution and flushed for 1 min by the nitrogen stream to allow the solvent (hexane) to evaporate. The desorption tube was then transferred to the thermodesorption device (TDS A) and processed by thermodesorption-GC/MS. Quantification of the residues sorbed on Twister bars was accomplished using a five-point external standard curve.

Data Processing. The experimentally determined time courses of the amounts of individual test substances on the Twister sampler were fitted by linear regression analysis using eq 4. The adjustable parameters were the intercept (M_0) and the slope ($C_W R_S$) of the linear uptake curve $M_S = f(t)$. Quality of the fit was characterized by the standard deviations of the optimized parameters, as well as the correlation coefficient adjusted for the degrees of freedom (r^2 adjusted), the fit standard deviation (SD), and the Fisher test criterion on the accuracy of the model. The sampling rates of the device R_S for individual test compounds were calculated by dividing the slope of the linear uptake curve by the mean aqueous analyte concentration during the exposure. The required variances of R_S values were calculated from the coefficients of variation of the uptake slope parameters and of the concentrations in the aqueous phase which were obtained according to the law of error propagation.

The free energies of solvation of the test substances in water $\Delta G_s(w)$ were calculated using the quantum chemical continuum-solvation model SM2.[30] For previous applications to calculate Henry's law constant from $\Delta G_s(w)$, the reader is referred to the literature.[31−33] The free energies of solvation of the test substances in octanol $\Delta G_s(o)$, were calculated as follows. Under standard thermodynamic conditions, the equilibrium partitioning of a compound between the air phase (a) and the octanol phase (o) in terms of molar concentrations c_a and c_o is governed by the solvation free energy $\Delta G_s(o)$

$$\Delta G_s(o) = -RT \ln \frac{c_o}{c_a} = 2.3RT \log \frac{K_{aw}}{K_{ow}} \quad (8)$$

For the application of eq 8, the air−water partition coefficient K_{aw} is derived from the calculated free energy of aqueous solvation,

$$\log K_{aw} = \Delta G_s(w)/2.3RT \quad (9)$$

The multilinear regression analyses were performed with Origin 5.0 (Microcal Software, USA).

RESULTS AND DISCUSSION

Passive Sampler Performance. *Batch Exposures.* Normal distribution of the errors for individual analytes in the Twister samples was confirmed. The coefficient of variation of individual substances extracted from the solution by the 16 Twister bars incubated under the same conditions ranged from 6% (PCB 28) to 19% (PCB 180). Twisters checked for repeatability were used for construction of MESCO samplers exposed in flow-through studies.

Flow-Through Exposures. The performance of the MESCO sampler was tested in continuous-flow exposures to constant concentrations of test chemicals. Concentrations of the analytes in water (C_W) and the amounts accumulated in the MESCO sampler (C_S) were two parameters measured regularly during the continuous-flow exposures. During exposure, the water concentration was held constant, which was confirmed by analyses of water samples.

Characteristic uptake curves are shown in Figure 2. For all test substances, the uptake was linear in all exposure studies during the whole exposure period and without any sign of a leveling-off in the uptake curve.

Satisfactory fits of kinetic eq 4 to the data from exposure were obtained for all test compounds. Correlation coefficient (r^2 adjusted) values of the regression (model versus experimental) ranged from 0.74 to 0.97 with the exception of HCB in experiment 2 (r^2 adjusted, 0.66). Coefficients of variation of the calculated slope did not exceed 29% in any case. A lag phase between approximately 0 and 46 h was observed for the test substances in experiment 1. In experiments 2 and 3, no significant ($p > 0.05$ in all tests) lag phases were detected for the test substances, except for PCB180 in experiment 2, for which a lag phase of 44 h was observed. The higher uncertainty in estimation of intercept values in these experiments results from lack of data in the initial uptake period (first sampling point available after 69 h). The average aqueous concentrations of individual analytes measured during exposures ranged from 50% to 130% of the nominal concentration. The maximum fluctuations of aqueous concentrations during exposure did not exceed 40% of the mean concentration for individual compounds.

Concentration Proportionality of Response. The results of flow-through exposures indicate that the passive sampler responded proportionally to the range of test analyte concentrations (20−50 ng L^{-1}, nominal). The independence of sampling rates R_S from aqueous solute concentrations was confirmed using an unpaired *t*-test ($p = 0.05$) for γ-HCH, DDE, PCBs, and hydrophobic PAHs ($\log K_{ow} > 5$) (Figure 3).

Time To Reach Steady State. The maximum exposure time in which the passive sampling system collects integratively

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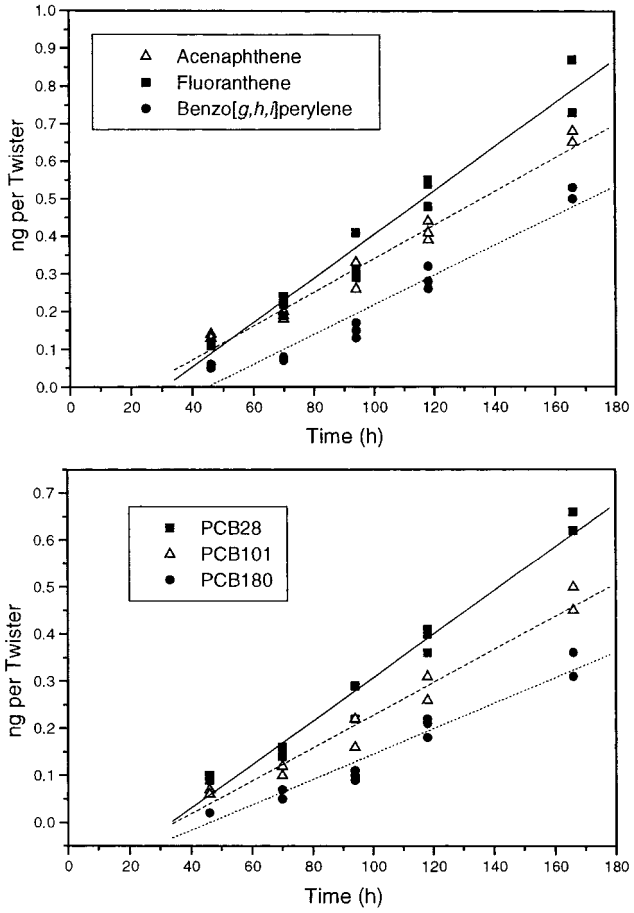

Figure 2. Uptake of selected PAHs and PCBs by the Twister-based MESCO sampler. The data used represent the 19 °C flow-through exposure (20 ng L^{-1}). The lines are predicted concentrations in the sampler obtained by linear regression using eq 4.

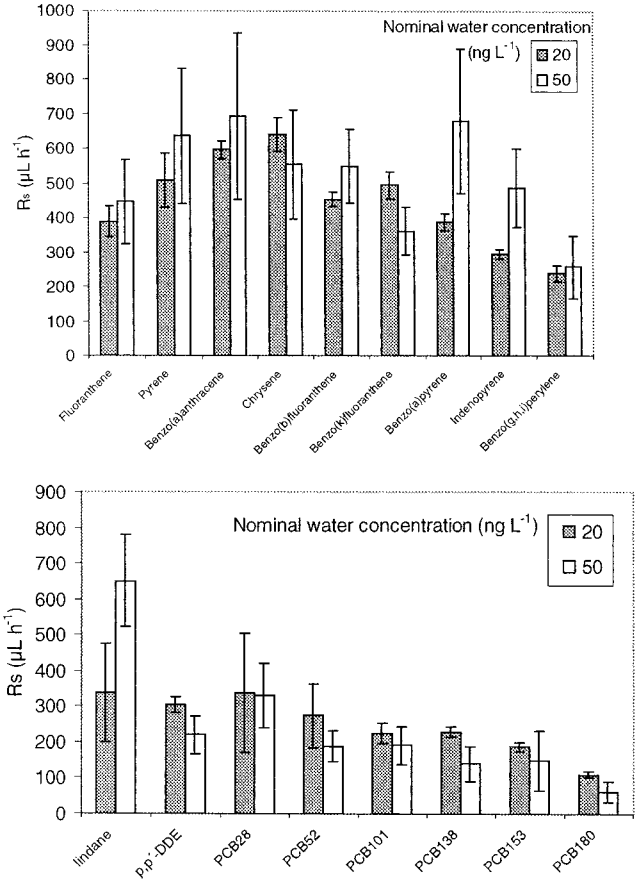

Figure 3. Relationship between aqueous concentration and MESCO sampling rate (R_S). The data used represent flow-through exposures at 19 °C. The independence of sampling rates from aqueous concentration was confirmed for the shown compounds using an unpaired *t*-test ($p = 0.05$).

under field conditions or time to reach 50% of the K_{SW} value was estimated using eq 7 and the R_S values from the flow-through exposure study conducted at 19 °C and 20 ng L^{-1} nominal concentration (experiment 1). Because of physical difficulties in determination of the K_{SW} values in batch experiments (depletive extraction of test substances by the Twister from 20 mL of a 100 ng L^{-1} aqueous solution), the apparent distribution constants K_f-(PDMS), obtained with glass fibers coated with 100-μm PDMS for the analyte's partitioning between PDMS coating and aqueous sample was used as a substitute for K_{SW} in the estimation.[34−36] The results of the first-order halftime t_{50} calculation are reported in Table 3. It is calculated that, for γ-HCH and acenaphthylene, a passive sampler may sample integratively less than one week. For the rest of the PAHs taken into the calculation, the passive sampler may remain in the linear uptake phase more than one week; for the HCB, DDE, and PCBs, the t_{50} may be several months.

The linear uptake of all test analytes in all exposure studies during the whole exposure period indicates that this condition of integrative sampling is fulfilled for at least one-week exposures. The t_{50} estimation indicates the possibility to use sampling rate data obtained under laboratory conditions for estimation of TWA concentrations of analytes from the contaminant amounts accumulated in MESCOs during environmental exposures of several weeks. In general, deviations from the linear uptake in prolonged exposures are expected for compounds with log $K_{ow} < 4.0$, with the assumption that K_{SW} correlates well with K_{ow} within the hydrophobicity range. For a more accurate estimate of t_{50} values, direct measuring of K_{SW} in a Twister−water batch or flow-through system is necessary.

Sampling Rate. The sampling rates R_S obtained in flow-through exposure studies conducted at 19 and 14 °C and 20 ng L^{-1} nominal concentration (experiments 1 and 2, respectively) are shown in Table 4. Over the range of controlled laboratory conditions, the magnitude of R_S values differed by 15-fold (i.e., from 47 to 700 μL h^{-1}). This range of sampling rates is narrow relative to the broad K_{ow} range of almost 5 orders of magnitude (log K_{ow} ranged from 3.7 to 8.27).

Using the average sampling rates for each chemical, a single MESCO deployed in water over 20 days would clear a total of 60−300 mL of water of the individual chemicals. This is a low volume when compared with clearance volumes of other common passive samplers, such as the triolein-filled SPMDs with standard configuration,[9] which would clear 20−160 L of water in 20 days. Despite the fact that the extraction efficiency of MESCO is 3 orders of magnitude lower than that of SPMD, the method

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Table 3. Estimation of the Maximal Exposure Time t_{50} in Which MESCO Samples Integratively under Field Conditions at 19 °C[a]

compound	log K_f(PDMS)	t_{50} (d)
HCB	4.3[b]	119
γ-HCH	3.2[c]	3
p,p′-DDE	5.2[b]	344
PCB28	4.7[b]	69
PCB52	5.0[b]	190
PCB101	5.3[b]	655
PCB138	5.4[b]	734
PCB153	5.4[b]	910
PCB180	5.2[b]	1020
acenaphthylene	3.40[d]	4
acenaphthene	3.63[d]	11
fluorene	3.71[d]	9
anthracene	3.98[d]	14
phenanthrene	3.96[d]	20
fluoranthene	4.71[d]	92
pyrene	4.86[d]	99
benzo[*a*]anthracene	5.26[d]	211
chrysene	5.69[d]	530
benzo[*b*]fluoranthene	5.17[d]	227
benzo[*k*]fluoranthene	5.33[d]	299
benzo[*a*]pyrene	5.39[d]	439
indeno[1,2,3-*cd*]pyrene	4.28[d]	45
benzo[*ghi*]perylene	4.43[d]	78

[a] Sampling rates taken for calculation were determined at nominal test substance concentrations of 20 ng L^{-1} at 19 °C. [b] The 100-μm PDMS fibers were exposed in 500 mL of stirred standard solution over a time sufficient to reach equilibrium distribution between the aqueous solution and fiber coating.[34] [c] Data from ref 36. [d] Data from ref 35.

Table 4. Summary of Passive Sampler Sampling Rates R_s Derived from Flow-Through Exposures at Different Temperatures at Nominal Analyte Concentration of 20 ng L^{-1}

	T = 19 °C		T = 14 °C	
compound	R_s (μL h^{-1})	CV (%)	R_s (μL h^{-1})	C (%)
HCB	114	7	47	50
γ-HCH	336	41	188	47
p,p-DDE	305	7	142	28
PCB28	337	49	497	57
PCB52	275	32	397	40
PCB101	226	13	266	28
PCB138	227	6	271	29
PCB153	188	7	229	30
PCB180	110	8	113	33
acenaphthylene	484	7	700	16
acenaphthene	280	8	238	14
fluorene	391	7	485	16
anthracene	462	15	543	21
phenanthrene	321	10	255	17
fluoranthene	389	11	217	31
pyrene	509	15	270	30
benzo[*a*]anthracene	597	4	212	33
chrysene	641	8	215	32
benzo[*b*]fluoranthene	453	5	234	26
benzo[*k*]fluoranthene	495	8	214	28
benzo[*a*]pyrene	388	7	301	18
indeno[1,2,3-*cd*]pyrene	294	5	*a*	
benzo[*ghi*]perylene	239	9	*a*	

[a] Indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene were not determined during the experiment conducted at 14 °C.

sensitivity of these two techniques is comparable. This is because the total amount of analyte sequestered by MESCO during deployment can be transferred to the GC system, whereas only a small portion of the SPMD extract is usually injected to the GC (to prevent introduction of large amounts of interfering contamination to the chromatographic system).

The advantage of low clearance volume (i.e., $R_S t$) of MESCO during exposure in comparison with other types of passive samplers (e.g., SPMDs) is the nondepletive extraction, which enables use of flow-through exposure calibration data also for TWA concentration estimation at sampling sites with very low exchange volumes of water in the vicinity of the sampler during an exposure (e.g., in wells with very low groundwater flux).[37]

The comparability of experimentally derived MESCO calibration data to actual values during field sampling generally depends on the similarity of laboratory and field exposure conditions. Besides temperature and biofouling, mainly flow velocity/turbulence may affect the uptake kinetics. An increase in uptake rate can occur with increasing water flow velocity or turbulence as reported for passive sampling devices fitted with polyethylene membranes.[18,29,38] On the other hand, Kingston et al.[18] observed only minor effects of turbulence on the accumulation kinetics in a passive sampler fitted with a hydrophilic polysulfone membrane. Nevertheless, examination of potential rate-limiting barriers to analyte uptake by MESCOs is necessary. It is assumed that the overall resistance ($1/k_{ov}$), to the uptake of a chemical is given by the sum of particular barrier resistances

$$\frac{1}{k_{ov}} = \sum_i \frac{\delta_i}{K_{iW} D_i} = \frac{\delta_M}{D_M K_{MW}} + \frac{\delta_W}{D_W} + \frac{\delta_S}{D_S K_{SW}} \qquad (10)$$

where δ_i is the particular barrier thickness, D_i is the diffusion coefficient in the barrier, and K_{iw} is the partition coefficient between the *i*th phase and water (designed as subscripts for the water (W), dialytic membrane (M), and receiving organic phase (S). The overall mass-transfer coefficient is expected to be affected mainly by the diffusion of solutes in individual phases (water, membrane pores, and the PDMS, respectively) and by their partitioning into the PDMS, since no accumulation of hydrophobic analytes is expected in the hydrophilic dialytic membrane (i.e., $K_{MW} \approx 1$).

As can be seen from eq 10, a resistance decrease in receiving organic phase is expected with increasing K_{SW} value for substances having a similar diffusion coefficient in the organic phase D_S.

To obtain more information on the processes involved in the contaminant uptake, clearance (elimination) rate constants (k_e) from the sampler into water are required for the test chemicals. In this study, we were able to make an estimation from the sampling rate and the PDMS/water partition coefficient (K_f(PDMS)) value only:

$$k_e = \frac{k_{ov} A \alpha}{K_{SW} V_S} \approx \frac{R_S}{K_f(\mathrm{PDMS}) V_S} \qquad (11)$$

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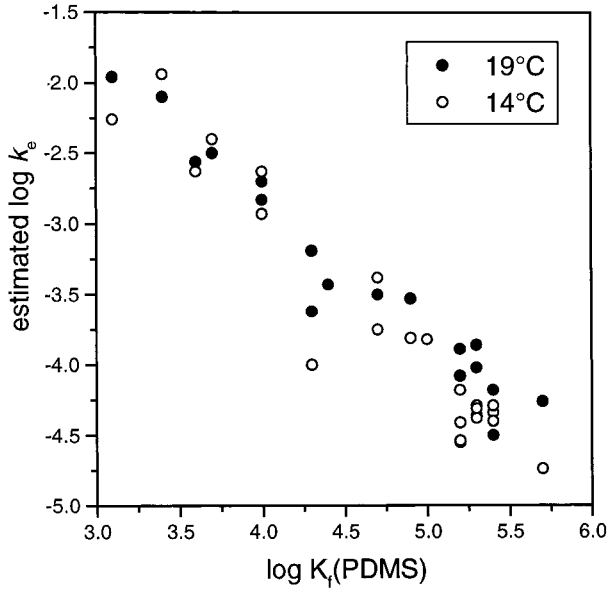

Figure 4. Logarithm of the clearance rate constant log k_e (h^{-1}) estimated using eq 11 versus the logarithm of PDMS/water partition coefficient log K_f(PDMS).

The combination of eqs 10 and 11 allows recognition of the dominant barriers to mass transfer. When the diffusive transport is limited by the resistance in the PDMS and the resistance in water and dialytic membrane is negligible (i.e., if $\delta_M/D_MK_{MW} + \delta_W/D_W \ll \delta_S/D_SK_{SW}$), the elimination rate constant k_e should be independent of K_{SW}. On the other hand, if the transport is limited by the resistance in water or dialytic membrane (i.e., if $\delta_M/D_MK_{MW} + \delta_W/D_W \gg \delta_S/D_SK_{SW}$), the elimination rate constant k_e should be inversely proportional to the equilibrium partition coefficient K_{SW}. Inspection of elimination rate constants estimated from our experimental data using eq 11 shows a linear decrease of log k_e with increasing log K_f(PDMS) at both experimental temperatures (i.e., 14 and 19 °C, respectively; Figure 4). This indicates that mass transfer of these chemicals between the MESCO sampler and the water is governed by the diffusion in the dialytic membrane or the aqueous-phase resistance rather than by the diffusion in the PDMS. We assume that the diffusion in membrane pore water, the inner aqueous phase, or both, are dominant diffusion-limiting steps since the aqueous boundary layer at the surface of the sampler presents only a small part of the total diffusion path and the net flux across the membrane is limited by the small pore area. The elimination rate constant k_e can be experimentally obtained from dissipation studies, and this issue will be addressed in further validation studies.

Predictive Equation for the Sampling Rate. The sampling rate R_S is directly proportional to the overall mass-transfer coefficient k_{ov} (eq 5). To find a predictive equation for the sampling rate, we attempted to correlate the sampling rate with the physicochemical properties of the test compounds (diffusion and partition coefficients). For a first approximation, it can be assumed that diffusion coefficients decrease with increasing molecular weight or size. No simple correlation could be found between R_S at 19 °C (from experiment 1) and logK_f(PDMS) or molecular weight (MW). When lindane (the only nonaromatic compound among test substances) is left out of the data set, bilinear regression for the sampling rate gives a good correlation:

$$R_s = (187 \pm 29)\log K_f(\text{PDMS}) - (2.51 \pm 0.28)\text{MW} + 103 \quad (12)$$

$$n = 22; \quad \text{SD} = 66.36; \quad r = 0.899; \quad F = 40$$

The results of the regression are also shown in Figure 5. The sampling rate (and also the overall mass-transfer coefficient) decreases with increasing molecular weight, which indicates that the sampling process is governed by the diffusion. An increase in sampling rate with increasing K_f(PDMS) value might indicate the loss of resistance to mass transfer in the PDMS with increasing K_{SW} (i.e., K_f(PDMS)) value.

A linear correlation between log K_{ow} and log K_f(PDMS) exists for several compound classes, but the correlation becomes poor when different chemical classes are included into one correlation ($r = 0.74$ in this case).[39] Thus, log K_f(PDMS) values in eq 12 cannot be substituted simply by log K_{ow} values to directly derive the sampling rate from molecular weight and corresponding octanol−water partition coefficient. However, to find a useful predictive equation, we attempted to substitute log K_f(PDMS) with the free energies of solvation in water ΔG_s(w) and in octanol ΔG_s(o), respectively. In a first approximation, nearly identical aqueous solvation energies are assumed in both the octanol−water and PDMS−water systems, respectively. The difference in behavior of both systems is expected to be related to the difference in the free energies of solvation in both organic phases.

Stepwise multilinear regression analysis for log K_f(PDMS) was performed using ΔG_s(w) and ΔG_s(o) as descriptors derived from molecular structure. The best fit was obtained using

$$\log K_f(\text{PDMS}) = (0.03 \pm 0.01)\Delta G_s(\text{w}) - (0.52 \pm 0.07)\Delta G_s(\text{o}) - (0.0049 \pm 0.0007)\Delta G_s^2(\text{o}) - 8.08 \quad (13)$$

$$n = 22; \quad \text{SD} = 0.27; \quad r = 0.92; \quad F = 35$$

The sign of the regression coefficient confirms that, in agreement with theory, increasingly negative free energy of aqueous solvation ΔG_s(w) leads to a decrease in log K_f(PDMS) values of the compounds. However, the ΔG_s(w) term only weakly contributes to the correlation. In the next step, the log K_f(PDMS) term in eq 12 was substituted by a linear combination of descriptors ΔG_s(o) and ΔG_s^2(o), respectively, and multilinear regression for the sampling rate R_s was performed.

This substitution yields a good correlation

$$R_s = -(2.2 \pm 0.3)\text{MW} - (97.8 \pm 19.2)\Delta G_s(\text{o}) - (0.94 \pm 0.19)\Delta G_s^2(\text{o}) - 1505 \quad (14)$$

$$n = 22; \quad \text{SD} = 74.5; \quad r = 0.87; \quad F = 20$$

and enables one to predict the sampling rate of a compound from its molecular weight and hydrophobicity. However, this approach must be further verified in the future.

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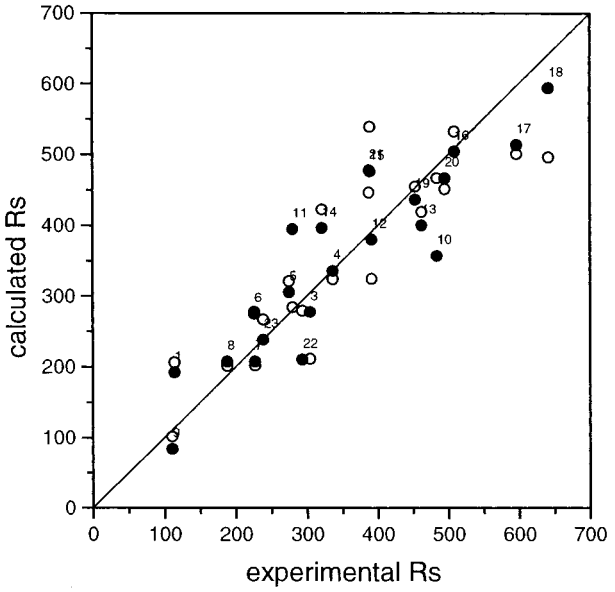

Figure 5. Calculated versus experimental sampling rate (R_S; μL h^{-1}) values at 19 °C according to regression models given in eq 12 (full circles) and eq 14 (hollow circles), respectively. The compounds are identified by numbers as listed in Table 1. Lindane was not included in the calculations.

The results of the regression are also shown in Figure 5. Unfortunately, correlations found for R_S data obtained at 14 °C were of poor quality.

Lag Phase. From the theory, the lag phase τ_0 can be interpreted as the time needed for the contaminant to pass the membrane. Thus, τ_0 is related to the overall mass-transfer coefficient k_{ov}

$$k_{ov} = \delta/\tau_0 \tag{15}$$

where δ is the total diffusion path length. The sampling rate is related to k_{ov} too (eq 5). Therefore, the lag phase is expected to be inversely proportional to the sampling rate, as results from combination of eqs 5 and 15

$$R_S = A\alpha\delta/\tau_0 \tag{16}$$

The higher uncertainty in estimation of intercept values in the experiments enabled us to obtain significant τ_0 values only from experiments conducted at 19 °C and 20 ng L^{-1} nominal concentration (experiment 1) and, for PCB180, from the experiment at 14 °C and 20 ng L^{-1} nominal concentration (experiment 2). Almost identical lag phases of 46 and 44 h were obtained for PCB180 in both experiments.

In agreement with the theory, a decrease in sampling rate with increasing lag phase was observed for PCBs and for very hydrophobic (log K_{OW} > 5.7) PAHs, too, with the exception of benzo[*k*]fluoranthene. For the rest of the tested substances, the dependence is less clear. For more insight into the connection between the sampling rate and the delay time, more detailed kinetic studies conducted in the initial uptake phase are needed.

Effect of Temperature. The relationship between sampling rates of the test analytes and temperature was compared at two temperatures (14 and 19 °C, Table 4). The ratios derived by dividing analyte R_S values determined at 19 °C by those determined at 14 °C ranged from 0.7 to 3.0. No significant differences (unpaired *t*-test; $p = 0.05$) in sampling rates were observed between 14 and 19 °C treatments for PCBs and for γ-HCH. Among PAHs, a significant decrease in sampling rates with decreasing temperature was observed for benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, and benzo[*k*]fluoranthene. Also, the sampling rate of HCB and *p,p′*-DDE decreased significantly with decreasing temperature. The effect of temperature on the sampling rate is not easy to model because of the complexity of the system. Both thermodynamic and kinetic parameters affecting the sampling rate are temperature dependent. For practical purpose, it is therefore necessary to determine the effects of temperature in the laboratory for each analyte of interest and to measure the environmental temperature during field deployment.

Method Sensitivity and Selectivity. MESCO has the potential to detect low TWA water concentrations (ng to pg/L) for two reasons: (1) A substantial enrichment factor is built into MESCO sampling, because dissolved aqueous concentrations are concentrated up to the factor K_{SW} into a Twister. (2) The entire analyte amount on the Twister is introduced to the GC and directed to the detector.

To estimate minimum quantifiable TWA aqueous concentrations, limits of quantitation in MESCO samplers $M_{S(LOQ)}$ were substituted into eq 6. The calculated concentration quantiation limits depend on the sampling rate R_S, and the method sensitivity increases with increasing exposure period of the samplers. When taking a sampler exposure of 20 days for the calculation, estimated quantitation limits range from 4 pg L^{-1} for PCB28 to 140 pg L^{-1} for benzo[*ghi*]perylene, respectively. Actual quantitation limits can be affected, e.g., by interfering substances or bleeding from the PDMS coating during thermodesorption.

The MESCO sampling approach aims at measuring trace concentrations in water that will always contain interfering substances. The selectivity of the MESCO extraction technique is enhanced in two ways: (1) The dissolved molecules become separated from colloids during their diffusion across the dialysis membrane. (2) Hydrophobic target analytes are selectively extracted from the inner aqueous solution by the PDMS sorbent coating.

CONCLUSIONS

The MESCO sampling system combines the passive sampling approach with solventless preconcentration of organic solutes from aqueous matrixes and subsequent desorption of the sequestered analytes on-line with a capillary GC/MS system. This combination presents a low-cost and robust alternative to the currently used passive sampling techniques. Moreover, the hydrophilic cellulose dialysis membrane is permeable for both nonpolar and polar organic species, whereas other passive sampling devices such as SPMDs allow for accumulation of nonpolar substances only. The user of MESCO can easily check the repeatability of the stir bars used for the preparation of the samplers. The Twister stir bar can be reused after each field deployment when no degradation or damage of the membrane occurs during exposure. The samplers are miniature and do not require use of large deployment devices in the field, which enables a nonconspicuous deployment

at sampling sites during monitoring campaigns. Instead of PDMS-coated stir bars, glass fibers coated with PDMS esc. may be used for construction of passive samplers. The advantage of SPME fibers is that accumulated analytes can be analyzed using conventional gas chromatographs without the need of a thermodesorption unit and a cold injection system. However, the volume, and thus also the accumulation capacity of the stir bars, is between 1 and 2 orders of magnitude higher than that of SPME fibers, which makes a sampler with SPME fiber less sensitive.

The performance of the MESCO sampler for integrative sampling of hydrophobic persistent organic pollutants has been demonstrated. The issues, which have to be addressed for further validation of MESCO, include testing (1) the stability of the dialysis membrane during in situ deployment and prevention of its possible degradation, (2) the effect of water turbulence on the uptake kinetics of analytes, (3) the effect of biofouling on the uptake kinetics, (4) the uptake capacity of Twister bars for individual analytes and determination of K_{SW}, (5) the dissipation kinetics of individual analytes from MESCO at varying conditions, and (6) the applicability of the sampler for monitoring polar analytes. As an alternative to thermodesorption, reextraction of analytes from Twister bars by small volumes of organic solvents could be used.[40] The extracts could be then subjected to analysis by HPLC or examined by bioassays.

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SUPPORTING INFORMATION AVAILABLE

Description of the flow-through exposure system, description of processing and analysis of water samples, and results of the fits of kinetic eq 4 to the data from flow-through exposure experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Environ. Sci. Technol. **2002**, *36,* 290−296

Calibrating the Uptake Kinetics of Semipermeable Membrane Devices in Water: Impact of Hydrodynamics

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The use of lipid-containing semipermeable membrane devices (SPMDs) is becoming commonplace, but the potential effects of environmental variables affecting the accumulation of contaminants into SPMDs had not been characterized sufficiently, yet. To characterize the effect of hydrodynamic conditions on the contaminant uptake kinetics, accumulation of pentachlorobenzene, hexachlorobenzene, and hexachlorocyclohexane isomers from water into SPMD was studied at various water flow rates. The accumulation kinetics of hydrophobic compounds (log K_{ow} > 4) are governed by the aqueous boundary layer in linear flow velocity range from 0.06 to 0.28 cm s^{-1} and sensitive to slight changes in flow rate. The effect of flow velocity on the exchange kinetics increases with increasing hydrophobicity. Under faster, but still laminar flow conditions (0.28−1.14 cm s^{-1}), the sensitivity to changes in flow decreases to a nonsignificant level for the substances under consideration. The results of this study confirm that the use of the laboratory-derived calibration data for estimation of analyte concentrations in the ambient environment is limited unless flow-sensitive performance reference compounds are used.

Introduction

Passive monitors are rapidly gaining wide acceptance for assessing integrated, or time-weighted, concentrations of organic chemicals in aquatic systems. One category of passive sampler, the lipid-containing semipermeable membrane devices (SPMD), introduced by Huckins et al. (*1*) has received a great deal of attention. The SPMD sampler consists of lay-flat polyethylene tubing containing a thin film of triolein, a high molecular weight neutral lipid. The polyethylene used in SPMD is commonly referred to as nonporous, even though transient cavities with diameters approaching ∼10 Å are formed by random thermal motions of polymer chains (*2*). The thermally mediated transport corridors of the polyethylene exclude larger molecules, as well as those that are adsorbed on sediments or humic acids. Only truly dissolved (but generally nonionized) contaminants are sequestered. The process mimics the transfer of organic contaminants through biomembranes. The utility of the SPMD has been shown for monitoring aqueous residues of polychlorinated biphenyls, various organochlorine pesticides, polychlorinated dibenzodioxins, polychlorinated dibenzofurans, and polycyclic aromatic compounds.

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Current research results show that the SPMD can be used to estimate time-weighted average (TWA) concentrations of organic contaminants in aquatic environments. The theory and several mathematical models at different levels of complexity required to compute TWA ambient concentrations of analytes from SPMD concentrations have been described earlier (*2*−*7*). The uptake rates of contaminants into SPMD are affected by several factors including the sampler design, molecular properties, and environmental conditions. The environmental factors include temperature, biofouling impedance, and water velocity/turbulence. For correct estimation of ambient chemical concentrations from the field SPMD data, and for development of adequate calibration methods, it is necessary to sufficiently characterize the potential effects of environmental variables, in particular the impact of hydrodynamics on the uptake kinetics.

Booij et al. (*6*) studied the effects of changes in flow turbulence on the exchange kinetics of organochlorine compounds with a wide range of K_{ow} values ($4 < \log K_{ow} < 8$) in diluted sediment suspensions. He showed that the average exchange rate of chemicals between SPMD and water decreased by a factor of 4 under conditions of low turbulence. Huckins et al. (*8*) found a 1.5-fold increase in exchange rates with a 50-fold increase in velocity (range of 0.004−0.2 cm s^{-1}). Most calibration studies have been conducted under low flow conditions; therefore, there is a need for characterization of the sensitivity of the calibration procedure to slight changes in laminar flow rate.

To characterize the effect of hydrodynamic conditions on the contaminant uptake from water into SPMD, we examined the effect of various low linear flow velocities (flow rates) on the uptake kinetics of several organochlorine compounds with K_{ow} values ranging from 3.8 to 5.5.

Modeling. To describe the uptake of contaminants from water to SPMD exactly, it would be necessary to use the Fick's second law for each compartment of the system, that is, for lipid, the SPMD membrane and water near the surface of the device, respectively (*9*). The inhomogeneity of each phase, which manifests itself by the presence of the diffusion layers, and the different solvations of the substances in different phases ought to be also taken into account. The resulting description would be most probably too complicated for a direct comparison with our experimental data. Its simplification can be based on the plausible assumption of quick diffusion within the bulks of the compartments with regard to the duration of experiments, which can be justified using the solution of Fick's second law for the one-dimensional diffusion into a plane sheet of isotropic medium (*9*). This greatly simplifies the description of the transport, and the second-order partial differential equations based on Fick's second law can be replaced by a set of linear differential equations of the first order.

The least complex approach for modeling the uptake of chemicals from water to SPMD given by Huckins et al. (*5*) is based on the description of the SPMD as a single compartment. The SPMD membrane is expressed as a lipid equivalent volume, and the SPMD sampler can be treated as a single compartment

$$K_{SPMD} = K_{Lw}(V_L + K_{mL}V_m)/V_{SPMD} \quad (1)$$

where K values are partition coefficients among SPMD components [designated as subscripts for the whole SPMD, SPMD lipid (L), and the SPMD membrane (m) and water (w)] and V is the volume of a phase designated by subscripts.

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When assuming a constant concentration in water, the concentration for the whole device uptake is given by

$$C_{SPMD} = C_w K_{SPMD}(1 - \exp[-k_e t]) \quad (2)$$

Here, C values are analyte concentrations and k_e is the elimination rate constant, which is also called the overall exchange coefficient. The chemical uptake into SPMD remains linear and integrative in the initial period of the exposure until the concentration factor (CF, ratio C_{SPMD}/C_w) in the SPMD reaches about half-saturation ($k_e t < \ln 2$) (*7*) and then eq 2 can be reduced to

$$C_{SPMD} = C_w K_{SPMD} k_e t = C_w R_s t / V_{SPMD} \quad (3)$$

where R_s is the apparent SPMD sampling rate. The elimination rate constant k_e can be broken down to several fundamental parameters

$$k_e = \frac{A}{K_{SPMD} V_{SPMD}} \frac{1}{(1/k_w + 1/k_{SPMD} K_{SPMD})} \quad (4)$$

where k_w is the mass transfer coefficient in the aqueous boundary layer and k_{SPMD} is the apparent mass transfer coefficient for transport in the SPMD sampler from the surface of the SPMD to the location of chemical storage in the SPMD. The term in parentheses is the overall resistance to the uptake of a chemical. Analogously to the theory for diffusion through two films in series (*10*), overall resistance is given by the sum of independent and additive resistances to mass transfer for the stagnant aqueous film at the surface of the SPMD ($1/k_w$) and for the SPMD ($1/k_{SPMD}K_{SPMD}$). These resistances can be expressed as SPMD-specific residence times τ_w and τ_{SPMD}, which combine with K_{SPMD} to model the elimination rate constant k_e (or overall residence time τ):

$$\frac{1}{k_e} = \frac{V_{SPMD}}{A}\left(\frac{K_{SPMD}}{k_w} + \frac{1}{k_{SPMD}}\right) = \tau_w K_{SPMD} + \tau_{SPMD} = \tau \quad (5)$$

The group V_{SPMD}/Ak_w is thus the aqueous boundary layer residence time τ_w, and V_{SPMD}/Ak_{SPMD} is the SPMD residence time τ_{SPMD}.

In extreme cases, the uptake rate for the whole device is controlled either by the SPMD (or, more specifically, by the polymeric membrane of the SPMD) or by the aqueous boundary layer, depending on the analyte properties and exposure conditions. Examination of eqs 4 and 5 indicates that a high partition coefficient between SPMD and water (K_{SPMD}) effectively reduces the resistance to mass transfer in the SPMD. Gale (*7*) predicted an SPMD control for the accumulation of large molecules with low polymer diffusivity or for accumulation at lower temperatures. On the other hand, aqueous film diffusion may control the accumulation of highly polymer-diffusive molecules and highly hydrophobic substances with low resistance to mass transfer in SPMD due to a high K_{SPMD} value. Similar uptake rate constants (i.e., $k_e \times K_{SPMD}$) of chemicals with widely different partition coefficients are an indicator of the limitation of mass transport to and from the SPMD by the resistance in the aqueous phase, whereas increasing uptake rate constants with increasing K_{SPMD} show that the membrane resistance likely governs the mass transport.

Huckins et al. (*2*, *5*) have suggested adding performance reference compounds (PRC) to SPMD lipid prior to deployment. PRCs are analytically noninterfering compounds with a low to moderate hydrophobicity (up to log K_{ow} of ~5.0), that can be used for in situ calibration of the exchange rates. This approach is based on the assumption that uptake rates of chemicals can be derived from measurements of loss rates of PRCs (*2*, *6*). Uptake and release are considered to be isotropic processes. The release of a PRC from the SPMD, when the concentration of this compound in the environment is negligibly low, can be described by a first-order-decay kinetic equation

$$C_{SPMD} = C_0 \exp(-k_e t) \quad (6)$$

where C_0 is the concentration of PRC in SPMD at the beginning of exposure.

Experimental Section

Materials and Chemicals. The solvents acetone, dichloromethane, hexane, and 2-propanol of LiChrosolv quality were obtained from Merck. Hexachlorobenzene (HCBz), pentachlorobenzene (PeCBz), hexachlorocyclohexane (HCH), [$^{13}C_6$]-α-HCH, [$^{13}C_6$]PeCBz, and [$^{13}C_6$]HCBz standards were obtained from Supelco. [$^2H_{10}$]Anthracene (D_{10}-ANT) (98% pure) was obtained from DeuChem, Leipzig, Germany.

SPMDs with standard configuration, designed by Huckins et al. at the U.S. Geological Survey in Columbia, MO, consisting of a thin film of 1 mL of triolein (95% pure) sealed in a low-density polyethylene lay-flat tube (2.54 × 91.4 cm, 75−90 μm wall thickness), were purchased from ExposMeter AB, Tavelsjö, Sweden. They were stored in original gastight metal paint cans until just before exposure.

Laboratory Exposures. *Static Exposures.* Batch exposures were conducted in amber glass flasks containing 1 L of double-distilled water and one SPMD each. Immediately before exposure, SPMD lipid was spiked with 1 μg of each HCH isomer or with PeCBz, HCBz, and D_{10}-ANT. For spiking a small cut was made at one end of the SPMD, and 50 μL of hexane solution of test chemicals in hexane (0.02 μg μL^{-1}) was injected into the membrane using an HPLC syringe (volume = 100 μL). The punctured SPMD was heat-sealed again, and the spiked solution was homogenized with the triolein by squeezing the SPMD content several times from one end to the other using latex gloves. For the HCH exposure study two replicate SPMDs were sampled on days 0, 1, 5, 14, and 22 of the exposure. For PeCBz, HCBz, and D_{10}-ANT, SPMDs were sampled on days 0, 35, and 47 of the exposure. Water samples (1 L) were taken at each SPMD sampling time. The triolein and the polyethylene membrane of each SPMD were analyzed separately as described below.

Flow-through Exposures. SPMDs were exposed to test chemicals at a nominal concentration of 50 ng L^{-1} and to control water in a flow-through exposure system. Exposures were conducted at 19 °C. The experimental setup consisted of a 1 m high glass column with either 15 or 7.5 cm inner diameter with a sieve-like perforated bottom (openings of 0.5 cm diameter). The column was covered with dark foil to prevent photodegradation of analytes during exposure. The exposure water was pumped from the bottom to the top of the column. Test chemicals were dissolved in methanol, and the appropriate amounts of stock solution were delivered into exposure water in a 1 L chamber positioned at the bottom of the column using a peristaltic pump (Minipuls 3, Gilson). The water in the chamber was mixed using a magnetic stirrer with the turning speed of 600 min^{-1}. The methanol concentration in the exposure water was held constant at 0.01% (v/v) in all exposure studies. This concentration was not expected to significantly affect the partitioning of test chemicals between SPMD and water. Tap water was fed to the chamber using a membrane pump (Prominent) at 36−180 L h^{-1}. This setup enabled the flow rate in the exposure column to be varied. Exposures were conducted at flow rates of 0.06, 0.18, and 1.14 cm s^{-1}, respectively. Before exposure, SPMDs were spiked with 25 μL of a hexane stock solution of D_{10}-ANT using an HPLC syringe (volume = 25 μL) to give a final concentration of 10 μg per SPMD. SPMDs were fixed in the column in a vertical position using Teflon rings at the top

TABLE 1. Summary of SPMD Flow-Through Exposure Experimental Conditions

expt	nominal concn of chemicals (ng L^{-1})	linear flow velocity (cm s^{-1})	exposure period (h)	no. of SPMDs sampled
0	<MDL[a]	0.06	0−408	8
1	50	0.06	0−760	10
2	50	0.28	0−336	14
3	50	1.14	0−498	10

[a] MDL, method detection limit.

and the bottom of the column. The exposures lasted from 14 to 31 days. The membranes were sampled at time intervals, and the content of test chemicals accumulated during exposure was determined. Duplicate samples of water (2 L) in the exposure column were taken at each time when SPMDs were sampled and analyzed according to the procedure described below. The experimental conditions of individual exposures are given in Table 1.

SPMD Processing. SPMDs from flow-through exposure studies were analyzed as described earlier (*12*). Briefly, the devices were first subjected to an exterior cleanup. SPMDs were then dialyzed three times with 250 mL of hexane per SPMD at 18 °C for 24 h. The dialysates were combined, and their volume was reduced by rotary evaporation and with streams of high-purity nitrogen to dryness. The residue was redissolved in dichloromethane and cleaned up by size exclusion chromatography. The fraction containing the compounds of interest was concentrated, redissolved in hexane to a 1 mL final volume, and used for GC analysis.

For SPMD from static exposures, polyethylene membrane and lipid were analyzed as separate samples. Empty membranes were processed according to a procedure used for whole SPMD with the difference that the dialysis step was repeated only twice. Lipid was quickly washed out from the SPMD using three rinses of hexane (5 mL per rinse), and the combined hexane rinses were filled into freshly prepared and contaminant-free polyethylene membranes and processed according to a procedure used for whole SPMDs.

The residues in the water samples were extracted using solid phase extraction (SPE) (see Supporting Information).

Instrumental Analysis and Quality Control. The quantitation and qualitative control of the compounds of interest was made by GC (HP 5890), interfaced to a mass spectrometric detector (280 °C), and a capillary column (30 m × 0.25 mm i.d.) with a nonpolar stationary phase ULTRA 2 (thickness = 0.5 μm). Temperature conditions were as follows: injector, 250 °C; column, 60 °C (1 min), raised at 30 °C/min to 150 °C, raised at 6 °C/min to 186 °C, and raised at 4 °C/min to 280 °C, which was held for 11.5 min. Quantitation of the residues was accomplished using a 10-point external standard curve.

An SPMD blank (unspiked and unexposed SPMD) was taken through the entire dialytic and cleanup procedure (procedural blank) for each batch of SPMD samples from the diluter and static studies. Spiked SPMDs were analyzed by fortifying fresh membranes and then processing them as a sample (see Supporting Information). Chemical concentrations found in different matrices (SPMD, membrane, lipid, and water) were corrected for losses during the sample handling using recovery rates derived from spiking studies.

Results and Discussion

Static Exposures. The partitioning of test substances between the SPMD compartments, that is, membrane and lipid, during the static exposure indicates that the system approached equilibrium distribution after ~100 h for all test substances. We used the data from longer times (i.e., >120 h) for calculation of partition coefficients of test substances between SPMD compartments and water. The K_{Lw} values estimated for HCH isomers from the static exposures are comparable with their octanol−water partition coefficients, which is in a good agreement with the study of Chiou (*18*), who observed almost equality of the partition coefficients for selected nondissociating organochlorine compounds with log K_{ow} < 5. For PeCBz, HCBz, and D_{10}-ANT the concentration in water did not exceed the limits of detection (2, 2, and 6 ng L^{-1}, respectively). Therefore, only K_{mL} values were obtained for these substances from static exposures, and the K_{Lw} values directly measured by Chiou (*18*) were taken for calculation of K_{SPMD} values of PeCBz and HCBz. K_{SPMD} values were calculated using eq 1. The K_{SPMD} value for D_{10}-ANT was interpolated from the linear dependence of log K_{SPMD} on log K_{ow} for the test substances. An estimate of K_{SPMD} values was also performed using the method detection limits in the aqueous phase as a substitute for the equilibrium aqueous concentration. K_{SPMD} values of 4.7, 4.9, and 3.9 were obtained for PeCBz, HCBz, and D_{10}-ANT, respectively. The difference in log K_{SPMD} values obtained by the two different approaches was not greater than 0.1 log unit. The mean values of determined partition coefficients are summarized in Table 2 together with related values from the literature.

TABLE 2. Summary of SPMD Partition Coefficients Derived from Static Exposures

compound	log K_{ow}[a]	log K_{Lw} (lit.)[b]	log K_{Lw} (exptl)	CV (%)	K_{mL}	CV (%)	log K_{SPMD}[c]
α-HCH	3.80		3.82	25	0.052	11	3.31
β-HCH	3.80		4.03	13	0.020	24	3.26
γ-HCH	3.70		3.66	16	0.057	13	3.22
δ-HCH	4.10		3.91	14	0.015	15	3.56
PeCBz	5.20	5.27	5.38[d]		0.095[c]	41	4.73[e]
HCBz	5.50	5.50	5.57[d]		0.122[c]	30	4.99[e]
D_{10}-ANT	4.54		4.58[d]		0.167[c]	32	4.04[f]

[a] Preferred or selected values from refs *16* and *17*. [b] Values from ref *18*. [c] $n = 4$. [d] Method detection limits were taken as a substitute for the equilibrium aqueous concentration. [e] Literature value of K_{Lw} was taken for calculation. [f] Value interpolated from linear dependence of log K_{SPMD} on log K_{ow} for the test substances.

Flow-Through Exposures. The effect of the aqueous film resistance to mass transfer can be investigated when exposure studies are conducted under various hydrodynamic conditions. The exposures were conducted at flow rates for which a laminar character of the flow in the major part of the exposure column was observed. This was checked by observing the dissolution of $KMnO_4$ grains in water flowing through the exposure column. Concentrations of the analytes in water (C_w) and in the SPMD (C_{SPMD}) were two parameters measured regularly during the continuous flow exposures. During the exposure the water concentration was held constant, which was confirmed by analyses of water samples. All SPMDs exposed to control water without addition of analytes, and also SPMD blank samples, contained less than method detection limits (MDL) of test substances. MDL values ranged from 8 ng/SPMD for α-HCH to 23 ng/SPMD for D_{10}-ANT. Average water concentrations of test substances in exposure water ranged from 27 to 62 ng L^{-1}. The independence of SPMD concentration factors (CFs) relative to aqueous solute concentrations was demonstrated previously (*1*−*3*, *5*). Therefore, CFs were used to express the data. The variance of calculated concentration factor values up to 16% was estimated from the coefficients of variation (CV) of the concentration in the SPMD (12%) and of the concentrations in the aqueous phase (11%), according to the law of error propagation. Characteristic uptake curves are shown in Figure 1.

The uptake was modeled using linear and nonlinear (Levenberg−Marquardt algorithm) regression analysis. Curve

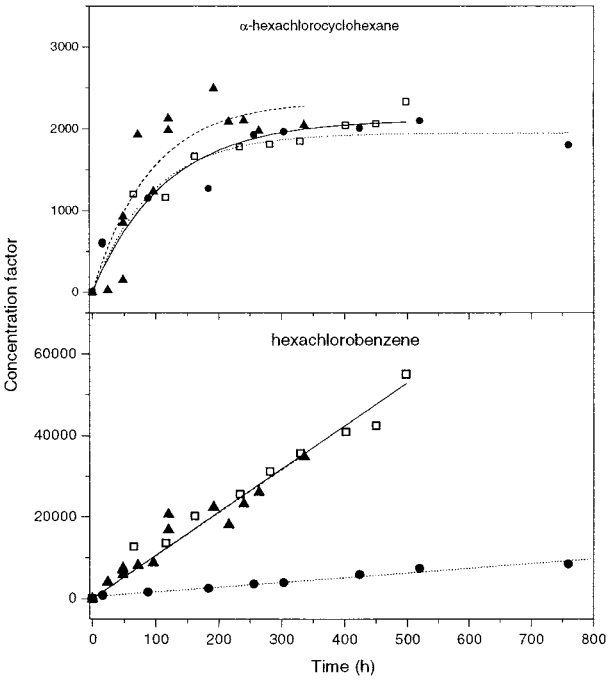

FIGURE 1. Uptake of α-hexachlorocyclohexane (top) and hexachlorobenzene (bottom) by SPMD exposed under conditions of different linear flow velocities: 0.06 cm s^{-1} (circles, dotted lines), 0.28 cm s^{-1} (triangles, dashed lines), and 1.14 cm s^{-1} (squares, solid lines). The flow-through exposures were conducted at 19 °C at nominal chemical concentrations of 50 ng L^{-1}. The lines correspond to eqs 2 and 3 with the optimized values of the parameters given in Table 3.

fitting was performed with Origin 5.0 (Microcal Software). The experimentally determined time courses of the CFs of individual HCHs in the SPMD were fitted by nonlinear regression analysis using eq 2 with K_{SPMD} and k_e as adjustable parameters. In the case when the CF of the compound did not reach half of the K_{SPMD} value (for PeCBz and HCBz), eq 3 with k_e as the only adjustable parameter was used for linear regression analysis of the uptake curves. The K_{SPMD} values needed for these calculations were taken from Table 2. Note that estimated values of K_{SPMD} were used for PeCBz, HCBz, and D_{10}-ANT, respectively.

A satisfactory fit of kinetic eq 2 to the experimental data was obtained for all HCH isomers in all exposure experiments. Relatively accurate values of the parameters K_{SPMD} (CVs not exceeding 14% of the estimate) and k_e (CV < 39%, except of one case for β-HCH, 49%) were obtained. The higher uncertainty in the estimation of k_e values results from lack of data in the initial linear uptake period. A variation between 9 and 40% was observed in K_{SPMD} values for individual HCHs among experiments conducted at different flow rates. A difference of up to a maximum of 0.5 log unit was observed between log K_{SPMD} estimates from flow-through exposure data and values from static exposures for individual HCHs.

With regard to PeCBz and HCBz, a good fit of eq 3 to the experimental data was obtained, too. CVs of the calculated k_e did not exceed 5%.

The release of D_{10}-ANT was modeled using eq 6 with C_0 and k_e as adjustable parameters. Figure 2 shows the release kinetics of this compound under different flow conditions. Estimates of C_0 ranged between 89 and 109% of the calculated value. CVs of the k_e for this compound varied between 12 and 17%.

Effect of Flow on the Exchange Kinetics. To examine the effect of flow velocity on the mass transfer, best fit values of k_e obtained for individual compounds under various flow

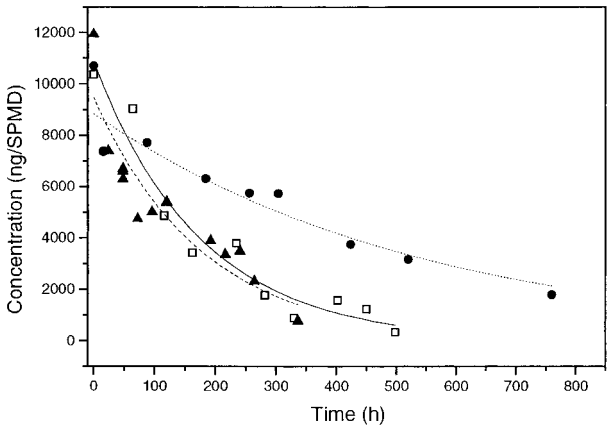

FIGURE 2. Release of [$^2H_{10}$]anthracene from SPMDs exposed at different linear flow velocities: 0.06 cm s^{-1} (circles, dotted lines), 0.28 cm s^{-1} (triangles, dashed lines), and 1.14 cm s^{-1} (squares, solid lines). The flow-through exposures were conducted at 19 °C. The lines correspond to eq 7 with the optimized values of the parameters given in Table 3.

conditions (0.06, 0.28, and 1.14 cm s^{-1}) were compared using an unpaired t test ($p = 0.05$). For HCHs, no significant difference was observed between k_e values determined at different flow rates. The only exceptions were the k_e values for β-HCH and δ-HCH at flow rates of 0.28 and 1.14 cm s^{-1}. However, in these cases the difference could not be attributed to the change of the aqueous film thickness, because the k_e values determined at higher flow rate (1.14 cm s^{-1}) were in both cases smaller than at the lower one (0.28 cm s^{-1}).

With regard to more hydrophobic chemicals, a significant difference was observed between k_e values determined at the lowest flow rate (0.06 cm s^{-1}) and at both higher flow velocities. At a flow rate of 0.28 cm s^{-1}, k_e for PeCBz is higher than that at 0.06 cm s^{-1} by a factor of 3 and for HCBz by a factor of 9. The further increase in flow rate from 0.28 to 1.14 cm s^{-1} did not cause any further significant increase in k_e values.

The release kinetics of D_{10}-ANT was used as an independent measure of the exchange kinetics between SPMD and water. It was significantly affected by the flow, too. A 5-fold increase in flow rate from 0.06 to 0.28 cm s^{-1} results in a 3-fold increase in k_e. Only a slight, but insignificant, decrease in k_e value was observed with the further 4-fold increase in flow velocity to 1.14 cm s^{-1}.

No significant effect of flow conditions on the uptake of moderately hydrophobic HCH, and, on the other hand, a strong effect increasing with the K_{ow} correspond well with the theory of diffusion through two films in series (*10*), which assumes a switch in the overall mass transfer to the aqueous phase control for very hydrophobic compounds (eq 5).

Mechanism of Accumulation. To obtain a more detailed insight into the mechanism of the accumulation process, we tried to characterize the contribution of aqueous and polymer film resistance to the overall mass transfer. For this purpose, k_e values were fitted to eq 5. K_{SPMD} values needed for the analysis were taken from Table 2. Direct linear regression of the data is not desirable because $1/k_e$ and K_{SPMD} vary over 2 orders of magnitude; thus, the regression is weighted heavily in favor of the larger values. Therefore, we preferred to perform the regression on the logarithmic quantities, assuming a log-normal distribution of the errors. In addition, the assumption was made that k_{SPMD} values are the same for all compounds and for all three exposure experiments and that k_w values are the same for all compounds within each single experiment, respectively. This assumption could be made because test compounds are nonpolar and they have

TABLE 3. Summary of SPMD Exchange Coefficients and Partition Coefficients Derived from Flow-through Exposures

	linear flow velocity											
	0.06 cm s^{-1}				0.28 cm s^{-1}				1.14 cm s^{-1}			
compound	$k_e \times 10^3$ (h^{-1})	CV (%)	log K_{SPMD}	CV (%)	$k_e \times 10^3$ (h^{-1})	CV (%)	log K_{SPMD}	CV (%)	$k_e \times 10^3$ (h^{-1})	CV (%)	log K_{SPMD}	CV (%)
α-HCH	10.56	28	3.29	6	10.98	33	3.37	13	8.67	18	3.32	5
β-HCH	18.09	49	2.91	9	9.99	18	2.87	8	4.65	32	3.17	14
γ-HCH	14.07	39	3.17	8	13.07	20	3.22	7	7.07	21	3.33	7
δ-HCH	7.94	35	3.01	10	9.66	19	3.09	8	4.71	24	3.34	10
PeCBz	0.57	5	—[a]		1.77	5	—[a]		1.40	3	—[a]	
HCBz	0.13	4	—[a]		1.25	5	—[a]		1.40	4	—[a]	
D_{10}-ANT	1.87[b]	17			5.66[b]	15			5.75[b]	12		

[a] Not used as adjustable parameter because equilibrium was not approached during the exposure. [b] k_e value determined from the dissipation rate.

TABLE 4. Values of Mass Transfer Coefficients for the SPMD (k_{SPMD}) and the Aqueous Boundary Layer (k_w) Obtained as Optimized Parameters of the Nonlinear Regression Analysis of the Elimination Rate Constant (k_e) as Dependent on the SPMD–Water Partition Coefficient (K_{SPMD}) Using Equation 7[a]

flow velocity (cm s^{-1})	log k_{SPMD} (m s^{-1})	τ_{SPMD} (h)	log k_w (m s^{-1})	τ_w (s)	R_s (L day^{-1})
0.06	-9.44 ± 0.09	79	-6.03 ± 0.12	112	3.6
0.28	-9.44 ± 0.09	79	-5.44 ± 0.15	29	14.0
1.14	-9.44 ± 0.09	79	-5.57 ± 0.14	38	10.4

[a] Statistical indices of the fit are the number of data points $n = 21$, the correlation coefficient $r = 0.94$, and the standard deviation of the fit $s = 0.70$. The aqueous boundary layer residence time τ_w and the SPMD residence time τ_{SPMD} were calculated as V_{SPMD}/Ak_w and V_{SPMD}/Ak_{SPMD}, respectively. The apparent sampling rate R_s of compounds accumulated under aqueous boundary layer control was calculated as k_wA.

similar molecular weights and sizes. Therefore, diffusion coefficients of the test substances and mass transfer coefficients determined at constant conditions in particular matrices (water or SPMD) are expected to be approximately the same. In this way, the nonlinear regression was simultaneously performed with all k_e values obtained in all experiments using the rearranged eq 5 as a fitting function

$$Y = \log(A/V_{SPMD}) - \log(\sum_{i=1}^{3} z_i \times 10^{X-A_i} + 10^{-B}) \quad (7)$$

where $X = \log K_{SPMD}$ is the independent variable; z_i are indicator variables taking the value $z_i = 1$ for experimental data from the ith experiment, for the rest of the data, $z_i = 0$; and $Y = \log k_e$ is the dependent variable. Adjustable parameters are the mass transfer coefficient in the aqueous film for the ith experiment $A_i = \log k_{wi}$, and in the SPMD $B = \log k_{SPMD}$, respectively. The fit results are summarized in Table 4 and shown in Figure 3. Note that also k_e values for D_{10}-ANT obtained from the kinetics of dissipation were included into the analysis.

Membrane Resistance. According to the two-resistance theory, the less hydrophobic compounds ($\log K_{SPMD} < 3.6$); that is, HCHs seem to be accumulated under sampler (membrane and lipid) control. The resistance to mass transfer in the SPMD can be viewed as two particular resistances acting in series, one for transport in the polymeric membrane and the other for transport in the receiving lipid phase. It can be shown that these resistances are additive

$$\frac{1}{k_{SPMD}K_{SPMD}} = \frac{\delta_m}{D_m K_{mw}} + \frac{\delta_L}{D_L K_{Lw}} \quad (8)$$

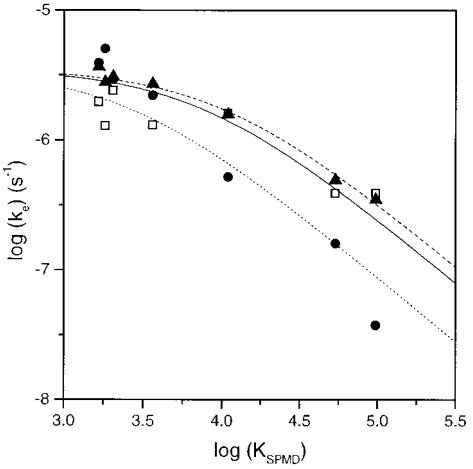

FIGURE 3. Dependence of the elimination rate constant k_e on the SPMD–water partition coefficient K_{SPMD} at different linear flow velocities: 0.06 cm s^{-1} (circles, dotted lines), 0.28 cm s^{-1} (triangles, dashed lines), and 1.14 cm s^{-1} (squares, solid lines). The lines correspond to eq 7 with the values of adjustable parameters log k_{SPMD} and log k_w given in Table 4.

where constant diffusion coefficients D_m and D_L in the phase films of thickness δ_m and δ_L are assumed for the membrane and the lipid, respectively. The last additive term in eq 8 can be neglected, because the resistance to diffusion in lipid is small in comparison with the resistance to diffusion in the membrane and in the aqueous boundary layer, respectively. From the estimated k_{SPMD} value of 3.7×10^{-10} m s^{-1} the corresponding polyethylene film diffusion coefficient D_m for the group of test substances was calculated using eq 8 after the introduction of $K_{mw} = K_{mL}K_{Lw}$, taking $\delta_m = 82.5$ μm and neglecting the resistance to diffusion in lipid. The value of D_m, ranging from 6×10^{-11} to 3×10^{-10} cm^2 s^{-1}, corresponds well with the value of 3×10^{-11} cm^2 s^{-1} estimated for phenathrene by Huckins et al. (*2*) and the value of the order of 10^{-10} estimated for a series of chlorinated hydrocarbons by Booij et al. (*6*), respectively. In general, the diffusion coefficient in polymer is a substance-specific quantity, which is controlled by physicochemical properties of diffusant molecules. For nonpolar molecules steric effects could control diffusion in the polyethylene membrane. Therefore, k_{SPMD} derived in this study has to be considered as a rough estimate valid only for a group of compounds with properties similar to the compounds tested (small nonpolar molecules). The SPMD residence time τ_{SPMD} of 79 h is calculated, which indicates that SPMD sampling exceeding 2 days (i.e., ln $2\tau_{SPMD}$) cannot be considered as integrative for substances accumulated under membrane control. For exposures exceeding about four halftimes of

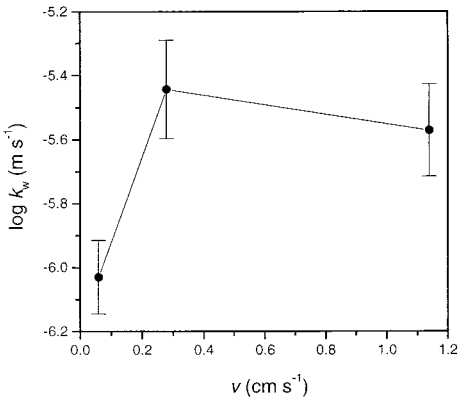

FIGURE 4. Dependence of the mass transfer coefficient in the aqueous boundary layer k_w as a function of linear flow velocity v in the flow-through exposure system.

the uptake curve [i.e., 4(ln $2\tau_{SPMD}$)], aqueous concentrations can be estimated using the equilibrium partitioning approach, that is, $C_w = C_{SPMD}/K_{SPMD}$. The actual concentration of a compound accumulated in SPMD will reflect concentration changes in the aqueous phase during exposure with a time delay of τ_{SPMD}.

Aqueous Boundary Layer Resistance. For more hydrophobic compounds (log $K_{SPMD} > 3.6$), the transport kinetics are governed by the aqueous boundary layer. This is indicated by the decrease in k_e values with increasing K_{ow} and also by the fact that k_w values are a function of the flow rate.

Aqueous film theory (*13*, *14*) hypothesizes a liquid boundary layer of thickness δ_w, which is postulated to be completely stagnant and nonconvected, so that a solute molecule crosses it by pure diffusion only. At steady state, the aqueous phase mass transfer coefficient is given by

$$k_w = \frac{D_w}{\delta_w} \tag{9}$$

where D_w is the diffusion coefficient in the aqueous phase. The film theory predicts an increase in k_w at faster flow rates because δ_w decreases.

The quantitative computations of the value of diffusional flux in a laminar fluid (*13*, *19*) show that the mass transfer coefficient k_w should be a function of the characteristic fluid velocity v, in accordance with law v^n, for a great variety of geometrical shapes of streamlined bodies and for different types of surface. When the flow is across the surface of a plate in a fluid under forced convection, the exponent n is equal to 0.5. The dependence of k_w observed in our study seems to follow this trend (Figure 4). The mass transfer coefficient increases initially with the flow rate, but later the increase becomes less expressive (insignificant in our case). Unfortunately, even for the simple experimental setup used in our study, the hydrodynamics of the system is fairly complicated, that is, SPMDs affect the current profile, entrance effects occur at the bottom of the exposure column, etc. Therefore, a quantitative comparison of the experimentally determined dependence $k_w = f(v)$ with theoretical computations is precluded and a direct comparison of the data with other calibration studies (*3*, *6*) is impossible, too.

The same type of dependence, that is, $k_w(v) = Av^{0.5}$, is expected to be valid also for uptake data based on SPMD placement at right angles to a very slow flow (*3*, *5*), provided that the streaming was laminar.

Almost equal values of aqueous diffusion coefficients D_w were estimated for the tested group of compounds ranging from 6×10^{-6} to 7×10^{-6} cm^2 s^{-1} (*15*). From eq 9, the estimated boundary aqueous film thickness decreases approximately from 780 to 170 μm with increasing flow rate. The magnitude of the boundary layer thickness corresponds with that of ~400 μm estimated by Gale (*7*) from uptake data obtained in a relatively quiescent dilutor system (i.e., flow < 1 cm s^{-1}). In environmental systems the effective thickness of the aqueous boundary layer can vary from ~10 μm (extremely turbulent/high flow conditions) to >1000 μm (deep stratified lakes of deep seas) (*20*). In practice, the variation of flow at the surface of in situ exposed SPMDs can be reduced by the use of appropriate SPMD deployment devices. The advantage of the aqueous boundary layer control in comparison with the membrane layer control is that the transport kinetics are of low selectivity for compounds with similar molar mass and K_{ow} value. Diffusion coefficients in water of the magnitude of 10^{-5} cm^2 s^{-1} are observed for the most compounds with molar masses up to 500 g mol^{-1}. Therefore, the exchange rate parameters are likely to be similar for compounds of similar size and hydrophobicity. On the other hand, calibration studies and field exposures must manage the effect of flow, because the hydrodynamic regime can strongly affect the resistance of the aqueous boundary layer to mass transfer. The results of this study indicate that the accumulation kinetics of hydrophobic compounds (log $K_{ow} > 4.5$) is sensitive to slight changes in flow approximately up to the flow rate of 0.28 cm s^{-1}. Under faster, but still laminar, streaming (0.28 cm s^{-1} < v < 1.14 cm s^{-1}), the sensitivity of the mass transfer to changes in flow decreases to a nonsignificant level for the substances under consideration.

Management of the Effect of Hydrodynamics on the Exchange Kinetics. This study confirms that for accurate estimation of aqueous contaminant concentrations from the amounts accumulated by SPMDs it is absolutely necessary to manage the effect of flow regime on the exchange kinetics. Achievement of a strictly controlled flow is rather complicated in laboratory experiments and almost impossible to reproduce in the field without expensive equipment. It is more realistic to conduct the calibrations under conditions of a low sensitivity to small changes in flow and to construct appropriate field deployment devices, buffering the flow efficiently so that a good correspondence of the exchange kinetics of contaminants in situ with the calibration data is obtained. The results of this study indicate that there might be an optimal regime under laminar flow conditions. In the case of a turbulent exterior flow, the theory leads to a proportionality of the limiting diffusional flux to the 0.8−0.9 power of velocity (*19*). Thus, an additional increase of k_w with increasing flow rate is expected when the flow regime switches from laminar to turbulent. Note that the change of k_w causes also a shift of the actual point of switch (i.e., analyte K_{SPMD} value) from aqueous layer control to membrane control (*20*).

For the necessary laboratory−field comparison of the exchange kinetics, PRCs should be used. The desired attribute of a PRC is the high sensitivity of k_{e^-PRC} to changes in flow. The release kinetics of D_{10}-ANT, a PRC compound used in this study, follows the changes in flow rate with a quite satisfactory sensitivity (note that anthracene is photosensitive and should be used with caution in the field studies). Compounds with moderate hydrophobicity (log K_{ow} < 4) are disqualified as flow regime sensors because they are accumulated under membrane control, and their exchange kinetics is insensitive to changes in water flow regime. More hydrophobic PRCs (log K_{ow} > 5) might produce more significant differences in release kinetics under varying hydrodynamic conditions. However, very long exposure times (months or so) would be needed to achieve a significant decrease in SPMD concentrations of such substances. Nevertheless, the dissipation rates of a flow-sensitive PRC (i.e., k_{e^-PRC}) from environmentally exposed SPMD can be compared to the k_{e^-CAL} derived for the same compound during a laboratory calibration study to determine the effect of

exposure conditions on sampling. This approach has been shown by Huckins et al. (*20*). For compounds that are accumulated under aqueous layer control (i.e., if $1/k_W \gg 1/k_{SPMD}/K_{SPMD}$), the apparent sampling rate can be calculated as $R_s = k_w A$. The values of apparent sampling rates R_s calculated for experiments conducted at different flow rates are given in Table 4. If the condition of equality of the temperature at the sampling site and in the laboratory calibration study is fulfilled, it can be shown that

$$R_{s-field} = R_{s-CAL}\frac{k_{e-PRC}}{k_{e-CAL}} \quad (10)$$

The $R_{s-field}$ value can be introduced to eq 3 to calculate the TWA aqueous concentration of the analyte. Finally, the results of this study confirm that the use of the laboratory-derived calibration data for the estimation of analyte concentrations in the ambient environment is limited unless flow-sensitive performance reference compounds are used.

Supporting Information Available

Estimation of the time to reach steady-state flux in individual SPMD compartments and the equations for the rate of transfer in steady state, determination of recovery rates of test chemicals from different matrices, extraction procedure of test substances from water, and an example of the use of PRCs to adjust the sampling rates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Development of an integrative passive sampler for the monitoring of organic water pollutants

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The development of convenient and competitive devices and methods for monitoring of organic pollutants in the aquatic environment is of increasing interest. An integrative passive sampling system has been developed which consists of a solid poly(dimethylsiloxane) (PDMS) material (tube or rod), acting as hydrophobic organic receiving phase, enclosed in a water-filled or an air-filled low-density polyethylene (LDPE) membrane tubing. These samplers enable the direct analysis of the pollutants accumulated during exposure in the receiving phase by thermodesorption–GC/MS, avoiding expensive sample preparation and cleanups. The capabilities of these sampling devices were studied for the sampling of 20 persistent organic pollutants (chlorobenzenes, hexachlorocyclohexanes, *p*,*p*′-DDE, PAHs, and PCBs) in laboratory exposure experiments. For the three sampler designs investigated the uptake of all target analytes was integrative over exposure periods up to 9 days (except PCB 101). The determined sampling rates range from 4 to 1340 μl h^{-1} for the water-filled samplers and from 20 to 6360 μl h^{-1} for the air-filled ones, respectively. The sampling rate of the analytes is dependent on their molecular weight, partition between water and sampler media (PDMS, polyethylene, water, air) and also of the sampler design. The passive samplers enable the estimation of time-weighted average (TWA) concentration of water pollutants in the lower ng l^{-1} to pg l^{-1} range.

Introduction

The monitoring of environmental pollutants in the ground and surface waters is of fundamental importance for both the protection of these ecosystems and the quality of human life. In particular the determination of persistent organic pollutants (POPs) is of ecotoxicological relevance due to their high toxic potential, their persistence and their tendency to bioaccumulate. As is known, these pollutants can be present in the aquatic environment both freely dissolved and particle-bound. For ecological risk assessment the bioavailable fraction is of substantial interest. This corresponds with the freely dissolved fraction. Using conventional sampling techniques (grab sampling) only the total content of the pollutants is obtained. Furthermore, the conventional sampling and analysis of grab water samples only provide information about pollutant burden at the moment of sampling.

Passive sampling techniques can overcome the problems mentioned above. These techniques allow the convenient determination of the time-weighted average concentration of the freely dissolved fraction of pollutants over several weeks or even months. Compared to conventional sampling the number of the samples and thus the expense of sampling and subsequent analysis can be reduced significantly. In addition, due to the accumulation of the pollutants over the whole sampling period, passive sampling allows the detection of even low analyte concentrations. Furthermore, the sampling devices are usually simple in design, small, inexpensive and require no power supply. This makes the technique inexpensive and suitable for use at remote sites. However, for the determination of TWA concentrations of organic pollutants in field studies samplers must be calibrated in laboratory experiments.

Today the passive sampling technique represents an attractive alternative to the conventional snap-shot sampling for water monitoring of semivolatile POPs. In the last few years various passive sampling devices were designed for monitoring of pollutants in the aquatic systems. These sampling devices are usually so-called membrane samplers. Such membrane samplers typically consist of a receiving medium with a high affinity for the organic contaminants enclosed by a diffusion-limiting semipermeable membrane.[1–4]

Semipermeable membrane devices (SPMDs), introduced by Huckins and co-workers,[5–9] attained the greatest importance and widespread application. Due to both their high membrane surface area and their relatively large volume of receiving medium SPMDs proved to be most effective in their capacity to accumulate lipophilic contaminants. The SPMD sampler consists of layflat low-density polyethylene tubing enclosing a thin film of triolein. The main disadvantage of the SPMD technique is the complex sample preparation procedure required to recover the accumulated pollutants from the collecting phase (triolein). This is achieved by dialysis using considerable amounts of organic solvents, followed by concentration of the extracts and an expensive cleanup before the chromatographic analysis.[9,10]

In the last few years several attempts have been made to develop passive sampling devices, which avoid the drawbacks mentioned above and also make passive sampling technology more attractive for routine monitoring programmes. Such passive samplers contain solid materials (granular adsorbents

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and compact polymeric sorbents, like PDMS, respectively) instead of the liquid organic receiving phase. That allows the thermodesorption of the accumulated pollutants without additional sample preparation.

Hardy *et al.*[11–13] created a passive sampler consisting of a glass tube, sealed at one side with a silicone–polycarbonate membrane. Depending on the target analytes this sampler can be filled with various granular materials, such as activated charcoal, Tenax-TA, XAD-7, Chromosorb 103 and Porapak Q. After exposure, the granular receiving phase can be desorbed either with a suitable solvent or thermally. This sampler was successfully applied for the enrichment of more volatile organic compounds, like monocyclic aromatic compounds[13] and phenols,[12] whereas the less volatile compounds were not enriched effectively.

At the end of the nineties Gratwohl and Martin[14,15] patented a so-called ceramic dosimeter for the integrative sampling of organic compounds in ground water. This sampler consists of a porous ceramic tube which was filled with different grained adsorbents, *e.g.* the ion exchange resin Amberlite IRA-743 and Tenax. The porous ceramic tube enables only the dissolved analytes to pass the membrane. This sampler was applied for the monitoring of several PAHs in ground water. Concerning the subsequent thermodesorption of the analytes from Tenax difficulties appear due to the unexpected water permeability of the ceramic membranes.

In a recently published paper, Vrana *et al.*[16] described the application of a solid sorbent on the basis of PDMS as receiving phase in a membrane sampler. This so-called MESCO (*m*embrane-*e*nclosed *s*orptive *co*ating) sampler consists of a stir bar coated with a thin PDMS layer (Gerstel Twister, a commercially available device used for stir bar sorptive extraction, SBSE[17]) enclosed in a water-filled dialysis membrane bag from regenerated cellulose. After exposure of the sampler, the PDMS coated stir bar is taken from the enveloping membrane and can be directly analysed by thermodesorption–GC/MS. Thus, laborious and time-consuming sample preparation can be avoided.

PDMS is recommended as a receiving phase in extraction and thermodesorption as it has a number of benefits compared with other sorbents.[18] The predominant mechanism of analyte extraction into the polymer PDMS phase is absorptive partitioning, which means that displacement effects of the analytes which are characteristic for adsorbents play no role.

Although the MESCO sampler is a miniaturised version, this passive sampling approach enables lower quantification limits for hydrophobic POPs in the pg l^{-1} level. The application of regenerated cellulose as a porous hydrophilic membrane material enables the widening of the applicability to a broader polarity range of pollutants including low-hydrophobic substances (log $K_{OW} < 4$). Unfortunately, this material has relatively low chemical and thermal stability and is subject to microbial degradation,[3] which potentially leads to the damage of the sampler in the field.

The aim of the work presented here was to develop and to test a membrane sampler combining the advantages of the MESCO sampler with those of more stable membranes, such as low-density polyethylene. LDPE membranes were successfully applied in SPMDs. These membranes are hydrophobic, resistant to solvents and biodegradation and they can be heat-sealed. Furthermore, the commercially available stir bars as receiving phase should be substituted by less expensive PDMS materials with a significantly enhanced volume to increase the maximum exposure time of the passive sampler in the field.

Theory

Previously, models have been developed describing the uptake kinetics of organic contaminants in water by passive samplers constructed as solvent filled dialysis membranes,[19] triolein filled polyethylene membranes[20] or membrane enclosed sorptive coatings[16] and can analogously be adapted for the description of the function of samplers designed in this study. These consist of a hydrophobic solid receiving phase (PDMS) enclosed in water-filled or air-filled semipermeable membrane made of nonporous LDPE.

The mass transfer of an analyte in a sampler includes several diffusion and interfacial transport steps across all barriers, *i.e.* the stagnant aqueous boundary layer, possible biofilm layer, the membrane, the inner fluid (aqueous or gas) phase, and the receiving organic phase as rate control step is not assumed *a priori*.

It can be shown that in the initial uptake phase, chemical uptake is linear or time-integrative. Under these conditions the concentration of a chemical in the organic phase is directly proportional to the product of the concentration in the surrounding aqueous medium C_W [kg m^{-3}] and the exposure time t [s]. For practical application, uptake can be described by eqn. (1)

$$M_S(t) = M_0 + C_W R_S t \quad (1)$$

where M_S [kg] is the amount of analyte accumulated in the receiving phase and M_0 [kg] the initial amount of analyte in the sampler. R_S [m^3 s^{-1}] is the sampling rate of the system:

$$R_S = k_{ov} A \quad (2)$$

where k_{ov} [m s^{-1}] is the overall mass transfer coefficient and A [m^2] is the membrane surface area. Sampling rate can be determined experimentally under fixed conditions at constant analyte concentration. Under environmental conditions, when the water concentration changes during the exposure, the term C_W represents a TWA concentration during the deployment period.

As described by Huckins *et al.*,[21] the uptake of an analyte into the passive sampler is linear and integrative approximately until the concentration factor of the sampler (ratio $C_S(t)/C_W$) reaches half-saturation. If sampling rates R_S and organic receiving phase/water partitioning coefficients K_{SW} are available, the maximum exposure time in which the sampling device works integrative under field conditions can be estimated using eqn. (3):

$$t_{50} \sim \ln 2 K_{SW} V_S / R_S \quad (3)$$

where t_{50} is the first-order half-time of the uptake curve and V_S the volume of the receiving phase.

Experimental

Chemicals and materials

The test substances (Table 1) include several groups of semivolatile persistent organic pollutants: hexachlorocyclohexanes (HCHs), chlorinated benzenes (CBs), 2,2′-bis(4-chloropheny)-1,1′-dichloroethylene (*p,p′*-DDE), PAHs, and PCBs.

HCH, chlorobenzene, PCB and PAH reference standards were obtained from Promochem (Wesel, Germany). The solvents *n*-hexane, methanol and dichloromethane (for organic trace analysis) were purchased from Merck (Darmstadt, Germany). HPLC-grade water was supplied by Baker (Deventer, The Netherlands). Layflat LDPE membrane tubing (layflat, 30 mm; wall thickness, 80 μm) was achieved from Polymer-Synthese-Werk GmbH (Rheinberg, Germany). Silicone tubing (3.0 mm × 3.6 mm) was obtained from Reichelt (Heidelberg, Germany). Silicone rod material (2.0 mm id) was purchased from Goodfellow (Bad Nauheim, Germany). Stir

Table 1 Selected physicochemical properties of the test analytes

Compound	Abbreviation	No.	MW[a]	log K_{OW}[b] at 25 °C	log K_{MW}[c] at 25 °C	K_{AW}[d] at 25 °C	D_A[e]/cm^2 s^{-1} at 20 °C	D_W[f]/cm^2 s^{-1} at 20 °C
1,2,4,5-Tetrachlorobenzene	TeCB	1	215.9	4.5	4.0	4.9×10^{-2}	0.06	6.2×10^{-6}
Pentachlorobenzene	PeCB	2	250.3	5.2	4.6	3.4×10^{-2}	0.057	5.8×10^{-6}
Hexachlorobenzene	HCB	3	284.8	5.5	4.8	5.3×10^{-2}	0.0543	5.5×10^{-6}
α-HCH	α-HCH	4	290.8	3.7	3.2	5.0×10^{-4}	0.05	6.2×10^{-6}
β-HCH	β-HCH	5	290.8	3.8	3.3	1.8×10^{-5}	0.05	6.2×10^{-6}
γ-HCH	γ-HCH	6	290.8	3.7	3.2	2.1×10^{-4}	0.05	6.2×10^{-6}
δ-HCH	δ-HCH	7	290.8	4.1	3.6	1.8×10^{-5}	0.05	6.2×10^{-6}
PCB 28	PCB 28	8	257.5	5.6	4.9	8.2×10^{-3}	0.0542	5.1×10^{-6}
PCB 52	PCB 52	9	292.0	6.1	5.2	8.2×10^{-3}	0.054	4.9×10^{-6}
PCB 101	PCB 101	10	326.4	6.8	5.6	1.4×10^{-2}	0.054	4.7×10^{-6}
p,p′-DDE	*p,p′*-DDE	11	318.0	5.7	5.0	1.7×10^{-3}	0.05	5.0×10^{-6}
Acenaphthylene	Ace	12	152.2	4.0	3.5	3.4×10^{-3}	0.063	6.5×10^{-6}
Acenaphthene	Acenaph	13	154.2	4.0	3.5	4.9×10^{-3}	0.063	6.3×10^{-6}
Fluorene	Flu	14	166.2	4.2	3.7	3.2×10^{-3}	0.06	6.0×10^{-6}
Phenanthrene	Phe	15	178.2	4.5	4.0	1.3×10^{-3}	0.058	5.8×10^{-6}
Anthracene	Ant	16	178.2	4.6	4.4	1.6×10^{-3}	0.058	5.9×10^{-6}
Fluoranthene	FLU	17	202.3	5.1	4.5	4.2×10^{-4}	0.055	5.5×10^{-6}
Pyrene	Pyr	18	202.3	5.1	4.5	3.7×10^{-4}	0.055	5.6×10^{-6}
Benzo[*a*]anthracene	BaA	19	228.3	5.9	5.1	2.3×10^{-4}	0.052	5.1×10^{-6}
Chrysene	CHR	20	228.3	5.7	5.0	2.6×10^{-5}	0.052	5.1×10^{-6}

[a]Molecular weight. [b]Octanol–water partition coefficient.[22,23] [c]Membrane–water partition coefficient estimated from eqn. (4).[28] [d]Henry's Law constant.[22,23] [e]Diffusion coefficient in air.[25] [f]Diffusion coefficient in water.[24] [g]δ_T = length of the diffusion path in the transfer medium = 0.3 cm.

bars for SBSE (PDMS coating: 0.5 mm thickness, 10 mm length) were obtained from Gerstel (Mülheim/Ruhr, Germany).

Physicochemical properties of substances

Henry's Law constants K_{AW} at 25 °C of substances under investigation were taken from the literature.[22,23] Almost equal values of aqueous diffusion coefficients D_W were estimated for the tested group of compounds ranging from 5×10^{-6} to 7×10^{-6} cm^2 s^{-1}.[24] Diffusion coefficients of the test analytes in air D_A at 20 °C range from 0.05 to 0.06 cm^2 s^{-1}.[25] An approximated value of 10^{-10} cm^2 s^{-1} was used as diffusion coefficient of the analytes in the LDPE membrane D_M.[26,27] The membrane/water partition coefficients K_{MW} were estimated from a predictive equation derived by Hofmans:[28]

$$\log K_{MW} = -0.0956(\log K_{OW})^2 + 1.7643 \log K_{OW} - 1.98 \quad (4)$$

Preparation and test of the sampler components

The materials provided for receiving phases in the passive sampling devices (silicone tubes and rods) were obtained from the manufacturers as endless materials. In order to obtain reproducible results the tubes and rods were carefully cut with a scalpel in pieces of each 40 mm length and then weighed. Outliers in the weight (CV > 1%) were discarded.

In order to clean and condition the silicone tubing and rods, in each case ten of these were placed into a vial (50 ml) containing 50 ml of *n*-hexane and horizontally shaken for 2 h (tubing) or 4 h (rods). The materials were dried in a desiccator under vacuum and then thermally conditioned for 3 h at 250 °C in a nitrogen flow of about 50 ml min^{-1}. For cleaning and conditioning of the stir bars these were placed separately into small vials filled with 2 ml of a mixture of dichloromethane and methanol (1 : 1) for 1 h. Then they were dried in a desiccator and subsequently heated at 250 °C for 90 min in a nitrogen flow. For cleaning of the layflat LDPE tubing, 3 pieces of this material with a length of each 1 m were put into a glass vessel (500 ml) containing 500 ml of *n*-hexane and shaken for 24 h. Then the solvent was rejected and the procedure was repeated once. The wet tubing was dried in a desiccator.

To investigate the applicability of some PDMS materials as organic receiving phases in the sampling devices these were tested within the complete extraction and thermodesorption procedures. For this purpose, the conditioned receiving phases were separately shaken in each 50 ml water spiked with the test analytes (100 ng l^{-1} of each compound). This solution was prepared by spiking a water sample with a mixture of test analytes dissolved in methanol. The vials containing the tubes and the rods were horizontally shaken for 2 h at 200 motions per min. The stir bars were stirred at 1000 rpm in Erlenmeyer flasks for 2 h. After extraction, the receiving phases were taken from the water sample, rinsed with a small volume of water, and dabbed dry with a lint-free tissue. It should be noted that the small water droplets inside the tubes should be carefully removed. The accumulated analytes were determined using thermodesorption–GC/MS as described later. The completeness of the desorption of the enriched analytes (carry over) was revised by a second desorption under equal conditions.

Membrane samplers

The membrane samplers used in this study (Fig. 1) consist of a layflat LDPE membrane tubing (length, 50 mm) enclosing a

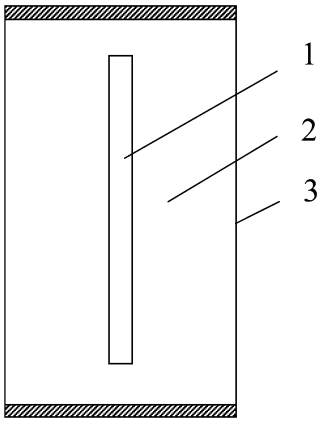

Fig. 1 Schematic diagram of the passive sampling device described here. The receiving phase (component 1, silicone tubes or rods) is enclosed in low-density polyethylene membrane tubing (component 3) filled with the transfer medium (component 2, water or air) and heat-sealed at each end.

silicone tube (length, 40 mm; referred to as tube sampler) or a silicone rod (length, 40 mm; referred to as rod sampler). The layflat LDPE tubing with the receiving phase inside was water-filled (about 8 ml) or air-filled and heat-sealed at both ends. For both samplers the volume of the receiving phase (about 125 μl) and the effective membrane surface area (30 cm^2) were equal. In order to enable a simultaneous exposure of a set of samplers, they were connected to a string.

Laboratory exposure experiments

A set of passive samplers were exposed to contaminated water with a nominal analyte concentration of each 50 ng l^{-1} in a flow-through exposure system. This system consisted of an exposure chamber, an 1 m high glass column (inner diameter 7.5 cm) with a perforated bottom. To prevent photodegradation of the analytes during exposure the column was covered with dark foil. In a mixing chamber (1 l) positioned at the bottom of the exposure column tap water (60 l h^{-1}) and the appropriate amount of the test analytes dissolved in methanol (400 μg l^{-1}) delivered by a peristaltic pump (Gilson, USA) were carefully mixed using a magnetic stirrer. The resulting methanol concentration in the exposure water did not exceed 0.01% (v/v). Tap water was fed to the mixing chamber by a membrane pump (Prominent, Germany). The spiked water flowed from bottom to top through the exposure chamber. Using a heating–cooling system the water temperature in the exposure chamber was held constant at the predetermined temperature. The passive sampler string was fixed in the exposure column in a vertical position.

The exposure experiments were performed at 14 and 8 °C, respectively, and at a linear flow velocity of the water of 0.38 cm s^{-1} (see Table 2). The samplers were removed one by one after predetermined exposure times. (The maximum exposure times varied between 176 and 236 h.) Then the receiving phases were immediately taken out of the enveloping LDPE tubing and carefully dried. The loaded receiving phases were stored in closed small glass vials at −18 °C in a freezer until thermodesorption–GC/MS analysis. Investigations concerning the loss of analytes during storage of the loaded receiving phases under these conditions resulted in the conclusion that these could be neglected.

In order to determine the concentration of the analytes under investigation in the water during exposure, samples were taken from the exposure column at each time when samplers were removed and analysed as described below.

Processing of the water samples

The extraction of the water samples taken from the exposure column was performed using SBSE. The procedure was as follows: 50 ml of the water sample was filled into an Erlenmeyer flask (50 ml), the stir bar was lowered in the flask and then the sample was stirred at 1000 rpm for 2 h. After this the stir bar was taken out, washed with water and dried. For external calibration, spiked water samples containing 10, 30, 50, 70, and 100 ng l^{-1} of each analyte were prepared using a mixture of test analytes dissolved in methanol and extracted as described above. It should be noted that the content of methanol in the calibration solutions should be held constant (<1%).

Thermodesorption–GC/MS analysis

The pollutants accumulated during the exposure experiments in the receiving phases of the passive samplers and in the stir bars were analysed using thermodesorption–GC/MS. The solid receiving material was placed into an empty glass desorption tube. Thermodesorption–GC/MS was performed on an Agilent Technologies system 6890/5973 (Palo Alto, CA, USA) equipped with a Gerstel thermodesorption device with auto-sampler. For cryofocusing of the analytes prior to the transfer into the capillary column a Gerstel cold injection system (CIS 4) with an empty liner was used. During thermal desorption the CIS 4 was cooled with liquid nitrogen to a temperature of −150 °C. For the desorption of the analytes from the receiving phases and the stir bars the following conditions were chosen: desorption temperature, 250 °C; helium flow rate, 100 ml min^{-1} and desorption time, 10 min. The transfer lines both from the thermodesorption device to the CIS 4 and from the GC to the MS ion source were set to 250 °C. After desorption of the receiving phase and cryofocusing of the analytes, the CIS 4 was heated to 250 °C at a rate of 12 °C s^{-1}, whereas the system was used in the splitless mode with a splitless time of 1.5 min. An HP-5 MS capillary column (30 m, 0.25 mm id, 0.25 μm film thickness) was employed with the following temperature program: 50 °C, 3 min isothermal, 15 °C min^{-1} to 160 °C, then at 3 °C min^{-1} to the final temperature of 280 °C, and held for 8 min. Helium was used as carrier gas at a linear velocity of 39 cm s^{-1}. The single ion monitoring (SIM) mode applying one or two characteristic ions per analyte was chosen for the detection.

For external calibration of the accumulated pollutants in the receiving phases, a plug of silanised glass wool (length, about 4 cm) which was positioned in the heated zone of a desorption tube was spiked with the calibration solution (2 μl). The desorption tube was flushed for 1 min with a nitrogen flow of 30 ml min^{-1} to allow the main part of the solvent (methanol) to evaporate and then thermally desorbed. In order to control analyte losses during the evaporation of methanol at external calibration, the flush time was varied in the range of 30 to 120 s. This investigations resulted in no significant decrease of the peak areas with increased flush time. Quantification of the analytes sorbed in the receiving phase was performed using a six-point calibration.

Results and discussion

Assessment of PDMS materials

In a preliminary study the applicability of some commercially available PDMS materials—silicone tubes and silicone rods—as organic receiving phase in the passive sampling devices were investigated to achieve information about the extraction efficiency, the repeatability, completeness of the thermodesorption process (carry over), and the handling of the materials. For this purpose, each eight pieces of the receiving phases were object of the complete extraction and thermodesorption procedures (see the Experimental section—Preparation and test of the sampler components). Additionally, stir bars were included in the experiments, because they should serve on the one hand for comparison and they were employed for the analysis of the water samples on the other hand. The results of

Table 2 Conditions of the flow-through exposure experiments

Experiment no.	Sampler design used	Nominal concentration/ng l^{-1}	Temperature/°C	Flow velocity/cm s^{-1}	Exposure period/h
1a	Water-filled tube sampler	50	14	0.38	176
1b	Air-filled tube sampler	50	14	0.38	224
1c	Water-filled rod sampler	50	14	0.38	224
2	Water-filled tube sampler	50	8	0.38	236

Table 3 Mean peak areas ($n = 8$), coefficients of variation (CV in %) and carry over (%) of different receiving phase materials obtained from extraction and thermodesorption–GC/MS analysis

	Stir bars			Tubes			Rods		
Compound	Peak area $\times 10^{-3}$	CV (%)	Carry over (%)	Rel. peak area[a] (%)	CV (%)	Carry over (%)	Rel. peak area[a] (%)	CV (%)	Carry over (%)
1,2,4,5-Tetrachlorobenzene	947	5.2	0.32	1.03	9.1	4.09	0.65	8.8	5.27
Pentachlorobenzene	965	6.0	0.15	0.65	6.8	1.36	0.68	6.5	4.37
Hexachlorobenzene	1004	6.9	0.12	0.65	15.5	nd	0.73	3.8	3.62
α-HCH	391	7.6	0.05	0.72	6.1	nd	0.85	5.2	3.03
β-HCH	57	9.6	3.00	1.33	4.5	2.25	1.71	19.7	4.28
γ-HCH	305	8.7	0.11	0.64	6.3	0.40	0.84	6.8	3.52
δ-HCH	117	8.5	0.86	0.85	7.8	2.64	1.10	20.6	0.70
PCB 28	1565	9.3	0.18	0.46	5.9	0.81	0.75	5.0	4.21
PCB 52	898	10.3	nd	0.43	5.2	0.28	0.74	6.9	4.73
PCB 101	510	11.1	0.09	0.36	11.1	0.33	0.67	16.5	6.07
p,p'-DDE	376	10.9	nd	0.36	13.2	0.09	0.65	20.5	5.78
Acenaphthylene	1272	5.5	0.26	1.00	6.9	1.31	0.82	7.4	3.41
Acenaphthene	1496	6.5	0.54	0.84	6.6	1.46	0.61	14.9	4.02
Fluorene	1287	7.6	0.50	0.72	7.3	1.36	0.84	4.6	3.72
Phenanthrene	2058	9.3	1.19	0.63	7.3	0.98	0.80	5.8	3.94
Anthracene	1386	9.8	0.14	0.54	5.9	0.42	p.i.		
Fluoranthene	1673	11.5	0.12	0.41	3.6	0.46	0.65	19.9	4.82
Pyrene	1643	11.2	0.12	0.41	6.7	0.44	0.55	20.9	5.17
Benzo[*a*]anthracene	281	12.8	nd	0.62	18.9	0.18	0.85	28.6	3.53
Chrysene	364	8.8	nd	0.52	14.0	0.25	0.89	25.5	3.97

[a]Related to the mean peak areas of the stir bars ($n = 8$). [b]nd = not detectable. [c]pi = peak interference.

these investigations are summarised in Table 3. The carry over provides information about the completeness of the thermodesorption process. For this purpose, the already thermally desorbed materials were desorbed again and the peak areas of the first and second desorption were compared, setting the areas of the first desorption to 100%. It should be noted that the volume of the PDMS phase of the stir bars (24 µl) and the other materials (125 µl) differ considerably. The extraction yields (relative peak areas) of the analytes investigated using tubes and rods were in the range of 0.37 to 1.33 compared to stir bars. From the three receiving phases, the best repeatability was found for the stir bars. The variation coefficients of the peak areas of the individual analytes extracted from the spiked solution by the 8 stir bars ranged from 5 to 13%. Comparing the tubes and the rods, the first ones showed a better repeatability with variation coefficients from 4 to 19% (tubes) and from 4 to 29% (rods), respectively. The values for the carry over of the stir bars indicate that the thermodesorption of the most compounds under the given conditions was nearly quantitative (<1% except β-HCH and phenanthrene). The values for the tubes were slightly higher (in most cases lower than 1.5%). In contrast, the carry over of the rods was significantly increased (between 3.0 and 6.1%). The reasons for this finding we assume in the significantly larger thickness of the PDMS layer of the rods (2 mm id) compared to the other materials (tubes, 0.3 mm; stir bars, 0.5 mm). Thus, an increased time is needed for the quantitative diffusion of the analyte molecules dissolved in the PDMS phase to the surface area of the rods. For this reason the silicone tubes were favoured as receiving phase material in the passive sampler devices. However, it was found that the handling of the rods is more convenient, especially by the preparation of the air bubble-free water-filled samplers and in consideration of drying (removing of the small water droplets on the inner surface area of the tubes). Therefore, in one exposure experiment rod samplers were included, too.

Calibration experiments

The capabilities of the passive sampling devices described here for the long-term water monitoring of the target analytes were investigated by performing exposure experiments in a flow-through exposure apparatus. In Table 2 the experimental conditions are summarised. Over the exposure periods the analyte concentrations in the water as well as the temperature and the flow rate of the water were held constant. As described above, during the exposure experiments water samples and passive samplers were taken from the exposure column at time intervals to determine the analyte concentrations in the water (C_W) and the amounts accumulated in the samplers (M_S).

The mean concentration of the individual analytes in the water samples within the exposures (C_W) were in the range of 78 to 131% of the nominal concentration (except *p,p'*-DDE in experiment 1). The calculated coefficients of variation of the average analyte concentrations were at maximum 11%.

The experimentally determined time courses of the accumulated amounts of individual analytes on the receiving phases (M_s) were fitted by the linear regression analysis. According to eqn. (1) the adjustable parameters are the slope ($C_W R_S$) and the intercept (M_0) of the linear uptake curve. The quality of the fit was characterised by the standard deviations of the optimised parameters, as well as the correlation coefficient (R) and the fit standard deviation (SD). Typical uptake curves are shown in Fig. 2.

Using tube samplers the uptake of all compounds was linear over the whole exposure time in all experiments. The correlation coefficients of the regression were in the range of

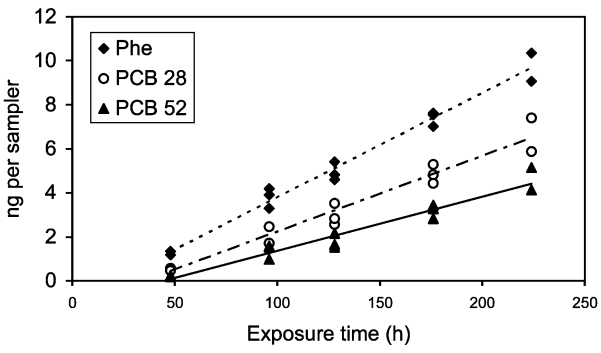

Fig. 2 Uptake of selected analytes by the air-filled tube sampler obtained from a flow-through exposure at 14 °C (nominal analyte concentration, 50 ng l^{-1}). For abbreviations see Table 1.

0.867 to 0.988. The variation coefficients of the calculated slope did not exceed 20%.

Using rod samplers (experiment 1c) the uptake of all analytes was linear except PCB 101. The correlation coefficients of the regression ranged from 0.698 to 0.990. The variation coefficients of the slope were in maximum 34%.

The uptake curves of the analytes show partly negative intercepts. From the theory[16] negative intercepts can be explained by the presence of a lag phase. This can be interpreted as the time needed for the analyte to pass the LDPE membrane. The duration of the lag phase or the so-called delay time is affected by the diffusivity of analyte and thickness of individual barriers (membrane and diffusion layers of fluid media). Moreover, steady-state flow of analyte from water to the receiving phase is not established immediately. However, the time to reach steady-state flux in the sampler can be estimated by the magnitude of the variable l^2/Dt, where l is the film thickness, D is the diffusion coefficient and t is time.[29] If the variable is less than unity, a steady-state flux is assumed. Using the thickness of the polyethylene membrane of 100 μm and a typical diffusion coefficient of small non-polar molecules in LDPE membranes of 10^{-10} cm^2 s^{-1}, steady-state should be achieved after one or two days in the polyethylene membrane. This corresponds well with the lag phase observed in our experiments. In most cases the calculated lag phases were in the range between 5 and 30 h, however, for the PCBs lag phases up to 48 h were found. In aqueous and air boundary layers, steady-state should be established after few minutes only. To use the sampler for the monitoring purposes, analytes should approach steady-state in the individual compartments quickly with regard to the duration of experiments, *i.e.* duration of the transition phase should not be much longer than 10% of the exposure period.

Sampling rates. The sampling rates R_S of the three types of passive samplers obtained in the exposure experiments 1 and 2 are given in Table 4. According to eqn. (1) the R_S values were calculated by dividing the slope of the linear uptake curve by the mean analyte concentration C_W in the water during exposure. The variances of the R_S values were calculated from both the coefficients of variation of the slope and of the analyte concentration in the aqueous phase, according to the law of error propagation.

Over the range of the controlled exposure conditions, the R_S values of the analytes under investigation covered a range of 2 to 3 orders of magnitude. For example, for the water-filled tube sampler at 14 °C the R_S values were in the range of 5 to 1340 μl h^{-1}. Comparing the sampling rates of the PAHs it can be seen that the values decrease with increasing molecular weight (size), increasing hydrophobicity (log K_{OW} ranged from 4.0 to 5.9) and decreasing water solubility of the compounds. A similar behaviour, significantly decreased sampling rates with increasing chlorination grade, was found for the chlorinated benzenes and the PCBs.

Originally, higher chlorinated PCBs (PCB 138, PCB 153 and PCB 180) and EPA PAHs with high molecular weights (benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*ah*]anthracene and benzo[*ghi*]-perylene) were to have been included in the exposure studies, too. However, in previous investigations it was found that these compounds were accumulated in the receiving phase only in very small amounts (near the detection limits). Therefore an accurate determination of the sampling rates was precluded.

The sampling rates of the samplers described here are low (0.12 to 32 ml per day for the individual analytes using the water-filled tube sampler) compared with those of other sampling devices, such as standard SPMDs[21] (1 to 8 l per day). That means, the sampling efficiency of the SPMDs is about 3 orders of magnitude higher. Nevertheless, the sensitivity of the two methods should be approximately the same, because in the case of the samplers described here, the total amount of the analyte accumulated in the receiving phase is transferred to the GC/MS. In contrast, only a small portion of the obtained SPMD extract (usually 1–2 μl) is injected.

Comparing the sampling rates given in Table 4 with those of the MESCO sampler[16] it can be seen that the R_S values are in the same order of magnitude (in the μl h^{-1} range), as expected, but the MESCO sampling rates are more uniform. Additionally, for the PCBs and PAHs with high molecular weights R_S values could be determined, too. That means that measurable amounts of these analytes were accumulated in the PDMS material during the exposure. The main difference between these both sampling devices is in the membrane material employed. The membrane of the MESCO sampler consists of porous hydrophilic polymeric material (molecular weight

Table 4 Sampling rates R_S of the 3 passive sampler designs derived from flow-through exposures at different temperatures (nominal analyte concentration 50 ng^{-1})

	Water-filled tube samplers				Air-filled tube samplers		Water-filled rod samplers	
	T = 8 °C		T = 14 °C		T = 14 °C		T = 14 °C	
Compound	R_S /μl h^{-1}	CV (%)	R_S/μl h^{-1}	CV (%)	R_S/μl h^{-1}	CV (%)	R_S/μl h^{-1}	CV (%)
1,2,4,5-Tetrachlorobenzene	737	9	647	9	6355	9	480	11
Pentachlorobenzene	201	11	192	11	4314	11	214	14
Hexachlorobenzene	21	13	56	22	904	14	87	18
α-HCH	229	11	185	13	136	8	283	9
β-HCH	31	16	69	11	34	17	69	14
γ-HCH	120	10	141	11	72	8	195	10
δ-HCH	44	11	96	10	24	9	138	11
PCB 28	96	10	57	15	921	13	64	20
PCB 52	52	12	41	18	621	13	33	35
PCB 101	5	13	[a]		104	15	4	80
p,p′-DDE	4	14	5	20	53	14	5	21
Acenaphthylene	988	9	730	9	1398	8	507	7
Acenaphthene	897	9	671	9	2226	7	481	7
Fluorene	907	9	1342	11	1876	6	753	8
Phenanthrene	541	10	269	11	929	8	259	11
Anthracene	515	11	265	14	988	12	125	12
Fluoranthene	69	10	56	9	122	10	37	14
Pyrene	42	11	34	10	99	13	30	15
Benzo[*a*]anthracene	13	15	10	19	31	16	8	14
Chrysene	9	14	9	19	20	13	6	27

[a]PCB 101 could not be determined in this experiment.

cutoff 1000). Thus, the analytes pass the membrane by diffusion through the water-filled pores. In contrast, the membrane of the samplers used in this study consists of nonporous polyethylene. The organic analytes can pass such a nonporous polymeric membrane only by dissolving in the polymeric phase and subsequent diffusion through the membrane layer. (LDPE membranes can be passed only by truly dissolved organic molecules with cross-sectional diameters up to about 1 nm.[20]) Thus, the diffusion coefficients of the individual organic substances in the polymer D_M and the membrane/water partition coefficients K_{MW} are of crucial importance for the sampling efficiency.

Influence of the transfer medium on the sampling rates. In order to investigate the influence of the medium, which is contained in the sampling device together with the receiving phase, water-filled and air-filled tube samplers were exposed together under the same conditions. The determined sampling rates and variances are listed in Table 4. Comparing the R_S values in the columns 4 and 6 it can be seen that the values of most of the analytes for the air-filled sampler are significantly higher as for the water-filled ones with exception of the four HCH isomers. Thus, for the chlorobenzenes and the PCBs the R_S values are increased 10- to 20-fold and for the PAHs up to 4-fold, respectively.

The comparability of experimentally derived sampler uptake rates to actual values during environmental sampling generally depends on the similarity of laboratory and site exposure conditions. When sampler calibration and field conditions are dissimilar, the magnitude of the differences in lab and field uptake rates for an analyte depends on the source of analyte rate control. Thus, examination of potential rate-limiting barriers is important.

The overall mass transfer coefficient is expected to be affected by the diffusion of solutes in individual phases (water, membrane, the inner transfer medium [air or water], and the PDMS, respectively) and by their partitioning into the PDMS and the LDPE membrane, since accumulation of hydrophobic analytes is expected also in the hydrophobic membrane. From the theory,[30,31] it is assumed that the overall resistance ($1/k_{ov}$), to the uptake of a chemical is given by the sum of particular barrier resistances to mass transfer [eqn. (5)]:

$$\frac{1}{k_{ov}} = \sum_i \frac{\delta_i}{K_{iw} D_i} \tag{5}$$

where δ_i is the particular barrier thickness, D_i is the diffusion coefficient in the barrier and K_{iw} is the partition coefficient between the i-th phase and water.

For water-filled tube sampler, the overall resistance ($1/k_{ovWS}$) is then given by eqn. (6):

$$\frac{1}{k_{ovWS}} = \frac{\delta_B}{D_W} + \frac{\delta_M}{D_M K_{MW}} + \frac{\delta_W}{D_W} + \frac{\delta_S}{D_S K_{SW}} \tag{6}$$

The subscripts B, M, W and S represent the boundary aqueous layer at the surface of the sampler [B], the membrane [M], the transfer aqueous layer inside the sampler [W], and the receiving organic phase [S].

The resistance to mass transfer in the air-filled tube sampler can be described analogously by eqn. (7):

$$\frac{1}{k_{ovAS}} = \frac{\delta_B}{D_W} + \frac{\delta_M}{D_M K_{MW}} + \frac{\delta_A}{D_A K_{AW}} + \frac{\delta_S}{D_S K_{SW}} \tag{7}$$

where the subscript A denotes the air layer between the receiving phase and the membrane, and K_{AW} is the dimensionless Henry's Law constant.

It is likely that the differences in the sampling rates determined under the same exposure conditions for two sampler designs differing from each other only in the composition of the filling medium (water or air) are caused by differences in the partial resistance to mass transfer in this medium. These particular resistances are described by the corresponding terms δ_W/D_W and $\delta_A/D_A K_{AW}$ in eqn. (6) and (7), respectively. The diffusion paths of analyte molecules through the inner transfer medium are approximately the same for both sampler designs (*i.e.* $\delta_W \approx \delta_A$). Practically, the exact distance between the membrane and the PDMS rod or tube cannot be measured because the PDMS rod or tube was not in a fixed position inside the membrane. This distance may vary between 1 and 5 mm and an approximate average value of $\delta_T = 3$ mm was taken for calculations of particular resistances of the inner medium to mass transfer of an analyte. Note that for both sampler designs, the mass transfer by convection in the inner transfer medium is assumed to be negligible. Thus, the differences in sampling rates for an analyte may originate in unequal transfer medium permeability for the two sampler designs.

To examine the effect of the inner transport medium on the mass transfer in the sampler, the sampling rate ratio for two sampler designs (R_{SAS}/R_{SWS}) determined for the same analyte under equal exposure conditions can be expressed using a combination of eqn. (2), (6) and (7):

$$\frac{R_{SAS}}{R_{SWS}} \approx \left(A + \frac{\delta_T}{D_W}\right) \Big/ \left(A + \frac{\delta_T}{D_A K_{AW}}\right) \tag{8}$$

where $A = \delta_B/D_W + \delta_M/D_M K_{MW} + \delta_S/D_S K_{SW}$ and δ_T is the length of the diffusion path in the inner transfer medium. The sampling rate ratio is then modulated by the value of analyte's diffusion coefficient in water, the diffusion coefficient in air and the Henry's Law constant, respectively. We assume that the diffusion in membrane and/or the inner transfer medium are dominant diffusion limiting steps. The aqueous boundary layer at the surface of the sampler and in the PDMS layer present only a small part of the total diffusion path. Therefore, the term A in eqn. (8) can be rewritten $A \approx \delta_M/D_M K_{MW}$

In order to prove the applicability of eqn. (8) for prediction of the R_{SAS}/R_{SWS} ratio from the physicochemical properties of analytes, a correlation of estimated and measured ratio was performed using linear regression analysis [eqn. (9)]:

$$(R_{SAS}/R_{SWS})_{calc} = -1.153 + 2.023(R_{SAS}/R_{SWS})_{exp} \tag{9}$$

$n = 19$; SD = 8.68; $r = 0.85$; $P < 0.0001$

The fit yields a good correlation (see also Fig. 3). However, the calculated ratio overestimates the experimental value on average by a factor of 2. The systematic error is likely introduced into the calculation by using an imprecise value of the distance between membrane and PDMS phase δ_T. A simulation of the effect of varying δ_T on the estimated R_{SAS}/R_{SWS} ratio showed that a 5-fold increase in δ_T from 1 to 5 mm results in a variation in the average slope of the linear dependence of calculated to measured R_{SAS}/R_{SWS} from 0.9 to 2.8. Despite this imprecision, experimental and estimated data correlate well for the whole range of simulated δ_T. Thus, it appears that the observed differences in experimental R_S values for two sampler designs can be explained based on physicochemical properties of analytes and theoretical considerations to mass transfer in samplers.

The calculation of particular resistances shown in eqn. (6) and (7) allows also recognizing the dominant barriers to mass transfer. Any step or layer with more than 50% of the total resistance is considered rate limiting. The comparison relative contribution of individual barriers to the total resistance for each compound shows that the uptake rate control depends not only on the sampler construction, but also on the analyte properties (Table 5). The estimation of the rate limiting barrier will be verified by experiments in the future.

Comparison of the tube and rod sampler. A comparison of the water-filled tube and rod samplers (Table 4, column 4 and

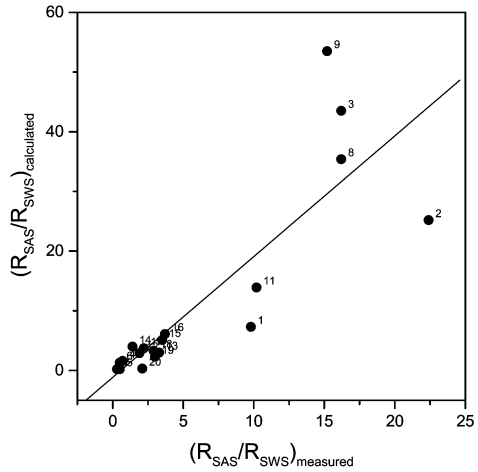

Fig. 3 Calculated *versus* experimental sampling rate ratio (R_{SAS}/R_{SWS}) for two sampler designs differing from each other only in the composition of the filling medium (air or water). The experimental ratio was determined for the two designs under the same exposure conditions in a flow-through experiment at 14 °C. The theoretical ratio R_S was calculated using eqn. (8). The line represents the linear regression given in eqn. (9).

8) shows that the sampling rates are similar. For the tube sampler the R_S values of PAHs are generally higher than those for the rod sampler. The variances of the sampling rates show increased values especially for the three PCBs for the rod sampler (PCB 28, 20%; PCB 52, 35% and PCB 101, 80%). A similar behaviour could be observed for chrysene (variation coefficient, 27%). The reason for this finding we assume in the relatively large thickness of the PDMS layer of the rods (2 mm id) and the associated deferred and incomplete desorption of these analytes. Because of the lower variances using the tube sampler this one has been favoured.

Effect of the temperature. In order to study the influence of the temperature on the sampling rates, the water-filled tube samplers were exposed at two different temperatures (14 and 8 °C; see Table 4). A significant decrease (*t*-test) of the sampling rates with decreasing temperature was observed for hexachlorobenzene, β-HCH and δ-HCH. In contrast, the more volatile PAHs, acenaphthylene, acenaphthene, phenanthrene, and anthracene, show a significant increase of the R_S values with decreasing temperature. The R_S values of the other PAHs (except fluorene) determined at the two exposure temperatures have no significant differences. The prediction of the temperature effect on the sampling rates is difficult because of the complexity of the system. Both thermodynamic and kinetic parameters affecting the sampling rate are temperature dependent.

Based on widely applied relationships such as the Wilke–Chang equation and the Heyduk and Laude equation[32] analyte diffusion coefficients in water are expected to be directly proportionally to temperature. On the other hand, the phenomenon of reduced or nearly constant solute permeability with increasing temperature has been observed in nonporous polymers such as LDPE.[33] Typically, increased temperature should enhance mass transfer in all media and the uptake of target analytes should exhibit Arrhenius dependences. However, in membrane systems, non-ideal solute-polymer interactions may affect activation energy required for molecular diffusion, increasing complexity of the temperature–R_S relationship. Also, partition coefficients K_{iw} may decline enough with increasing temperature to offset increases in diffusion coefficients.[34]

Maximum exposure time t_{50}. Maximum exposure time in which the passive sampling device accumulates a pollutant integrative under field conditions can be estimated according to eqn. (3) and the sampling rates R_S from the exposure experiments. As described in an earlier paper,[16] the determination of distribution constants K_{SW} for the analyte partitioning between PDMS coating and aqueous sample in batch experiments causes difficulties. Therefore, the apparent distribution constants $K_{f(PDMS)}$, obtained from SPME experiments with PDMS coated fibers (100 μm) was used as a substitute for the K_{SW} values in the estimation.[16] The results of the t_{50} estimation for the water-filled tube sampler are given in Table 6. From the calculation results that for acenaphthylene, acenaphthene and fluorene the passive sampler may accumulate integrative about 2 to 3 weeks. Maximum exposure times from 3 to 10 weeks were estimated for HCHs. For the other PAHs investigated, HCB, DDE and PCBs, the t_{50} values may

Table 5 Estimation of the main barrier to mass transfer in water-filled and air-filled passive sampler designs according to eqn. (6) or (7)

	Water-filled sampler			Air-filled sampler		
Compound	Membrane (%)	Water (%)	Rate limiting barrier	Membrane (%)	Air (%)	Rate limiting barrier
1,2,4,5-Tetrachlorobenzene	14	86	W	99	1	M
Pentachlorobenzene	4	96	W	93	7	M
Hexachlorobenzene	2	98	W	92	8	M
α-HCH	49	51	W+M	79	21	M
β-HCH	43	57	W+M	10	90	A
γ-HCH	49	51	W+M	62	38	M
δ-HCH	27	73	W	5	95	A
PCB 28	2	98	W	60	40	M
PCB 52	1	99	W	41	59	M + A
PCB 101	0	100	W	34	66	A
p,p′-DDE	1	99	W	20	80	A
Acenaphthylene	33	67	W	94	6	M
Acenaphthene	32	68	W	96	4	M
Fluorene	23	77	W	90	10	M
Phenanthrene	13	87	W	66	34	M
Anthracene	11	89	W	66	34	M
Fluoranthene	4	96	W	15	85	A
Pyrene	4	96	W	14	86	A
Benzo[a]anthracene	1	99	W	3	97	A
Chrysene	1	99	W	0	100	A

[a]W = Water. [b]M = Membrane. [c]A = Air.

Table 6 Estimated maximum exposure times t_{50} of the analytes using water-filled tube samplers in the field at 14 °C

Compound	log $K_{f(PDMS)}$	t_{50}/day
Hexachlorobenzene	4.3[a]	1283
α-HCH	3.2[b]	29
β-HCH	2.7[b]	24
γ-HCH	3.2[b]	40
δ-HCH	3.3[b]	74
PCB 28	4.7[a]	3158
PCB 52	5.0[a]	8761
p,*p*′-DDE	5.2[a]	108749
Acenaphthylene	3.40[c]	12
Acenaphthene	3.63[c]	23
Fluorene	3.71[c]	14
Phenanthrene	3.96[c]	121
Anthracene	3.98[c]	129
Fluoranthene	4.71[c]	3287
Pyrene	4.86[c]	7625
Benzo[*a*]anthracene	5.26[c]	63769
Chrysene	5.69[c]	188469

[a]Data from reference 16. [b]Data from reference 36. [c]Data from reference 35.

be several months and more. The results of the t_{50} calculation indicate that the passive sampler under investigation enables the estimation of TWA concentrations of pollutants from the amounts accumulated during field exposures of several weeks.

As described above, the change of the inner transfer medium (from water to air) used in the samplers results in significantly increased sampling rates for most of the analytes investigated (except the HCH isomers) and thus, according to eqn. (3), in decreasing t_{50} values. It could be estimated, that the air-filled tube sampler may integrative sample the low molecular weight PAHs (acenaphthylene and acenaphthene) only up to one week. However, in the calibration experiment linear uptake were found to be up to nine days for these compounds.

Sensitivity. The calculated sampling rates were used to estimate the potential of the sampling devices under study to detect low TWA concentrations of the target analytes. Based on eqn. (1), the minimum quantifiable TWA concentration of the analytes in ambient water were estimated, whereas the M_S values were replaced by the limits of quantification $M_{S(LOQ)}$. According to the correlation mentioned above, the sensitivity of the entire analytical method depends on the sampling rate R_S and the exposure time of the sampler. That means, presuming the integrative uptake of the analyte from the sampler over the entire exposure period, the sensitivity improves with increasing exposure time. Assuming an exposure of 10 days, limits of quantification in the range of 3 pg l^{-1} (fluorene) to 2.4 ng l^{-1} (*p*,*p*′-DDE) could be estimated for the water-filled tube sampler (at 14 °C). The use of the air-filled tube sampler enables a significant improvement in sensitivity for most of the target analytes except the HCH isomers. Therefore this sampler design is recommended if very low concentrations of pollutants are expected in the field. These results demonstrate that the sampling devices described here enable the detection of the target analytes in the lower ng l^{-1} to pg l^{-1} range.

Conclusions

Based on a previously described sampler (MESCO)[16] a new passive sampler was designed which has on one hand the advantages of the earlier one, and overcomes its weakness (the low chemical and thermal stability as well as biodegradability of the dialysis membrane from regenerated cellulose) on the other hand. The membrane was substituted by a stable, in the SPMD technique successfully applied, LDPE membrane. Moreover, the stir bars used as receiving phase were substituted by less expensive PDMS materials (tubes and rods), which enabled additionally a significant increase of the PDMS volume and thus the accumulation capacity. The study of the PDMS materials regarding reproducibility and completeness of enrichment and thermodesorption yielded in comparable good results of tubes and stir bars.

The investigation of the capability of three versions of the sampler (water-filled tube and rod sampler as well as air-filled tube sampler) resulted in the new samplers enabling the effective accumulation of the POPs under study and thus the estimation of low TWA concentrations of these water pollutants. The first comparison of samplers which differ only in the filling medium (water and air, respectively) was done, to our knowledge. This resulted in a significant increase of the sampling rates of most of the analytes and thus in enhanced sensitivities for the air-filled sampler. This finding could be confirmed by calculation of the sampling rates based on physico-chemical parameters.

The new samplers are stable in field exposure (as tested in on-site experiments) and enable longer exposure times compared with the MESCO sampler because of their enlarged accumulation capacity.

However, there is a lack in efficient sampling of analytes with larger molecular size, such as PCBs and PAHs with high molecular weights because of the application of the non-porous LDPE membranes.

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Príloha 6

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PAPER

Performance optimisation of a passive sampler for monitoring hydrophobic organic pollutants in water

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The performance of an integrative passive sampler that consists of a C18 Empore disk sorbent receiving phase fitted with low density polyethylene membrane was optimised for the measurement of time-weighted average concentrations of hydrophobic micropollutants in water. A substantial improvement of sampling characteristics including the rate of sampling and the sampling precision was achieved by decreasing the internal sampler resistance to mass transfer of hydrophobic organic chemicals. This was achieved by adding a small volume of *n*-octanol, a solvent with high permeability (solubility × diffusivity) for target analytes, to the interstial space between the receiving sorbent phase and the polyethylene diffusion-limiting membrane.

Introduction

There is an increasing requirement for monitoring the water quality across Europe, with particular emphasis on the contaminants in the list of priority pollutants in the Water Framework Directive (WFD) and in various water conventions, *e.g.* the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR). Among priority pollutants, persistent organic pollutants (POPs), such as organochlorine pesticides, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons (PAHs) are of great importance. Due to their low aqueous solubilities and hydrophobic nature, the concentrations of POPs dissolved in water are very low, usually <1 ppb. POPs associate easily with particulate matter and are finally deposited in the sediment. The fraction of the chemical truly dissolved in water is very small. Nevertheless, because organisms often bioconcentrate these low levels of contaminants in water to relatively high levels in their tissues, determination of the dissolved portion of environmental pollutants is critical for assessing the potential for detrimental biological impacts.

The only monitoring method legally accepted for this purpose is spot sampling. This is both expensive and labour intensive and measures only instantaneous concentrations, which may not be representative of long-term average pollutant concentrations. There are a number of methods that attempt to overcome these problems, *e.g.* on-line continuous monitoring, biomonitoring or passive sampling.[1] Among these methods passive sampling technology has the potential to become a reliable, robust, and cost-effective tool, that could be used in monitoring programmes across Europe.[2,3]

Integrative passive sampling involves the measurement of the concentration of an analyte as a weighted function of the time of sampling.[2] Ideally, the sampling device acts as an infinite sink for contaminants of interest and the uptake of analytes is time proportional. The use of passive sampling methods to monitor POPs has increased greatly over the past decade. Much has been published on the use of semipermeable membrane devices (SPMD) for evaluating ultra-low concentrations of hydrophobic contaminants.[4–7] Although SPMDs are widely used and very sensitive for assessment of waterborne POPs, laborious and time-consuming separation of lipid matrix components from target analytes using solvent dialysis and size exclusion chromatography is required.[8]

We developed previously a novel passive sampling system for the measurement of time-weighted average (TWA) concentrations of micropollutants in aquatic environments.[9,10] The system is based on the diffusion of target compounds through a membrane and the subsequent accumulation of these pollutants in a bound, solid receiving phase. Accumulation rates and selectivity are regulated by the choice of both the diffusion-limiting membrane and solid-phase receiving material.

One of the prototypes was designed for the sampling of non-polar organic compounds with log octanol/water partition coefficient (log K_{ow}) values greater than 3.[9] This system used a 47 mm C18 Empore® disk as the receiving phase and a low-density polyethylene (LDPE) diffusion-limiting membrane. The LDPE is a nonporous material with no fixed pores, only transient cavities with a typical size of 1 nm. This solute size limitation excludes large molecules as well as those that are adsorbed on colloids or humic acids. Only truly dissolved and non-ionised contaminants diffuse through the LDPE membrane and can be sequestered by the sampler. The C18 Empore® disk has a very high affinity and capacity for the sampled non-polar organic pollutants.

For a good sampler performance, a sufficiently high sampling rate is essential, *i.e.* the rate at which the sampler accumulates chemicals from water, usually expressed as volume of water cleared of a chemical per unit of time (*e.g.* L d^{-1}). High sampling rates are needed, especially for non-polar chemicals due to their low concentrations in the water column. The sampling rate depends on the physicochemical properties of the analyte, the environmental conditions and the sampler design.[2] An optimal sampler design can be achieved in two ways: by maximising the surface area of the sampler; *i.e.* the area through which the analytes are accumulated in the receiving phase, and by minimising the resistance of mass

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transfer across the various phases for the analytes being measured.

The Empore® disk used for the receiving phase[9] in our sampler design consists of octadecyl (C18) bonded silica stationary phase particles, immobilised by polytetrafluoroethylene (PTFE) fibrils. The disk presents a porous medium with a total porosity (inter-particle and intra-particle) of 0.52.[11] When the LDPE diffusion-limiting membrane is placed over the C18 disk a thin layer of air, or in some cases water, remains trapped between the inner surface of the membrane and the adsorbing surface of the C18 silica particles embedded inside the PTFE disk. This layer of air or water both fills the pores in the Empore® disk and forms a thin macroscopic film that fills the gap between the surfaces of receiving phase disk and diffusion-limiting membrane. The analytes taken up by this design of sampler by diffusion across the surface of the LDPE membrane are hydrophobic; air and water are media with very low permeability (solubility × diffusivity) for most of these chemicals. This layer trapped inside the sampler acts as (or represents) a significant additional barrier to mass transfer and potentially reduces the sampling rate of the analytes of interest.

The aim of this study was to improve the performance of the passive sampler by minimizing its internal resistance to obtain higher sampling rates that are required for the measurement of low concentrations of non-polar organic pollutants. The effect of various gap-filling fluids (*i.e.* air, water and *n*-octanol) on the performance of the passive sampler was evaluated for a number of PAHs. These are non-polar compounds with a range of physicochemical properties (Table 1) and thereby provide a convenient test set of compounds.

Theory

The mass transfer of a given chemical through a passive sampling device includes several diffusion and interfacial mass transport steps across the different barriers that maybe present *i.e.* the stagnant aqueous boundary layer, possible bio-film layer, the diffusion-limiting membrane, the inner fluid (aqueous or gaseous) phase, and the receiving phase (Fig. 1).

In the initial exposure phase, analyte uptake is expected to be linear or time-integrative after steady state flux of chemicals into the sampler has been achieved.[4,12] Under these conditions the amount of a chemical in the receiving phase is directly proportional to the product of the concentration in the surrounding water (C_w) and the exposure time (t). For practical purposes, uptake in the linear phase can be described by:

$$M_S(t) = M_0 + C_w R_s t \quad (1)$$

where M_S is the amount of analyte accumulated in the receiving phase, M_0 is the initial amount of analyte in the receiving phase, and R_S is the sampling rate of the system:

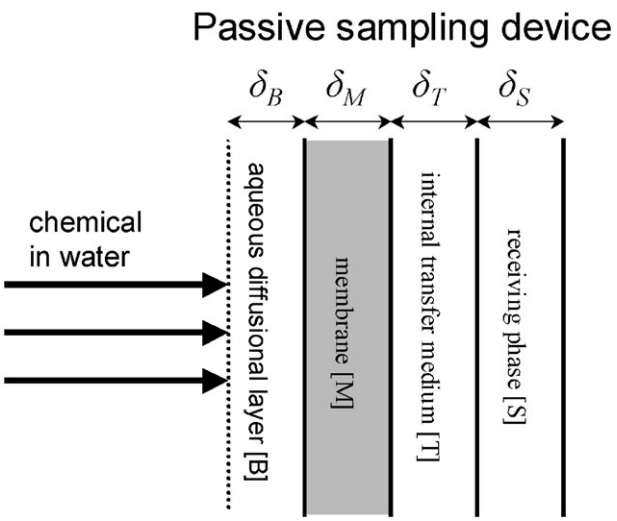

Fig. 1 Profile of the passive sampling device showing the barriers to analyte mass transfer into the sampler.

$$R_S = k_{ov} A \quad (2)$$

where k_{ov} [m s^{-1}] is the overall mass transfer coefficient and A [m^2] is the surface area of the membrane. The uptake of an analyte is linear and integrative approximately until the concentration factor of the sampler (ratio $M_S(t)/C_W$) reaches half-saturation.

The sampling rate of an individual chemical can be determined experimentally under fixed conditions at constant analyte concentration. Under environmental conditions, when the water concentration changes during the exposure, the term C_W represents a TWA concentration during the deployment period.

Materials and methods

Physicochemical properties of substances

Henry's Law constants (K_{AW}) at 25 °C, of substances under investigation were taken from literature.[13,14] Nearly equal values of aqueous diffusion coefficients (D_W) were estimated for the test compounds, ranging from 5×10^{-6} to 6×10^{-6} cm^2 s^{-1}.[15] Diffusion coefficients of the test analytes in air, D_A, at 20 °C ranged from 0.05 to 0.06 cm^2 s^{-1}.[16] An approximated value of 10^{-10} cm^2 s^{-1} was used as diffusion coefficient (D_M) of the analytes in the LDPE membrane.[17] Diffusion coefficients of test analytes in *n*-octanol (D_o) of 7×10^{-7} cm^2 s^{-1} were calculated from the assumption that the D_o values are lower

Table 1 Selected physicochemical properties of test analytes at 20 °C

Compound	M_W[a] g mol^{-1}	log K_{ow}[b]	S[c] g m^{-3}	K_{AW}[d]	D_A[e] cm^2 s^{-1}	$D_W \times 10^6$[f] cm^2 s^{-1}	$D_O \times 10^7$[g] cm^2 s^{-1}
Acenaphthene	154.2	4.0	3.8	4.9×10^{-3}	0.063	6.3	7.5
Fluorene	166.2	4.2	1.9	3.2×10^{-3}	0.06	6.0	7.2
Anthracene	178.2	4.6	0.045	1.3×10^{-3}	0.058	5.9	6.9
Phenanthrene	178.2	4.5	1.10	1.6×10^{-3}	0.058	5.9	7.0
Fluoranthene	202.3	5.1	0.26	4.2×10^{-4}	0.055	5.5	6.6
Pyrene	202.3	5.1	0.132	3.7×10^{-4}	0.055	5.6	6.6
Benzo[*a*]anthracene	228.3	5.9	0.011	2.3×10^{-4}	0.052	5.1	6.1
Chrysene	228.3	5.7	0.0019	2.6×10^{-4}	0.052	5.1	6.0
Benzo[*b*]fluoranthene	252.3	5.8	0.0015	3.4×10^{-5}	0.05	5.0	6.0
Benzo[*k*]fluoranthene	252.3	6.0	0.0008	3.4×10^{-5}	0.05	5.0	6.0
Benzo[*a*]pyrene	252.3	6.2	0.0038	4.6×10^{-5}	0.05	5.0	6.0

[a] Molecular weight (M_W). [b] *n*-Octanol/water partition coefficient K_{ow}. [c] Aqueous solubility S. [d] Dimensionless Henry's Law constant. [e] D_A diffusion coefficient in air. [f] D_W diffusion coefficient in water. [g] D_O diffusion coefficient in *n*-octanol.

than those in water because of the higher viscosity of 1-octanol (7.49 cP at 25 °C) compared with water (0.89 cP at 25 °C).[18] The LDPE membrane/water partition coefficients (K_{MW}) were estimated from Hofman's predictive equation.[19] The values of physicochemical properties are summarised in Table 1.

Materials and chemicals

C18 Empore® disks (47 mm diameter) were purchased from Varian Inc., Walton-on-Thames, UK. LDPE membrane material (40 μm thickness) was obtained from Fisher Scientific, Loughborough, UK. The solvents (HPLC grade quality or equivalent), acetone; *n*-hexane; 2,2,4-trimethyl pentane; ethyl acetate; *n*-octanol; *n*-nonane; methanol and water were obtained from Fisher Scientific. Certified pure (purity >98% in all cases) reference standards of the test compounds; surrogates, and internal standards were obtained from Qm_x Laboratories, Saffron Walden, UK. Certified external calibration solutions of target analyte mixtures at a concentration of 10 μg mL^{-1} in cyclohexane were obtained from Qm_x Laboratories.

Sampler design

The patented design of the passive sampler has been described previously.[9,20] Briefly, the sampling device consisted of a PTFE body containing a C18 Empore disk as a receiving phase. A 40 μm thick LDPE disk (47 mm diameter) of diffusion-limiting membrane was placed on the top of the receiving phase. The PTFE body supported both the receiving phase and the diffusion-limiting membrane and sealed them in place.

Three variants of sampler design were tested in this study. They differed only in the composition of the medium, filling the space between the receiving phase and the LDPE membrane: air (variant 1), water (variant 2) or *n*-octanol (variant 3). The effect of the filling medium on performance (sampling rate and sampling precision) of the sampler was evaluated.

Preparation of the samplers

C18 Empore® disks were conditioned by soaking them in methanol for 20 min until translucent and then stored in methanol until required. The Empore® disks were prepared in a 47 mm diameter disk vacuum manifold platform (Varian Inc.). Methanol (10 mL) was slowly passed through the disk, followed by 20 mL ultrapure water. 500 mL of 5 μg L^{-1} aqueous solution of D_{12}-benzo(*a*)anthracene (internal standard) was filtered through the disk. The subsequent treatment of the disks differed for the three sampler variants:

Variant 1

A vacuum was applied for 30 min to ensure that the disk was completely dry at the end of the procedure.

Variant 2

The filtration procedure was stopped immediately before the last portion of the 500 mL aqueous internal standard solution passed the disk. It was assured that the disk remained saturated with water after this procedure and the disk did not dry out during any of the preparation steps. To prevent the disk from drying between conditioning and exposure in the flow-through test system, the devices were loaded immediately before deployment.

Variant 3

A vacuum was applied for 30 min to ensure that the disc was completely dry. The Empore® disk was then put on the sampler PTFE support disk. 1 mL solution of *n*-octanol in acetone (45% v/v) was applied. The acetone was allowed to evaporate from the disk for 10 min in the fume hood. The resulting volume of applied *n*-octanol was 450 μL.

The final preparation step was the same for all sampler variants. The LDPE membrane was put on the top of the Empore® disk. Prior to sampler assembly, the LDPE membranes were pre-cleaned by soaking for 24 h in *n*-hexane and dried. Any air bubbles were smoothed away from between the two layers by gently pressing the top surface of the membrane using a clean paper tissue. The PTFE supporting disk was placed into the sampler body and fixed in place to form a watertight seal between the membrane and the top section of the sampler.

Exposure experiments

In each experiment up to 16 passive samplers were exposed in a constant concentration flow-through exposure system. A nominal concentration of 100 ng L^{-1} for each test analyte was maintained throughout the experiment. The configuration of the flow-through exposure system has been described.[9] Briefly, it consisted of a 20 L glass tank with an overflow to waste. Water was fed to the exposure tank using a peristaltic pump at 2 L h^{-1}. Test chemicals were dissolved in methanol (30 μg L^{-1}) and the appropriate amounts of stock solution (100 μL min^{-1}) were delivered into the exposure tank using a small peristaltic pump. The water in the chamber was mixed using an overhead stirrer. The resulting methanol concentration in the exposure water did not exceed 0.5% (v/v). To allow for the sorption of chemicals to exposed surfaces (*e.g.* glass walls of the tank), the system was allowed to equilibrate with the test solution for 48 h before samplers were deployed. The passive samplers were placed at the bottom of the exposure tank. Exposures were conducted at 11 °C. The exposures lasted 14 days, during which duplicate samplers were sampled at set time intervals and analysed (see below) to determine the concentrations of accumulated test chemicals. Duplicate samples (500 mL each) of water, sampled from the outlet of the exposure tank, were also taken each time the samplers were removed, and the concentration of test analyte in the water was determined. The experimental conditions of individual exposures are given in Table 2.

Extraction of analytes from the passive samplers

After exposure, the sampler was carefully disassembled and the LDPE membrane removed and rinsed with 5 mL acetone. Compounds were extracted from the Empore® disks in an ultrasonic bath (5 min) using acetone (5 mL) followed by 5 min in 50 : 50 (v/v) ethyl acetate: 2,2,4-trimethylpentane (5 mL). The disks were removed, the solvent extracts combined with the LDPE membrane rinsate and filtered through a drying cartridge containing 1 g of sodium sulfate (Varian Inc.).

In the case where no *n*-octanol was used in the sampler construction, 100 μL of *n*-nonane was added to the extract to act as a solvent keeper. The solvent extract was gradually

Table 2 Summary of flow-through exposure conditions[a] used for the different designs of passive sampler

Sampler variant	Permeation medium[b]	Exposure period/h	Number of samplers
1	Air	0–336	16
2	Water	0–288	11
3	*n*-Octanol	0–284	15

[a] The nominal concentration of analytes in water was 100 ng L^{-1} at 11 °C. [b] The medium filling the gap between the Empore® receiving disk and the LDPE diffusion-limiting membrane.

reduced in volume under nitrogen to approximately 100 μL, 800 μL of *n*-hexane was added and transferred to a 2 mL vial for analysis. 100 μL of 10 ng μL^{-1} solution of D_{10}-anthracene in *n*-hexane was added as an internal standard. The final volume was adjusted to 1 mL with *n*-hexane.

When *n*-octanol was used in sampler conditioning, the extract was gently reduced under nitrogen. Approximately 450 μL of extract in *n*-octanol remained after this preparation step (*n*-octanol has a very low volatility). The reduced extract was transferred to 2 mL vials prior to analysis. 50 μL of the 10 ng μL^{-1} internal standard solution of D_{10}-anthracene in *n*-octanol was added. The final volume was adjusted to 500 μL with *n*-octanol.

In all cases, the percentage recovery of the test compounds from the C18 Empore® disks was between 95 and 100%.

Extraction of analytes from water

The test analytes in water samples taken from the outlet of the flow-through exposure system were extracted using solid-phase extraction (SPE) on Bondelut C18 LO SPE cartridges (3 mL/200 mg sorbent; Varian Inc.). The sorbent was first activated by the passage of 2 mL methanol followed by 10 mL doubly-distilled water through the bed. The water sample (500 mL) was passed through the cartridge at 30 mL min^{-1} using low-pressure. After the entire water sample has passed through the cartridge, the sorbent was dried by aspirating air through the bed. Extracted analytes were eluted with 1 mL *n*-hexane. 50 μL of internal standard (10 ng μL^{-1} D_{10}-anthracene in *n*-hexane) was added prior to analysis.

Water was spiked at multiple concentrations to estimate the recoveries of the test compounds using the SPE procedure. A procedural blank and four recovery solutions (20–100 ng L^{-1}) were extracted concurrently with the water samples. The recovery standards were analysed alongside spiking standards and a mean percentage recovery for the four spiking concentrations was calculated. SPE recoveries of the test compounds were between 80 and 95%.

Extraction of analytes from the PTFE sampler body

To check the potential analyte adsorption to the PTFE material of the sampler, PAHs accumulated in a sampler body were extracted after 284 h of exposure in experiment 3. The sampler body was extracted in an ultrasonic bath (15 min) using acetone (200 mL). The extraction step was repeated twice. The extracts were combined and 100 μL of *n*-nonane was added. The extract was gradually reduced in volume under nitrogen to approximately 100 μL, 800 μL of *n*-hexane was added and transferred to a 2 mL GC vial for analysis. 100 μL of 10 ng μL^{-1} solution of D_{10}-anthracene in *n*-hexane was added as an internal standard. The final volume was adjusted to 1 mL with *n*-hexane.

Instrumental analysis

The concentrations of all target analytes accumulated in samplers during the exposure studies were quantified using GC/MS. Analysis was performed with a 6890A series GC equipped with a mass-selective detector 5973 (Agilent Technologies, Bracknell, UK).

GC/MS analysis of *n*-hexane sampler extracts (variants 1 and 2) and exposure tank water extracts

The sampler extract (1 μL) was injected into the GC/MS system. Injections were carried out in splitless mode at an inlet temperature of 250 °C. The injector was coupled to a 30 m × 0.25 mm id, 0.25 μm film HP-5 MS capillary column (Varian Inc.). Helium was used as carrier gas at a column flow rate of 2 mL min^{-1}. The GC oven temperature programme was 60 °C (2 min) and then increased at 30 °C min^{-1} to 150 °C and then at 6 °C min^{-1} to 280 °C (5 min). Quantification of the test analytes was accomplished using a 7-point external calibration curve. All external standards were prepared in *n* -hexane.

GC/MS analysis of *n*-octanol sampler extracts (variant 3)

The sampler extract (1 μL) was injected into the GC/MS system. Injections were carried out in pulsed splitless mode at an inlet temperature of 250 °C. The injector was coupled to a methyl deactivated fused silica retention gap (2.5 m × 0.25 mm id) The other end of the retention gap was connected to a 30 m × 0.25 mm id, 0.25 μm film HP-5 MS capillary column (Varian Inc.). The pulse pressure was 50 psi for 2 min. Helium was used as carrier gas at a column flow rate of 2 mL min^{-1}. The GC oven temperature programme was 120 °C (2 min) and then increased at 6 °C min^{-1} to 300 °C (5 min). Quantification of the test analytes was accomplished using a 7-point external calibration curve. All external standards were prepared in *n*-octanol.

MS parameters

The MS parameters for both GC methods were: interface temperature 280 °C, ion source temperature 250 °C, electron impact (EI) ionization mode at 70 eV. Analysis was performed by selected ion monitoring (SIM) applying two or three characteristic ions for each compound in both detection and quantification.

Data processing

The experimental time course accumulation rates of individual test substances on the Empore® disks were fitted by linear regression analysis using eqn. (1). The adjustable parameters were the intercept (M_0) and the slope ($C_W \times R_S$) of the uptake curve $M_S = f(t)$. Quality of the fit was characterized by the standard deviations of the optimised parameters, as well as the correlation coefficient adjusted for the degrees of freedom (r^2 adjusted), the fit standard deviation, and the Fisher test criterion on the accuracy of the model. The sampling rates R_S for individual test compounds were calculated by dividing the slope of the linear uptake curve by the mean aqueous analyte concentration during the exposure period. The required variances of R_S values were calculated from the coefficients of variation (relative standard deviations) of the uptake slope parameters and the concentrations in the aqueous phase, which were obtained according to the law of error propagation.

Results and discussion

Flow-through exposures

The performance of the three sampler design variants was tested by exposure to constant concentrations of test chemicals in a continuous flow-exposure tank. Concentrations of the analytes in water (C_w) and the amounts accumulated in the receiving phase (M_S) were two parameters measured regularly during the continuous flow-exposures. During exposure the concentrations of the test compounds in water were held constant, and this was confirmed by regular analysis of water samples. Characteristic analyte uptake curves for the sampler variant 3 are shown in Fig. 2.

Variant 1 (air-filled sampler)

Satisfactory fits of the exposure data using eqn. (1) were obtained for all compounds ($P < 0.05$) excepting benzo[*b*]-fluoranthene, benzo[*k*]fluoranthene and benzo[*a*]pyrene. For

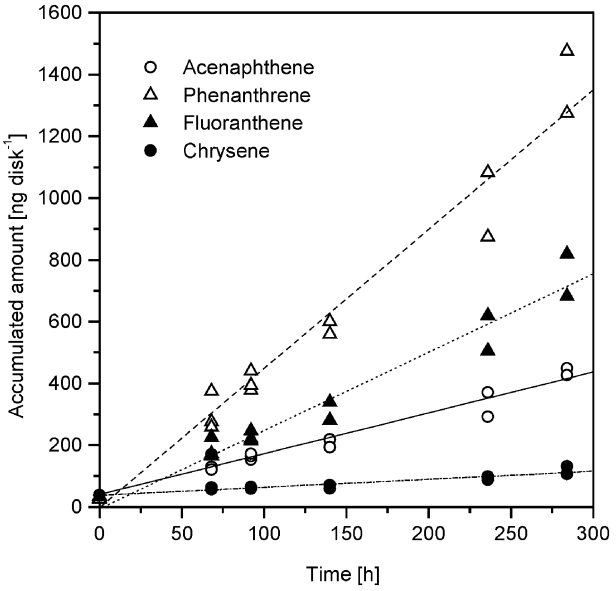

Fig. 2 Uptake of selected PAHs and by the passive sampler variant 3, where the pores in the receiving phase were filled with *n*-octanol. The data used represent the 11 °C flow-through exposure at 100 ng L^{-1} nominal water concentration of each analyte. The lines are predicted concentrations in the sampler obtained by linear regression using eqn. (1).

these three compounds, no significant uptake was observed. Correlation coefficient (r^2 adjusted) values of the regression (model *versus* experimental) of the satisfactory fits ranged from 0.66 (acenaphthene) to 0.76 (fluoranthene). Coefficients of variation of the calculated sampling rate did not exceed 43% in any case, excepting acenaphthene (57%).

Variant 2 (water-filled sampler)

Satisfactory fits of the exposure data using eqn. (1) were obtained only for phenanthrene, anthracene, fluoranthene and pyrene ($P < 0.05$). For the rest of the PAH compounds, deviation of the data from linear uptake was observed. No significant uptake was observed for acenaphthene, fluorene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*a*] pyrene. Correlation coefficient (r^2 adjusted) values of the regression (model *versus* experimental) of the satisfactory fits ranged from 0.36 (anthracene) to 0.65 (fluoranthene). Coefficients of variation of the calculated sampling rate did not exceed 44% for any of these compounds.

Variant 3 (*n*-octanol-filled sampler)

Satisfactory fits of the exposure data using eqn. (1) were obtained for all test compounds. For all analytes the uptake was linear ($P < 0.05$) during the whole exposure period, without any sign of a levelling-off (reaching equilibrium). Correlation coefficient (r^2 adjusted) values of the regression (model *versus* experimental) ranged from 0.72 (benzo[*a*]pyrene) to 0.96 (acenaphthene). Coefficients of variation of the calculated sampling rate did not exceed 32% in any case.

The maximum fluctuations of water concentrations during exposures did not exceed 30% of the mean concentration for individual compounds.

Performance comparison of the three sampler variants

The sampling rates determined for the three sampler variants are shown in Fig. 3. The highest sampling rates (R_S up to 0.19 L d^{-1}) were determined for the sampling device filled with *n*-octanol (variant 3). The sampling rates obtained with the water-filled sampler (variant 2) were the lowest, except for

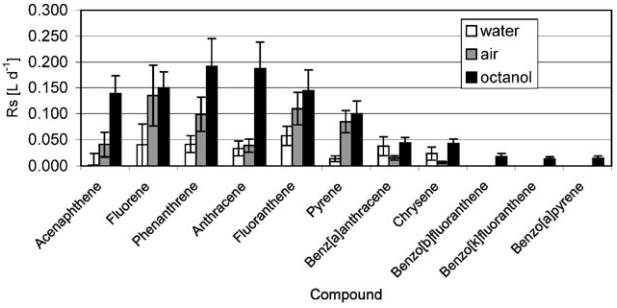

Fig. 3 Sampling rates R_S of polycyclic aromatic hydrocarbons determined for the three passive sampler designs. The passive samplers consist of a receiving phase (47 mm C18 Empore® disk) fitted with a 40 μm thick low-density polyethylene membrane. The pores in the receiving phase were filled with different media: water, air or *n*-octanol. R_s data were derived from 14-day flow-through exposures at 11 °C at the nominal analyte concentration of 100 ng L^{-1}.

benzo[*a*]anthracene and chrysene. For these two compounds, the uptake rates were comparable with the other two sampler variants. The sampler performance can be ranked from the slowest to the fastest as follows: water-filled sampler (variant 2) < air-filled sampler (variant 1) < *n*-octanol-filled sampler (variant 3). In general, sampling rates were lower for very hydrophobic PAHs with high molecular weight. The uptake of larger ringed PAHs (benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*a*]-pyrene) into the air and water-filled variant was so slow, that sampling rates could not be measured. A hydrophobicity profile (with an optimum at log $K_{ow} \approx$ 4.5) of sampling rates was observed for the *n*-octanol-filled device (variant 3). A similar hydrophobicity profile was described by Huckins *et al*. for lipid-filled SPMDs.[21] The best precision of the calculated sampling rates was obtained for the *n*-octanol-filled sampler. The worst precision, accompanied by non-linear sampling behaviour, was observed for the water-filled sampler.

Theoretical examination of the mass transfer

To explain the observed differences in performance of the three sampler variants, a theoretical examination of the mass transfer processes involved was undertaken.

The individual mass transfer layers through which a chemical must diffuse to reach the receiving phase are shown in Fig. 1. The overall mass transfer coefficient is affected by the diffusion of solutes in the individual layers (*i.e*. aqueous boundary layer, diffusion-limiting membrane, the inner transfer medium [air, water or *n*-octanol] and the receiving phase) and by their partitioning into the LDPE membrane and receiving phase; since accumulation of hydrophobic analytes is expected also in the membrane material.[21] Moreover, accumulation is expected also in the *n*-octanol layer in sampler variant 3.

From theory[22,23] it is assumed that the overall mass transfer resistance ($1/k_{ov}$), to the uptake of a chemical is given by the sum of particular barrier resistances to mass transfer:

$$\frac{1}{k_{ov}} = \sum_i \frac{\delta_i}{K_{iw} D_i} \qquad (3)$$

where δ_i is the particular barrier thickness, D_i is the diffusion coefficient in the particular barrier and K_{iw} is the partition coefficient between the *i*-th phase and water.

The overall resistance ($1/k_{ov}$) is then given by:

$$\frac{1}{k_{ov}} = \frac{\delta_B}{D_W} + \frac{\delta_M}{D_M K_{MW}} + \frac{\delta_T}{D_A K_{TW}} + \frac{\delta_S}{D_S K_{SW}} \qquad (4)$$

The subscripts B, M, W and S represent the boundary aqueous layer at the surface of the sampler [B], the membrane [M], the

inner transfer layer (air, water or *n*-octanol) [T] and the receiving phase [S]. The group $D_M K_{MW}$ is the commonly used membrane permeability coefficient. In case where the medium that fills the space between the receiving phase and the membrane is air, water or *n*-octanol, the partition coefficient K_{TW} in eqn. (4) stands for the dimensionless Henry's Law constant K_{AW}, the unity (the number 1) or the octanol/water partition coefficient K_{ow}, respectively. Eqns. (3) and (4) show that an individual resistance increases with the increasing thickness of the barrier and with decreases in the diffusion and partition coefficients, respectively.

A layer with more than 50% of the total resistance is considered rate-limiting.[25] It is likely that the differences in the sampling rates for similar (but differing from each other in the composition of the fluid between the membrane and the receiving phase) sampler designs are caused by differences in the partial resistance to mass transfer of the type of interstitial fluid. The diffusion path of analyte molecules through the inner transfer medium is approximately the same for all sampler designs, because all three sampler designs have the same geometry. For all sampler designs, the mass transfer by convection in the inner transfer medium is assumed to be negligible. Thus, the difference in sampling rates is likely to originate in unequal inner transfer medium permeability of the individual sampler designs.

To examine the effect of the inner transfer medium of the sampler on the mass transfer, an estimate of the magnitude of the resistance of this layer was made. This resistance ($1/k_T$) was calculated as:

$$\frac{1}{k_T} = \frac{\delta_T}{D_A K_{TW}} \quad (5)$$

The estimated values of ($1/k_T$) are shown in Fig. 4 together with the estimated resistance $1/k_M$ of the LDPE membrane, which was calculated as:

$$\frac{1}{k_M} = \frac{\delta_M}{D_M K_{MW}} \quad (6)$$

The calculation was made using the available physicochemical properties of the test analytes including diffusion and partition coefficients (Table 1). The thickness of the transfer medium δ_T was set to be approximately 1 mm (depth of pores in an Empore disk) and the thickness of the LDPE membrane δ_M was 40 μm.

A theoretical examination shows that the resistance to mass transfer of the water or air layer is expected to be several orders of magnitude higher than that of the *n*-octanol layer. Despite the fact that the diffusion coefficients of the analytes in water and air are much higher than those in *n*-octanol, the permeability of these media is low due to very low solubility or vapour pressure of the PAHs in them. Moreover, the resistance of water and air is expected to increase with increasing the molecular weight of the analytes, whereas the resistance in *n*-octanol will decrease. This reduced internal resistance to uptake becomes significant when sampling (and successfully detecting) large ringed PAHs, which are present (in the dissolved form) only at trace levels in the aquatic environment.

Furthermore, the resistance to mass transfer of the water layer is expected to be comparable to or even higher than the resistance of the LDPE membrane. Thus, in sampler variant 2, the water filling the pores of the Empore® disk is likely to be the rate-limiting barrier to the uptake of chemicals.

Although the resistance of the air layer is expected to be lower than that of LDPE membrane for smaller PAHs (up to three aromatic rings), it is expected to dramatically increase for larger PAHs. The inner air layer is then expected to take control over the sampling kinetics in the variant 1 of the sampler.

From theory,[23] the individual resistances to mass transfer are additive. Fig. 5 shows sampling rates estimated (using eqn. (3)) theoretically for a combined mass transfer through the LDPE membrane and the inner transfer medium. The theoretical uptake scenario for the air (variant 1) and water-filled (variant 2) sampler designs estimate the maximum achievable values of sampling rates of 1.4 and 0.3 L d^{-1}, respectively. In contrast, the predicted sampling rates for the *n*-octanol-filled sampler (variant 3) are much higher (up to 30 L d^{-1}). Significant differences in favour of the *n*-octanol variant (3) are predicted especially for the larger ringed PAHs.

Experimental sampling rates *vs.* theoretical predictions

All experimentally determined sampling rates were lower than 26% of the theoretically calculated values.

To compare the theoretically estimated kinetic parameters with the experimentally measured values, it is necessary to consider the simplifications made in the above calculations.

Firstly, only the mass transfer of chemicals in physical sampler components (membranes and well-defined layers of fluid) was discussed. However, the first and very important step in uptake is the diffusion through the stagnant aqueous boundary layer at the surface of the membrane. This presents an additional barrier for the uptake of chemicals in the

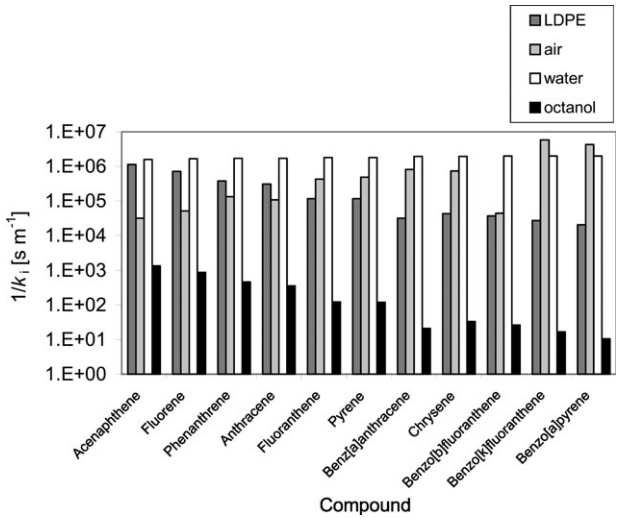

Fig. 4 Estimate of various individual barrier resistances (LDPE membrane and inner transfer media air, water and *n*-octanol) to mass transfer ($1/k_i$) inside a passive sampler. The calculations were made using eqns. (5) and (6).

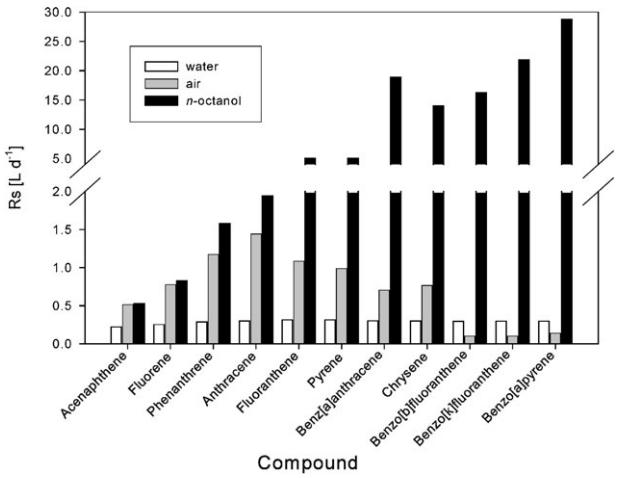

Fig. 5 Estimate of sampling rates (R_s) of the target analytes calculated for mass transfer through the LDPE membrane and the inner transfer medium layer of air, water or *n*-octanol using eqn. (4). The resistance of aqueous boundary layer at the outer surface of the sampler was not considered in the calculation.

sampler. The thickness of the aqueous boundary layer varies with exposure conditions; increased water turbulence during the sampling period reduces the thickness of the boundary layer and thus its resistance to mass transfer. For hydrophobic chemicals (with high values of K_{MW}, K_{TW} or K_{SW}) the aqueous boundary layer may become the rate-limiting barrier of the whole sampling process.[24] Our ongoing calibration experiments with sampler variant 3 at varying exposure conditions have demonstrated that the sampling rates of PAHs can be increased by more than one order of magnitude by increasing the water turbulence around the face of the sampler.[25] This confirms that the uptake of these compounds is indeed governed by diffusion across the aqueous boundary layer. The mass transfer conditions at the boundary layer for a non-streamlined body with a complicated geometry (*e.g.* the sampling device evaluated in this study) are difficult to model and for practical purposes are non-predictable.[17]

Secondly, limitations due to molecular size exclusion of the LDPE membrane were not taken into account. In the LDPE membrane resistance calculation, a uniform membrane diffusion coefficient ($D_M = 10^{-10}$ cm^2 s^{-1}) for the analytes was used. In reality, the D_M value is related to molecular size and it is expected to significantly decrease with increasing molecular weight.[19] The complex interactions of non-porous polymers with the diffusing analytes have so far prevented the establishment of a precise relationship between molecular size and the polymer diffusion coefficients.[26]

Thirdly, the theoretically derived kinetic parameters represent a situation at 25 °C, for which literature data of physicochemical properties were available. A direct comparison with experimental data obtained at 11 °C would introduce a certain systematic error. However, this is expected to be only of minor importance, because the diffusion and partition coefficients are not expected to change dramatically (orders of magnitude or so) within the chosen temperature range (11–25 °C).

Finally, the resistance to mass transfer of the receiving phase was assumed to be negligible in comparison to the other sampler layers.

Hence, the theoretically predicted very high (up to 30 L d^{-1}) sampling rates for high molecular weight PAHs are not realistic. The aqueous boundary layer, in combination with the low membrane permeability and the high resistance to mass transfer in the internal water or air may result in unfavourably low sampling rates for these and similar hydrophobic compounds. This assumption was confirmed by the observed very low or non-measurable uptake rate of large ringed PAHs. A steep decline in sampling rates for very hydrophobic compounds was observed also for lipid filled SPMDs; Huckins *et al.*[26] discussed possible reasons for this phenomenon, which include: (a) a higher order rise in resistance to mass transfer across the aqueous boundary layer for large hydrophobic analytes; (b) a sharp reduction in solubility and permeability in the LDPE for analytes with large molecules; and (c) uncontrollable partitioning of very hydrophobic substances into the colloidal phase in water.

Although measured sampling rates are expected to be lower than those estimated from theory, the calculations of the combined resistances of the LDPE membrane and the inner transfer medium represent an estimate of the best (highest accumulation rate) possible sampling performance. This could potentially be achieved for small molecules in an extremely turbulent environment where the thickness of the aqueous boundary layer is close to zero.[23]

The factors outlined above, that could not be estimated with the required precision, preclude a direct quantitative comparison of the model predictions with the experimental data. However, the theoretical considerations satisfactorily explain the observed differences in performance of the three sampler variants investigated.

Robustness of the calibration data

The factors affecting a chemical's sampling rate include sampler design, molecular properties and environmental conditions. This study was performed to find the optimum sampler design. The effects of environmental conditions such as temperature and water turbulence were not addressed, but will be reported separately.[25]

The fact that all experimentally determined sampling rates were lower than the theoretically derived values (*i.e.* which did not consider the resistance of the aqueous boundary layer) indicates that all sampling devices used in this study accumulated the target analytes under aqueous boundary layer control. Moreover, Fig. 4 illustrates that even a thin (1 mm) layer of water presents a more efficient barrier to mass transfer than the LDPE membrane. As a consequence, it is likely that the performance of the passive sampler will be susceptible to changes in water flow and turbulence during deployment.

When the uptake of analytes is controlled by the diffusion in the aqueous boundary layer, the presence of the LDPE membrane in the sampler does not affect the sampling kinetics. Nevertheless, its role is crucial for the selectivity of sampling. LDPE allows only small (smaller than the size exclusion limit of 1 nm) and truly dissolved molecules to be sorbed by the receiving phase; contaminants bound to humic acids and colloids are excluded.

In order to sufficiently validate the performance of the passive sampler, calibration at various flow and turbulence conditions as well as exposure temperatures was performed and will be reported separately. In addition, the *in situ* calibration concept of performance reference compounds can be applied to support the laboratory calibration data.[27] This will also be reported along with investigations into the effects of biofouling of the membrane surface during field deployments.

Practical aspects of the *n*-octanol usage in sampler construction

When selecting a suitable solvent for application as an internal transfer medium in the sampler the following factors were taken into account. The most important factor is a good permeability (*i.e.* the diffusion coefficient × solubility) for the hydrophobic organic pollutants. Another factor is a low volatility and diffusivity to prevent solvent loss due to evaporation and diffusion from the device during prolonged (*i.e.* weeks to months) field deployments. Furthermore a viscous solvent helps to prevent unwanted spillage and leakage from the sampler during preparation, exposure and disassembly.[28,29]

The use of *n*-octanol (boiling point 195 °C) as a solvent which remains in the sample after its processing has consequences for the subsequent GC/MS analyses. Enriched residue extracts in *n*-octanol can, in principle, be directly injected into a hot split/splitless inlet of a GC. To ensure that the chromatographic peaks do not tail, an initial column temperature of at least 120 °C is necessary. Hence, only compounds with boiling points above 250 °C (*e.g.* PAHs with 3 or more rings) can be determined reproducibly by this analytical method. Furthermore, other practical details have to be considered when analysing hydrophobic compounds contained in *n*-octanol. These include the use a viscosity delay in the automatic injection cycle, use of pulsed splitless injection and the installation of a retention gap before the chromatographic column. Mixed solvents should generally not be used for samples analysed by GC and external standards dissolved in *n*-octanol are required for quantification of the accumulated residues.

There are, however, several advantages to the use of *n*-octanol. Firstly, *n*-octanol does not represent a severe matrix interference. The extract from the sampler can be analysed by GC without the need of special cleanup procedures, unlike that from the widely used lipid-filled SPMDs. For the latter devices, laborious and time-consuming separation of lipid matrix com-

ponents from target analytes using solvent dialysis and size exclusion chromatography is required.[8] Secondly, *n*-octanol acts as an efficient solvent keeper preventing the loss of target analytes due to evaporation during the sample preparation steps and subsequent storage prior to the chemical analysis. Thirdly, *n*-octanol is a well-characterised substance. Physicochemical parameters such as partition coefficients between *n*-octanol and other media (*e.g.*, water, air) are available in the literature for a large number of environmental pollutants. The availability of physicochemical property data facilitates the modeling of analyte uptake by the passive sampler.

Comparison with other passive sampling devices

The performance of the passive sampler optimised in this study can be compared with those of other types of sampling devices designed to collect hydrophobic organic pollutants. Calibration data for PAHs are available in the literature for SPMDs[21] and the membrane enclosed sorptive coating (MESCO) sampling devices.[30] These devices differ in their design geometry and their use of construction materials. However, for all of these, the sampling rates are directly proportional to the sampler surface area. Consequently, the highest sampling rates will be achieved with passive samplers having a very large surface area, such as the standard size SPMDs (450 cm^2 in comparison to 17.5 cm^2 for the sampler used in this study). Nevertheless, the sampling performance of these devices can be compared on the surface specific basis, *i.e.* when their sampling rates are expressed as volume of water cleared for a chemical, per unit time and unit surface area, or L d^{-1} cm^{-2}.

Furthermore, it is necessary to take into account that the reported sampling rates are likely to be affected by environmental variables (temperature, water turbulence, biofouling) and vary depending on the exposure conditions used to collect the laboratory derived calibration data. Although the most calibration studies reported in the literature were performed in flow-through systems, they were not conducted under the same exposure conditions or using water of a comparable quality (*e.g.*, the presence of variable levels of dissolved organic carbon [DOC]).

Taking into account these limitations, an approximate comparison of sampling rates can be made. Fig. 6 shows that the surface specific sampling rates of the three passive sampling devices are very similar for PAHs compounds with 3 and 4 aromatic rings, ranging from 5 to 13 mL d^{-1} cm^{-2}. This indicates that the uptake of these compounds by the three different samplers is governed overall by a similar mass transfer process; most likely diffusion across the aqueous boundary layer. The uptake of PAHs with 5 and more aromatic rings in the molecule by our sampling device is up to one order of magnitude slower than that of the SPMD or MESCO. As has previously been mentioned, ongoing calibrations have demonstrated that the sampling of these chemicals can be accelerated (by an order of magnitude or more) by increasing the water turbulence around the face of the sampler.[25] Thus, it is likely that the uptake of these compounds is also governed by diffusion across the aqueous boundary layer.

However, there are a number of other possible explanations for the observed decrease in sampling rates for the very hydrophobic (5-ringed) PAHs. A decrease in the concentration of these compounds in the exposure tank over the time course of the experiments can be excluded as we have shown that the flow-through system provided a constant level of analyte. Once equilibrated, the potential losses of these compounds to the surfaces of the glass tank and the PTFE sampler bodies were compensated for by the continuous replenishment of analyte solution.

Loss of analytes due to adsorption to the PTFE parts in close proximity to the active sampling area of the sampler (*i.e.* near the LDPE membrane) is one possibility. We have investigated the amount of PAHs accumulated in the PTFE sampler body after 284 h of exposure in experiment 3 (see Table 1). The amounts ranged from 0 to 130 ng, with higher accumulation observed for the more hydrophobic PAHs. For one sampler, the total PTFE surface area in contact with the test solution in the calibration tank was 140 cm^2. The surface of the walls of the sampling cavity represents only 20% of this area (30 cm^2). Assuming a homogeneous uptake by the PTFE surfaces, the amounts of PAHs adsorbed to the PTFE walls of the sampling chamber ranged from 0 to 28 ng. This represents only up to a maximum of 15% of the amount of analyte accumulated by both the receiving phase and the LDPE membrane. Such a small accumulation by the PTFE material therefore does not fully explain the observed decrease in sampling rates found for 5-ring PAHs.

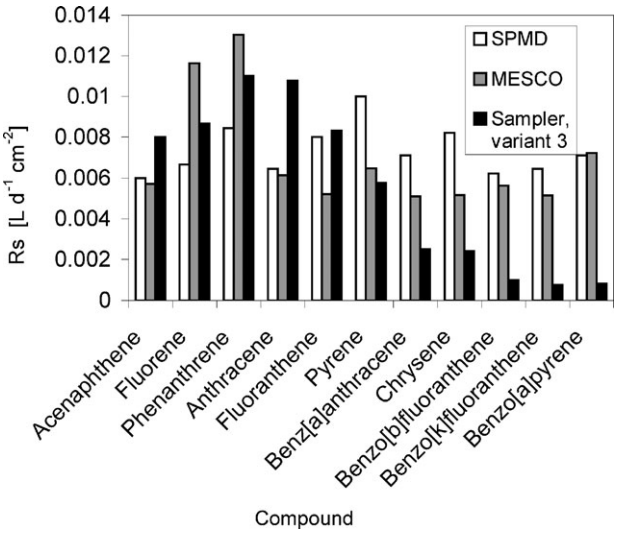

Fig. 6 Comparison of surface area specific sampling rates of the *n*-octanol-filled sampler (variant 3) with two other passive devices designed for time-integrative sampling of PAHs. SPMD calibration data reported by Huckins *et al.*[21] represent a flow-through exposure in quiescent water at 10 °C; the MESCO sampler calibration data reported by Vrana *et al.*[30] were obtained under laminar flow conditions at a water temperature of 14 °C.

A second explanation concerns the potential overestimation of dissolved aqueous concentrations of the very hydrophobic compounds due to their sorption to DOC. It has been shown that DOC levels from 1 mg L^{-1} very efficiently reduce the truly dissolved fraction of chemicals with log $K_{ow} > 6$.[31] In our calibration system, DOC would be present in the water as a result of microbial activity during the 12-day exposure period. When analysing (by SPE) the water samples from the exposure tank, the concentration of analytes represents both the truly dissolved and colloidally bound fraction. However, the passive sampler sequesters only the truly dissolved fraction. This phenomena can lead to an underestimation of the calculated sampling rates for highly hydrophobic compounds. We speculate that this is the likely cause for the observed decrease in sampling rates for 5-ring PAHs compared to calibration studies with SPMD and MESCO samplers. The influence of DOC is a common problem for the laboratory calibration for all designs of passive sampling devices and further research is necessary to address this issue.[32,33]

Conclusions

The performance of a passive sampler for integrative (TWA) sampling of hydrophobic organic pollutants has been optimised. Substantial improvements in sampling characteristics including the magnitude of sampling rate and the sampling precision were achieved by applying a small volume of

n-octanol, to the space between the receiving sorbent phase and the LDPE diffusion-limiting membrane.

The resulting device is simple to construct and deploy, and the procedures used for the analysis of compounds retained in the receiving phase are compatible with existing instrumental methods used by environmental laboratories that measure non-polar organic compounds in water. However, in situations where pollutant concentrations are very low (sub ppt levels) where high sampling rates would be required to sequester a sufficient amount of chemical for analysis, the SPMD would still remain the passive sampling method of choice.

The issues that will be addressed in the further validation of the passive sampler include testing (1) the effect of environmental variables, *i.e*. water temperature and turbulence, on the uptake kinetics of analytes; (2) the dissipation kinetics of individual analytes or performance reference compounds from the sampler at varying conditions as an independent measure of the exchange kinetics between the sampler and water; (3) the uptake capacity of passive sampler for individual analytes; (4) adsorption of compounds by the part of the PTFE body in close proximity to the active sampling surface and (5) the effect of DOC and biofouling on sampler performance.

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Passive sampling techniques for monitoring pollutants in water

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We review the state of the art in using passive sampling technology for environmental monitoring of waterborne organic and inorganic pollutants. We discuss strategies for sampler design, calibration, *in situ* sampling and quality-control issues, and advantages and challenges associated with passive sampling in aqueous environments. We then review typical applications of passive samplers in assessing the aquatic environment.
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Keywords: Environmental monitoring; Environmental pollutants; Passive sampling; Sample preparation; Water analysis

Abbreviations: ASV, Anodic stripping voltammetry; BTEX, Benzene, toluene, ethyl benzene and xylene; DET, Diffusion equilibrium in thin films; DGT, Diffusive gradient in thin films; GC, Gas chromatography; HPLC, High-performance liquid chromatography; LDPE, Low-density polyethylene; MESCO, Membrane-enclosed sorptive coating; nd-SPME; Negligible depletion solid-phase microextraction; NOM, Natural organic matter; OSPAR, The Convention for the Protection of the Marine Environment of the North-East Atlantic; PAH, Polycyclic aromatic hydrocarbon; PCB, Polychlorinated biphenyl; PCDD, Polychlorinated dibenzo[p]dioxin; PCDF, Polychlorinated dibenzo[p]furan; PDB, Polyethylene diffusion bag; PDBS, Passive diffusion bag sampler; PIMS, Passive integrative mercury sampler; PLM, Permeation liquid membrane; POCIS, Polar organic chemical integrative sampler; PRC, Performance reference compound; QA, Quality assurance; QC, Quality control; SBSE, Stir-bar sorptive extraction; SLM, Supported liquid membrane; SLMD, Stabilised liquid-membrane device; SPATT, Solid-phase adsorption toxin tracking; SPMD, Semi-permeable membrane device; SPME, Solid-phase microextraction; SVOC, Semi-volatile organic compound; TLC, Thin-layer chromatography; TRIMPS, Trimethylpentane-containing passive sampler; TWA, Time-weighted average; VOC, Volatile organic compound

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1. Introduction

It is necessary to monitor pollutants in the aquatic environment to satisfy the requirements of legislative frameworks and directives, as many of these compounds can pose a threat to both human health and ecosystems. A number of toxic compounds have been designated priority pollutants [e.g., those on lists of the US Environmental Protection Agency (EPA) and the Water Framework Directive of the European Union (EU)] and their measurement is necessary to ensure that water-quality standards are maintained. Sampling and analysis of such a broad range of organic (e.g., chlorophenols, organo- chlorine pesticides, polyaromatic hydrocarbons, polychlorinated biphenyls) and inorganic (e.g., heavy metals and some of their organo-metallic species) compounds represents an ongoing challenge to the environmental chemist.

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Most aquatic monitoring programmes rely on collecting discrete grab, spot or bottle samples of water at a given time. Often, where pollutants are present at only trace levels, large volumes of water need to be collected. The subsequent laboratory analysis of the sample provides only a snapshot of the levels of pollutants at the time of sampling. However, there are drawbacks to this approach in environments where contaminant concentrations vary over time, and episodic pollution events can be missed. One solution to this problem is to increase the frequency of sampling or to install automatic sampling systems that can take numerous water samples over a given time period. This is costly and in many cases impractical, since a secure site and significant pre-treatment of water are required. Such systems are rarely used in widespread monitoring campaigns. Spot sampling yields different apparent concentrations of pollutants depending on the pre-treatment applied (e.g., filtering) and does not provide information on the truly dissolved, bioavailable fraction of the contaminants.

Another approach that yields information on biologically relevant concentrations of pollutants uses biota. A number of test species can be used, depending on the water body being investigated. These organisms can be deployed for extended periods of time, during which they passively bioaccumulate pollutants in the surrounding water. Analysis of the tissues or lipid extracts of the test organism(s) can give an indication of the equilibrium level of waterborne contamination. A number of factors can influence the results – metabolism, depuration rates, excretion, stress, viability and condition of test organism. Furthermore, extraction of analytes from the tissue of animals prior to instrumental analysis is complex.

Estimates of pollutant concentrations in water can also be made by measuring concentrations in benthic sediments and then using equilibrium distribution coefficients to derive levels of dissolved analytes. This approach is limited by the assumption of equilibrium between the sediments and the water column, and the potential effects of organic carbon quality differences among sediments or the formation of non-extractable, sediment-bound residues that are not accounted for in current equilibrium-partition models.

In the last two decades, alternatives have been sought to overcome some of these difficulties. Of these, passive sampling methods have shown much promise as tools for measuring aqueous concentrations of a wide range of priority pollutants. Passive samplers avoid many of the problems outlined above, since they collect the target analyte *in situ* and without affecting the bulk solution. Depending on sampler design, the mass of pollutant accumulated by a sampler should reflect either the concentration with which the device is at equilibrium or the time-averaged concentration to which the sampler was exposed. Such devices have been available for monitoring air quality since the early 1970s. These diffusion-based dosimeters have been employed extensively by industry to measure toxic chemicals in workplace air.

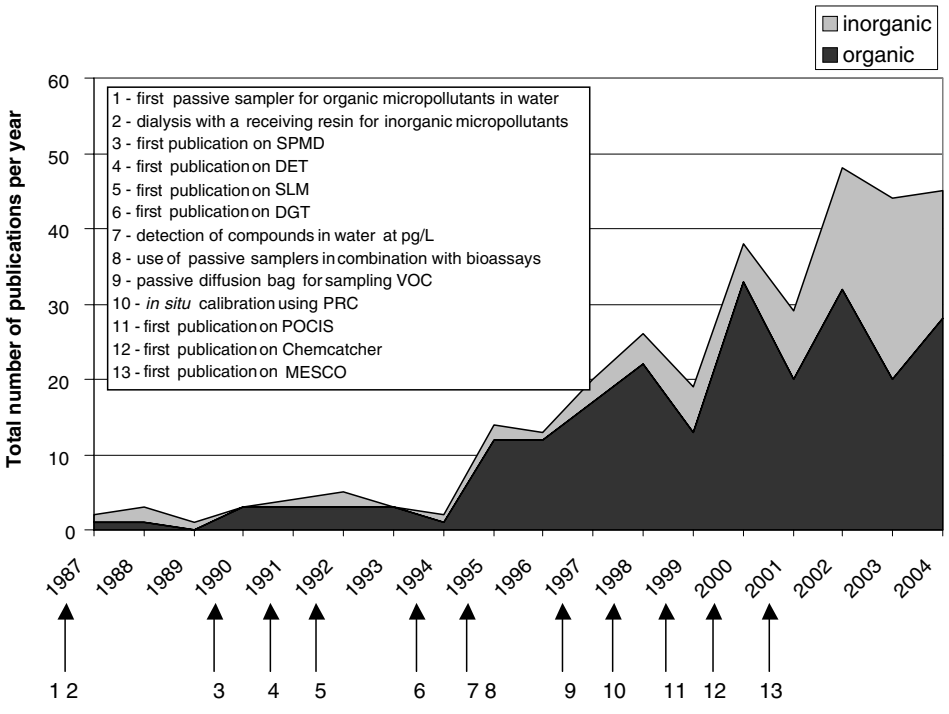

Figure 1. Milestones in the development of passive sampling techniques. The figure shows the annual number of peer-reviewed publications on the development and the application of passive samplers for monitoring of organic contaminants in water.

Later, the principles of passive dosimetry were applied in monitoring in aqueous environments. Milestones in the development of passive sampling devices for monitoring of water pollutants are shown in Fig. 1.

This article reviews the state of the art of different passive sampling methods that have been developed to measure both organic and inorganic pollutants in water and highlights their range of applicability. Their potential for use in monitoring programmes is considered alongside other issues, such as quality control and detection limits. We discuss recent developments to extend their use (e.g., extracts from the devices being incorporated into bioassay-based ecotoxicology tests), challenges and limitations of the technology.

2. Principles

Passive sampling can be defined in its broadest sense as any sampling technique based on free flow of analyte molecules from the sampled medium to a receiving phase in a sampling device, as a result of a difference between the chemical potentials of the analyte in the two media. The net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system, or until the sampling period is stopped [1]. Sampling proceeds without the need for any energy sources other than this chemical potential difference.

Analytes are trapped or retained in a suitable medium within the passive sampler, known as a reference or receiving phase. This can be a solvent, chemical reagent or a porous adsorbent. The receiving phase is exposed to the water phase, but without the aim of quantitatively extracting the dissolved contaminants. Pollutant adsorption or absorption from water into most passive sampling systems generally follows the pattern shown in Fig. 2. The exchange kinetics between a passive sampler and water phase can be described by a first-order, one-compartment mathematical model:

$$C_S(t) = C_W \frac{k_1}{k_2}(1 - e^{-k_2 t}), \quad (1)$$

where $C_S(t)$ is the concentration of the analyte in the sampler at exposure time t, C_W is the analyte concentration in the aqueous environment, and k_1 and k_2 are the uptake and offload rate constants, respectively. Two main accumulation regimes, either kinetic or equilibrium, can be distinguished in the operation of a sampler during field deployment.

2.1. Equilibrium-passive samplers

In equilibrium sampling, the exposure time is sufficiently long to permit the establishment of thermodynamic equilibrium between the water and reference phases. In this situation, equation (1) reduces to:

$$C_S = C_W \frac{k_1}{k_2} = C_W K. \quad (2)$$

Knowledge of the phase-water partition coefficient (K) allows estimation of dissolved analyte concentration. An overview of equilibrium-passive sampling devices has been published by Mayer et al. [2]. The basic requirements of the equilibrium-sampling approach are that stable concentrations are reached after a known response time, the sampler capacity is kept well below that of the sample to avoid depletion during extraction and the device response time needs to be shorter than any fluctuations in the environmental medium. Passive diffusion bag samplers (PDBSs) have been used extensively for monitoring volatile organic compounds (VOCs) in water [3,4].

2.2. Kinetic passive samplers

With kinetic sampling, it is assumed that the rate of mass transfer to the reference/receiving phase is linearly

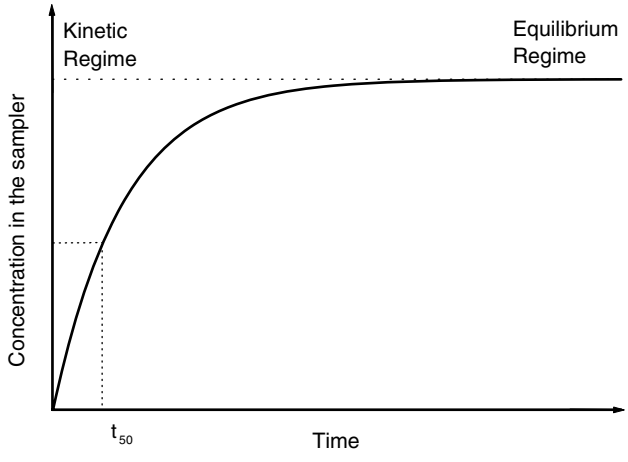

Figure 2. Passive sampling devices operate in two main regimes (kinetic and equilibrium).

proportional to the difference between the chemical activity of the contaminant in the water phase and that in the reference phase. In the initial phase of sampler exposure, the rate of desorption of analyte from the receiving phase to water is negligible, the sampler works in the linear uptake regime, and equation (1) reduces to:

$$C_S(t) = C_W k_1 t. \quad (3)$$

Equation (3) can be rearranged to an equivalent relationship:

$$M_S(t) = C_W R_S t, \quad (4)$$

where $M_S(t)$ is the mass of analyte accumulated in the receiving phase after an exposure time (t) and R_S is the proportionality constant (sampling rate), which is the product of the first-order rate constant for uptake of pollutant (k_1) and the volume of water that gives the same chemical activity as the volume of receiving phase. R_S may be interpreted as the volume of water cleared of analyte per unit of exposure time by the device.

When R_S is known, C_W [the time-weighted average (TWA) concentration of a pollutant in the water phase] may be calculated from the sampling rate (R_S), exposure time (t) and the amount ($M_S(t)$) of the analyte trapped by the receiving phase. For most devices operating in the kinetic mode, R_S does not vary with C_W, but is often affected by water flow or turbulence, temperature and biofouling. The advantages of kinetic or integrative sampling are that they sequester contaminants from episodic events commonly not detected with spot sampling, and can be used where water concentrations are variable. They permit measurement of ultra-trace, yet toxicologically relevant, contaminant concentrations over extended time periods.

2.3. Sampler design

Although many different types of kinetic passive sampler exist, nearly all share common design characteristics, the most important being the presence of a barrier between the sampled medium and the receiving phase. The barrier should determine the rate at which analyte molecules are collected at a given concentration. The barrier may also define the selectivity of the sampler and restrict certain classes of analyte or species sampled. Based on the properties of the barrier, samplers fall into one of the two categories – diffusion-based or permeation-based devices [1]. The sampling process is similar for both. Once exposed to water, they collect analyte molecules reaching the receiving phase by diffusion through a static layer of water contained in well-defined opening(s) in the sampler (diffusion samplers), or by permeation through a porous or non-porous membrane (permeation samplers).

The uptake rate of analytes depends on the sampler design, physicochemical properties of the analytes and environmental variables (i.e., water turbulence, water temperature and fouling). Passive samplers are designed to maximise the amount of analyte sampled in order to detect the generally low levels of analytes present in water, whilst ensuring a quantitative correlation between the mass of chemical separated and its concentration in the sampled medium.

Diffusional kinetic samplers mostly use a ''tube'' design, where the receiving phase is located inside a long, narrow inert tube or a capillary. The space between the edge of the sampler and the surface of the receiving phase, characterised by a diffusion distance (L), is filled with a stagnant layer of the sampled medium, and this defines the sampling rate. To avoid fluctuations in L, caused by the disturbance of the stagnant diffusion layer by facial water velocity/turbulence, tube-type diffusion samplers are characterised by a relatively low ratio of surface area of the receiving phase A to L. Since the amount of analyte sampled is directly proportional to the surface area of the sampler, tube-type samplers are generally less sensitive than so-called badge-type samplers, characterised by a high A/L ratio. The tube design is usually used in air monitoring. However, sampling kinetics in flat badge-type samplers with a large surface area are more affected by fluctuations in water velocity. To alleviate the impact of these fluctuations, a diffusion-limiting membrane is generally used to separate the receiving phase from the sampled medium and to control the mass transfer of analyte to the receiving phase. In water monitoring, badge-type samplers predominate.

2.4. Calibration of passive samplers

The theoretical background of passive sampling in water has been described previously [1,5–7]. The substance-specific kinetic constants, k_1 and k_2, and the distribution coefficient, K, can be determined in two ways. In theory, kinetic parameters characterising the uptake of analytes can be estimated using semi-empirical correlations between mass-transfer coefficients, physicochemical properties (mainly diffusivities in various media) and hydrodynamic parameters [8]. However, because of the complexity of the water flow around passive sampling devices during exposure (usually non-streamlined objects), it is often difficult to estimate uptake parameters from first principles. For K, which characterises the affinity of a pollutant to the receiving phase relative to water, more substance-specific information is usually available from the literature.

In a practical approach, calibration of passive sampling exchange kinetics is performed in the laboratory at known exposure concentrations [9–12]. To predict TWA water concentrations of contaminants from levels accumulated in passive samplers, extensive calibration studies are necessary to characterise the uptake of chemicals under various exposure conditions. Uptake kinetics of chemicals depends upon not only the physicochemical properties of the diffusand, but also the sampler

design and environmental variables, such as temperature, water turbulence and biofouling of the sampler surface [13,14].

2.5. Environmental factors affecting passive sampling

It is important to consider the mechanisms of the exchange process between the aqueous phase and the sampler components. The rate-limiting step in the uptake to the receiving phase (in the absence of fouling) may be controlled by diffusion in the diffusion-limiting membrane or across the aqueous diffusive boundary layer at the membrane–water interface [15]. Water turbulence affects the thickness of the unstirred layer of water that forms part of the diffusion-limiting barrier near the sampler surface, and consequently also affects the mass transfer of the analytes. The rate-limiting step depends on the type and properties of the membrane, the environmental conditions prevailing during sampling and the properties of the compound being sampled.

A number of methods have been developed to compensate for the effect of environmental variables on the sampler performance. Booij et al. [16,17] described a method to estimate the uptake kinetics in both laboratory and field situations by spiking devices prior to exposure with a number of performance reference compounds (PRCs) that do not occur in the environment. Where factors influencing uptake kinetics affect the offloading kinetics of PRCs in an identical manner, the release rate of these compounds is a measure of the exchange kinetics between the sampler and water, and can be used in field exposures to compensate for variations in environmental conditions.

2.6. Biofouling

Unprotected surfaces submersed in water eventually become colonised by bacteria and various flora and fauna that may ultimately form a biofilm. The thickness of this biofilm varies from not only exposure to exposure but also spot to spot on the same diffusion-limiting membrane. The composition of biofilms varies significantly depending on the aquatic system. Biofouling can affect the overall resistance to mass transfer by increasing the thickness of the barrier and by blocking any water-filled pores in the diffusion-limiting membranes. Colonising organisms may damage the surface of membranes, if made of a degradable material. Huckins et al. [18] reported 20–70% impedance in uptake of polyaromatic hydrocarbons (PAHs) in severe cases, but also showed that, for biofouled semi-permeable membrane devices (SPMDs), PRCs can be applied to correct for biofouling during deployment. Their model describing the mass transfer in a biofilm indicates that, ideally, it behaves like an immobilised water layer, with a resistance independent of the biofilm/water partition coefficient, which would mean a similar mobility of compounds in biofilm, independent of their hydrophobicity [18]. The problem of sampler fouling may be reduced by selecting suitable construction materials. For example, polyethersulphone used in one design of the Chemcatcher and in the polar organic chemical integrative sampler (POCIS) is less prone to fouling than polyethylene used in SPMDs [19]. In addition, certain solvent-filled membrane devices are protected from fouling by slow seeping of the fouling-inhibiting solvent (e.g., *n*-hexane) from the sampler during exposure. Protective screens made of copper or bronze mesh have also been shown to inhibit biofouling; however, their use is restricted when monitoring for heavy metals.

3. Passive sampling devices

Passive samplers usually combine sampling, selective analyte isolation, pre-concentration and, in some cases, speciation preservation in one step. They simplify the operations performed at the sampling site. They eliminate the need for an energy/power supply and allow the entire sampling set-up to be simplified and miniaturised. Once the sample is collected, further steps in its processing are usually the same as for other sampling/sample pre-concentration methods in analysis. They include extraction/desorption of the analytes, final instrumental analysis and processing the data.

A review of passive samplers used for monitoring pollutants in various media has been published by Namiesnik et al. [20]. Tables 1 and 2 present an overview of devices used to measure organic and inorganic contaminants in water. In the following sub-sections, we present in detail several (but not all) samplers with a potential for use in environmental monitoring programmes to illustrate the manifold applications of this technology.

3.1. Passive samplers for organic pollutants

3.1.1. Semi-permeable membrane devices. SPMDs comprise lay-flat tubing made of low-density polyethylene (LDPE) filled with a high-molecular weight lipid, typically high-purity synthetic triolein. LDPE is a non-porous material with no fixed pores, only transient cavities with a typical size of 1 nm. This solute size limitation excludes large molecules as well as those that are adsorbed on colloids or humic acids. Only truly dissolved and non-ionised contaminants diffuse through the LDPE membrane and can be separated by the sampler. Triolein represents a receiving phase with a high capacity for compounds with octanol/water partition coefficients $\log K_{OW} > 3$ [21]. The design of the SPMD was first published in 1990. Since then, nearly 200 studies have been reported, and this is the most mature technique for sampling organic pollutants [22]. Several reviews and one monograph have been published on this technology [18,23–25].

Table 1. Overview of passive sampling devices for organic contaminants

Sampler	Full name	Construction	Analytes	Sampling purpose	Typical deployment	Advantages	Drawbacks	Sample preparation for chemical analysis	Ref.
Ceramic dosimeter	Ceramic dosimeter and toximeter	Ceramic tube (5 × 1 cm) filled with a solid-phase sorbent material, closed with PTFE lids	PAHs, BTEX, chlorinated hydrocarbons	Integrative sampling in ground-water	Up to 1 year	No need for extensive laboratory calibrations. Robust design, suitable for long-term monitoring. Sorbent material of the ''Toximeter'' variant can be tested in contact bioassays	Low sensitivity	Solvent extraction or thermal desorption	[32]
Chemcatcher	Universal passive sampler using Empore disk	A housing made of inert plastic (e.g., PTFE), containing a disk of solid receiving phase bound in a porous polymer, and a disk of diffusion-modulating membrane.	Polar and non-polar organics	Integrative	14 days –1 month	Selectivity of the sampler can be adjusted using appropriate combination of membrane and Empore disks. Calibration data available for many chemicals		Solvent extraction	[27]
Dosimeter		Activated carbon receiving phase in a perforated acrylic housing	BTEX and atrazine	Integrative	Up to 2 months			Solvent extraction	[72]
Ecoscope	A sampler based on solvent-filled dialysis membranes and chelating sorbent discs	A plastic housing containing a chelating sorbent disc for sampling metals and dialysis membrane filled with solvents	Non-polar organics	Qualitative screening					[73]
Gaiasafe		Paper or fabric strips impregnated with a solution of binding agent	Metals, anions, organic compounds	Screening	2 days –2 months			Solvent extraction	[74]
Gore-Sorber		Various sorbent materials filled in a carrier hose made of Gore-Tex	BTEX, MTBE, PAHs, VOCs, SVOCs	Equilibrium	14 days			Thermal desorption	[75]

LDPE and silicone strips		Low-density polyethylene or silicone strips	Hydrophobic organic compounds	Integrative	1 month	Simple construction, inexpensive, simple sample processing, and calibration data available for many analyte classes	Smaller sampling capacity than SPMDs	Solvent extraction	[76]
MESCO	Membrane–enclosed sorptive coating	PDMS-coated stir bar used in SBSE or a PDMS rod enclosed in a membrane made of regenerated cellulose or low-density polyethylene	PAHs, PCBs, organochlorine pesticides	Integrative	2 weeks	Miniaturised sampler, non-depletive matrix extraction, solventless sample processing, and both non-polar and polar analytes are accumulated in the sampler equipped with a cellulose membrane	Low membrane stability of the sampler variant with cellulose dialysis membrane	Thermal desorption	[31]
nd-SPME	Negligible depletion-solid phase microextraction	A fibre coated with a liquid (polymer), a solid (sorbent), or a combination of both	Hydrophobic chemicals, including PAHs, PCBs, petroleum hydrocarbons, organochlorine pesticides, aniline, phenols	Equilibrium	Hours	Negligible depletion extraction, a cheap, disposable device	Low sensitivity	Thermal desorption in GC inlet	[30]
Passive	Sampler according to Lee and Hardy	Silicone polycarbonate permeation membrane and an adsorbent receiving phase	Chlorobenzenes, nitrobenzenes and nitrotoluenes	Integrative	Up to 1 day			Solvent extraction	[77]
PDB	Passive diffusion bag samplers	Dialysis membrane or a low-density polyethylene bag filled with distilled water	Polar organic compounds, VOCs, metals, trace elements	Equilibrium sampling in groundwater	2 weeks	Relatively inexpensive, and sample recovery is rapid	Not suitable for sampling semi-volatile organic compounds	Conventional analysis of the receiving water phase	[35]
PISCES	Passive *in situ* concentration-extraction sampler	Hexane in a polyethylene membrane	PCB	Integrative	2 weeks			Volume reduction of the receiving phase	[78]
POCIS	Polar organic chemical integrative sampler	Solid sorbent receiving phase material enclosed in a polyethersulphone membrane	Herbicides and pharmaceuticals with $\log K_{Ow} < 3$	Integrative	Up to 2 months	High sensitivity; capacity of the sampler can be adjusted using appropriate sorbent materials, membrane has low susceptibility to biofouling, and calibration data available for many chemicals		Solvent extraction	[26]

(*continued on next page*)

Table 1 (*continued*)

Sampler	Full name	Construction	Analytes	Sampling purpose	Typical deployment	Advantages	Drawbacks	Sample preparation for chemical analysis	Ref.
Porous	Sampler according to De Jonge and Rothenberg	A water permeable porous sampler that acts as a semi-infinitive adsorptive sink	Wide range of contaminants	Flux-proportional sampling in soil and ground-water	1 month	Tracers integrated in the sampler store information of water volume that passed the sampler during deployment		Solvent extraction	[79]
Stainless steel housing	Sampler according to Kot-Wasik	A stainless steel housing, containing organic solvent in a chamber separated from water by a membrane	Phenols, acid herbicides, triazines	Integrative	1 month	A sample of the receiving phase solvent can be taken without affecting the integrity of the sampler	Low-sensitivity, receiving phase solvent may diffuse out of the sampler during field deployment	Analysis of a sub-sample of solvent is taken and analysed without further clean-up steps	[80]
Solvent-filled dialysis membranes		Non-polar solvent immiscible with water filled in a cellulose dialysis membrane	Hydrophobic organic compounds	Integrative	1 month	Not prone to biofouling	Low sensitivity for very hydrophobic compounds, and solvent diffuses out of the sampler during deployment	Volume reduction of the receiving phase	[81]
SPATT	Solid-phase adsorption toxin tracking	Porous synthetic resin filled polyester fabric sachets	Polar phytotoxins	Integrative	1 week			Solvent extraction	[82]

SPMD	Semi-permeable membrane devices	Flat tube of LDPE filled with triolein	Hydrophobic semi-volatile organic compounds	Integrative	1 month	Widely used method, commercially available, well-established standard operation procedures, and calibration data available for many analyte classes, and high sensitivity	Complicated sample clean-up, susceptible to biofouling	Dialysis in organic solvents, size exclusion chromato-graphy	[21]
TLC plate	Thin-layer chromatography plate		Organo-phosphates	Screening	1 month	Good sensitivity because of a large surface area		Solvent extraction	[83]
TRIMPS	Trimethyl-pentane-containing passive sampler	2,2,3-Trimethylpentane filled in a low density polyethylene membrane	Pesticides	Integrative	1 month	Simple sample clean-up and analysis	Receiving phase solvent diffuses out of the sampler during field deployment	Direct analysis of the receiving phase solvent	[84,85]
TWA-SPME	Solid-phase microextraction applied for determination of TWA concentrations	A fibre coated with a liquid (polymer), a solid (sorbent), or a combination of both	BTEX	Integrative	A few minutes	No need for extensive laboratory calibrations, and sampling rates can be estimated using empirical mass-transfer models	Short-term sampling only, and fibre susceptible to damage or fouling in the field	Thermal desorption in GC inlet	[86]

Table 2. Overview of passive sampling devices for inorganic contaminants

Sampler	Full name	Construction	Analytes	Sampling purpose	Typical deployment period	Advantages	Drawbacks	Sample preparation for chemical analysis	Ref.
Chemcatcher		Comprises an immobilized chelating acceptor resin on a PTFE base and a cellulose acetate membrane filter acting as a thin diffusion layer	Cd, Cu, Ni, Pb and Zn	*In situ* sampling, integrative, speciation	14 days –1 month	Selectivity of the sampler can be adjusted using appropriate combination of membrane and Empore disks, and calibration data available for many chemicals		Acid extraction	[53]
DGT	Diffusion gradients in thin films	Two layers of acrylamide gel mounted in a holder device, one containing an acceptor phase, the other acting as a thin diffusion layer	55 metallic elements including the common heavy metals, phosphorous, sulphide and ^{99}Tc	Integrative, speciation, screening, mimicking biological uptake	1 week	Versatile, well documented	Complicated preparation of device	Acid extraction	[87]
PIMS	Passive integrative mercury sampler	LDPE lay-flat tubing	Neutral Hg species	Pre-concentration, screening	Weeks–months	Membrane characteristics may be altered for control of sampling rates	Further development necessary for aquatic conditions	Direct analysis of the receiving phase	[52]
PLM	Permeation liquid membrane	Microporous hydrophobic support separating test solution from receiving solution	Cu, Pb	Bioavailable metal species	Hours	Selectivity of the sampler can be adjusted using appropriate combination of carrier media and receiving phase	Complicated preparation of device	Solvent extraction	[88]
SLM	Supported liquid membrane	A strip solution with strong complexing agent is separated from the test solution by a macro-porous hydrophobic membrane	Doubly charged cations	Integrative field sampling, pre-concentration of trace elements, mimicking biological membranes	Days	Versatile, selectivity of the sampler can be adjusted		Direct analysis, can be coupled on-line for real-time monitoring	[89]
SLMD	Stabilized liquid membrane device	LDPE lay-flat tubing containing an acidic solution with high affinity for the target elements	Divalent metal ions	Pre-concentration, *in situ* sampling, determination of labile metal ions in grab samples	Days–weeks		Early development stage	Acid extraction	[47]

3.1.2. Polar organic chemical integrative sampler. The POCIS is used to monitor hydrophilic contaminants, such as pesticides, prescription and over-the-counter drugs, steroids, hormones, antibiotics and personal-care products [26]. Such compounds are entering water and ecosystems on a global scale and some have been linked with chronic toxicities. POCIS samples from the dissolved phase and thereby enables the biologically available fraction to be estimated. This sampler permits determination of TWA concentration in water over extended periods (several weeks).

The POCIS comprises a solid receiving phase material (sorbent) sandwiched between two microporous polyethersulphone diffusion-limiting membranes. The type of sorbent used can be changed to target specifically certain compounds or chemical classes. Two configurations are commonly used:

- a 'generic' configuration contains a mixture of three solid-phase sorbents (Isolute ENV+ polystyrene divinylbenzene and Ambersorb 1500 carbon dispersed on S-X3 Biobeads); it is used to monitor most pesticides, natural and synthetic hormones, many wastewater-related chemicals, and other water-soluble organic chemicals and
- the 'pharmaceutical' configuration contains a single (Oasis HLB) solid-phase sorbent and is designed for drug residues [26].

3.1.3. Chemcatcher (organic version). This system uses a diffusion-limiting membrane and a bound, solid-phase receiving phase. Accumulation rates and selectivity are regulated by the choice of both the diffusion-limiting membrane and the solid-phase receiving material; both are supported and sealed in place by an inert plastic housing. For a range of priority pollutant classes, a number of designs are available with different combinations of receiving phase and diffusion-limiting membrane [27].

One design is used for the sampling of non-polar organic compounds with $\log K_{OW}$ values greater than 4 [27]. This uses a 47-mm C_{18} Empore disk as receiving phase and an LDPE diffusion-limiting membrane. The C_{18} Empore disk has a high affinity and capacity for non-polar organic pollutants. Another design used for the sampling more polar organic contaminants combines a 47-mm C_{18} Empore disk as the receiving phase with a polyethersulphone diffusion-limiting membrane [27]. Other devices are being developed for a range of emerging pollutants, including alkylphenols, anti-inflammatory drugs and other pharmaceuticals, polybrominated flame retardants, steroids, sulphonamides and metals (e.g., mercury, tin and their organometallic species) [28].

3.1.4. Negligible depletion-solid-phase microextraction. Solid-phase microextraction (SPME) was developed by Pawliszyn et al. [29] as a simple extraction method with several advantages over liquid–liquid extraction and solid-phase extraction. The use of organic solvents is diminished and the SPME technique is simple, precise, and it may be automated easily, and the apparatus is inexpensive. The extraction medium is a thin layer of a polymer coating on an optical silica fibre, with a typical volume of 10–150 nL. Extraction equilibrium may generally be reached in 30 min. The mass of analyte on the fibre can be measured by either gas chromatography (GC) or high-performance liquid chromatography (HPLC). While most applications of SPME aim at the highest possible extraction efficiency, negligible depletion SPME (nd-SPME) represents a specific application to measure free concentrations based on negligible analyte extraction from the sampled matrix. In addition to the advantages of SPME, existing equilibria within the sample remain undisturbed during nd-SPME. The disadvantage of nd-SPME is the small amount of analyte that is available for analysis (typically only a few percent of the total amount in the sample), and this may lead to quantification problems. A review of nd-SPME has been published by Heringa and Hermens [30].

3.1.5. Membrane-enclosed sorptive coating. This adaptation of the SPME technique to enable integrative passive sampling of hydrophobic organic pollutants has been reported. The device, referred to as the MESCO (membrane-enclosed sorptive coating), comprises a Gerstel Twister stir bar used for stir-bar sorptive extraction (SBSE) or a silicone polymer rod enclosed in a membrane made of regenerated cellulose. The receiving phases may be surrounded by air or water within the bag [31]. The miniature MESCO sampling system combines sampling with solventless pre-concentration. The sampler enables direct analysis of the accumulated contaminants by thermodesorption coupled on-line to GC, thereby avoiding time-consuming sample preparation and clean-up. Despite the small surface area and volume of the sampler, its sensitivity is comparable with other passive sampling systems, since the entire amount of analyte contained in the receiving phase is introduced into GC and subsequently detected.

3.1.6. Ceramic dosimeter. The ceramic dosimeter [32] uses a ceramic tube as the diffusion-limiting barrier to enclose a receiving phase comprising solid sorbent beads. Recently, the utility of the ceramic dosimeter as a robust groundwater-sampling device was demonstrated for benzene, toluene, ethyl benzenes, xylenes (BTEX) and naphthalenes, using Dowex Optipore L-493 as the receiving phase [33]. In up to 90 days of sampling in a contaminated aquifer, the ceramic dosimeter showed an excellent performance, as judged by comparing TWA contaminant concentrations derived from dosimeters with average aqueous concentrations determined by

frequent conventional spot-sampling methods. Based on the same principle, researchers proposed using Amberlite IRA-743 as a solid receiving phase for the measurement of PAHs [32,34].

3.1.7. Polyethylene diffusion bags. There is potential for loss of volatiles during the collection of VOCs from groundwater. Polyethylene diffusion bag (PDB) samplers help to eliminate this problem [35,36]. The sampler comprises a membrane sealed in the form of a long cylindrical bag, filled with deionised water. The bag is made of LDPE and acts as a semi-permeable membrane allowing the passage of most chlorinated VOCs. VOCs in groundwater diffuse across the membrane into the de-ionised water in the bag until equilibrium is reached. Typically, PDBs take about 2 weeks to equilibrate in an aquifer [37]. Once this equilibration has occurred, sample recovery takes place.

3.2. Passive samplers for inorganic pollutants

3.2.1. Dialysis in situ. Equilibrium dialysis is a simple, size-based separation method applicable to the study of trace-metal speciation [38]. Sampling with a dialysis cell is based on a diffusive flux of species able to pass through the cell membrane towards a small volume of water as the acceptor solution, until equilibrium is reached. Metals associated with colloids and humic acid complexes, which are larger than the pores of the membrane, are excluded [39].

3.2.2. Dialysis with receiving resins. An alternative configuration to the above is to add a receiving phase (e.g., a chelating resin) with a high affinity for the species being measured in the cell. Under these conditions, the diffusion rate is theoretically directly proportional to the metal concentration in the water being sampled [40]. If a suitable chelating resin is selected, the bioavailable metal species can be separated. In this case, diffusion across the dialysis membrane may simulate metal-transport processes across biological barriers. The use of the chelating resin, Chelex 100, showed a measurable, reproducible uptake of the soluble fraction of Cd, Pb and Zn at low ambient water concentrations [41]. Coefficients of variations were lower than for mussels, making this resin a promising acceptor phase for the measurement of dissolved metal species in sea-water. These devices have also been deployed in storm-water run-off and variations in the uptake rates of metals could be correlated to hydrological/hydrochemical parameters, such as rainfall volume and pH [42].

3.2.3. Liquid membrane devices. Supported liquid membranes (SLMs) pre-concentrate trace elements from water and have been developed to mimic uptake across biological membranes. This system comprises an organic solvent with a complexing agent that is selective for the target element and is immobilised on a thin macroporous hydrophobic membrane (either as a flat sheet or as a hollow fibre with a small lumen) [43,44]. One side of the membrane is exposed to the aqueous environment, while the other is in contact with a strip solution containing a complexing agent with a higher affinity towards the metals being separated than the one immobilised in the membrane. A proton, an anion or a metal-ion counter gradient drives the transport across the device. The device can be tailored to separate specific metal species by a careful selection of complexing agents or by altering the lipophilicity of the diffusion membrane [45,46]. SLM devices have been used to measure Cd, Co, Cu, Ni, Pb and Zn in natural waters. Effects of turbulence, pH and concentration variations on the performance of SLM devices have been reported [47].

The permeation liquid membrane (PLM) device is the result of further development of the SLM. This technique is based on carrier-mediated transport of metals across a hydrophobic membrane. The microporous support is impregnated with a hydrophobic organic solvent and placed between the sample and a receiving solution [48]. The transport of Cu and Pb complexes through a PLM with a neutral macrocyclic carrier has been described [49].

3.2.4. Diffusive gradient in thin films. The diffusive gradient in thin-films (DGT) device is a development of a similar sampler – the diffusion equilibrium in thin-films (DET) device – initially suggested by Davison and co-workers in 1991 [50]. The first reported use of the improved DGT device was in 1994 for measuring Zn in sea-water. The DGT device comprises a gel-layer incorporating a binding agent (which acts as a solute sink) and a hydrated acrylamide diffusion gel separating it from the water column. This creates a diffusion layer of well-defined thickness. The initial design of the DGT utilised an ion-exchange resin as the receiving phase. Later, Zhang and co-workers [51] demonstrated the applicability of the technique to determination of trace metals (Cd, Cu, Fe and Mn) in sea-water. With a chelating resin embedded in the gel layer, metals could be quantified as low as 4 pmol/L after deployment for 1 h.

The subsequent refinement of the design and the extended range of inorganic pollutants that may be sampled indicate the versatility and the widespread use of the DGT device. In principle, it is possible to sample any labile species for which a suitable binding agent can be embedded into the receiving phase gel.

3.2.5. Passive integrative mercury sampler. Attempts have been made to use the passive integrative mercury sampler (PIMS), originally designed for air sampling, to sample neutral Hg species in water [52]. The device comprises lay-flat LDPE tubing containing a reagent mixture of nitric acid and gold stock solution.

Experiments were performed in simulated freshwater and sea-water environments. The uptake rates remained linear for 2 weeks and preliminary results indicate that sampling of neutral Hg species from water is feasible. Sampling in freshwater was more effective than in sea-water, likely to be because a larger fraction of the total Hg in sea-water was present as charged chloro-anion complexes that could not readily permeate through the membrane.

3.2.6. Chemcatcher (inorganic version). An alternative configuration of the Chemcatcher (see Section 3.1.3) has been developed for the separation of metals. The device comprises a commercially available 47 mm diameter chelating extraction disk as receiving phase and a cellulose acetate diffusion-limiting membrane [53]. The sampler has been used to monitor Cd, Cu, Ni, Pb and Zn, in various aquatic environments, such as a storm-water pond, where the uptake of metals was compared with flow-weighted bottle samples. Results indicated a good correlation with the electro-available Cu fraction but were somewhat less clear for Zn [53].

The diffusion-limiting membrane can be treated with a low surface-energy coating (e.g., polyfluorinated sulphonic acid polymer (Nafion)) to reduce biofouling on the surface of the membrane. The diffusion characteristics of the membrane, the influences of water turbulence and the radius of metal ions monitored have been investigated [54].

4. Applications of samplers

The first publications on the use of passive samplers to monitor aquatic contaminants were in 1980s (Fig. 1) and these devices have since received widespread recognition as effective tools in environmental research. Passive sampling technology is widely applicable in monitoring studies and the results obtained can be interpreted at different levels of complexity. Passive samplers have been employed in field studies aimed at:

(a) screening for the presence and absence of pollutants;
(b) investigating temporal trends in levels of waterborne contaminants;
(c) monitoring spatial contaminant distribution and tracing point and diffusive pollution sources;
(d) speciation of contaminants;
(e) assessing pollutant fate and distribution between environmental compartments;
(f) measuring TWA concentrations of waterborne pollutants;
(g) comparing contaminant patterns in biota and passive samplers – biomimetic sampling to estimate organism exposure; and,
(h) assessing toxicity of bioavailable pollutants in extracts from the receiving phase of passive samplers.

Tables 3 and 4 illustrate the different field applications. These tables are not intended to be comprehensive, but rather to give the reader an overview of the variety of applications. A detailed review of the organic contaminant classes and aqueous matrices that can be sampled by passive samplers was recently published by Stuer-Lauridsen [55].

4.1. Use in chemical monitoring

There are several advantages in using passive samplers for monitoring pollutants in water including:

(a) non-mechanical or passive operation;
(b) ability to sample large volumes of water and
(c) reduced effort required for deployment and sample processing compared to other commonly used methods.

Currently available passive sampling devices are applicable to monitoring chemicals with a broad range of physicochemical properties (Fig. 3) and the detection limits obtained or the lowest measured concentrations (Fig. 4) suggest that passive samplers may find application in monitoring programmes.

Stuer-Lauridsen [55] indicated that passive sampling devices can be used to monitor more than 75% of the organic micropollutants listed in water-quality criteria of the EU and US, the EU Water Framework Directive and the recommendations of The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR).

4.2. Contaminant speciation

Speciation of environmental contaminants includes not only physicochemical speciation of the forms in which analytes are present in the sampled matrix (e.g., freely dissolved, colloidal and particle-bound forms), but also chemical speciation (e.g., the valency state of metals in the sampled water). Trace metals are present in water in various forms (hydrated ions, and inorganic and organic complexes) together with species associated with heterogeneous colloidal dispersions. The particulate phase also contains elements in a range of chemical associations, from weak adsorption to binding in the mineral matrix. These species coexist, although they may not necessarily be in thermodynamic equilibrium.

The difficulty in differentiating the various forms arises from the low levels present in natural waters. The fractionation of species is recognised as an essential step in assessing bioavailability and toxicity in water. A problem is that solution equilibria may change after sample collection through adsorption or desorption of analytes to particulate and colloidal surfaces. A representative

Table 3. Examples of field applications of passive sampling devices for monitoring organic contaminants

Application	Sampler	Environment	Analytes	Short description	Ref.
Screening of contaminant for presence or absence	*n*-Hexane-filled dialysis membranes	Lake water	Organochlorine compounds	Detection of contaminants in passive samplers and mussels	[90]
	POCIS	Wastewater effluents	Polar wastewater-related contaminants and pharmaceuticals	Screening of contaminants	[19]
	SPMD	River	Hydrophobic organic contaminants	Screening of contaminants	[91,92]
Speciation of contaminants	SPMD	Seawater	PAHs	Distribution of particulate, dissolved, and colloidal PAHs in the water column	[57]
	nd-SPME	River water	PCBs, chlorobenzenes	Determination of freely dissolved contaminant fraction in presence of humic acids	[58]
	SPMD	River	PAHs	Relationship between freely dissolved contaminant levels and the quality of dissolved organic matter	[59]
Monitoring of temporal pollution trends	SPMD	Seawater	Organochlorine compounds	Temporal trend in sea-water pollution by outflow of contaminated freshwater following a flood episode	[93]
	SPMD	Seawater	PCBs and hexachloro-benzene	Time evolution in air, sea-water, and at the sea-air boundary layer	[94]
Monitoring of spatial distribution and tracing pollution sources	SPMDs	River	PCBs	Identification and contribution of point and diffusive sources to the total contaminant flux	[95]
	SPMD	River	PCDDs, PCDFs and PCBs	Spatial distribution of contaminants in a river basin	[96]
	SPMD	River and sea-water	PAHs	Spatial distribution of contaminants	[97]
	SPMD	Surface water	UV filter compounds	A regional mass-balance study	[98]
	PISCES	Surface water and effluent wastewater	PCBs	Tracing a point source of pollution	[99]
	SPMD	Discharge from wastewater-treatment plants	Alkylphenol ethoxylates	Spatial distribution of contaminants and their degradation products in the aqueous phase and their distribution between sediment and water column	[100]
	SPMD	River	PBDEs	Assessment of spatial contaminant levels and contaminant-pattern profiles and their relation to contaminant sources	[101, 102]
	SPMD	Seawater contaminated by discharged oilfield-produced water	PAHs	Spatial levels and patterns of bioavailable contaminant fraction	[103]

Table 3 (*continued*)

Application	Sampler	Environment	Analytes	Short description	Ref.
	SPMD	Seawater	Organotin compounds	Spatial levels and patterns of contaminants sampled by passive samplers and mussels compared to those with water samples	[104]
Assessment of contaminant fate and distribution between environmental compartments	SPMD	Irrigation water canal	PAHs	Measuring the residence times (or persistence) of analytes in the dissolved phase water	[105]
	SPMD	Discharge from an industrial source to sea-water	PCBs, chlorophenols, chlorobenzenes	Comparison of contaminant levels in SPMD, mussel and sediment	[106]
	SPMD	Freshwater, wastewater-treatment plants	Triclosan	Fate of a bactericide in the aquatic environment	[107,108]
	Low-density polyethy-lene strips	Seawater	PCBs, PAHs and hexachloro-benzene	Distribution of dissolved contaminants between sediment, pore-water and overlying water column	[109]
	SPMD	River	PCBs, PAHs, PCDDs, PCDFs and substituted benzenes	Comparison of dissolved contaminant levels and patterns estimated using sediment, fish and SPMD	[110–113]
	SPMD	River	Petroleum hydrocarbons	Pre-concentration of sub-part per billion levels for studying source, transport, and bioremediation using carbon- and hydrogen-isotope analysis	[114]
Measurement of time-weighted average aqueous concentrations	SPMDs	River	PCDDs, PCDFs	Comparison of levels and congener profiles of extremely hydrophobic compounds in SPMDs and water	[115,116]
	Ceramic dosimeter	Groundwater	PAHs	Comparison of passive samplers with spot sampling	[34]
	SPMD	Groundwater	PAHs	Comparison of passive samplers with spot sampling	[70]
	POCIS	Effluent of wastewater-treatment plants	Polar pharmaceuticals	Assessment of prescription and illicit drugs in treated sewage effluents	[117]
	Chem-catcher	Harbour	Antifouling agents	Comparison of passive samplers with spot sampling	[27]
Estimate of organism exposure	SPMD	Harbour	Organochlorine pesticides	Comparison of contaminant levels and patterns in mussels and SPMDs	[118]
	SPMD	Seawater	PAHs	Assessment of contaminant accumulation in mussels, fish and SPMDs exposed to dispersed crude oil	[119]
	SPMD	Laboratory exposure in groundwater spiked with contaminant	PCBs and Organochlorine pesticides	Comparison of uptake kinetics in SPMDs and fish	[120,121]

(*continued on next page*)

Table 3 (*continued*)

Application	Sampler	Environment	Analytes	Short description	Ref.
	SPMD	Seawater	PAHs	Assessment of chemical exposure in a side-by-side deployment of SPMD and bivalves	[122,123]
	TRIMPS	River polluted by field run-off by pesticides	Endosulfan	Correlation of contaminant levels in passive samplers with population densities of macroinvertebrates	[124]
	SPMD	Wastewater-treatment plant	Synthetic musks	Comparison contaminant levels and patterns in fish, mussels and SPMDs	[125]
	SPATT	Seawater	Algal toxins	Assessment of shellfish contamination by toxins using samplers and mussels deployed side by side	[82]
Biomimetic extraction for toxicity assessment of aqueous contaminants	Equilibrium sampling using Empore disk (sampling is not performed *in situ*)	Effluents and surface water	A complex mixture of hydrophobic chemicals	Estimate of total body residues in biota after exposure to complex chemical mixtures	[126,127]
	SPME	A methodical study	A complex mixture of hydrophobic chemicals	Estimate of total body residues in biota after exposure to complex chemical mixtures	[65]
	SPMD	Effluents of wastewater-treatment plant	Organochlorine pesticides, PCBs, PAHs	Instrumental analysis and bioindicator tests to determine toxic potential of bioavailable contaminants	[128]
	SPMD	River	A complex mixture of hydrophobic chemicals	Bioassay-directed fractionation to identify bioavailable and toxic chemicals	[129]
	SPMD	Urban stream	PAHs	Assessment of toxic potency of compounds collected by SPMDs using an *in vitro* bioassay	[130]

value is particularly difficult to identify through conventional sampling procedures in environments where concentrations fluctuate [56].

4.2.1. Organic contaminants. Passive samplers can be applied to characterise the distribution of organic contaminants between particulate, dissolved and colloidal phases in the water column [57–59]. The selectivity of devices may be adjusted to sample a desired fraction of an analyte present by choosing membrane materials with desired properties (e.g., pore size and charge on the surface).

Most passive samplers collect only the truly dissolved fraction of chemicals, since: (a) the truly dissolved molecules become separated from colloids and particles during their diffusion across the membrane that separates water from the receiving phase [21]; and, (b) only dissolved molecules are sorbed by the receiving phase [30].

4.2.2. Inorganic contaminants. Passive samplers have been used to gain understanding of the species of metals in the aquatic environment. Speciation of metals with the DGT device relies on two effects: the relative difference in diffusion coefficients; and, the relative difference in affinity to the binding agent between the species to be characterized. It is possible to differentiate between inorganic labile species and organic labile species by employing a systematic variation of diffusion gel pore sizes, resulting in a size-discriminating uptake in a similar fashion to voltammetry. However, diffusion coefficients of the model species have to be determined individually to make accurate measurements of the concentration of the labile species [60].

Table 4. Examples of field applications of passive sampling devices for monitoring inorganic contaminants

Application	Sampler	Environment	Analytes	Short description	Ref.
In situ metal speciation	SLM	Natural waters	Cd, Cu and Pb	The transport mechanisms through supported liquid membrane devices for metal-ion separation and pre-concentration were studied and optimised	[45,46,131]
	SLMD	Natural waters	Cd, Co, Cu, Ni, Pb, Zn	Effects of environmental conditions on the sampling of metals were investigated	[47]
	Chem-catcher	Natural waters	Cd, Cu, Ni, Pb, Zn	Integrative metal sampling was compared with spot sampling and attempts made to reduce biofouling	[53,54]
	DGT and DET	Natural waters	Cr	Simultaneous application of DGT and DET to determine Cr(III) and Cr(III)/Cr(VI) fractions in resin layer and diffusive equilibrium layer, respectively	[132]
	DGT	Lake water	Cu, Fe, Mn and Zn	Study of DGT performance in five different lakes (pH 4.7–7.5) and comparison between dialysis and predictions of a speciation model	[133]
	DGT	Natural freshwater	Cu and Zn	Comparison of DGT, competitive ligand exchange and voltammetric measurements, as well as examining the agreement of the results with predictions made by several speciation models	[134]
	DGT	Synthetic freshwater	Cd	Examination of DGT lability of Cd in solutions containing various synthetic (nitrilo-triacetic acid (NTA) and diglycolic acid) and natural (extracted fulvic acid) ligands. Diffusion gel of reduced pore size used to estimate portion of Cd complexed by fulvic acid	[135]
	DGT	Natural water	Ni and Zn	*In situ* determination of Zn and Ni speciation between humic and fulvic acid complexes through the use of diffusive gel layers with different pore sizes. Comparison with ASV results and predictions of speciation model	[136]
Mimics bioavailability	DGT	Ion-poor water	Cu	Comparison of Cu binding to trout gills and results for ion-selective electrode and DGT measurements. Examination of the influence of NOM on Cu bioavailability	[137]
	DGT	Freshwater	Cu	Investigation of the performance of DGT in the evaluation of toxic fraction of Cu to *Daphnia magna*, using synthetic ligands (EDTA, NTA, glycine and humic acids)	[138]

(*continued on next page*)

Table 4 (*continued*)

Application	Sampler	Environment	Analytes	Short description	Ref.
	DGT	Seawater	Cd, Cu, Pb and Zn	Parallel use of DGT devices and transplanted mussels to assess metal levels in marine environment	[139]
	DGT	Freshwater	Al	Comparison of the relevance of DGT performance to the observed bioavailability of Al with trout (*Salmo trutta* L.) compared with a pyrocatechol violet fractionation procedure	[140]
	PLM	Natural waters	Cu, Pb	Transport of metal complexes through the permeation liquid membrane depends on the lipophilicity of the complexes	[88,141]
Determination of radionuclides	DGT	Freshwater	^{134}Cs	Use of ammonium molybdophosphate binding agent to collect and determine ^{134}Cs in laboratory tests and applied to a natural freshwater lake	[142]
Determination of metal remobilization	DGT	Freshwater	Al, Ba, Co, Cu, Fe, Mn and Ni	A novel sediment trap device was used together with a DGT device to determine the metal remobilization from settling particles in a well-mixed lake	[143]

4.3. Quantification of concentrations in water

Passive sampling methods can be used to calculate the concentrations of compounds in the aqueous phase, using the principles described in Section 2. Fig. 5 illustrates the way in which integrative passive samplers can provide representative information on TWA contaminant concentrations over a long period of time with a sampling frequency lower than in spot sampling. However, it is important to recognise that, in most cases, the aqueous concentration estimated using passive samplers reflects only the truly dissolved contaminant fraction and is not necessarily equal to the concentration measured in spot samples, particularly in very hydrophobic compounds in the presence of elevated levels of dissolved organic matter. Nevertheless, the comparison is possible, if all species and fractions of contaminants present in the sampled matrix are characterised (see Section 1).

In many aquatic systems, contaminant concentrations are not constant, but fluctuate or occur in the form of unpredictable pulses. Concentrations reflected by integrative passive samplers are TWAs over the exposure period, but more research is needed to quantitate the uptake in passive samplers in scenarios involving pulsed and discontinuous exposure. Such research will provide sufficient evidence of realistic concentration estimates using passive samplers and convince the regulators of the application of passive samplers in monitoring programmes.

4.4. Estimate of organism exposure

Sijm et al. [61] reviewed biomimetic passive sampling methods to study the bioavailability of chemicals in soil or sediment. Biomimetic equilibrium sampling approaches using SPME [29] and Empore disks can mimic partitioning of contaminants between the pore water and the organism. Both approaches assume that the freely dissolved contaminant concentrations will represent bioavailability. However, for substances that may be biotransformed in the organism, the methods will overestimate the concentration in the organism. For organisms that have several routes of uptake (in addition to via the water phase), the biomimetic method will underestimate the concentration in the organisms.

Biomimetic sampling devices have been applied to sense dissolved sediment pore-water concentrations

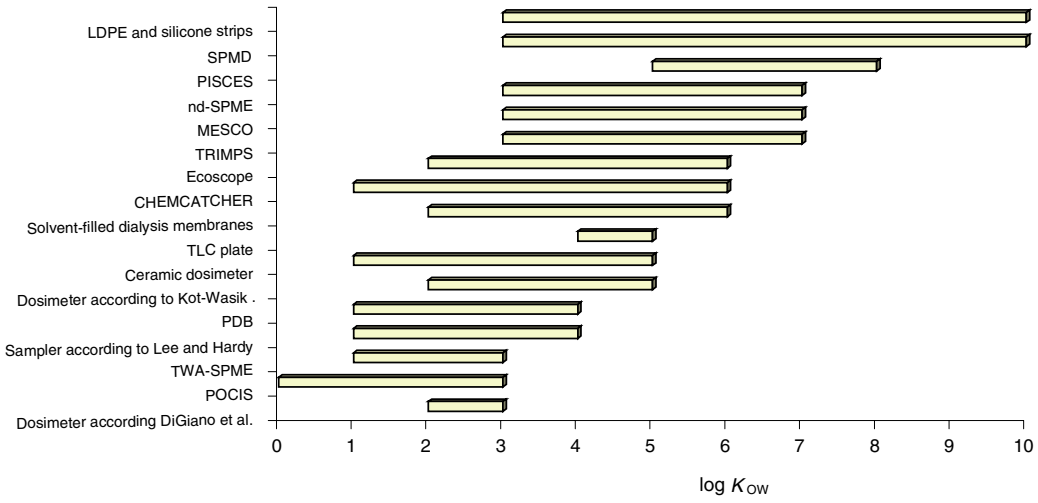

Figure 3. Typical hydrophobicity range of organic compounds sampled by selected passive sampling devices (characterised by the value of octanol/water partition coefficient, log K_{OW}).

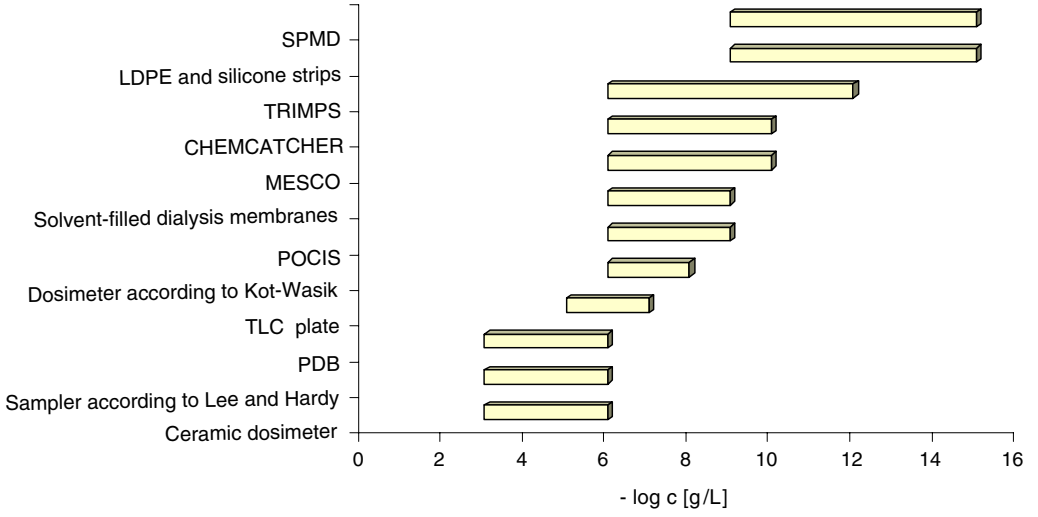

Figure 4. Typical detectable concentrations of organic compounds by selected passive sampling devices.

of contaminants [62,63] and to estimate the bioaccumulation potential in effluents and surface waters [64,65].

4.5. Bioassays

The pre-concentrated extracts obtained from the elution of receiving phases of passive samplers (particularly those used to measure organic pollutants) can subsequently be combined with a variety of bioassay procedures to assess both the level and the biological effects of water contaminants [66]. In some *in vitro* bioassays used to assess the health of an ecosystem, problems can occur due to the difficulty of obtaining suitable water samples for testing. For example, most hydrophobic organic contaminants are present in aquatic environment only at trace levels (i.e., <1 μg/L). The extraction of several litres of water would be required to yield sufficient amounts of analyte for subsequent bioassay.

The use of ''bio-mimetically'' separated extracts from passive samplers can overcome this problem [67].

It has been shown that the baseline toxicity of chemicals can be predicted (based on total body residue estimates) from the concentration of contaminants separated by passive samplers [68].

5. Quality control

The level of quality control (QC) applied to passive sampling varies with project goals and analytical procedures

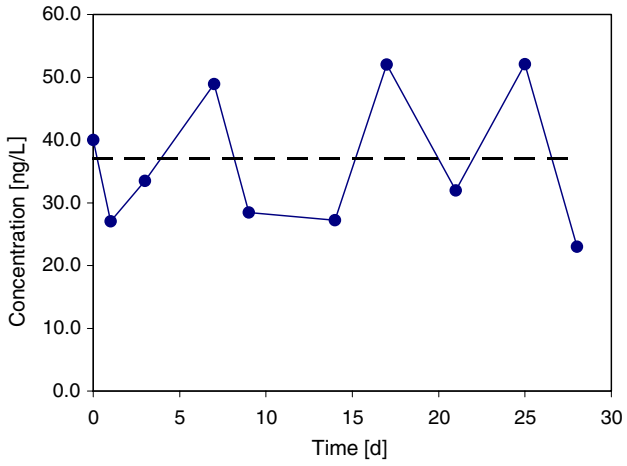

Figure 5. Comparison of a 28-day TWA concentration of simazine obtained using passive sampling (dashed line; the Chemcatcher integrative sampler variant for polar organic chemicals) with the concentrations determined in filtered spot samples (circles) from the Meuse River, The Netherlands, in Spring 2004 [144].

involved. The application of appropriate QC procedures and parameters is a mandatory consideration in both sampler deployment and subsequent analysis. QC samples should address issues of purity of materials used to construct a device, and potential contamination during transport, deployment, retrieval and subsequent storage. QC protocols are also required for analyte recovery and further processing (enrichment and fractionation operations). Control charts are recommended for monitoring analyte recoveries throughout a project. The QC samples relevant to passive sampler studies include fabrication blanks, process blanks, reagent blanks, field blanks and sampler spikes.

DeVita and Crunkilton [69] examined the QC issues associated with using SPMDs for monitoring PAHs in water. Their results showed that QC measures applied to SPMDs met or surpassed conventional guidelines (EPA method 610 for PAHs in water) for precision and accuracy.

However, assessing the accuracy and the trueness of determinations made by passive samplers may prove difficult, as the results may not be directly comparable with total concentrations found in spot samples or by other sampling techniques. This is because only very few methods, other than passive samplers, can truly measure dissolved contaminant fractions.

When environmental conditions at an exposure site differ from laboratory calibration conditions or calibration data are not available, samplers spiked with PRCs serve as a special type of QC sample. These provide information about *in situ* uptake kinetics [16,17].

QC samples involved in using passive sampling devices are shown in Fig. 6.

Stuer-Lauridsen [55] discussed the quality assurance (QA) that would be required for passive samplers to be accepted in water-quality-monitoring programmes.

6. Future trends

There are several major trends in the future development of passive sampling technology.

The first is towards miniaturisation of devices. Small devices offer the advantages of inexpensive transportation to and from the sampling site, the requirement for small deployment devices and a low consumption of solvents and reagents during their subsequent processing. Moreover, miniaturised devices allow application in situations with limited space and volume of water (e.g., in groundwater boreholes [70]). Miniaturisation goes hand in hand with the trend to develop solventless sample-preparation techniques. Passive samplers based on *in situ* analyte preconcentration using SPME or similar techniques allow sample processing (following exposure) using thermal desorption GC [31] or solvent microextraction followed by HPLC [71]. However, the practical application of SPME-based techniques in *in situ* passive sampling of aqueous trace contaminants will require their robustness and sensitivity to be further enhanced.

The second trend is the development of passive sampling technology to monitor a wider range of chemicals. Recently, attention has been focused on compounds with medium-to-high polarity (e.g., polar pesticides and drugs [26]).

Precise calibration of passive sampling devices for monitoring trace metals is essential for quantifying the various metal species and complexes found in water.

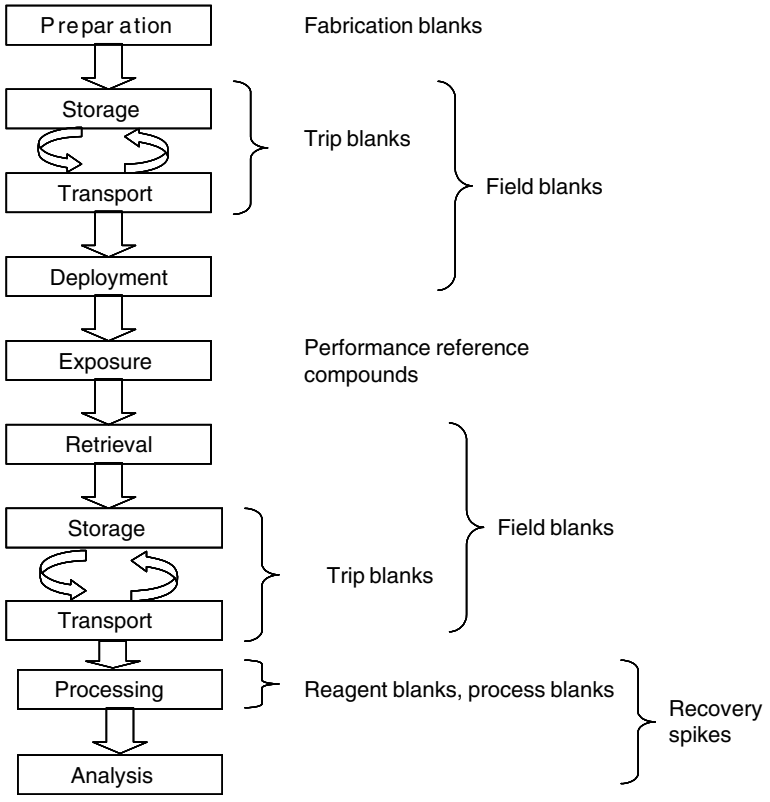

Figure 6. Quality control samples involved in passive sampling.

This requires knowledge of the uptake kinetics of different metal moieties. Configuration of specific devices for monitoring well-defined fractions of metals will increase their potential as regulatory tools.

A further challenge is to improve robustness by reducing or controlling the impacts of environmental conditions and biofouling on the sampler performance. Internal and external PRCs are being tested for improving the accuracy of TWA concentrations of contaminants.

Another trend is the coupling of chemical and biological analysis of samples collected using passive samplers, with detection and identification of toxicologically relevant compounds. The marriage of passive samplers and bio-marker and bio-indicator tests offers many avenues of investigation to provide information concerning the relative toxicological significance of waterborne contaminants.

Finally, the development of efficient QA, QC and method-validation schemes for passive sampling techniques is essential to gain broader acceptance for the technology in regulatory programmes.

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Príloha 8

Vrana B., Paschke A., and Popp P., Calibration and field performance of membrane-enclosed sorptive coating for integrative passive sampling of persistent organic pollutants in water, ***Environ. Pollut.*, 2006, 144, 296–307**.

PAPER

Performance of semipermeable membrane devices for sampling of organic contaminants in groundwater†

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Lipid-filled semipermeable membrane devices (SPMDs) are receiving increasing attention as passive, *in situ* samplers for the assessment of environmental pollutant exposure. Although SPMDs have been successfully used in a variety of field studies in surface waters, only a few studies have addressed their characteristics as groundwater samplers. In this study, the performance of the SPMDs for monitoring organic contaminants in groundwater was evaluated in a pilot field application in an area severely contaminated by chemical waste, especially by chlorinated hydrocarbons. The spatial distribution of hydrophobic groundwater contaminants was assessed using a combination of passive sampling with SPMDs and non-target semiquantitative GC-MS analysis. More than 100 contaminants were identified and semiquantitatively determined in SPMD samples. Along the 6 field sites under investigation, a large concentration gradient was observed, which confirms a very limited mobility of hydrophobic substances in dissolved form in the aquifer. The *in situ* extraction potential of the SPMD is limited by groundwater flow, when the exchange volume of well water during an exposure is lower than the SPMD clearance volume for the analytes. This study demonstrates that SPMDs present a useful tool for sampling and analyzing of groundwater polluted with complex mixtures of hydrophobic chemicals and provides guidance for further development of passive sampling technology for groundwater.

Introduction

The monitoring of temporal and spatial trends in concentration levels of groundwater pollutants is essential for ecological risk assessment for chemical stressors as well as for surveillance of the success of remediation measures. This may be impossible without extensive repetitive sampling, when the conventional approach of spot sampling is used. This approach is to sample a quantity of a groundwater and determine the quantity of contaminant or analyte present, and then calculate the total concentration. It is both expensive and labour intensive, and measures only instantaneous concentrations, which may not be representative of long-term average pollutant concentrations. Moreover, measurements of organic chemicals in groundwater are highly prone to bias stemming from the choice of sampling techniques. Many hydrophobic chemicals tend to be particle- or colloid-associated, and not truly dissolved in groundwater.[1] Thus, if the sampling method tends to increase the amount of suspended solids in groundwater samples (by re-suspending sediments in the well or by remobilizing particles from the aquifer), reported levels of organic chemicals may be erroneously high. In addition, groundwater sampling with pumps leads to a change in the hydraulic flow field, potentially causing a dilution of the contaminants. Furthermore, the use of conventional sampling methods is affected by sorption of the nonpolar analytes to the bailers, bags, filters, and tubing used.[2]

To overcome these limitations, improved sampling and analytical methods are needed, suitable for the characterization of contaminants in groundwater. Various sampling techniques have been developed to avoid aggravated disturbance of the groundwater wells and the surrounding aquifer during sampling.[3]

Passive samplers present a novel, non-invasive technology suitable for long-term monitoring of organic pollutants in groundwater.[4] Passive sampling involves the deployment of a device, which uses a diffusion gradient to collect pollutants over a period of days to weeks, followed by extraction and analysis of pollutants in a laboratory to provide a measure of concentrations of pollutants to which the sampler was exposed. Two main regimes can be distinguished in passive sampler operation, these are integrative and equilibrium sampling.

In the case of equilibrium sampling, the exposure time is sufficiently long to permit the establishment of thermodynamic equilibrium between the water and the reference phase. Equilibrium groundwater sampling devices called passive diffusion bag (PDB) samplers have been widely applied in groundwater monitoring.[5] This sampler is suitable for sampling of volatile organic compounds, but its application for sampling of semi-volatile organic compounds is restricted.

With integrative sampling, it is assumed that the rate of mass transfer to the reference phase is linearly proportional to the difference between the chemical activity of the contaminant in the water phase and in the reference phase. Unlike spot sampling, kinetic or integrative sampling methods also sequester contaminants from episodic events, can be used in situations of variable concentrations, and permit measurement of time-weighted average (TWA) concentrations over extended

† Electronic supplementary information (ESI) available: Tables with detailed information on the contaminants identified in the SPMD extracts. See http://www.rsc.org/suppdata/em/b4/b411645c/

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time periods. A comprehensive review with a full listing of available passive sampling techniques has recently been published by Namiesnik *et al.*[6]

Along with other passive sampling techniques, semipermeable membrane devices (SPMDs) present a convenient sampling and preconcentration method for instrumental methods of chemical analysis, as well as for bioassays.[7]

In the SPMD extraction, hydrophobic chemicals are sampled more efficiently than less hydrophobic chemicals, simulating the way xenobiotics are accumulated from the aqueous phase by biota.[8,9] Moreover, the SPMD extraction allows restriction of sampling to the truly dissolved fractions in the aqueous phase of the water samples, while most of the sampling techniques include the fraction of the chemicals associated with suspended particles or colloids. SPMD is especially suitable for sampling of semivolatile organic compounds.

In this study, we wanted to test the performance of the lipid-filled SPMDs for monitoring of organic contaminants in groundwater in a pilot field application, by evaluating a procedure that combines an innovative groundwater sampling technique with subsequent chemical screening and semiquantitative analysis of accumulated contaminants.

The aim was to evaluate the potential of SPMDs to become a competitive tool for monitoring spatial and temporal distribution of organic groundwater pollutants in an area severely contaminated by chemical production residues, especially chlorinated hydrocarbons. Moreover, the study was conducted to provide an informative basis about the character of pollution with semivolatile organic compounds in order to target future method validation at the most relevant identified contaminants.

The study was performed in the Bitterfeld region in Saxony-Anhalt, Germany, as part of the interdisciplinary joint research program called SAFIRA (SAnierungsForschung In Regional kontaminierten Aquiferen = Remediation Research in Regionally Contaminated Aquifers; abbreviation from German).[10] In this program, suitable and innovative *in situ* remediation procedures have been developed and tested. The region was heavily polluted by mining, chemical industry and the uncontrolled deposition of chemical wastes over nearly 100 years. Groundwater in the area is still severely contaminated by chemical waste. A conservative estimate puts the volume of contaminated groundwater in the Bitterfeld region at some 200 million cubic metres. Serious ecological impact is to be expected when the groundwater contaminant plume reaches the zone of interaction with the nearby biosphere reservation area of the Mulde river floodplain. Although the main groundwater contaminants in the area are thought to be water soluble and volatile, the contribution of hydrophobic semivolatile contaminants is not known. Whilst hydrophobic compounds are present in groundwater in low concentrations (μg L^{-1}), they potentially can be accumulated by biota, and all the compounds in combination may cause severe biological effects.

Experimental

Materials and chemicals

The solvents acetone, dichloromethane, hexane and isopropanol in LiChrosolv quality were obtained from Merck (Germany). Dimethylsulfoxide was obtained from Fluka (Germany). Perdeuterated polyaromatic hydrocarbons (D-PAHs) were obtained as pure neat compounds (purity >99%) from Promochem (Germany). Organic pollutant standards of 33 organic contaminants for determination of relative molar response factors and calculation of GC retention indices were prepared from neat compounds of high purity (>99%). These were purchased from Dr Ehrenstorfer (Germany), Promochem (Germany), Riedel de Haen (Germany), Sigma Aldrich (Germany) and from Merck (Germany).

Physicochemical properties of contaminants

The octanol–water partition coefficient (K_{ow}) and the normal boiling point of substances identified in SPMD extracts were estimated using an incremental method.[11,12] In cases where the substitution pattern of atoms in the identified molecular structure was ambiguous, K_{ow} values were estimated for substances with all possible isomeric structures, and average values were calculated and utilised.

Sampling devices

SPMDs with standard configuration (2.54 × 91.4 cm, 75–90 μm membrane thickness, total mass 4.3 g each), assembled from low-density polyethylene lay-flat tubing and containing a thin film of 95% pure triolein (1 mL), were purchased from Exposmeter, Tavelsjö, Sweden. SPMDs were stored in original, gas-tight, metal paint cans until just before field deployment. Before groundwater exposure, SPMDs used for later quantification of accumulated compounds using GC-MS were spiked with performance reference compounds (PRCs), a mixture of D-PAHs including $^2H_{10}$-biphenyl, $^2H_{10}$-fluorene, $^2H_{10}$-phenanthrene (D-PHE), $^2H_{10}$-anthracene, $^2H_{10}$-fluoranthene, $^2H_{10}$-pyrene and $^2H_{12}$-benz(*a*)anthracene. D-PAHs were spiked in 100 μL of a hexane stock solution using an HPLC syringe (volume 100 μL) to give a final concentration of 10 μg of individual compound per SPMD. SPMDs without D-PAH addition were used for toxicity screening using bioassays.

Sampling sites

The study was performed in the Bitterfeld region in Saxony-Anhalt, Germany. The place of the SAFIRA project is located in an area of Bitterfeld free of previous mining activities, where a quaternary (Wechselion Mulde river gravel) and a tertiary (Bitterfeld mica sand) aquifer are separated by a lignite seam of 5–9 m thickness. In order to study the aquifer and the groundwater quality, almost 40 boreholes were installed and expanded to form groundwater monitoring wells in the past. Aquifer material analysis has shown that volatile chlorinated aliphatic hydrocarbons and chloroaromatics are present at elevated concentrations in the aquifers but are distributed differently above and below the coal horizon. In the upper aquifer, monochlorobenzene is the most important groundwater contaminant (20–30 mg L^{-1}), whereas chloroethenes dominate in the aquifer below the lignite seam.[13] The locations of the sampling wells used in this study are shown in Fig. 1 and their selected geophysical parameters are given in Table 1. The area near the well GWM 19/91 has been directly polluted by seepage of spilled chemicals in the past and represents the source zone of the contamination plume. In consideration of the main groundwater flow direction and known geological conditions, transport of organic pollutants in groundwater is expected toward the east and south from the source zone. Sampling was performed at the depth of the quaternary aquifer (19–32 m in the subsurface), except for the borehole SafBit 2/96, where groundwater from a greater depth (45 m) was also sampled.

SPMD sampling

The SPMDs were lowered into 5 groundwater wells in the study area for 20 days during spring 2000. SPMDs were mounted in perforated stainless steel deployment cages (5 × 5 × 80 cm long). Two SPMDs were mounted inside the deployment cage to form two open loops bent in the middle. Each loop was stretched between stainless steel pins at opposite ends of the deployment cage. Two sampling containers were

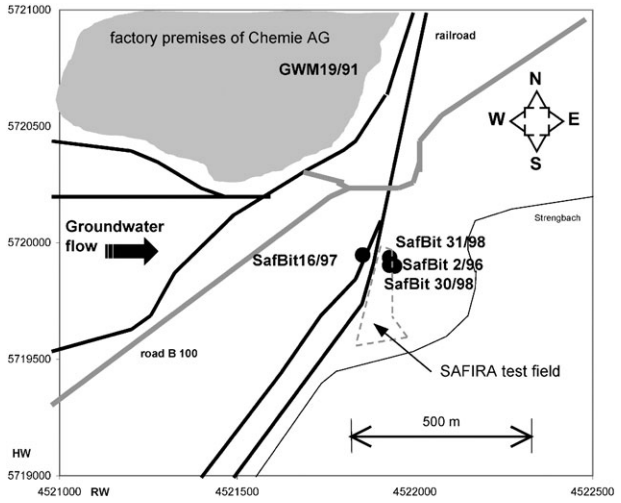

Fig. 1 Map of the sampling area in Bitterfeld, Saxony-Anhalt, Germany. Circles indicate groundwater wells, where SPMDs were deployed. The area near to the well GWM 19/91 has been directly polluted by seepage of spilled chemicals in the past and represents the source zone of the contamination plume.

deployed in each of the sampling wells. The first deployment cage contained two SPMD samples spiked with PRCs, which were used later for instrumental chemical analysis. Two SPMDs without PRCs were mounted in the second container and examined by bioassays after exposure. The results of the bioassay responses to the SPMD extracts will be reported separately. On day 20, SPMDs were removed from the deployment devices and immediately sealed in individual contaminant-free metal cans. The cans were transported on the same day, approximately within 6 hours, to the processing laboratory on ice and in darkness and were kept in a freezer at −20 °C until processing.

SPMD processing

The SPMD processing was described previously.[14] Briefly, the devices were subjected to exterior cleanup. In contrast to our previous field studies with SPMDs in surface water (*e.g.* ref. 14), no fouling was observed at the surface of membranes after 20 days of exposure. This can be explained by a low activity of microorganisms in groundwater compared to that in surface water. SPMDs were then dialysed twice with 250 mL hexane per SPMD at 18 °C for 24 hours. The dialysate was concentrated to approximately 10 mL by rotary evaporation. Nonane (100 μL) was added as a keeper and the volume was reduced using high-purity nitrogen. The residue was redissolved in dichloromethane. The concentrated extract was cleaned by size exclusion chromatography (SEC) using a high performance SEC column (22.5 mm i.d. × 250 mm, 10 μm particles, Lichrogel PS 20 (Merck, Germany)) with dichloromethane (5 mL min^{-1}) as mobile phase. The SEC fraction containing the contaminants (85–100 mL) was collected. This step results in the elimination of nearly all lipid materials and polyethylene oligomers. Solvent exchange from dichloromethane to 1 mL hexane was performed prior to examination by instrumental analysis.

Instrumental analysis

GC-MS non-target analysis (without standards[15]) was used for the identification and semiquantitative analysis of the contaminants in the SPMD extracts. The extracts were injected *via* an autosampler (1 μL, splitless) into a GC (HP 5890) and separation of the contaminants was performed using a capillary column (30 m × 0.25 mm i.d.) with a nonpolar stationary phase HP5-MS (thickness 0.25 μm). The temperature conditions were as follows: injector 250 °C, column 50 °C (5 min)–5 °C min^{-1}–280 °C (10 min), detector transfer line 280 °C. Ultra high purity helium was used as carrier gas.

Detection was performed using a mass spectrometric detector operating in electron impact ionisation mode at 70 eV. The detector temperature conditions were: ion source temperature 230 °C and quadrupole temperature 150 °C. The detector was operated in the full-scan mode in the m/z range from 30 to 450. Quantification of D-PHE and other PRCs was accomplished in selected-ion monitoring mode (MS-SIM) using a six-point external standard curve under the same chromatographic conditions.

Identification of contaminants

The identification of substances in the SPMD extracts was performed by comparing the mass spectra obtained from the total ion chromatograms with the NIST 98 mass spectral library. The criterion for identifying a substance was the quality of match with the mass spectrum entry in the spectral database. A spectrum match quality value higher than 80% was considered sufficient for preliminary substance identification (see Electronic Supplementary Information†, protocols from GC-MS analyses). It was verified by peak purity evaluation that each integrated peak resulted from only a single component, without co-elution of a major interference. The identity of the substances in samples from different sampling wells was confirmed also by the consistency of the retention times. To achieve a higher degree of certainty for correct component identification, retention time information was also incorporated into the identification. For this purpose, the Lee retention index (LRI) system was used.[16,17] This system employs the polycyclic aromatic hydrocarbons naphthalene, phenanthrene and chrysene as the retention time markers. D-PAHs were used in our case since their LRIs do not differ

Table 1 SPMD sampling wells and selected geophysical parameters

Sampling well	Sampling depth/m	Aquifer	Flow direction	Groundwater temperature/°C	Hydraulic gradient (‰)	Hydraulic conductivity/m s^{-1}	TOC/mg L^{-1}
SafBit 30/98	19.5–20.5	Quaternary	West → east (partially to the south)	13.8	0.2–0.8	5.50E-04	16.5
SafBit 31/98	19.0–20.0	Quaternary	West → east (partially to the south)	13.7	0.2–0.8	2.20E-04	15.0
SafBit 2/96 (tert.)	44.5–46.0	Tertiary	West → east	16.1	1.0–3.0	8.00E-06	—[a]
SafBit 2/96 (quat.)	30.5–32.0	Quaternary	—	16.1	1.0–3.0	—	—
SafBit 16/97	20.0–21.0	Quaternary	West → east	15.2	1.0–3.0	2.60E-05	—
GWM 19/91	24.5–25.5	Quaternary	—	16.5	—	—	—

[a] — Indicates no information about the parameter.

substantially from those of native substances. These compounds are assigned LRI values of 200 ($n = 2$), 300 ($n = 3$), and 400 ($n = 4$), respectively. LRIs of unknown compounds were calculated by linear interpolation:

$$\mathrm{LRI} = [100 \times (RT_{\mathrm{unknown}} - RT_n)/(RT_{n+1} - RT_n)] + 100(n) \quad (1)$$

where RT_{unknown} is the retention time of the unknown compound; RT_n and RT_{n+1} are the retention times of the markers that elute before and after the unknown. To prove the applicability of the Lee retention index system at the gas chromatographic conditions used in this study, LRI values were also calculated for 32 compounds chosen to reflect the contaminant spectrum identified in SPMD samples. The standard LRI values were compared with their published LRI values[17] or their normal boiling point, if literature LRI data were not available (Table 2).

Semiquantitative analysis of contaminants

Determination of molar concentrations (expressed as μmol of substance per SPMD sample) of the identified components was performed as follows. The total ion current (MS-TIC) technique was used for quantification. Concentrations of individual components were calculated using the approach shown by van Loon *et al.*[18] For this purpose, relative molar response factors (RMRFs) compared to D-PHE were determined for 33 compounds chosen to reflect the contaminant spectrum identified in SPMD samples (Table 2). The RMRF is defined in eqn. (2). Here, k_{i} and $k_{\mathrm{D\text{-}PHE}}$ are the molar response factors of compound i and D-PHE, respectively. These values correspond to the slopes of a linear dependence $S = k_i C$ of the TIC area (S) on the molar amount injected (C). The k_i values were calculated from ten-point calibration curves (injected concentration range 1–50 μg mL^{-1}).

$$\mathrm{RMRF} = k_i/k_{\mathrm{D\text{-}PHE}} \quad (2)$$

An average RMRF value determined for the test set of 33 compounds was used for quantification of contaminants in SPMD extracts. The molar concentrations of individual components in SPMD extracts, C_i, were calculated as

$$C_i = \frac{1}{\mathrm{RMRF}_{\mathrm{average}}} \frac{C_{\mathrm{D\text{-}PHE}}}{S_{\mathrm{D\text{-}PHE}}} S_i \quad (3)$$

where $C_{\mathrm{D\text{-}PHE}}$ is the molar amount of D-PHE quantified separately in each sample using MS-SIM technique, $S_{\mathrm{D\text{-}PHE}}$ and S_i are TIC areas of D-PHE and of the selected component in the full scan chromatogram of the same SPMD sample.

Quality control

Fresh SPMDs were taken through the entire dialytic and cleanup procedure (procedural blanks for instrumental analysis).

Table 2 Molecular weight, boiling point, relative molar response factors (RMRF) as compared to $^2H_{10}$-phenanthrene and Lee retention indices of 33 organic standards as determined by GC-MS; extraction recovery of selected organic standards from procedural spikes is given in the last column

No.	Compound	MW[a]	BP[b]	RMRF[c]	LRI[d]	Recovery rate[e] (%)
1	2-Bromotoluene	171.0	182	0.28	171	
2	3-Bromotoluene	171.0	184	0.26	169	
3	4-Bromotoluene	171.0	184	0.32	170	
4	1,3-Dichlorobenzene	147.0	173	0.28	162	10
5	1,4-Dichlorobenzene	147.0	173	0.35	163	10
6	1,2-Dichlorobenzene	147.0	181	0.29	168	12
7	3-Nitroanisole	153.1	258	0.24	228	
8	Bromobenzene	157.0	155	0.28	150	5
9	1-Chloro-3-nitrobenzene	157.6	236	0.25	210	
10	1-Chloro-4-nitrobenzene	157.6	242	0.27	212	
11	1-Chloro-2-nitrobenzene	157.6	246	0.25	213	
12	1-Bromo-2-chlorobenzene	191.4	204	0.40	188	
13	2,5-Dichloroaniline	162.0	251	0.36	229	
14	2-Chloronaphthalene	162.6	256	0.94	237	
15	2-Chlorotoluene	126.58	159	0.34	151	
16	3-Chlorotoluene	126.5	161	0.30	150	
17	4-Chlorotoluene	126.5	162	0.34	151	
18	1,3,5-Trichlorobenzene	181.4	208	0.52	190	70
19	1,2,4-Trichlorobenzene	181.4	214	0.51	199	55
20	1,2,3-Trichlorobenzene	181.4	219	0.49	207	50
21	*trans*-Azobenzene	182.2	293	0.41	278	62
22	2,4-Dichlorotoluene	161.0	200	0.43	187	
23	1-Bromo-4-chlorobenzene	191.5	196	0.45	188	
24	1,2-Dichloro-3-nitrobenzene	192.0	258	0.37	241	51
25	Azoxybenzene	198.2	—	0.34	—	
26	1,2,3,5-Tetrachlorobenzene	215.9	246	0.56	228	83
27	1,2,4,5-Tetrachlorobenzene	215.9	246	0.78	229	80
28	1,2,3,4-Tetrachlorobenzene	215.9	254	0.61	237	82
29	Pentachlorobenzene	250.3	277	1.04	262	84
30	1,1,2,3,4,4-Hexachloro-1,3-butadiene	260.8	210	0.84	—	
31	Hexachlorobenzene	284.8	332	1.06	291	100
32	α-Hexachlorocyclohexane	290.8	288	0.72	289	82
33	γ-Hexachlorocyclohexane	290.8	323	0.70	298	75
	Average RMRF			**0.47**		
	Standard deviation			**0.23**		
	Relative standard deviation (%)			**50%**		

[a] Molecular weight/g mol^{-1}. [b] Normal boiling point/°C. [c] Relative molar response factor; see Experimental section. [d] Lee retention index. [e] Extraction recovery from procedural spikes.

In addition, trip blanks were used to define contamination of the SPMDs during transportation and handling as described by Petty *et al.*[19] Spiked SPMDs were also analysed by fortifying fresh membranes and then processing them as samples. The PRCs were spiked at 500 ng per SPMD for each single component. Procedural spikes were also analysed by fortifying fresh membranes with selected analytes and then processing them as samples (Table 2). The standards were spiked at 500 ng per SPMD for each single component.

Results and discussion

Identification of contaminants in SPMD samples

Fig. 2 illustrates the results of the analysis of SPMD extracts from two of the sampling locations, and of an associated SPMD control. Up to 167 components were identified in the SPMD samples by mass spectrum library search and the identity of 123 substances characterized by a mass spectrum could be confirmed using LRI. For confirmation, calculated LRI were compared with published LRI data[17] or normal boiling points of the substances identified by the mass spectrum library search as has been shown by Eckel.[16]

First, the applicability of the LRI system was confirmed for 32 standards chosen to reflect the spectrum of groundwater contaminants. The LRI values of the standards calculated from GC retention times using eqn. (1) correlated well with the normal boiling points of the respective substances (Fig. 3). The identity of a substance preliminarily characterized by a mass spectrum was confirmed only when the absolute difference between the boiling point (in °C) and the corresponding LRI was lower than 50 (Fig. 3). Identified contaminants included aliphatics and cycloaliphatics, chloroaliphatics, chlorinated and brominated benzenes, toluenes and xylenes, alkylated benzenes and naphthalenes, alkyl- and arylsulfides, sulfur containing heterocyclic aromatics, methylated and chlorinated aromatic amines, hexachlorocyclohexanes (HCHs), alkylphenols and nitrobenzenes.

Matrix impurities identified in extracts from fresh procedural SPMD blanks (up to 20 compounds) included alkanes (C9–C16), bis(2-ethylhexyl)phthalate (DEHP), decahydrodimethyl naphthalene, methyl oleate and fatty acids (C18). During groundwater exposures, some of the impurities dissipated from

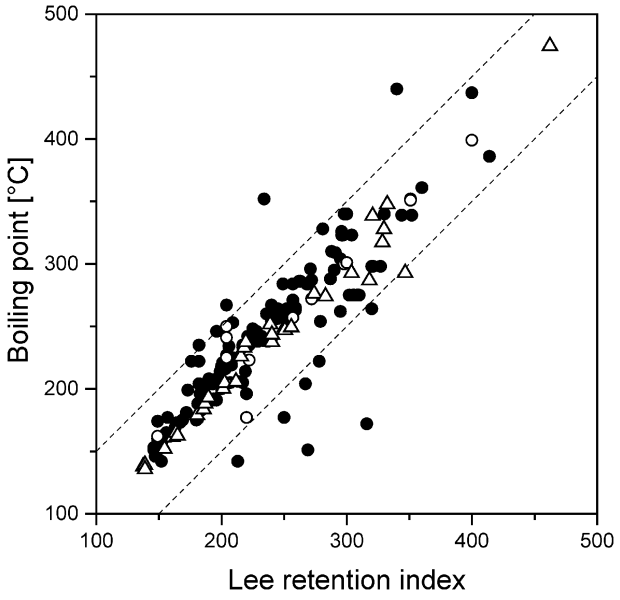

Fig. 3 A plot of the Lee retention index (LRI) of preliminarily identified compounds (by a mass spectrum library search) in SPMD extracts (full circles) and of 32 standards chosen to reflect the spectrum of groundwater contaminants (triangles) *versus* their normal boiling points or LRI values published by Rostad *et al.* (ref. 17; hollow circles). Identity of a substance was confirmed only when the absolute difference between the boiling point and the corresponding LRI was lower than 50 (within the band given by the dotted lines).

SPMDs. On average, only 5% of the initial amount of DEHP, 3% of the methyl oleate and less than 10% of the fatty acids were found in SPMD extracts after groundwater exposure. This finding indicates the need for specially adapted negative controls for bioassays, because these substances might cause additional inhibitory effects when SPMD extracts are subject to toxicity screening.

Quantification of contaminants

The applicability of the GC-MS method for total molar determinations strongly depends on the variation of the molar

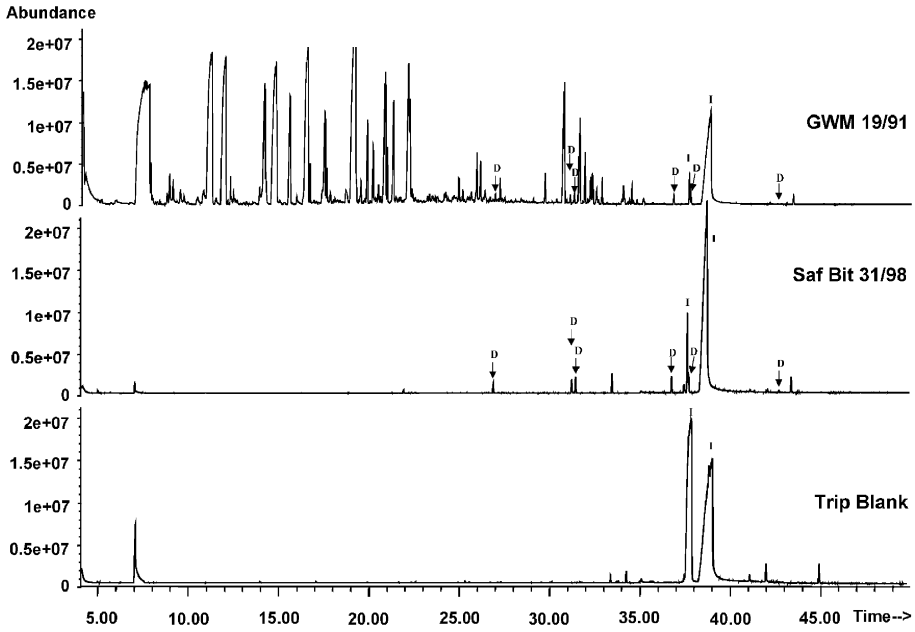

Fig. 2 GC-MS chromatograms of 2 SPMD sample extracts and a control (trip blank) SPMD. Samplers were deployed for 20 days in groundwater monitoring wells in Bitterfeld, Saxony-Anhalt, Germany. Peaks denoted by (D) are PRCs. Matrix impurities identified in procedural blanks are denoted by (I). Some of the matrix impurities dissipate from SPMDs during groundwater exposure.

response factors of organic contaminants.[18] Since MS signals are not absolute, RMRFs were determined using D-PHE as internal standard. The average molar response factor relative to D-PHE of the test set of 33 substances was 0.47. The overall variation of the RMRFs was 50% for the test set (Table 2). Although this is a significant variation, it is not very large, when compared to the overall variability of the method (9% to 55%, see below). Information on molar concentrations, which are accurate within a factor of 2, is still highly relevant for environmental risk assessment purposes.[18]

Recovery rate values of the fortified PRCs from SPMDs were good and reproducible. Average percentage recoveries of PRCs varied from 50% to 100% and the relative standard deviation of three spiked samples did not exceed 10% for any PRC used. The analysis of procedural spikes (Table 2, last column) showed that elevated component volatility causes low recovery of accumulated analytes from SPMDs due to their partial loss during sample transport and processing. There is also a trend of decreasing precision of the entire sampling, cleanup and analytical procedure with decreasing boiling point of the analyte. Acceptable recoveries (>50%) were determined for analytes with normal boiling point higher than 200 °C and thus only concentrations of identified semivolatile compounds with a normal boiling point higher than 200 °C were reported in this study. For quantitative recovery of more volatile compounds from SPMDs, a specific sample treatment would be required, *e.g.* application of purge and trap techniques.

The results of the analysis of SPMD extracts after 20 days of groundwater exposure are presented in Fig. 4 and are reported in detail in the Supplementary Information.† On the basis of total semivolatile contaminant residues, the wells can be ranked from lowest to highest as follows: SafBit 2/96 (quat.), SafBit 31/98, SafBit 2/96 (tert.), SafBit 16/97, SafBit 30/98, and GWM 19/91. The observed extreme concentration gradient of contamination is a clear indicator of a low mobility of hydrophobic semivolatile contaminants in the aquifer over a short distance of less than 760 m between the two most distant sampling wells.

The semiquantitative contaminant concentrations in SPMD extracts (given as a sum of all quantifiable semivolatile substances) ranged from 0.4 nmol per SPMD from well SafBit 31/98 to 20 μmol per SPMD from well GWM 19/91. The average

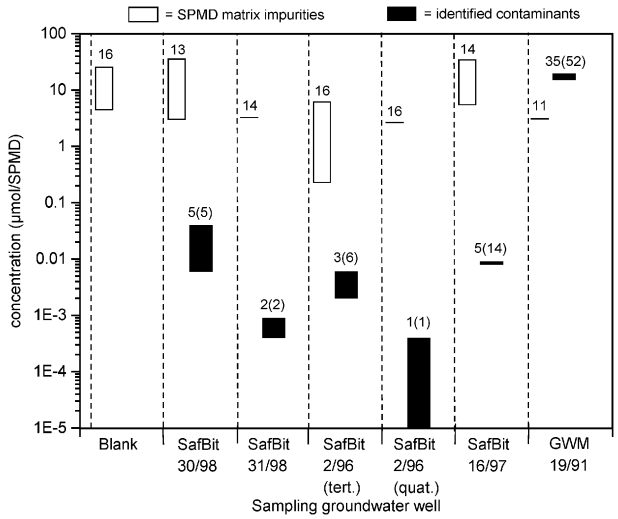

Fig. 4 Molar amounts of semivolatile compounds (boiling point >200 °C) identified in extracts from SPMDs deployed for 20 days in groundwater monitoring wells in Bitterfeld. Floating bars show the concentration range determined in two samplers exposed side by side. The numbers above the bars denote the number of components quantified in the extracts followed by the total number of components identified (in brackets). Detailed information is listed in the Supplementary Information.†

relative percentage difference between total concentrations of contaminants in duplicate SPMD samples from the same sampling site was in the range 14% (SafBit 31/98) to 61% (SafBit 30/98).

The cummulative uncertainty u_c (%) of the method employed for semivolatile organic chemicals sampling using SPMDs and their semiquantitative analysis can be estimated from the uncertainties of each sampling or analytical step (groundwater sampling, extraction, cleanup and gas chromatography),

$$u_c(\%) = \sqrt{u_s^2 + u_e^2 + u_a^2} \quad (4)$$

where u_s represents the uncertainty of sampling, u_e represents the uncertainty of the extraction and cleanup procedure and u_a represents the uncertainty of the analytical procedure.

The uncertainty of sampling u_s can be deduced from the average relative percent difference of two parallelly deployed sampling devices, which varied between 14% and 61%. The uncertainty of the extraction and cleanup step can be estimated as the average relative standard deviation of extraction recovery of spiked samples. This was lower than 30% for the tested analytes with a boiling point higher than 200 °C ($u_e \approx 30\%$). Finally, the uncertainty of the analytical procedure was estimated by calculating the overall variation of the RMRFs for the test set of chemicals ($u_a \approx 50\%$). Thus, the overall uncertainty of the method employed in this study is expected to vary between 60% and 80%. As a result, the method gives semiquantitative information about the concentration levels with a precision within one order of magnitude. Although this is a relatively low precision, it is sufficient for a preliminary characterization of the pollution situation at the sampling sites. Further, substance-specific method validation for major identified (and environmentally relevant) analytes will enable a substantial improvement of the method precision.

SPMDs have been developed as kinetic passive samplers, which integratively accumulate contaminants over a prolonged time period (days or weeks). Using known kinetic parameters, it is possible to calculate time-weighted average concentrations of the contaminants in the sampled medium from the amounts accumulated in the SPMD and the exposure time.[7]

There is sufficient evidence that the exchange kinetics of most organic analytes between SPMD and water can be described by first-order kinetics.[20] Moreover, the kinetics are isotropic, *i.e.* both uptake and loss of an analyte are governed by the same mass transfer law. However, the sampling kinetics are affected by many factors including the physicochemical properties of the sampled analytes as well as the environmental conditions.

To estimate the *in situ* sampling kinetics of SPMDs in groundwater in this study, the performance reference compound (PRC) approach was used. This approach was developed by Huckins *et al.*[20] to enable estimation of exchange kinetics of contaminants between SPMDs and the sampled medium. PRCs are analytically non-interfering organic compounds that are added to the sampling device prior to exposure. The release of a PRC from the SPMD, when the concentration of this compound in groundwater is negligibly low (*i.e.* $C_w = 0$), can be described by a first-order-decay equation

$$C_{SPMD(t)} = C_{SPMD(0)}\exp(-k_e t) \quad (5)$$

Here, C_{SPMD} is the PRC concentration in the SPMD, k_e is the first-order exchange rate constant, which is also called the overall exchange coefficient and t stands for time. Assuming that isotropic exchange kinetics can be applied and that SPMD–water partition coefficients are known, measurement of PRC first order elimination rate constants k_e during SPMD exposure permits estimation of the sampling rate, *i.e.* the volume of water that the SPMD has the potential to clear per day.

Huckins *et al.*[21] showed that the daily SPMD clearance volume or sampling rate R_S is related to k_e by

$$R_S = k_e K_{SPMD} V_{SPMD} \quad (6)$$

where K_{SPMD} is the SPMD–water partition coefficient and V_{SPMD} is the SPMD volume.

Measuring the sampling kinetics by taking samples in a time series appeared to be impractical because of a number of physical limitations. A maximum of two cages can be deployed at the depth of the screen, where groundwater is exchanged between the borehole and aquifer. Further, the manipulation of cages during the sampling would disturb the conditions of groundwater in the well. Moreover, the decreasing number of samplers in the well during the sampling period would likely cause temporal changes in analyte water concentrations, thus making the modelling of the sampling kinetics more complicated. Therefore, knowing the type of exchange kinetics from the literature, it was sufficient to measure PRC levels in SPMDs only at the beginning and the end of the field exposure. D-PAHs were used as PRCs in this study. To calculate the apparent first order exchange rate constant k_e, eqn. (5) was solved to permit a two-point derivation of k_e (assuming first-order kinetics):

$$k_e = \frac{\ln\left[C_{SPMD(0)}/C_{SPMD(t)}\right]}{t} \quad (7)$$

Blanks spiked with D-PAHs were used to determine $C_{SPMD(0)}$. A significant decrease of concentration in SPMD extracts during exposure was determined for PRCs with log K_{ow} < 4.5. On the other hand, no significant decreases in the concentrations of $^2H_{10}$-fluoranthene, $^2H_{10}$-pyrene, and $^2H_{12}$-benz(*a*)anthracene were observed after exposure in any of the SPMD samples. The calculated values of k_e for PRCs determined for different sampling wells are shown in Fig. 5.

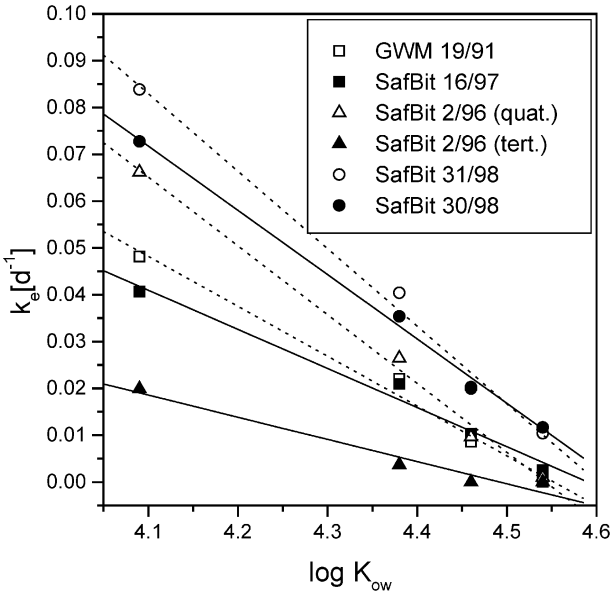

Fig. 5 Dependence of the apparent first-order elimination rate constant (k_e) of performance reference compounds ($^2H_{10}$-biphenyl, $^2H_{10}$-fluorene, $^2H_{10}$-phenanthrene, $^2H_{10}$-anthracene) in sampling wells on the octanol–water partition coefficients K_{ow}. The lines correspond to linear regression analysis of the data (see Table 3). No significant decreases in the concentrations of $^2H_{10}$-fluoranthene, $^2H_{10}$-pyrene and $^2H_{12}$-benz(*a*)anthracene were observed after exposure in any of the SPMD samples.

Partitioning of chemicals between SPMD and groundwater

The PRC approach can be applied to estimate appropriate exposure times needed to achieve equilibrium between SPMD and water for a specific group of compounds. The time required to reach 90% of the equilibrium concentration for uptake of contaminants or to offload 90% of the PRC from an SPMD can be considered as an approximation of equilibration time t_{eq}.[22] This can be calculated using eqn. (7).

PRCs having an elimination rate constant k_e of 0.115 d^{-1} or higher are expected to achieve partitioning equilibrium between SPMD and groundwater within 20 days of exposure. The maximum log K_{ow} value allowed for a substance in groundwater to achieve partitioning equilibrium within this time period was calculated by interpolation from the linear dependence $k_e = f(\log K_{ow})$ for each well as a value corresponding to $k_e = 0.115$ d^{-1}. Obtained threshold log K_{ow} values are given in Table 3.

Compounds having log K_{ow} equal to or lower than the threshold value achieve equilibrium partitioning between groundwater and SPMD within 20 days of exposure and their groundwater concentration can be estimated using the equilibrium partitioning model

$$C_w = C_{SPMD}/K_{SPMD} \quad (8)$$

For the remaining compounds, ambient groundwater concentrations can be estimated using a kinetic model described by Huckins *et al.*[21]

$$C_w = C_{SPMD}/K_{SPMD}(1 - \exp[-k_e t]) \quad (9)$$

SPMD extracts from wells GWM 19/91 and 2/96 (tert.) contained large amounts (50% and 60% on a molar basis) of chemicals with log K_{ow} higher than the calculated threshold log K_{ow} values. For these sites, additional accumulation of chemicals from groundwater to SPMDs is expected during prolonged exposure periods. For the remaining sampling sites, no significant additional increase in total molar concentrations is expected after sampling longer than 20 days and the equilibrium partitioning model can be applied for estimating their concentration in groundwater from the levels accumulated in SPMDs.

SPMD sampling kinetics limitation due to groundwater flow

As can be seen in Fig. 5, differences in PRC release kinetics between different sampling wells are evident. Environmental variables including water velocity/turbulence, fouling and temperature may affect the exchange kinetics of SPMDs.[23,24] We suppose that these factors only marginally contributed to the observed differences in contaminant uptake kinetics. It has been shown[25] that for chemicals with log K_{ow} < 4.0 uptake rates are probably controlled by the diffusion through the polyethylene membrane rather than through the aqueous boundary layer at the SPMD surface, and therefore are not subject to effects caused by fluctuating hydrodynamic conditions. For these compounds there is little reason to believe that the observed variability in the data is due to exposure conditions other than the depletion of ambient environmental levels of measured analytes.

Thus, it is more likely that the SPMD uptake is limited by groundwater flow.[4] SPMDs are very efficient extractors with typical sampling rates of several litres of water per day.[21] The model (eqn. (5)) describing the uptake of analytes assumes a constant concentration in the water surrounding the sampler and is relevant to the surface water situation when the water surrounding the membrane is exchanged quickly. This model may be inappropriate for use in groundwater in wells with low flow and low volume of the filtered zone (the span where samplers are deployed during the sampling). Permeability in a fine-grained aquifer can be very low, which may result in the depletion of target solutes at the membrane surface due to depletive sampling.

As a consequence of the decreasing water concentration surrounding the SPMD due to depletion by the sampler, the

Table 3 Summary of the linear regression analysis of the dependence of the apparent elimination rate constant (k_e) of performance reference compounds as dependent on the octanol–water partition coefficient using $k_e = A + B \times \log K_{ow}$ and estimated maximum log K_{ow} threshold value for a substance in groundwater to achieve equilibrium partitioning during 20 days of SPMD exposure in groundwater (also shown in Fig. 5). The analysis was performed with 4 PRC compounds ($^2H_{10}$-biphenyl, $^2H_{10}$-fluorene, $^2H_{10}$-phenanthrene and $^2H_{10}$-anthracene; $N = 4$)

Sampling well	A	B	Correlation coefficient	log K_{ow} threshold
GWM 19/91	0.48	−0.11	−0.99	3.5
SafBit 16/97	0.38	−0.08	−0.99	3.2
SafBit 2/96 (quat.)	0.67	−0.15	−0.99	3.8
SafBit 2/96 (tert.)	0.21	−0.05	−0.98	2.1
SafBit 31/98	0.76	−0.17	−0.99	3.9
SafBit 30/98	0.63	−0.14	−0.99	3.8

SPMD can accumulate analytes at a rate (contaminant amount per day) lower than that expected from the laboratory-derived sampling rate value R_S (determined at constant aqueous concentrations). To verify this, the groundwater flux in sampling wells Q was compared with the actual daily clearance volumes of SPMDs deployed in groundwater wells, represented by the *in situ* sampling rate R_S. These were calculated from the release kinetics of PRCs in each sampling well.

Groundwater flux in sampling wells was estimated using Darcy's Law:[4]

$$Q = KiA \tag{10}$$

where K is the hydraulic conductivity, i is the hydraulic gradient and A is the cross-sectional area, assumed to be the SPMD deployment device length (*ca.* 1 m) times twice the diameter of the well.[4] The permeability and gradient parameters were available from previous site assessments and were not obtained specifically for this study (Table 1). Calculated groundwater flow ranged from approximately 1 L d^{-1} in the well SafBit 16/97 to 5.3 L d^{-1} in the well SafBit 30/98. Due to a lack of information about the geophysical parameters, the calculation could not be performed for wells GWM 19/91 and SafBit 2/96 (quat).

R_S values between 0.9 and 5.2 L d^{-1} were measured by Huckins *et al.*[21] (for PAHs with log $K_{ow} < 5.3$ and a standard SPMD at constant aqueous concentration under quiescent flow conditions and a temperature similar to that in groundwater at sampling sites). These published sampling rates are comparable to or smaller than turnover rates actually encountered in groundwater wells examined in this study. For the actual *in situ* R_S calculation, k_e values from the dissipation rate of PRCs during SPMD exposure and K_{SPMD} values of PAHs published by Huckins *et al.*[21] were utilized and R_S values were calculated using eqn. (6). Fig. 6 confirms that the estimated *in situ* R_S values are affected by groundwater flow when the daily turnover volume in monitoring wells was lower than approximately 3 L d^{-1}. Under low flow conditions, when the water in wells is refreshed slowly, the aqueous concentration of contaminants will not remain constant during the whole SPMD deployment period as the SPMD removes contaminants from surrounding water. Thus, the *in situ* extraction potential of the SPMD is limited by groundwater flow, when the exchange volume of well water during an exposure is lower than the SPMD clearance volume for the analytes. This limitation has to be taken into account when applying SPMDs as integrative passive samplers in groundwater.

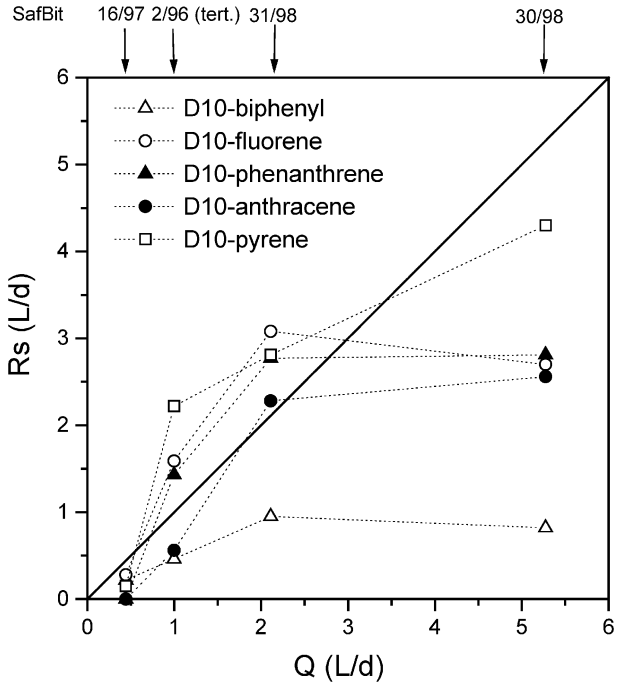

Fig. 6 Dependence of estimated sampling rates of polycyclic aromatic hydrocarbons (R_S) on the groundwater flow (daily turnover volume; Q) in the sampling wells. R_S values were calculated with eqn. (6) using k_e values from the PRC dissipation rate and log K_{SPMD} values published by Huckins *et al.*[21] The solid line represents $Q = R_S$.

To avoid the complications caused by the possibility of a depletive SPMD extraction, the use of smaller SPMDs (with corresponding lower clearance volumes) is recommended for groundwater sampling. However, to apply the linear uptake model (non-depletive extraction), it must be assured that the calculated SPMD sampling rate is much lower than the daily groundwater turnover volume in the well. Alternatively, passive samplers with very low clearance volumes can be used, such as ceramic dosimeters.[26] Recently a promising sampler design called Membrane Enclosed Sorptive Coating (MESCO) has been developed.[27] This integrative passive sampler is based on non-depletive extraction. Generally, MESCO clearance volumes are lower than 1 ml h^{-1}. Despite the low sampling rate, the sensitivity of this device is comparable to that of the SPMD, because the total amount of analyte sequestered by the MESCO during deployment can be transferred to the GC system, whereas only a small portion of the SPMD extract is usually injected into the GC (to prevent introduction of large amounts of interfering contaminants to the chromatographic system).

Conclusions

This study demonstrates performance of a procedure combining groundwater passive sampling using semipermeable membrane devices with chemical analysis of accumulated contaminants. Sampling the groundwater present in the screen zone using SPMDs provides the greatest chance of obtaining samples without increased turbidity and with minimal alteration of the groundwater chemistry caused by sampling. The SPMD method eliminates the need to dispose of potentially highly contaminated wastewaters produced by purge-type sampling methods. Cross contamination of samples is reduced by the use of SPMDs because the sampling equipment does not come into contact with water from multiple wells, unlike

sampling conducted with non-dedicated pumps, tubing, or bailers. SPMDs have a minimal effect on water circulation within a well and thus preserve any stratification of water, whereas purging can induce vertical mixing of the water. Thus, SPMDs have the potential to provide representative concentrations of aqueous contaminants as they exist in the undisturbed subsurface. Although the methods employed in this study need further validation, our investigation provided a valuable informative basis about the character of pollution with semivolatile organic compounds in order to target future method calibration at the most relevant identified contaminants.

The methodology demonstrated in this study is applicable for semivolatile organic groundwater contaminants. For accurate monitoring of a broad spectrum of contaminants, including volatile organic chemicals, a modification of the sample treatment procedure would be required, *e.g.* by application of purge and trap techniques. Alternatively, several passive samplers with a complementary selectivity, *e.g.* SPMD and PDB, can be deployed for screening/monitoring in multicomponent pollution situations. Use of sampling devices with low clearance volume is recommended to prevent limitation of the extraction potential by groundwater flow.

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Calibration and field performance of membrane-enclosed sorptive coating for integrative passive sampling of persistent organic pollutants in water

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A robust calibration method of a passive sampling device for monitoring of persistent organic pollutants in water is described.

Abstract

Membrane-enclosed sorptive coating (MESCO) is a miniaturised monitoring device that enables integrative passive sampling of persistent, hydrophobic organic pollutants in water. The system combines the passive sampling with solventless preconcentration of organic pollutants from water and subsequent desorption of analytes on-line into a chromatographic system. Exchange kinetics of chemicals between water and MESCO was studied at different flow rates of water, in order to characterize the effect of variable environmental conditions on the sampler performance, and to identify a method for in situ correction of the laboratory-derived calibration data. It was found that the desorption of chemicals from MESCO into water is isotropic to the absorption of the analytes onto the sampler under the same exposure conditions. This allows for the in situ calibration of the uptake of pollutants using elimination kinetics of performance reference compounds and more accurate estimates of target analyte concentrations. A field study was conducted to test the sampler performance alongside spot sampling. A good agreement of contaminant patterns and water concentrations was obtained by the two sampling techniques.
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Keywords: Organic pollutants; Passive sampling; Semipermeable membrane devices; Water monitoring

1. Introduction

Monitoring of pollution of ecosystems by persistent organic pollutants (POPs) is an ongoing challenge for the analytical chemist. For qualitative and quantitative assessment of pollution, a large number of samples must be taken from a given location over the entire monitoring period, when spot/grab sampling is applied as the method of choice. This approach is time-consuming, laborious and can be very costly. Grab samples provide information only about the situation in the moment of sampling and may fail to account for episodic contamination events.

Solutions for such situation are methods of passive sampling and/or extraction of analytes, which involve measurement of any analyte as a weighted average over the sampling time. The concentration of analyte is integrated over the whole exposure time, making such a method less bias-prone to fluctuations of pollutant concentrations. Long-term overview of pollutant levels at the sampling site is obtained in this way. Passive monitors are rapidly gaining wide acceptance for assessing time-weighted average (TWA), concentrations in aquatic systems. The current state-of-the art

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of passive sampling and extraction methods for long-term monitoring of environmental pollutants has recently been published by Namiesnik et al. (2005).

The common disadvantage of most passive sampling techniques is a laborious recovery of analytes from samplers using solvent extraction. To make the passive sampling technology more suitable for routine monitoring, low-cost and less time-consuming sample processing methods are required. Sample processing with reduced solvent consumption would also minimize the risk of sample contamination during handling in the laboratory and enable to improve quality control measures.

Recently, a solventless and simple technique for preconcentration of organic solutes from aqueous matrixes, the stir bar sorptive extraction (SBSE), was developed by Baltussen et al. (1998, 1999). The applicability of this extraction technique has been demonstrated for determination of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in water (Popp et al., 2001, 2003; Leon et al., 2003). SBSE is suitable also for analysing real environmental samples including drinking water (Garcia-Falcon et al., 2004a), run-off water (Garcia-Falcon et al., 2004b) and precipitation water (Niehus et al., 2002). The method is very sensitive, with detection limits well below 10 ng L^{-1} level. Garcia-Falcon et al. (2004b) have shown that, in contrast to other extraction techniques, SBSE is suitable for determination of freely dissolved fraction of PAHs in environmental water samples. The determination of freely dissolved fraction of contaminants in water is important especially for assessment of organism exposure and bioavailability. Absorptive partitioning is the predominant extraction mechanism of analytes into poly(dimethylsiloxane) (PDMS), the sorptive material used in SBSE.

Although SBSE was originally developed as method for batch extraction of water samples, we recently described an adaptation of SBSE for long-term continuous passive sampling of persistent organic pollutants in water (Vrana et al., 2001b). This so-called MESCO (membrane-enclosed sorptive coating) sampler consists of a stir bar coated with a thin PDMS layer [Gerstel Twister, a commercially available device used for SBSE (Baltussen et al., 1998)] enclosed in a water-filled dialysis membrane bag from regenerated cellulose. After exposure of the sampler, the PDMS coated stir bar is taken from the enveloping membrane and can be directly analysed by thermodesorption–GC–MS. The performance of the MESCO sampler had been demonstrated for integrative sampling of hydrophobic persistent organic pollutants including γ-hexachlorocyclohexane (γ-HCH), hexachlorobenzene (HCB), 2,2′-bis(4-chlorophenyl)-1,1′-dichloroethylene (DDE), PAHs, and polychlorinated biphenyls (PCBs) (Vrana et al., 2001b).

In general, the sampler performance depends on the sampler design, physicochemical properties of the sampled analyte and the environmental conditions. To be able to apply laboratory-derived calibration data for calculation of TWA water concentrations in the field, it is necessary to consider (or determine) the effect of environmental variables, including temperature, hydrodynamics and biofouling, on the sampler performance.

Because it appears impractical to conduct calibration studies for all exposure scenarios (e.g. for many combinations of temperature and water turbulence), a novel in situ calibration approach was developed by Huckins et al. (2002) for lipid-filled semipermeable membrane devices (SPMDs), passive samplers with working principle similar to MESCO. This involves the use of performance reference compounds (PRC), which are analytically non-interfering organic compounds with moderate to low affinity to the passive sampler that are added to the receiving phase (in our case to the PDMS) of the sampler prior to membrane enclosure. This approach is based on theory and experimental evidence that PRC dissipation rate constants are related to the uptake rates of target compounds.

In order to test the robustness of MESCO performance against variable environmental conditions, exchange kinetics of PAHs, OCPs and PCBs between water and MESCO were studied under condition of varying flow rate. The PRC approach was tested to identify a method for in situ correction of the laboratory-derived calibration data. Also, a field study was conducted to test the sampler performance alongside spot sampling.

2. Theory

The mass transfer of an analyte in a sampler includes several diffusion and interfacial transport steps across all barriers, i.e. the stagnant aqueous boundary layer, possible biofilm layer, the membrane, the inner aqueous phase, and the receiving organic phase. It has been shown that, the amount of the chemical accumulated in the MESCO sampler from water with constant chemical concentration can be described by (Vrana et al., 2001b):

$$M_S(t) = M_0 + (C_W K_{SW} V_S - M_0)\left[1 - \exp\left(-\frac{k_{ov} A \alpha}{K_{SW} V_S}\right) t\right] \quad (1)$$

where M_S is the mass of analyte in the receiving phase (PDMS), M_0 is the amount of analyte in the sampler at the start of the exposure, C_W represents the water concentration during the deployment period, K_{SW} is the receiving phase/water distribution coefficient, V_S is the volume of the receiving phase, k_{ov} is the overall mass transfer coefficient, A is the membrane surface area, α is the pore area of the membrane as fraction of total membrane area (membrane porosity), and t equals time. The coefficient in the exponential function is referred to as the overall exchange rate constant k_e.

$$k_e = \frac{k_{ov} A \alpha}{K_{SW} V_S} \quad (2)$$

In the initial uptake phase, when the exponential term is very small ($<<1$) or $M_S/V_s C_W << K_{SW}$, chemical uptake is linear or integrative. Thus, in the linear region Eq. (1) can be reduced to

$$M_S(t) = M_0 + C_W k_{ov} A \alpha t \quad (3)$$

For practical application, the Eq. (3) can be rewritten

$$M_S(t) = M_0 + C_W R_S t \quad (4)$$

where R_S is the sampling rate of the system.

$$R_S = k_{ov} A \alpha = k_e K_{SW} V_S. \quad (5)$$

Adding PRCs to the receiving phase prior to exposure of the passive sampler has been suggested as a means to calibrate the exchange rates in situ (Booij et al., 1998; Huckins et al., 2002). When PRCs are used that are not present in water ($C_W = 0$), Eq. (1) reduces to

$$M_S(t) = M_0 \exp(-k_e t) \quad (6)$$

which is a one-parameter equation, because the amount of PRC added to the MESCO sampler (M_0) is known.

3. Experimental

3.1. Materials and chemicals

Test chemicals (Table 1) included several groups of persistent organic pollutants: γ-hexachlorocyclohexane (γ-HCH), hexachlorobenzene (HCB), 2,2′-bis(4-chlorophenyl)-1,1′-dichloroethylene (DDE), PAHs and PCBs. γ-HCH reference material was obtained from Riedel-de Haen. HCB, DDE and PAH reference materials were obtained from Dr. Ehrenstorfer. PCB reference material and test chemicals in high purity (>99%; γ-HCH, HCB, DDE, PAHs and PCBs) were purchased from Promochem. Perdeuterated polycyclic aromatic hydrocarbons (D-PAHs) were obtained from Promochem. Physicochemical properties of test analytes are given in Table 1. Dialysis membrane Spectra/Por 6 (molecular weight cutoff 1000 Da) was obtained from Spectrum Laboratories. Twister™ stir bar for sorptive extraction was obtained from Gerstel. Lichrolut (R) (diameter of particles 40–63 μm) was purchased from Merck. The solvents methanol and hexane were used in LiChrosolv quality from Merck.

Table 1
Selected physicochemical properties of test analytes at 25 °C

No.	Compound	MW[a] (g mol^{-1})	log K_{OW}[b]	S[c] (g m^{-3})	log K_f[d] (PDMS)
1	HCB	284.8	5.5	0.005	4.4[e]
2	γ-HCH	290.8	3.7	7.3	2.6[e]
3	*p,p′*-DDE	318.0	5.7	0.04	5.3[e]
4	PCB28	257.5	5.6	0.16	4.8[e]
5	PCB52	292.0	6.1	0.03	5.1[e]
6	PCB101	326.4	6.8	0.01	5.5[e]
7	PCB138	360.9	7.6	0.0015	5.7[e]
8	PCB153	360.9	7.8	0.001	5.7[e]
9	PCB180	395.3	8.3	0.0003	5.6[e]
10	Acenaphthylene	152.2	4.0	16.1	3.40[f]
11	Acenaphthene	154.2	4.0	3.8	3.63[f]
12	Fluorene	166.2	4.2	1.9	3.71[f]
13	Anthracene	178.2	4.6	0.045	3.98[f]
14	Phenanthrene	178.2	4.5	1.10	3.96[f]
15	Fluoranthene	202.3	5.1	0.26	4.71[f]
16	Pyrene	202.3	5.1	0.132	4.86[f]
17	Benzo[*a*]anthracene	228.3	5.9	0.011	5.26[f]
18	Chrysene	228.3	5.7	0.0019	5.69[f]
19	Benzo[*b*]fluoranthene	252.3	5.8	0.0015	5.17[f]
20	Benzo[*k*]fluoranthene	252.3	6.0	0.0008	5.33[f]
21	Benzo[*a*]pyrene	252.3	6.2	0.0038	5.39[f]
22	Indeno[1,2,3-*cd*]pyrene	276.3	6.8	0.0005	4.28[f]
23	Benzo[*g,h,i*]perylene	276.3	6.9	0.0003	4.43[f]

[a] Molecular weight (MW).
[b] Octanol–water partition coefficient K_{OW} (Mackay et al., 1992).
[c] Aqueous solubility S (Mackay et al., 1992).
[d] PDMS/water distribution coefficient.
[e] Data from Paschke and Popp (2003).
[f] Data from Doong and Chang (2000).

3.2. Sampler design

The passive sampling device, referred to as the Membrane-Enclosed Sorptive Coating sampler (MESCO) has been described previously (Vrana et al., 2001b). It consists of a GERSTEL-Twister™ bar used for SBSE enclosed in a dialysis membrane bag made from regenerated cellulose (Spectra/Por 6, molecular weight cutoff 1000 Da, 18 mm flat width, 30 mm length; component). Twister is a stir bar (15 mm length) consisting of a magnetic core sealed inside a glass coated with 22 mg PDMS. The PDMS sorptive layer (receiving phase) is 500 μm thick and its volume is 24 μL.

3.3. Sampler preparation

Prior to use, the stir bar was placed into a vial containing 1 mL of a 1:1 mixture of methylene chloride and methanol, and treated for 5 min with sonication. Then the solvent mixture was rejected and the procedure repeated three times. The stir bar was dried in a desiccator at room temperature. Prior to each use, the stir bar was conditioned by heating for 180 min at 280 °C with a nitrogen stream of about 100 mL min^{-1}.

Perdeuterated PAHs were utilised as PRCs. For loading the Twister stir bars with (PRC_s), 20 mL of aqueous solution of containing $^2H_{10}$-biphenyl (D_{10}-BIP), $^2H_{10}$-fluorene (D_{10}-FLU), $^2H_{10}$-phenanthrene (D_{10}-PHE), $^2H_{10}$-anthracene (D_{10}-ANT), $^2H_{10}$-fluoranthene (D_{10}-FLT), $^2H_{10}$-pyrene (D_{10}-PYR) and $^2H_{12}$-benz(*a*)anthracene (D_{12}-BaA) was pipetted to a 25 mL amber glass vial with a flat base with a screw cap. The solution was prepared by spiking bi-distilled water with a PRC-mixture dissolved in methanol to give nominal concentration of individual analytes of 1 μg L^{-1}. The vial was then placed on a magnetic stirrer. The pre-cleaned Twister stir bar was placed in the vial with the PRC solution and stirred at 1000 min^{-1} for 30 min at room temperature. In order to accelerate the procedure, up to six Twister bars were loaded in parallel. Following the loading with PRCs, Twisters were washed with bi-distilled water, dried with a soft paper tissue and stored closed in an amber glass GC vial in the freezer until use.

For sampler assembly, the Twister was placed inside the dialysis membrane bag. The bag was filled with 3 mL of bi-distilled water and sealed at each end with 35 mm Spectra Por enclosures. As a direct relationship exists between the surface area and the rate of uptake, the area of the membrane was held constant at 1100 mm^2. To enable a simultaneous exposure of a series of samplers, they were connected to a string, which

was then exposed to organic analytes in a continuous-flow system.

3.4. Flow-through exposures

MESCO samplers were exposed to test chemicals at a nominal concentration of 20 ng L^{-1} in a flow-through exposure system. Exposures were conducted at 19 °C. The experimental conditions of individual exposures are given in Table 2. The experimental setup of the flow-through exposure system has been described (Vrana et al., 2001b; Vrana and Schüürmann, 2002). Briefly, exposure water was pumped from the bottom to the top of a 1 m high glass column with either 7.5 or 15 cm inner diameter. Test chemicals were dissolved in methanol and the appropriate amounts of stock solution were delivered into exposure water in a 1 L chamber positioned at the bottom of the column using a peristaltic pump. The water in the chamber was mixed using a magnetic stirrer. The methanol concentration in the exposure water was held constant at 0.01% (v/v). This setup enabled to vary the flow rate in the exposure column. The string of MESCO samplers was fixed in the column in a vertical position between the top and the bottom of the exposure column.

Exposures were conducted at linear flow velocities of 8, 35 and 68 cm min^{-1}. The exposures lasted up to 10 days, during which the samplers were sampled at time intervals and their contents analysed to determine accumulated concentrations of test chemicals as described below. Duplicate water samples from the exposure column (1 L) were taken at each time when samplers were sampled and analyte concentration in water was determined.

3.5. Field performance test

To assess the performance of MESCO for monitoring POPs in the field, samplers were deployed in a river. The sampler data were compared with spot sampling. The sampling site was located in the stream Spittelwasser flowing through a highly polluted industrial area of Bitterfeld in Saxony-Anhalt, Germany (Vrana et al., 2001a). The MESCOs were deployed for 20 days during summer 2000 (15th June–4th July). During the exposure, the water temperature at the sampling site varied from 18.9 to 20.5 °C. Four samplers were deployed at the sampling site. On the day of deployment, MESCOs were freshly prepared in laboratory and transported to the field in amber glass jars filled with bi-distilled water to prevent drying of the dialysis membrane during transport. At the sampling site, MESCOs were removed from the jars and placed into a protective deployment device made of a stainless steel conduit of 5 cm inner diameter with perforated surface (5 mm openings). The deployment device protected MESCOs from abrasion and protected the sequestered pollutants from light. The depth below the water surface at which devices were deployed was 20 cm. On day 20, MESCOs were removed from the deployment device, checked visually for mechanical damage and immediately sealed in individual amber glass jars filled with bi-distilled water. The jars were transported to the laboratory in a portable icebox (on ice and in darkness). Additional trip blank sampler was exposed to air while MESCOs were being deployed and collected. Trip blank was processed exactly as deployed samples and was used to define contamination of the MESCOs during transportation and handling. Two 2 L water samples were taken from the sampling site at the beginning and the end of the exposure period, extracted and analysed for contaminant content using solid-phase extraction technique.

Table 2
Summary of passive sampler flow-through exposure experimental conditions

Experiment no.	Flow velocity (cm min^{-1})	Exposure period (h)	Number of MESCOs sampled
1	35	0–163	16
2	8	0–233	15
3	68	0–168	12

Exposures were conducted at 19 °C and 20 ng L^{-1} nominal analyte concentrations in water.

3.6. Sampler processing

Following exposure, MESCOs were dismantled, Twister bars were washed with bi-distilled water, dried with a paper cloth, checked visually for possible damage of the sorptive layer, and analysed for accumulated target analyte and PRC content by thermodesorption–GC–MS.

3.7. Processing of water samples

The residues in the water samples from the calibration apparatus and river water samples were extracted using solid-phase extraction (SPE) using Lichrolut (*R*) sorbent or SPME technique as described earlier (Vrana et al., 2001b).

3.8. Instrumental analysis

The quantitation of the compounds accumulated during exposures in Twister bars was performed by thermodesorption–GC–MS under conditions described previously (Vrana et al., 2001b). Briefly, thermodesorption–GC–MS was performed on an Agilent Technologies (Palo Alto, CA, USA) system equipped with a Gerstel (Mülheim/Ruhr, Germany) thermodesorption device TDS A. A cold injection system from Gerstel (CIS-4) with an empty liner was used for cryofocusing the analytes prior to the transfer onto the analytical column. The single ion monitoring (SIM) mode of the mass selective detector applying one or two characteristic ions per compound was chosen for the detection.

For the external calibration, a small bunch of glass wool was positioned to an empty desorption tube. The desorption tube was then connected to the cool injector of a GC and flushed with 20 mL min^{-1} of nitrogen. The desorption tube with glass wool was then spiked with 2 μL of a calibration standard solution and flushed for 1 min by nitrogen stream to allow the solvent (hexane) to evaporate. The desorption

tube was then transferred to the thermodesorption device (TDS A) and processed by thermodesorption–GC–MS. Quantification of the residues sorbed on Twister bars was accomplished using a five-point external standard curve. Method quantification limit for the analytes under investigation ranged from 0.01 to 0.2 ng/Twister.

3.9. Data processing

The experimentally determined time courses of the amounts of individual test substances on the MESCO sampler were fitted by linear regression analysis using Eq. (4). The adjustable parameters were the intercept (M_0) and the slope ($C_W \times R_S$) of the linear uptake curve $M_S = f(t)$. Quality of the fit was characterized by the standard deviations of the optimized parameters, as well as the correlation coefficient adjusted for the degrees of freedom (r^2 adjusted), the fit standard deviation, and the Fisher test criterion on the accuracy of the model. The sampling rates of the device R_S for individual test compounds were calculated by dividing the slope of the linear uptake curve by the mean aqueous analyte concentration during the exposure. The required variances of R_S values were calculated from the coefficients of variation of the uptake slope parameters and of the concentrations in the aqueous phase, according to the law of error propagation.

The release of PRC from the MESCO sampler was fitted by non-linear regression analysis using Eq. (6) with M_0 and k_e as adjustable parameters. Quality of the fit was characterized by the standard deviations of the optimized parameters, as well as the correlation coefficient adjusted for the degrees of freedom (r^2 adjusted), the fit standard deviation, and the Fisher test criterion on the accuracy of the model.

4. Results and discussion

4.1. Flow-through exposures

4.1.1. Uptake kinetics

The performance of the sampler was tested by exposure to constant concentrations of test chemicals in a continuous-flow exposure tank at three various linear flow velocities. Concentrations of the analytes in water (C_W) and the amounts accumulated in the receiving phase (M_S) were two parameters measured regularly during the continuous-flow exposures. During exposure the water concentration was held constant, which was confirmed by analyses of water samples. Characteristic analyte uptake curves are shown in Figs. 1 and 2.

Satisfactory linear regression fits of the Eq. (4) to the uptake data of analytes from water to MESCO were obtained for all test compounds in all experiments. Correlation coefficient (r) values of the regression ranged from 0.79 to 0.99 except of PCB138, fluoranthene and pyrene in experiment 2, for which r values ranged from 0.59 to 0.69. Coefficients of variation (CV) of the calculated slopes of uptake curves ranged from 5 to 25% with a few exceptions of PCB138, fluoranthene and pyrene in experiment 2, for which CV ranged from 33 to 40%. The maximum fluctuations of aqueous concentrations during exposure did not exceed 30% of the average concentration for individual compounds.

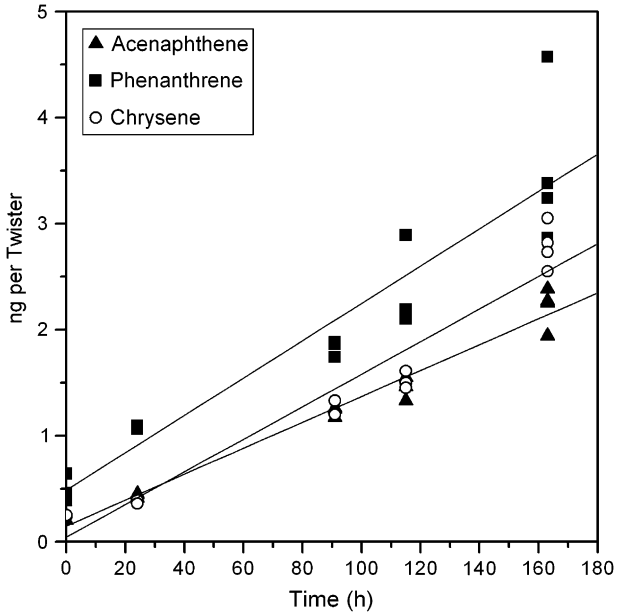

Fig. 1. Uptake of selected PAHs by the TWISTER-based MESCO sampler. The data represent the 19 °C flow-through exposure at linear flow velocity of 35 cm min^{-1} and nominal water concentration of analytes 20 ng L^{-1}. The lines are predicted concentrations in the sampler obtained by linear regression using Eq. (4).

4.1.2. Sampling rate

The sampling rates R_S obtained in flow-through exposure experiments conducted at 20 ng L^{-1} nominal water concentration and 19 °C and various linear flow velocities are shown in

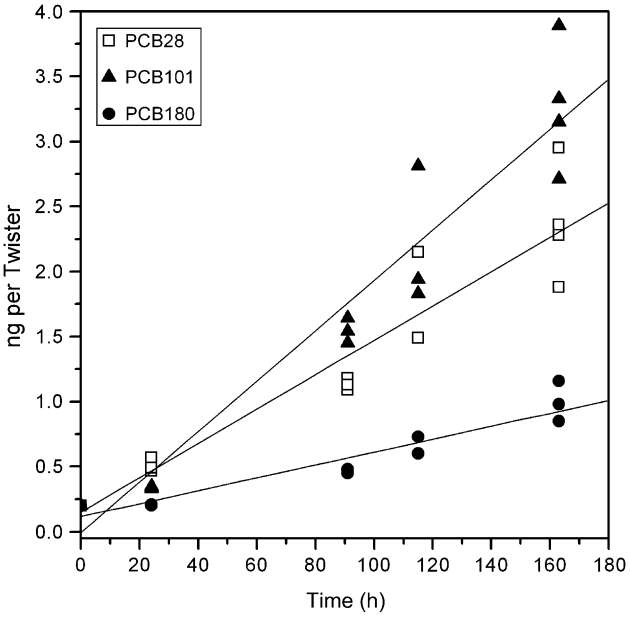

Fig. 2. Uptake of selected PCBs by the TWISTER-based MESCO sampler. The data represent the 19 °C flow-through exposure at linear flow velocity of 35 cm min^{-1} and nominal water concentration of analytes 20 ng L^{-1}. The lines are predicted concentrations in the sampler obtained by linear regression using Eq. (4).

Table 3. Over the range of controlled laboratory conditions, the magnitude of R_S values differed by 10-fold (i.e. from 100 to 983 μL h^{-1}). This range of sampling rates is narrow relative to the broad K_{OW} range of nearly 5 orders of magnitude. This is in a good agreement with our earlier observations (Vrana et al., 2001b).

4.1.3. Release kinetics

The release of PRCs from the MESCO sampler to water was fitted by non-linear regression analysis using Eq. (6) with M_0 and k_e as adjustable parameters. Fig. 3 shows the release kinetics of D_{10}-BIP under various flow conditions. Satisfactory fits of the first order decay Eq. (6) to the elimination data were obtained for D_{10}-BIP and D_{10}-FLU, with correlation coefficient (r^2 adjusted for degrees of freedom) values of the regression (model versus experimental) between 0.79 and 0.93. Coefficients of variation of the k_e for these compounds varied between 7 and 20%. For the remaining PRCs, satisfactory fit of the first order kinetic decay Eq. (6) to the PRC elimination data was obtained only for D_{10}-PHE in experiments 1 and 2, and for D_{10}-ANT in experiment 1, with r^2 (adjusted) values between 0.72 and 0.73. Coefficients of variation of the k_e for these compounds varied between 22 and 33%. The release of the remaining PRCs from the MESCO was too slow to statistically evaluate the release kinetics. The results of the first order decay fits were poor and estimates of k_e values for D_{10}-FLT, D_{10}-PYR and D_{12}-BaA were statistically not significantly different from zero ($p = 0.95$).

4.1.4. Verification of isotropic exchange kinetics: absorption versus desorption

Assuming that the uptake rate of target analytes R_S and the exchange rate constant k_e of its labeled analogue (PRC) are measured under the same conditions and that the distribution coefficient K_{SW} is measured at the same temperature, comparison of the R_S derived using the PRC elimination (Eq. (5)) to the directly measured R_S of the target analytes can be viewed as a check of the isotropic exchange kinetics.

For this purpose, we simultaneously measured the sampling rate of native fluorene and phenanthrene, and the exchange rate k_{ePRC} of their deuterated analogues in three exposure experiments. These exchange coefficients were determined at 19 °C and at various water flow conditions. The K_{SW} values used for the estimation of PRC-derived R_S of fluorene and phenanthrene were approximated by PDMS/water distribution coefficients taken from the literature (Doong and Chang, 2000). These are listed in Table 1.

Directly measured R_S and PRC-derived $R_{S\text{-}PRC}$ for MESCOs in experiment 1 were as follows: fluorene, $R_S = 680$ μL h^{-1} and $R_{S\text{-}PRC} = 341$ μL h^{-1}; phenanthrene, $R_S = 734$ μL h^{-1} and $R_{S\text{-}PRC} = 390$ μL h^{-1}. For the experiment 2, sampling rate values for the same compounds were as follows: fluorene, $R_S = 403$ μL h^{-1} and $R_{S\text{-}PRC} = 271$ μL h^{-1}; phenanthrene, $R_S = 451$ μL h^{-1} and $R_{S\text{-}PRC} = 394$ μL h^{-1}. Finally, for the experiment 3, sampling rate values for the fluorene were as follows: $R_S = 675$ μL h^{-1} and $R_{S\text{-}PRC} = 246$ μL h^{-1}. Because of the bad quality of the fit of the PRC elimination data, the comparison in this experiment for phenanthrene was precluded.

Table 3
Summary of passive sampler sampling rates R_S derived from flow-through exposures at different flow velocities at nominal analyte concentration of 20 ng L^{-1}

Flow velocity (cm min^{-1})	8		35		35		68	
	R_s (μL h^{-1})	C.V. (%)	R_s (μL h^{-1})	C.V. (%)	R_s[a] (μL h^{-1})	C.V. (%)	R_s (μL h^{-1})	C.V. (%)
Compound								
HCB	347	29	218	22	114	7	278	11
γ-HCH	183	33	287	22	336	41	347	19
p,p-DDE	287	35	334	26	305	7	179	36
PCB28	545	30	568	23	305	49	546	54
PCB52	349	29	409	21	337	32	471	57
PCB101	365	35	443	21	275	13	232	43
PCB138	404	31	311	23	188	6	160	34
PCB153	359	33	309	22	227	7	165	10
PCB180	287	36	238	21	110	8	172	24
Acenaphthylene	214	26	624	20	484	7	607	31
Acenaphthene	348	26	529	20	280	8	676	31
Fluorene	403	26	680	22	391	7	675	31
Phenanthrene	451	27	734	22	462	15	604	31
Anthracene	521	26	N.D.		321	10	983	31
Fluoranthene	322	30	720	21	389	11	280	32
Pyrene	332	32	371	30	509	15	242	31
Benzo[*a*]anthracene	307	47	N.D.		597	4	318	31
Chrysene	101	45	640	21	641	8	226	31
Benzo[*b*]fluoranthene	198	36	N.D.		453	5	293	32
Benzo[*k*]fluoranthene	188	37	N.D.		495	8	280	32
Benzo[*a*]pyrene	439	36	N.D.		388	7	478	32
Indeno[1,2,3-*cd*]pyrene	304	26	N.D.		294	5	261	34
Dibenzo[*a,h*]anthracene	153	26	N.D.			9	158	39
Benzo[*g,h,i*]perylene	260	26	N.D.		239		268	33

N.D. – not determined.
[a] Data from Vrana et al. (2001b).

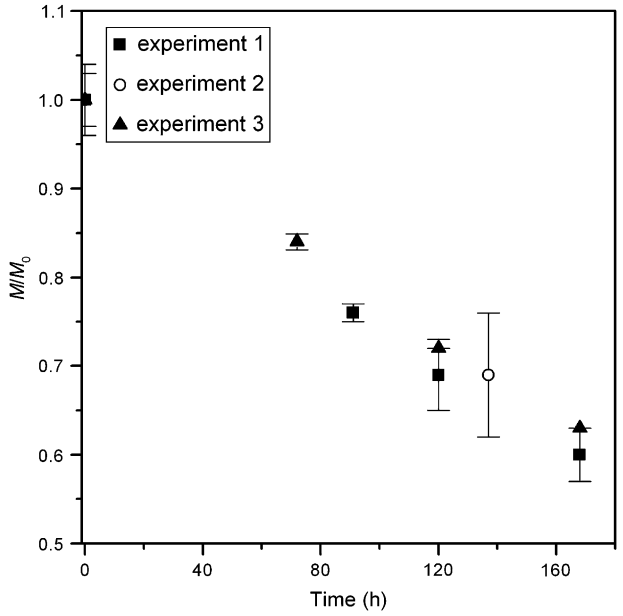

Fig. 3. Release of $^2H_{10}$-biphenyl from MESCOs (expressed as the mass fraction M/M_0 of the initial amount M_0 remaining in the sampler) exposed at different linear flow velocities: 8 cm min^{-1} (experiment 2), 35 cm min^{-1} (experiment 1), and 68 cm min^{-1} (experiment 3). The flow-through exposures were conducted at 19 °C.

By dividing R_S values by $R_{S\text{-}PRC}$ values, the bias or error encompassing the difference between predicted and measured values of R_S can be estimated. Application of this approach to our sampling rate data gave the following $R_S/R_{S\text{-}PRC}$ ratios: fluorene, ranging from 1.5 to 2.7; phenanthrene, ranging from 1.1 to 1.9. The predicted values of $R_{S\text{-}PRC}$ were lower than measured values. Overall, the mean $R_S/R_{S\text{-}PRC}$ bias ratio was 2.0, and the coefficient of variation was 34%. This is a good agreement between sampling rate values calculated from uptake and elimination kinetic data, when taking into account three separate sources of error accumulated in the $R_S/R_{S\text{-}PRC}$ ratio, originating in the measurement of the uptake (R_S) and elimination (k_e) kinetics, as well as the distribution coefficient K_{SW}. Huckins et al. (2002) have demonstrated a similar accuracy and variance (i.e. 2-fold difference and 35% variance) in comparison of measured and PRC-predicted sampling rates for lipid-filled semipermeable membrane devices.

The aforementioned experiments prove the isotropy of the uptake (absorption) and the elimination (desorption) of two analytes (fluorene and phenanthrene) onto and from a MESCO sampler. It is likely that isotropic exchange kinetics is valid also for a broad range of compounds, including the rest of analytes under investigation in this study. Using a similar approach, Chen and Pawliszyn have demonstrated the isotropy of the exchange kinetics between PDMS and water for BTEX aromatic compounds (Chen and Pawliszyn, 2004). The test is practicable only for compounds with moderate/low affinity to the receiving PDMS, for which elimination kinetics can be measured in a reasonable time period (two weeks or so). The experiment demonstrates the isotropic exchange kinetics. By knowing the behavior of either the absorption or desorption, the opposite one will also be understood.

4.1.5. Time limit for integrative sampling

Both uptake and elimination of a particular compound are characterized by the same exchange rate constant k_e, according to the Eq. (1). This fact can be used to determine the maximum exposure time for integrative sampling with MESCO.

The chemical uptake into passive sampler remains linear and integrative approximately until concentration factor reaches half saturation:

$$\frac{M_S(t_{50})}{V_S C_W} = \frac{K_{SW}}{2} \tag{7}$$

where t_{50} is the time required to accumulate 50% of the equilibrium concentration. Under these conditions, linear model (Eq. (4)) can be used to calculate TWA concentration of the analyte in water. The maximum exposure time t_{50} can be estimated, if both partition coefficient K_{SW} and the sampling rate R_S are known.

$$t_{50} \approx \ln 2 \frac{K_{SW} V_S}{R_S}. \tag{8}$$

However, the K_{SW} values are not always available and the sampling rate in the field may differ from the value determined under laboratory conditions. Because the isotropic exchange kinetics applies, the first order halftime t_{50} for uptake and is mathematically identical to $t_{1/2}$ for elimination, i.e. time required to lose 50% of the initial residue concentration in an exposure scenario, when the analyte is initially applied to the receiving phase ($M_0 \neq 0$) and not present in water ($C_W = 0$). Thus, t_{50} of an analyte can be approximated by the elimination halftime $t_{1/2}$ of a PRC with similar physicochemical properties. $t_{1/2}$ can be calculated using Eq. (6) and $M_S(t_{1/2}) = M_0/2$:

$$t_{50} \approx t_{1/2} = \frac{\ln 2}{k_{ePRC}}. \tag{9}$$

The results of the first order halftime calculation for PRCs used in this study are reported in Table 4. It is calculated that, for a compound with physicochemical properties similar to D_{10}-BIP or D_{10}-FLU, MESCO would sample integratively for more than 10 days under conditions similar to flow-through exposures in this study. According to Eq. (8), t_{50} increases with increasing sampler capacity (K_{SW}) and with decreasing sampling rate (R_s). It has been shown that the range of sampling rates is relatively narrow over a broad hydrophobicity range. Thus, it is expected that the main factor determining the t_{50} is the magnitude of the partition coefficient K_{SW}. For practical purpose, the apparent distribution constants K_f (PDMS), obtained with glass fibres coated with 100 μm-PDMS for analyte's partitioning between PDMS coating and aqueous sample can be used as substitute for K_{SW} (Doong and Chang, 2000; Valor et al., 2001; Paschke and Popp, 2003). With a few exceptions of γ-HCH, acenaphthylene and acenaphthene, K_{SW} values are higher than for that of fluorene. This implicates that, for most of the analytes under investigation and exposure conditions similar to the test exposures described in this study,

Table 4
Summary of exchange coefficients derived from flow-through exposures

Flow velocity (cm min^{-1})	8			35			68		
	$k_e \times 10^3$ (h^{-1})	CV (%)	$t_{1/2}$ (d)	$k_e \times 10^3$ (h^{-1})	CV (%)	$t_{1/2}$ (d)	$k_e \times 10^3$ (h^{-1})	CV (%)	$t_{1/2}$ (d)
Compound									
D_{10}-biphenyl	2.7	11	11	3.0	13	10	2.6	8	11
D_{10}-fluorene	2.2	14	13	2.8	15	10	2.0	20	14
D_{10}-phenanthrene	1.8	33	16	1.8	23	16			
D_{10}-anthracene				1.8	23	16			

integrative uptake period is expected to be longer than t_{50} values indicated by D_{10}-BIP and D_{10}-FLU.

4.1.6. Robustness of sampler performance

The comparability of experimentally derived MESCO calibration data to actual values during field sampling generally depends on the similarity of laboratory and field exposure conditions and the robustness of the sampler performance against fluctuations in environmental conditions. Besides temperature and biofouling, flow velocity/turbulence may affect the uptake kinetics. The uptake kinetics is sensitive to changes in flow velocity/turbulence when the dominant barrier to mass transfer of analytes is in the laminary aqueous boundary layer at the surface of the sampler. Such effect has been observed for passive sampling devices fitted with non-porous membranes made of low-density polyethylene (Booij et al., 1998; Vrana and Schüürmann, 2002), but also for samplers fitted with macroporous polyethersulphone membranes (Kingston et al., 2000; Alvarez et al., 2004).

The effect of flow velocity on the mass transfer of analytes to the MESCO samplers in the calibration experiments can be examined in three ways: (a) by examining the potential rate-limiting barriers to mass transfer of an analyte in MESCO; (b) by testing whether the varying flow conditions significantly affected the uptake of target analytes or (c) the elimination of PRCs.

4.1.7. Examination of the mass transfer in the sampler

Accumulation of target analytes in MESCO requires their movement out of the bulk sample medium, across multiple layers of barriers, and into the sampler matrix. It is assumed that the overall resistance ($1/k_{ov}$), to the uptake of a chemical in steady state is given by sum of particular barrier resistances

$$\frac{1}{k_{ov}} = \sum_i \frac{\delta_i}{K_{iW} D_i} = \frac{\delta_M}{D_M K_{MW}} + \frac{\delta_W}{D_W} + \frac{\delta_S}{D_S K_{SW}} \quad (10)$$

where δ_i is the particular barrier thickness, D_i is the diffusion coefficient in the barrier and K_{iw} is the partition coefficient between the ith phase and water (designed as subscripts for the water [W], dialytic membrane [M] and the receiving organic phase [S]). The overall mass transfer coefficient is affected mainly by the diffusion of solutes in individual phases (water, membrane pores and the PDMS, respectively) and by their partitioning into the PDMS, since no accumulation of hydrophobic analytes is expected in the hydrophilic dialytic membrane (i.e. $K_{MW} \approx 1$).

As can be seen from Eq. (10), a resistance decrease in receiving phase (PDMS) is expected with increasing K_{SW} value for substances having similar diffusion coefficient in this material D_S.

When the diffusive transport is limited by the resistance in the PDMS and then the resistance in water and dialytic membrane being negligible (i.e. if $\delta_M/D_M K_{MW} + \delta_W/D_W << \delta_S/D_S K_{SW}$), the exchange rate constant k_e should be independent of K_{SW}, and the sampling rate R_S should increase with increasing K_{SW}. On the other hand, if the transport is limited by the resistance in the water or dialytic membrane (i.e. if $\delta_M/D_M K_{MW} + \delta_W/D_W >> \delta_S/D_S K_{SW}$), the exchange rate constant k_e should be inversely proportional to the equilibrium partition coefficient K_{SW} and sampling rate should be independent of K_{SW} (Eqs. (2) and (10)).

Inspection of exchange rate constants determined from the PRC release kinetics shows a decrease of k_e with increasing $\log K_f$ in all experiments (Table 4). Further, there is no increasing trend of the sampling rate R_S versus $\log K_f$. for neither of the contaminant classes under investigations (Figs. 4 and 5). On the contrary, the sampling rates of PCBs decrease with increasing $\log K_f$, likely due to decreasing diffusivity in the rate-limiting barrier with the increasing molecular size/volume.

The examination of potential rate-limiting barriers to analyte uptake by MESCO indicates, that the slowest kinetic step in the mass transfer is the diffusion in one of the aqueous barriers (i.e. in the pores in the cellulose membrane, in the water filling the sampler, or in the aqueous boundary layer, respectively) rather than the diffusion in the receiving phase (PDMS). Since the aqueous boundary layer presents only a small part of the total diffusion path, it is likely that the dominant rate-limiting barrier to mass transfer is in the cellulose membrane. Moreover, the net flux of non-polar molecules across the cellulose membrane is limited by the small area of the membrane pores and by small permeability (i.e. diffusivity × solubility) of the cellulose material for non-polar compounds. Further experiments were conducted in order to confirm the robustness of the MESCO calibration data against the fluctuation in hydrodynamic conditions.

4.1.8. Effect of flow hydrodynamics on the analyte uptake

A one-way ANOVA test was also performed to check whether there was any significant difference between the R_S of individual compounds obtained in experiments conducted under conditions of varying water flow velocity. The ANOVA test was performed on sampling rates that included also previously published data. The extra data included in the test were

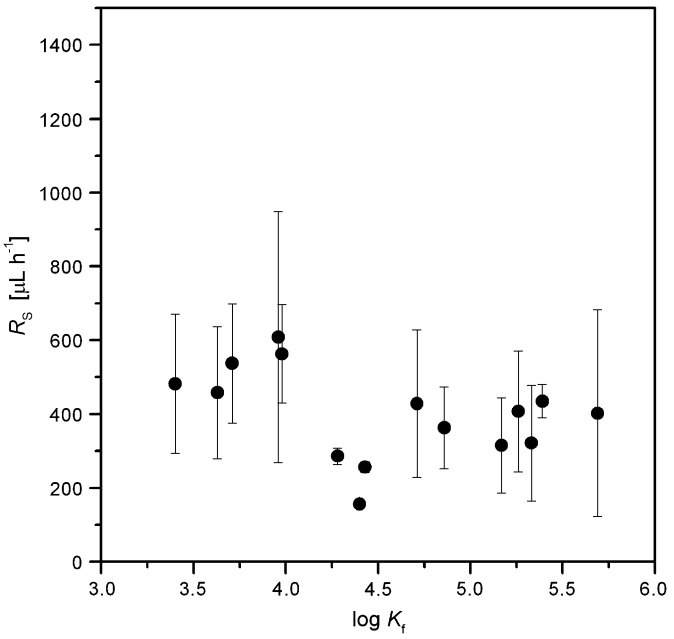

Fig. 4. Mean values of sampling rates R_S of PAHs from all calibration exposures conducted at 19 °C as dependent on PDMS/water distribution coefficient K_f.

obtained using the same experimental conditions as in this study; the experimental flow rate was 35 cm min^{-1} (Vrana et al., 2001b). Thus, these data represent a repeated experiment 1.

With exception of PCB28, PCB 52, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenzo[*a*,*h*]anthracene and benzo[*g*,*h*,*i*]perylene, a significant difference ($\alpha = 0.05$) between the R_S means of individual compounds obtained in experiments with varying water flow velocity was observed.

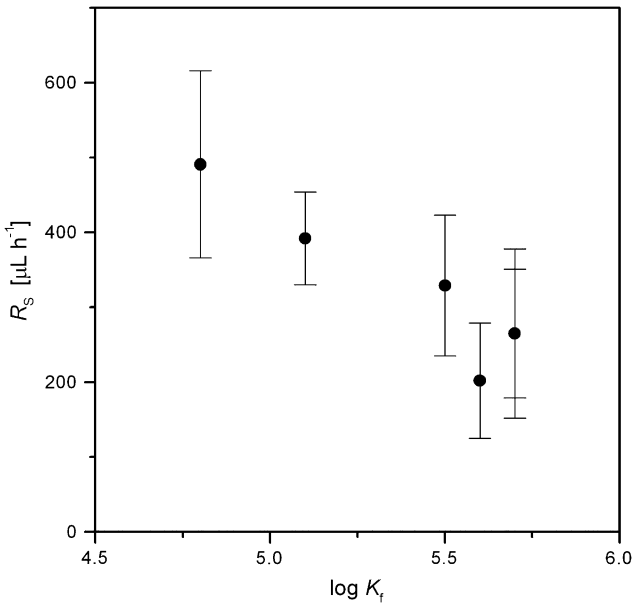

Fig. 5. Mean values of sampling rates R_S of polychlorinated biphenyls from all calibration exposures conducted at 19 °C as dependent on PDMS/water distribution coefficient K_f.

All experiments were conducted under the same exposure conditions; the only parameter that was varied was the water flow velocity. The uptake kinetics would be sensitive to changes in flow velocity/turbulence, if the dominant barrier to mass transfer of chemicals was in the laminar aqueous boundary layer at the surface of the sampler. From the theory, an increase in the sampling rate with the increasing flow velocity is expected, because the thickness of the boundary layer, and its resistance to the mass transfer, decreases. An increasing trend of sampling rate with the increasing flow velocity can be observed only for γ-HCH, acenaphthylene, anthracene, fluorene and phenanthrene. On the other hand, a decrease of sampling rate with the increasing flow velocity was observed for PCB 138, PCB 153 and PCB 180. For the remaining compounds, no trend could be observed.

The observed differences in the uptake kinetics cannot be unambiguously attributed to the effect of varying hydrodynamics. The conclusion is that, the observed difference in the sampling rate must be attributed to the error introduced by the process of sampling rate determination. This error is cumulative, stemming from two independent sources: the determination of amount of chemical accumulated in the sampler, and the determination of water concentration in the calibration system. Its magnitude is likely greater than the effect of hydrodynamics.

4.1.9. Effect of hydrodynamics on the PRC elimination

To examine the effect of flow velocity on the elimination rate of PRCs, best fit values of k_e obtained for individual PRCs under various flow conditions (8, 35 and 68 cm min^{-1}) were compared using a one-way ANOVA test. For the PRCs with significant elimination kinetics (D_{10}-BIP, D_{10}-FLU and D_{10}-PHE), no significant difference was observed between k_e values determined at different flow rates ($\alpha = 0.05$).

The uncertainty of the elimination kinetics determination is much lower than that of the sampling rate determination, because it is based solely on the measurement of analyte amount in the sampler. Moreover, with the assumption that the elimination of PRCs follows the first order kinetics (which is concentration independent), the k_e estimate determined from the elimination data is not affected by the potential bias in external calibration, which was used for determination of PRC amounts remaining on MESCO.

No significant effect of the hydrodynamics on the elimination from and, no observable effect on the uptake of compounds to the MESCO sampler indicate that, within the range of hydrodynamic conditions tested in this study, the MESCO sampling is robust and not affected by the water flow.

4.2. Field performance test

Table 5 shows the mass of each test analyte accumulated in the MESCO samplers following a 20-day deployment in a river. For substances exceeding the method limit of quantitation, the variation between the masses recovered from three

replicate passive sampling devices was lower than 60%. The time-averaged waterborne concentrations of PAHs, PCBs, HCB and γ-HCH at the sampling site were estimated from the contaminant amounts quantified in MESCOs after field exposure using the average values of sampling rates obtained in all laboratory flow-through exposures conducted at 19 °C. Eq. (4) was used to calculate the TWA waterborne concentrations of compounds. The amount of analyte found in the trip blank sample was taken for M_0 value. A possible fractional reduction in the uptake flux or sampling rate due to biofouling impedance was not respected in the estimation, although a thin biofilm was observed at the surface of samplers after exposure. Also, a simplifying assumption of linear uptake of γ-HCH and PAHs with $\log K_{OW} < 4.5$ during the exposure was made, although the uptake might have been curvilinear for these substances, as indicated by the t_{50} estimates. The estimated ambient concentrations C_W of selected contaminants are presented in Table 5 and were compared with grab sampling data (water samples; C_{WG}). There are no major differences in contaminant patterns in water concentrations obtained by the two different techniques. The slight concentration difference can be explained by the fact that C_W represents only the truly dissolved fraction of contaminants in water, whereas C_{WG} includes both contaminants dissolved and bound to the dissolved organic matter. The dissolved fraction of hydrophobic compounds is strongly affected by the dissolved organic carbon (DOC) content of the water. Especially very hydrophobic PAHs, PCBs and DDE are likely to be partitioned to DOC to a great extent. To relate the dissolved concentrations of analyte, derived from MESCO levels, to total aqueous concentrations (i.e. mass sorbed plus dissolved residues divided by the volume of water), an estimation using equilibrium partitioning model (Chiou et al., 1986) was made

$$C_{WT} = C_W(1 + [DOC]K_{DOC}) \quad (11)$$

where C_{WT} is the apparent solute concentration estimation in water containing DOC (as co-solute) at concentration [DOC] ($g\,mL^{-1}$ of water), and K_{DOC} is the corresponding organic-carbon-based partition coefficient. An estimation of K_{DOC} was made from the octanol–water partition coefficient using a predictive relationship of $K_{DOC} = 0.08K_{ow}$ (Burkhard, 2000). The dissolved organic carbon (DOC) content of the water samples ranged from 6.9 to 7.9 $mg\,L^{-1}$; an average value of 7.4 $mg\,L^{-1}$ was taken for calculation.

C_W represents TWA concentration estimation, whereas C_{WG} is an average value of two measurements of samples taken at the beginning and the end of the field study. Therefore, possible episodic fluctuations in pollutant concentrations during the field study are not reflected in the C_{WG} value. Nevertheless, the small relative percent differences in concentrations determined in bulk water samples taken with a time

Table 5
Mass of organic analytes accumulated in the MESCOs (M_S), dissolved (C_W) and total (C_{WT}) time-weighted average concentrations of organic analytes estimated from passive sampling data, and from grab sampling (water samples extracted by SPE; C_{WG}) at the site in the Spittelwasser River during a 20-day exposure

Compound	M_S (ng)	CV (%)	M_0 (ng)	C_W ($ng\,L^{-1}$)	C_{WT} ($ng\,L^{-1}$)	C_{WG} ($ng\,L^{-1}$)	RPD[d] (%)
HCB	2.57	17	0.02	22.3	26.4	NR[c]	
γ-HCH	15.98	19	ND[a]	115.6	115.9	89.1	6
p,p′-DDE	<0.002		0.02	<0.01	<0.01	ND	
PCB28	0.05	62	0.01	0.2	0.3	ND	
PCB52	NQ[b]		ND			ND	
PCB101	0.006	51	0.005	<0.01	<0.05	ND	
PCB153	0.005	78	0.007	<0.04	<1.0	ND	
PCB138	0.005	87	0.007	<0.02	<0.7	ND	
PCB180	ND		<0.006	ND	ND	ND	
Acenaphthylene	0.23	14	0.03	0.9	0.9	NR	
Acenaphthene	3.52	10	0.11	15.5	15.6	NR	
Fluorene	1.53	17	0.08	5.6	5.7	NR	
Anthracene	1.57	21	0.05	4.8	4.9	5.4	10
Phenanthrene	1.50	20	0.27	5.0	5.1	12.8	7
Fluoranthene	3.10	19	0.06	14.8	15.9	21.5	15
Pyrene	2.93	21	0.05	16.5	17.7	20.4	10
Benzo[*a*]anthracene	0.15	29	0.03	0.6	0.9	ND	
Chrysene	0.10	52	0.03	0.4	0.5	ND	
Benzo[*b*]fluoranthene	NQ		NQ			ND	
Benzo(*k*)fluoranthene	NQ		NQ			ND	
Benzo[*a*]pyrene	NQ		NQ			ND	
Indeno[1,2,3-*cd*]pyrene	NQ		NQ			ND	
Benzo[*g,h,i*]perylene	NQ		NQ			ND	

M_0 represents the amount of analytes found in the trip blank MESCO samplers. C_{WG} represents a recovery-corrected average of two 2 L samples of water taken at the beginning and the end of MESCO exposure. C_W and C_{WT} represent concentration estimation from amounts of analytes accumulated by three passive samplers. Average values of all calibration data obtained at 19 °C and were used for estimation.

[a] ND – not detectable.
[b] NQ – not quantifiable – presence of interfering peaks.
[c] NR – not reproducible recovery.
[d] RPD – relative percent difference.

difference of 20 days indicate rather stable concentration conditions during the field study.

A comparison of concentrations estimated by grab sampling (C_{WG}) to those estimated by passive sampling (C_{WT}) was possible for five of the test substances including γ-HCH, anthracene, phenanthrene, fluoranthene and pyrene. For these substances, limit of quantification was exceeded and good reproducibility was achieved in both methods. The ratio of concentrations C_{WG} to C_{WT} for each analyte ranges from 0.8 to 2.5, which is a good agreement, despite limitations in a direct comparison.

5. Conclusions

This study demonstrated that, within the range of tested experimental conditions, the MESCO sampling was robust and not affected by the variation of the water flow. This fact does not exclude the possibility of an effect of hydrodynamics under exposure conditions very different from those tested in this study, e.g. in highly turbulent water. Because it appears impractical to conduct calibration studies for all possible exposure scenarios (e.g. for many combinations of temperature and water turbulence), it is very useful to know that the exchange kinetics of analytes between MESCO sampler and water is isotropic. The implication of the isotropic exchange kinetics is that, by knowing the behavior of either the absorption or desorption, the opposite one will also be understood. The measurement of in situ exchange rate constant k_e of a particular compound, and the knowledge of its corresponding distribution coefficient K_{SW}, enables to estimate the in situ sampling rate using Eq. (5). This study demonstrates that the error of such estimate is within an acceptable limit, if good quality data are available. From this point of view, the availability of precise PDMS/water distribution coefficient values is crucial. The application of PRCs to estimate site-specific sampling rates of POPs should generally improve the accuracy of water concentration estimates and reduce the amount of calibration data required for the use of this passive sampling device.

Recently, attempts were made to replace the GERSTEL-Twister™ bar used in MESCO construction in this study by a cheaper material, which can be discarded if contaminated, eliminating the need for expensive cleaning. Silicone rods have been identified as a good alternative, and their applicability for extraction of chlorobenzenes, polychlorinated biphenyls and PAHs from water samples (Montero et al., 2004; Popp et al., 2004). Note that the thermal desorption of POPs (and of many other accumulated analytes) from the collector phases can be substituted by solvent microextraction (Popp et al., 2004). This approach offers several advantages: (a) there is no need to use the thermodesorption/cold injection system before the gas chromatographic analysis; (b) it enables repeated instrumental analysis of the sample and (c) the liquid extracts can be subject to bioassay screening. Further tests to use this inexpensive and flexible silicon material in passive sampler construction are recently performed at the UFZ Centre for Environmental Research in Leipzig, both in flow-through calibration experiments, and in field trials.

The application of regenerated cellulose in MESCO construction principally enables the widening of the applicability to a broader polarity range of pollutants including hydrophilic substances ($\log K_{OW} < 4$). However, this material has relatively low chemical and thermal stability and is subject to degradation, which potentially leads to the damage of the sampler in the field. An alternative membrane material with similar properties to regenerated cellulose, but resistant against degradation in the environment is needed. The replacement of cellulose in MESCO construction by non-porous polymeric membranes such as low-density polyethylene (LDPE) does not seem to be a viable solution. The sampling rates, and thus also the sensitivity, of devices fitted with LDPE are much lower than those of the device used in this study and the mass transfer of analytes in such devices is also more complicated than in the device described here (Wennrich et al., 2003). A promising alternative can be polypropylene-membrane bags with a wall thickness of 30 μm that have been successfully applied for the membrane-assisted solvent extraction of different compound classes within a wide range of pH (Hauser et al., 2004; Schellin and Popp, 2005).

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Calibration of the Chemcatcher passive sampler for the monitoring of priority organic pollutants in water

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A calibration method and data that are required for in situ measurement of the time-weighted average concentrations of hydrophobic priority organic pollutants in water using Chemcatcher passive sampling device are presented.

Abstract

An integrative passive sampler consisting of a C_{18} Empore® disk receiving phase saturated with *n*-octanol and fitted with low-density polyethylene diffusion membrane was calibrated for the measurement of time-weighted average concentrations of hydrophobic micropollutants, including polyaromatic hydrocarbons and organochlorine pesticides, in water. The effect of temperature and water turbulence on kinetic and thermodynamic parameters characterising the exchange of analytes between the sampler and water was studied in a flow-through system under controlled conditions. It was found that the absorption of test analytes from water to the sampler is related to their desorption to water. This allows for the in situ calibration of the uptake of pollutants using offload kinetics of performance reference compounds. The sampling kinetics are dependent on temperature, and for most of the tested analytes also on the flow velocity. Sampler–water partition coefficients did not significantly change with temperature.
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Keywords: Calibration; Chemcatcher; Passive sampling; Performance reference compounds; Priority organic pollutants; Semi-permeable membrane devices; Water monitoring

1. Introduction

There is an increasing requirement for the monitoring of water quality across Europe, with particular emphasis on the contaminants in the list of priority pollutants contained in the Water Framework Directive (WFD) and in the various water conventions, e.g. Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR). Among priority pollutants, persistent organic pollutants (POPs), such as organochlorine pesticides, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) are of great importance. Due to their low aqueous solubilities and hydrophobic nature, the concentrations of POPs dissolved in water are very low, usually less than 1 part per billion. POPs bind strongly to particulate matter and are finally deposited in the sediment. The fraction of the chemical truly dissolved in water is very small. Nevertheless, because organisms often bioconcentrate these low levels of contaminants in water to relatively high levels in their tissues, determination of the dissolved portion of environmental pollutants is critical for assessing the potential for detrimental biological impacts.

The only monitoring method legally accepted for this purpose is spot or grab sampling. This is both expensive and labour intensive, and measures only instantaneous concentrations, which may not be representative of long-term average pollutant concentrations. There is a number of methods that attempt to overcome these problems, e.g. on-line continuous monitoring, biomonitoring or passive sampling (Koester et al., 2003). Among these methods passive sampling technology has the

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potential to become a reliable, robust, and cost-effective tool that could be used in monitoring programmes across Europe (Namiesnik et al., 2005). A range of passive sampling devices have been developed for the monitoring of organic pollutants in water. Some of these include the lipid-filled semi-permeable membrane device (SPMD; Huckins et al., 1993), solvent-filled dialysis membrane samplers and the membrane-enclosed sorptive coating (MESCO; Vrana et al., 2001) for non-polar compounds and the polar organic chemical integrated sampler (POCIS; Alvarez et al., 2004) for polar compounds. The design and field performance of a wide range of passive samplers for organic micropollutants has been reviewed recently (Namiesnik et al., 2005; Stuer-Lauridsen, 2005; Vrana et al., 2005a).

We previously developed a novel passive sampling system for the measurement of time-weighted average (TWA) concentrations of micropollutants in aquatic environments (Kingston et al., 2000; Vrana et al., 2005b). The sampler is based on the diffusion of target compounds through a membrane and the subsequent accumulation of these pollutants in a bound, solid-receiving phase. Accumulation rates and selectivity are regulated by the choice of both the diffusion-limiting membrane and the solid-phase receiving material. One of the prototypes was designed for the sampling of non-polar organic compounds with log octanol/water partition coefficient (log K_{OW}) values greater than 3 (Kingston et al., 2000). This system uses a 47 mm C_{18} Empore® disk as the receiving phase and a low-density polyethylene (LDPE) diffusion-limiting membrane. The C_{18} Empore® disk has a very high affinity and capacity for the sampled non-polar organic pollutants.

For a good sampler performance, a sufficiently high sampling rate, i.e. the rate at which the sampler accumulates chemicals from water is essential. High sampling rates are needed especially for non-polar chemicals due to their low concentrations in the water column. The sampling rate depends on the physicochemical properties of the analyte, the environmental conditions and the sampler design.

Recently, the optimisation of the sampler design has been reported (Vrana et al., 2005b). This involved the improvement of sampling characteristics including the enhanced sampling kinetics and precision by decreasing the internal sampler resistance to mass transfer of hydrophobic organic chemicals (log $K_{OW} > 5$). This was achieved by adding a small volume of *n*-octanol, a solvent with high permeability (solubility × diffusivity) for target analytes, to the interstitial space between the receiving sorbent phase and the polyethylene diffusion-limiting membrane.

The aim of this study was to characterise the effect of temperature and hydrodynamics on kinetic and thermodynamic parameters characterising the exchange of analytes between the sampler and water in order to calibrate the passive sampler for the measurement of TWA concentrations of non-polar organic pollutants.

2. Theory

A number of authors have presented models describing the uptake kinetics of organic contaminants in water by passive sampling devices constructed from a receiving phase and a diffusion-limiting membrane (Johnson, 1991; Huckins et al., 1993; Gale, 1998). A comprehensive overview of theory and modeling of organic contaminant exchange between SPMDs and water has also recently been published by Huckins et al. (in press). The principles of analyte uptake described for SPMDs are also applicable to the sampler described in this study.

The mass transfer of an analyte from water to the sampler includes diffusion, interfacial transport steps across several barriers (compartments), including the stagnant aqueous boundary layer, possible biofilm layer, the diffusion-limiting membrane, and finally the receiving phase, which is in this case an *n*-octanol-saturated C_{18} Empore® disk. Assuming a rapid establishment of steady-state conditions, the flux of an analyte is constant and equal in each of the individual compartments. This also assumed that sorption equilibrium exists at all compartment interfaces. The resistances of each barrier to the mass transfer of analytes are then additive and independent (Scheuplein, 1968; Flynn and Yalkowsky, 1972).

Applying the assumptions given above, it can be shown that the amount of the chemical accumulated from water in the receiving phase of the sampler with constant analyte concentration can be described by the following equation:

$$m_D(t) = m_D(0) + (C_W K_{DW} V_D - m_D(0)) \times \left[1 - \exp\left(-\frac{k_o A}{K_{DW} V_D}\right) t\right] \quad (1)$$

where m_D is the mass of analyte in the receiving phase, $m_D(0)$ is the analyte mass in the receiving phase at the start of exposure, C_W represents the water concentration during the deployment period, K_{DW} is the receiving phase–water distribution coefficient, V_D is the volume of the receiving phase, k_o is the overall mass transfer coefficient, A is the membrane surface area, and t equals time.

The overall mass transfer coefficient k_o is affected by the diffusion of analytes in the individual layers (i.e. aqueous boundary layer, diffusion-limiting membrane and the receiving phase) and by their partitioning into the LDPE membrane and receiving phase; since accumulation of hydrophobic analytes is expected also in the membrane material (Huckins et al., 1999). From theory (Scheuplein, 1968; Flynn and Yalkowsky, 1972), the overall mass transfer resistance to the uptake of a chemical is given by the sum of particular barrier resistances to mass transfer.

Optimisation of the sampler design has been performed previously with the aim to minimise the internal resistance of the sampler to mass transfer of hydrophobic analytes (Vrana et al., 2005b). Thus, the contribution of the receiving phase to the overall resistance should be negligible.

The coefficient in the exponential function is referred to as the overall exchange rate constant k_e.

$$k_e = \frac{k_o A}{K_{DW} V_D} \quad (2)$$

In the initial uptake phase, when the exponential term is very small ($\ll 1$), chemical uptake is linear or integrative. Thus, in the linear region Eq. (1) can be reduced:

$$m_D(t) = m_D(0) + C_W k_o A t \quad (3)$$

For practical applications, Eq. (3) can be rewritten:

$$m_D(t) = m_D(0) + C_W R_S t \quad (4)$$

where R_S is the sampling rate of the system, representing the equivalent extracted water volume per unit of time.

$$R_S = k_o A = k_e K_{DW} V_D \quad (5)$$

Adding chemical standards called performance reference compounds (PRCs) to the receiving phase prior to exposure of the passive sampler has been suggested as a means to calibrate the exchange rates in situ (Booij et al., 1998; Huckins et al., 2002). The use of PRCs can be based on the evidence, that analyte uptake and offload kinetics are governed by the same mass transfer law, and obey first order isotropic exchange kinetics. When PRCs are used that are not present in water ($C_W = 0$) and isotropic exchange kinetics applies, Eq. (1) reduces to:

$$m_D(t) = m_D(0) \exp(-k_e t) \quad (6)$$

which is a one-parameter equation, since the amount of PRC added to the sampler ($m_D(0)$) is always known.

3. Materials and methods

3.1. Physicochemical properties of substances

Values of physicochemical properties, including octanol/water partition coefficients ($\log K_{OW}$), aqueous solubilities (S) and aqueous diffusion coefficients (D_W) are summarised in Table 1S in the supplementary information (Mackay and Shiu, 1992; Mackay et al., 1992). Values of aqueous D_W were estimated using Hayduk and Laude equation (Lyman et al., 1982).

3.2. Materials and chemicals

C_{18} Empore® disks (47 mm diameter) were purchased from Varian Inc., Walton-on-Thames, UK. LDPE membrane material (40 μm thick) was obtained from Fisher Scientific, Loughborough, UK. The solvents (HPLC grade quality or equivalent), acetone, ethyl acetate, methanol, *n*-hexane, *n*-octanol, *n*-nonane, 2,2,4-trimethyl pentane, and water were obtained from Fisher Scientific. Certified pure (purity >98% in all cases) reference standards of the test compounds, surrogates, and internal standards were obtained from Qm_x Laboratories, Saffron Walden, UK. Certified external calibration solutions of target analyte mixtures at a concentration of 10 μg mL^{-1} in cyclohexane were obtained from Qm_x Laboratories.

3.3. Sampler design

The patented design of the passive sampler has been described previously (Kingston et al., 2000; Vrana et al., 2005b). Briefly, the sampling device consists of a PTFE body containing a C_{18} Empore® disk as a receiving phase. A 40-μm thick LDPE disk (47 mm diameter) of diffusion-limiting membrane is placed on the top of the receiving phase. A small volume (450 μL) of *n*-octanol, a solvent with high permeability (solubility × diffusivity) for target analytes, is added to the interstitial space between the receiving sorbent phase and the diffusion-limiting membrane. The PTFE body parts (components 1 and 4, Fig. 1) supported both the receiving phase (component 2, Fig. 1) and the diffusion-limiting membrane (component 3, Fig. 1) and sealed them in place. The sampler was sealed by means of a screw cap (component 5, Fig. 1) for storage prior to use. The original design used by Kingston et al. (2000) contained a protective mesh that prevented mechanical damage to the surface of the membrane. Preliminary field studies showed some disadvantages (adsorption of analytes, fouling); therefore, the mesh was not used in this calibration study.

3.4. Preparation of the sampler

C_{18} Empore® disks were conditioned by soaking in methanol for 20 min until translucent and then stored in methanol until required. The Empore® disks were prepared in a 47-mm diameter disk vacuum manifold platform (Varian Inc.). Perdeuterated polycyclic aromatic hydrocarbons were utilised as PRCs. For loading the Empore® disks with PRCs, 10 mL methanol was slowly passed through the disk, followed by 20 mL ultrapure distilled water. Aqueous solution (500 mL) of PRCs, containing 5 μg L^{-1} of each of the following chemicals: D_{10}-biphenyl, D_{10}-acenaphthene, D_{10}-phenanthrene, D_{10}-pyrene and D_{12}-benzo[*a*]anthracene was filtered through the disk. A vacuum was applied for 30 min to ensure that the disc was completely dry. The extraction efficiency of the loading procedure for individual PRCs was between 50 and 100%, with the maximum coefficient of variation of 9%.

The Empore® disk was then put on the sampler PTFE support disk (component 4, Fig. 1). One millilitre solution of *n*-octanol in acetone (45% v/v) was applied. The acetone was allowed to evaporate from the disk for 10 min in the fume cupboard. The resulting volume of *n*-octanol was 450 μL. The LDPE membrane (pre-cleaned by soaking for 24 h in *n*-hexane and dried) was put on the top of the Empore® disk. Any air bubbles were smoothed away from between the two layers by gently pressing the top surface of the membrane using a clean paper tissue. The PTFE supporting disk was placed in the sampler body and fixed in place to form a watertight seal between the membrane and the top section of the sampler.

3.5. Volume of the receiving phase and the membrane

To calculate the distribution coefficients of compounds among the sampler compartments it is necessary to know the volumes of media of the receiving phase and membrane, i.e. the combined volume of C_{18} material and the

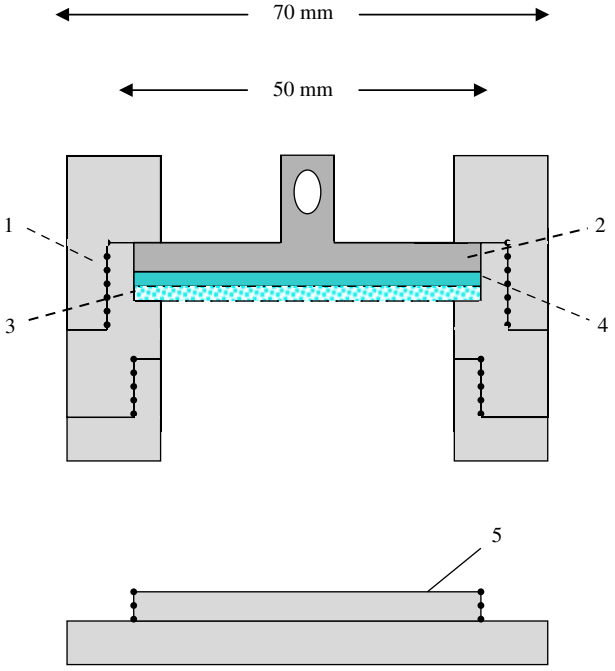

Fig. 1. Schematic diagram of the Chemcatcher passive sampling device.

n-octanol, and the LDPE membrane material. The receiving phase was not homogenous but consisted of a solid sorbent and a liquid (*n*-octanol) in a porous PTFE matrix. According to the manufacturer's documentation accompanying the Empore® disks, they consist of 10% (w/w) of PTFE fibres with 90% (w/w) of silica particles, chemically bonded octadecyl (C_{18}) groups. The organic carbon content of this silica–C_{18} material is 17% (w/w) (Verhaar et al., 1995), so 1 g of the silica–C_{18} material contains 0.20 g of C_{18}. Assuming the density of the bonded C_{18} is equal to that of octadecane (0.78 g mL^{-1}), 1 g of the disk contains 0.25 mL of the C_{18} material. The 47 mm disk weighs 572 mg, so the volume of C_{18} in the whole disk is 144 μL (Green and Abraham, 2000). The thickness of the disk is 0.5 mm. Four hundred and fifty microlitres of *n*-octanol was added to the disk before sampler assembly. The resulting total combined volume of the receiving phase V_D is 600 μL. The 47-mm diameter LDPE membrane disk used for construction of the sampler weighs 55 mg. The thickness (δ_m) of the LDPE membrane disk is 35 μm. The density of LDPE is 0.91 g cm^{-3}; the resulting volume of the membrane disk is 60.4 μL.

3.6. Exposure experiments

In each experiment up to 14 passive samplers were exposed in a constant concentration flow-through exposure system. This system was devised to allow calibration of the sampling devices to be made under controlled conditions of temperature, water turbulence, and analyte concentration. It was operated in a temperature-controlled dark room. The system consisted of a 20 L glass tank with an overflow to waste. The water and the solution of test analytes dissolved in methanol were pumped into the exposure tank separately at known and controlled rates. Water was fed to the exposure tank using a peristaltic pump at 2 L h^{-1}, allowing a complete renewal of water in the tank every 10 h. Test chemicals were dissolved in methanol (30 μg L^{-1}) and the appropriate amounts of stock solution (100 μL min^{-1}) were delivered into exposure tank using a second peristaltic pump. A nominal concentration of 100 ng L^{-1} for each analyte was maintained throughout the experiment. The resulting methanol concentration in the exposure water did not exceed 0.5% (v/v). Prior to each exposure, the apparatus was operated for a minimum of 48 h without samplers to allow for stabilization of the water concentration of analytes. To ensure uniform hydrodynamic conditions in the vicinity of all samplers, 14 samplers were placed on two horizontal turntables (seven samplers on each turntable) at two levels (Fig. 2). The turntables were vertically interconnected by a shaft, which was driven by an overhead stirrer. All parts of the turntable in contact with water were made of PTFE to prevent excessive sorption of chemicals. The carousel device was placed in the glass tank. The carousel device was rotated at a selected stirring speed using an overhead stirrer. The exposures lasted 14 days, during which duplicate samplers were removed at set time intervals and analysed (see below) to determine the concentrations of accumulated test chemicals. Every time a sampler was removed for analysis it was replaced by an empty (without a disk and membrane) sampler body. This was necessary to keep constant hydrodynamic conditions within the calibration system.

No carousel device was used in experiments, where conditions were set as "no stirring". Samplers were placed at the bottom of the exposure tank. To prevent the forming of concentration gradients in the calibration tank during the exposure, water in the tank was slowly stirred using a stainless steel propeller stirrer (diameter 60 mm) at 30 rpm.

Following exposure, the devices were removed and dismantled, and the receiving phase of the exposed system was extracted to determine the mass of each analyte and PRC present in the sampler. In addition, a minimum of three samplers were analysed prior to exposure to determine the initial levels of PRCs and analytes in blank samplers.

Duplicate samples (500 mL each) of water from the outlet of exposure tank were also taken at each time the samplers were removed, and the concentration of test analyte in the water determined (Vrana et al., 2005b).

3.7. Experimental design

The calibrations were set up to measure the uptake of target analytes at different combinations of temperatures and hydrodynamic conditions in a full factorial design. The calibration data were gathered in order to determine the sampling parameters and to observe how they are affected by environmental conditions. Each factor (temperature, stirring speed) was tested at three levels, resulting in the total number of nine experiments. The experimental conditions of individual exposures are given in Table 1.

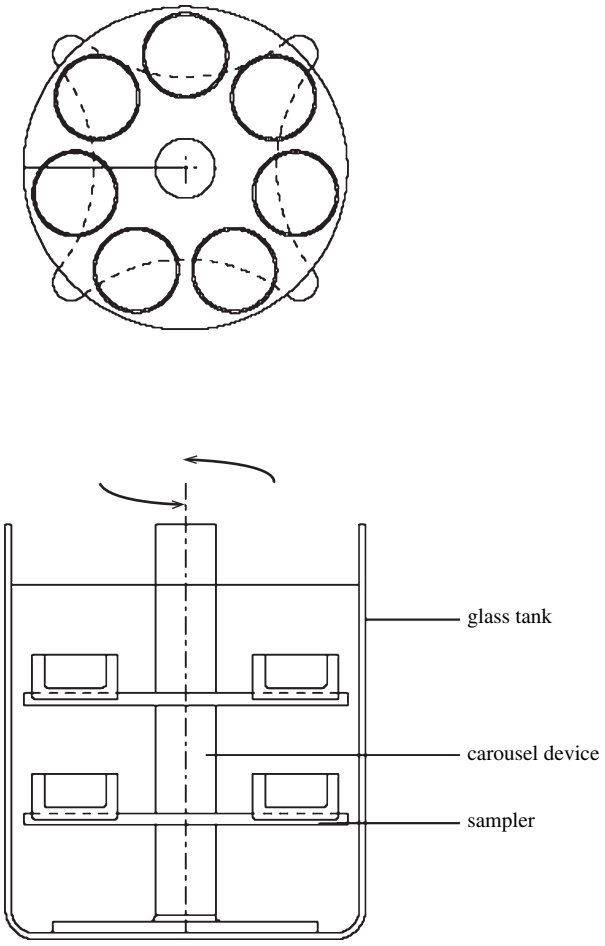

Fig. 2. Exposure tank and a carousel device used in flow-through calibration of passive sampling devices.

3.8. Extraction of analytes from passive samplers and from water

After exposure the sampler was carefully disassembled and the compounds were extracted from the Empore® disk using a two-step extraction procedure with organic solvents, described by Vrana et al. (2005b).

The test analytes in water samples taken from the outlet of flow-through exposure system were extracted using solid-phase extraction (SPE) on Bondelut C_{18} LO SPE cartridges (3 mL/200 mg sorbent; Varian Inc.). The extraction procedure has been described by Vrana et al. (2005b).

3.9. Instrumental analysis

The concentrations of all target analytes in water and sampler extracts were quantified using GC/MS as described by Vrana et al. (2005b). Analysis was performed with a 6890A series GC equipped with a mass-selective detector 5973 (Agilent Technologies, Bracknell, UK).

3.10. Data processing

The experimental time course accumulation rates of individual test substances on the Empore® disks were fitted by linear regression analysis using

Table 1
Summary of sampler flow-through exposure experiments

	Experiment no.								
	1	2	3	4	5	6	7	8	9
Temperature (°C)	6			11			18		
Exposure period (h)	0–336	0–336	0–336	0–284	0–264	0–336	0–336	0–360	0–360
Rotation speed (min^{-1})	0	40	70	0	40	70	0	40	70
Linear sampler velocity ($cm\ s^{-1}$)[a]	0	40	70	0	40	70	0	40	70
No. of samplers analysed	16	16	16	15	14	12	17	18	18

[a] Linear velocity v_S was calculated as $2\pi rf$, where r is the radius between the centre of the calibration carousel and the centre of the sampler and f is the rotation speed.

Eq. (4). The adjustable parameters were the intercept ($m_D(0)$) and the slope ($C_W \times R_S$) of the uptake curve $m_D = f(t)$. Quality of the fit was characterised by the standard deviations of the optimised parameters, as well as the correlation coefficient adjusted for the degrees of freedom (r^2 adjusted), the fit standard deviation, and the Fisher test criterion on the accuracy of the model. The sampling rates R_S for individual test compounds were calculated by dividing the slope of the linear uptake curve by the mean aqueous analyte concentration during the exposure period. The required variances of R_S values were calculated from the coefficients of variation (relative standard deviations) of the uptake slope parameters and the concentrations in the aqueous phase, which were obtained according to the law of error propagation.

The release of PRCs from the sampler was fitted by non-linear regression analysis using Eq. (6) with $m_D(0)$ and k_e as adjustable parameters. Quality of the fit was characterised by the standard deviations of the optimised parameters, as well as the correlation coefficient adjusted for the degrees of freedom (r^2 adjusted), the fit standard deviation, and the Fisher test criterion on the accuracy of the model.

4. Results and discussion

4.1. Flow-through exposures

The performance of the sampler was tested by exposure to constant concentrations of test chemicals in a continuous flow-exposure tank. Concentrations of the analytes in water (C_W) and the amounts accumulated in the receiving disk (m_D) were two parameters measured regularly during the continuous flow-exposures. During exposure the water concentration was held constant, and this was confirmed by analyses of water samples. Characteristic analyte uptake curves for the sampler are shown in Fig. 3.

Satisfactory linear regression fits of the Eq. (4) to the uptake data of analytes from water to the sampler discs were obtained for all test compounds in all experiments.

4.2. Sampling rate

The sampling rates R_S obtained in flow-through exposure experiments conducted at 100 $ng\ L^{-1}$ nominal water concentration and various linear flow velocities and temperatures are shown in Tables 2S–4S in the supplementary information. Over the range of controlled laboratory conditions, the magnitude of R_S values spanned over two orders of magnitude (i.e. from 0.008 for benzo[*a*]anthracene at 18 °C and a stirring speed of 0–1.380 $L\ d^{-1}$ for fluoranthene at 18 °C and a stirring speed of 40 rpm). This range of sampling rates is narrow relative to the broad K_{OW} range of nearly five orders of magnitude.

4.3. PRC offload kinetics

The offload of PRCs from the Empore® disks was fitted by non-linear regression analysis using Eq. (6) with $m_D(0)$ and k_e as adjustable parameters. Characteristic PRC offload curves are shown in Fig. 4 and the results are listed in Tables 5S–7S in the supplementary information.

Satisfactory fits of the first order decay, Eq. (6), to the offload data were obtained for D_{10}-biphenyl, D_{10}-acenapthene, D_{10}-fluorene and D_{10}-phenanthrene. The release of D_{10}-pyrene and D_{12}-benzo[*a*]anthracene from the sampler was too slow to be able to evaluate the kinetics statistically. For these PRCs, the results of the first order decay fits were poor and estimates of k_e values for D_{10}-pyrene and D_{12}-benzo[*a*]anthracene were statistically not significantly different from 0 ($P > 0.05$).

4.4. Verification of isotropic exchange kinetics: absorption versus desorption

When the uptake rate of a target analyte R_S and the exchange rate constant k_e of its deuterated analogue (PRC)

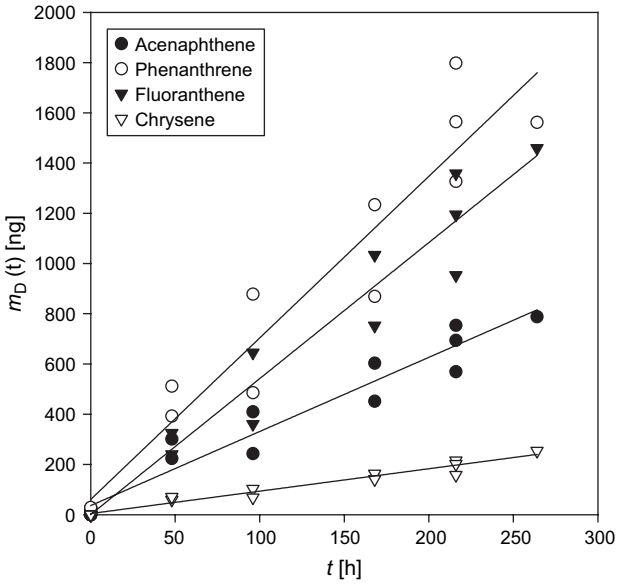

Fig. 3. Typical uptake curves of the analytes in the sampler. Data are presented from the flow-through exposure conducted at 11 °C and the carousel rotation speed 40 min^{-1} (experiment 5). The drawn lines show the linear fits of the data using Eq. (4).

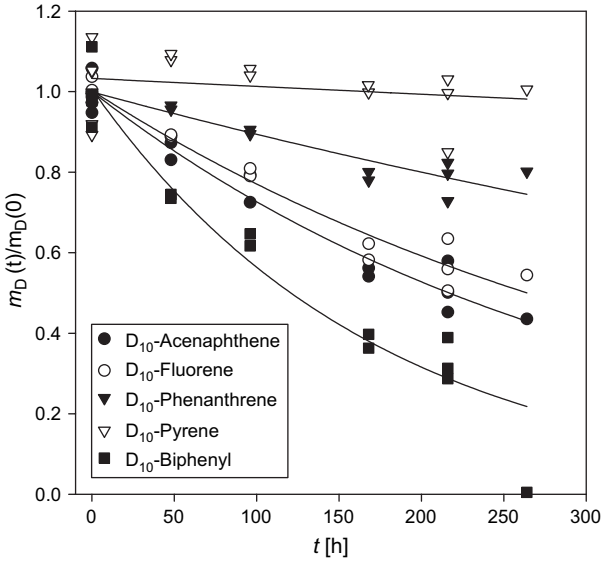

Fig. 4. Typical offload curves of PRCs from the sampler. Data are presented from the flow-through exposure conducted at 11 °C and the carousel rotation speed 40 min^{-1} (experiment 5). The drawn lines show the best fits of the data using Eq. (6).

are measured under the same conditions, the correlation between uptake and offload kinetic parameters can be viewed as a preliminary check of the isotropic exchange kinetics. Fig. 5 demonstrates that, for a broad range of environmental conditions (temperatures and water flow rates), there is a very good correlation between uptake and offload kinetic parameters of analytes and their deuterated analogues.

A good correlation has been found not only for uptake of analytes and offload of their labelled analogue PRCs, but for a broad variety of analyte/PRC combinations (Table 8S, supplementary information). This indicates that the mass transfer

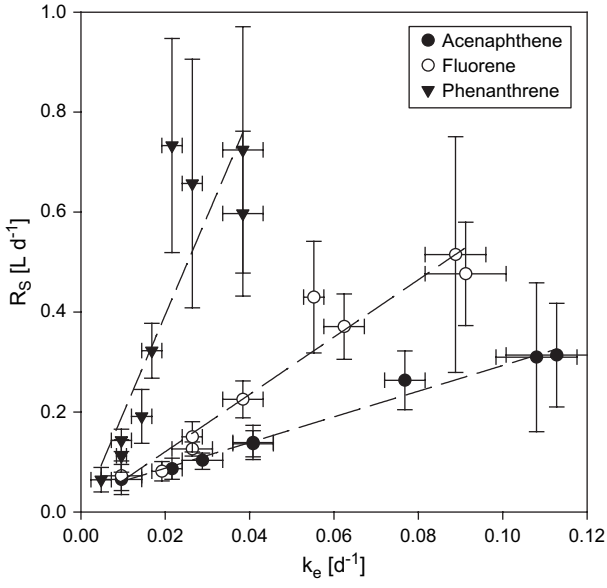

Fig. 5. Correlation between sampling rates R_S of three polycyclic aromatic hydrocarbons and offload rate constants k_e of their perdeuterated analogues (PRCs). The data represent nine flow-through exposures performed at various combinations of temperature and water turbulence.

of many analytes and PRCs is governed by the same law and the isotropy of the uptake (absorption) onto and the offload (desorption) from the sampler. The test is practicable only for compounds with moderate/low affinity for the receiving phase, and for which significant offload can be measured within the time period of the experiment.

A full demonstration of the isotropic exchange kinetics would require a direct comparison of the exchange rate constants k_e of a particular compound obtained from both offload and uptake curves. During the 2 weeks of sampler exposure, the uptake curves of the analytes under investigation remained in the linear uptake phase. Thus, the calculation of k_e from the fit of an exponential function to the uptake data was precluded. A prolonged sampler exposure would enable to measure the whole uptake curve. However, such experiments were not performed in this study because of practical difficulties such as a progressive deterioration of water quality due to increasing microbial activity in the exposure tank during exposures longer than several weeks. Moreover, 14 days is the typical time scale for deployment of the devices in the field.

4.5. Receiving phase–water distribution coefficients

The conventional approach to measuring the distribution coefficient between the receiving phase of the sampler and water is to perform a static exposure of the sampler in water and to measure concentration of the target analyte in water and in the receiving phase after equilibration. This approach is complicated for hydrophobic compounds, where difficulties might occur with the measurement of very low equilibrium concentrations in the water phase. Moreover, a time series of measurement needs to be performed to assure that the partitioning equilibrium has been reached.

In this work, a kinetic approach to the measurement of the distribution coefficients was adopted. In the flow-through exposures, kinetic parameters for several compounds and their perdeuterated analogues (PRCs) were determined at a broad range of exposure conditions. These parameters included the sampling rates R_S for absorption and the desorption rate constants k_e. Assuming the isotropy of the exchange kinetics of chemicals under investigation, and the validity of the model used to describe the kinetics, the value of the apparent receiving phase–water distribution coefficient can be calculated as a ratio of the absorption and desorption transport parameters for a particular compound:

$$K_{DW} = \frac{R_S}{k_e V_D} \tag{7}$$

There are only minimum differences in physicochemical properties of a compound and its deuterated analogue (PRC). Thus, it was assumed that the actual differences in their kinetic parameters were smaller than the experimental error associated with their determination. There were four compounds, for which the absorption and the desorption rate parameters of the corresponding PRC were measured in each experiment. These were acenaphthene, fluorene, phenanthrene and pyrene.

The volume of the receiving phase V_D is estimated to be 600 μL. The K_{DW} value was calculated using Eq. (7) and the required variance was calculated from the coefficients of variation of the uptake and elimination rate parameters. These were obtained according to the law of error propagation. Up to nine values of K_{DW} for each compound were calculated from the data available from individual exposure experiments (Table 9S, supplementary information). Among the exposure conditions that were varied in the experiments, only temperature is expected to affect the magnitude of K_{DW}. Thus, up to three independent measurements of K_{DW} were obtained for each of the three exposure temperatures.

The temperature effect on K_{DW} is shown in Fig. 6. Parameters of the temperature dependence were estimated using the Van't Hoff plot for the temperature range from 6 to 18 °C in the form:

$$\ln K_{DW} = A/T - B \quad (8)$$

where A and B are parameters of the linear dependence characterising the enthalpy and entropy components of the free energy, respectively, and T is the absolute temperature (K).

The elevated variance of some of the calculated K_{DW} values precludes the closer investigation of the temperature effect on the distribution coefficients. Nevertheless, the experimental evidence indicates that K_{DW} values are not significantly affected by temperature in the range from 6 to 18 °C. This enables all log K_{DW} data to be described by a linear empirical function of log K_{OW} (Fig. 7):

$$\log K_{DW} = 1.382 \log K_{OW} - 1.77 \quad (R = 0,\ s = 0.13,\ n = 31) \quad (9)$$

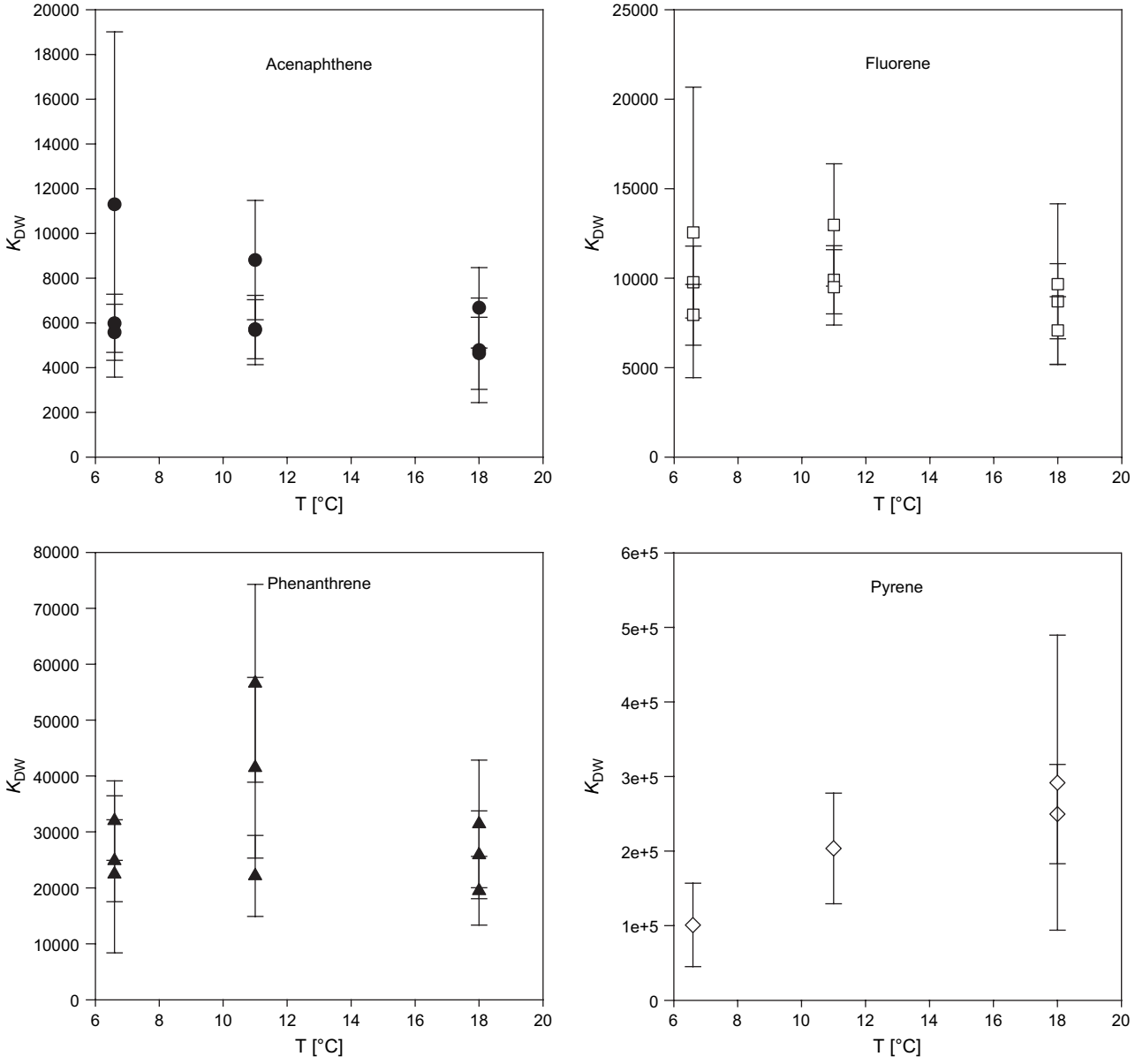

Fig. 6. Temperature dependence of apparent distribution coefficients between the sampler receiving phase (*n*-octanol-saturated C_{18}-Empore® disk) and water K_{DW}.

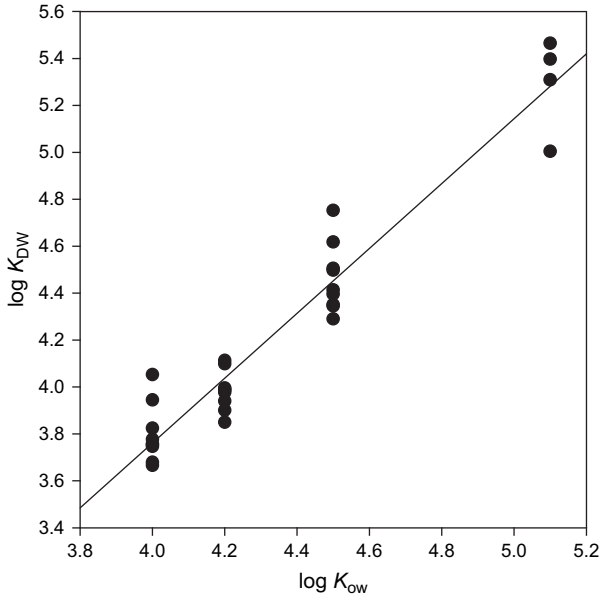

Fig. 7. The apparent receiving phase–water distribution coefficient log K_{DW} as a function of log K_{OW}.

Huckins et al. (in press) have shown that for SPMDs, the log K_{OW} versus log SPMD/water partition coefficient plot for compounds with log $K_{OW} > 5.0$ deviated from linearity. This phenomenon has also been observed for plots of log bioconcentration factor versus log K_{OW} (Connell, 1990). It was not possible to show in our study whether a deviation from linearity occurs for very hydrophobic compounds.

4.6. Time limit for integrative sampling

The chemical uptake into the passive sampler remains linear and integrative approximately until concentration factor reaches half saturation:

$$m_D(t_{50})/V_D/C_W = m_D(\infty)/2 = K_{DW}/2 \quad (10)$$

where t_{50} is the time required to accumulate 50% of the equilibrium concentration. Under these conditions, a linear model (Eq. (4)) can be used to calculate the TWA concentration of the analyte in water. The maximum exposure time t_{50} can be estimated, if both partition coefficient K_{DW} and the sampling rate R_S are known:

$$t_{50} \approx \ln 2\, K_{DW} V_D / R_S \quad (11)$$

According to Eq. (11), t_{50} increases with increasing K_{DW} and with decreasing R_S. It has been shown that the range of sampling rates is relatively narrow over a broad hydrophobicity range. Thus, the main factor determining the t_{50} is the magnitude of the apparent distribution coefficient K_{DW}. However, the t_{50} estimate using this approach is not very precise because the sampling rates in the field differ from those determined under laboratory conditions.

If the isotropic exchange kinetics apply, the first order halftime t_{50} for uptake is mathematically identical to $t_{1/2}$ for offload, i.e. the time required to lose 50% of the initial residue concentration in an exposure scenario, when the analyte is initially applied to the receiving phase ($m_D(0) \neq 0$) and is not present in the water ($C_W = 0$). Thus, t_{50} of an analyte can be approximated by the offload halftime $t_{1/2}$ of a PRC with similar physicochemical properties. $t_{1/2}$ can be calculated using Eq. (12) and $m_D(t_{1/2}) = m_D(0)/2$:

$$t_{50} \approx t_{1/2} = \ln 2/k_e \quad (12)$$

In general, shorter halftimes are predicted at elevated temperatures and under turbulent hydrodynamic conditions, when the exchange kinetics is faster. It is calculated that, for compounds with hydrophobicity similar to D_{10}-biphenyl or D_{10}-fluorene (log $K_{OW} \approx 4$), the sampler would sample integratively during a time period between 1 and 10 weeks, depending on the temperature and turbulence level. For more hydrophobic compounds, this time period can be much longer. For example, the halftime of more than three months is calculated for compounds with log $K_{OW} > 5$.

4.7. Sampling rates: effect of analyte properties

The sampling rate is strongly affected by the physicochemical properties of the compounds. Among the non-polar priority pollutants under investigation, the highest sampling rates were observed for small, moderately hydrophobic compounds: anthracene, phenanthrene, fluoranthene and pyrene. The maximum sampling rates were measured for compounds with log K_{OW} of 4.5. The lowest sampling rates were measured for indeno[1,2,3-*cd*]pyrene, dibenzo[*a*,*h*]anthracene and benzo[*g*,*h*,*i*]perylene; large and extremely hydrophobic compounds. The typical dependence of sampling rates on hydrophobicity is illustrated in Fig. 8.

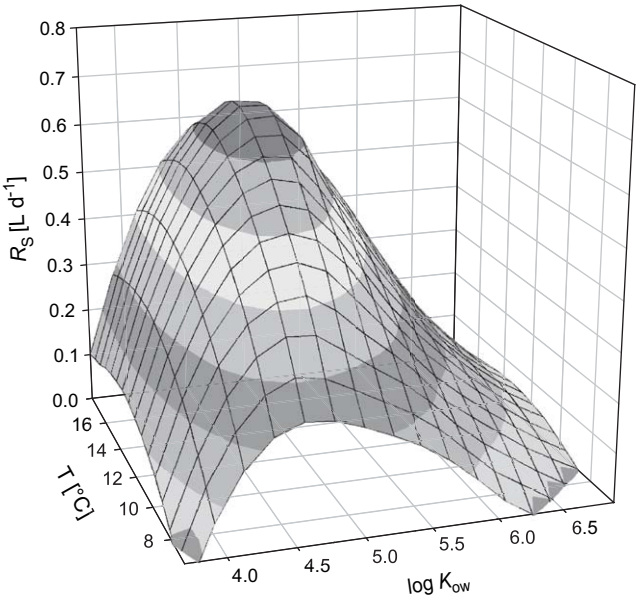

Fig. 8. Effect of temperature and log K_{OW} on analyte sampling rate values at 70 rpm rotation speed to illustrate the response surface.

4.8. Effect of temperature

The relationship between sampling rates of the test analytes and temperature can be compared at three temperatures (6, 11 and 18 °C). In general, the sampling rate increases with the increasing exposure temperature. The typical dependence of sampling rate on temperature is shown in Fig. 9.

We demonstrated that for the four polycyclic aromatic hydrocarbons with log K_{OW} range from 4.0 to 5.1, the apparent receiving phase-water distribution coefficient K_{DW} was not significantly affected by temperature within the range from 6 to 18 °C. Thus, the temperature is expected to affect mainly the magnitude of the kinetic component of the sampling rate (k_e; Eq. (7)).

Typically, increased temperature should enhance mass transfer in all media. The temperature dependence of the sampling rate R_S can then be described by the Arrhenius-type equation:

$$\ln R_S = \ln A - \frac{\Delta E_a}{RT} \quad (13)$$

where R is the universal gas constant (kJ mol^{-1} K^{-1}), A is the pre-exponential factor expressing the maximum sampling rate at infinite temperature, T is the absolute temperature (K) and ΔE_a is the activation energy (kJ mol^{-1}). Values of ΔE_a were obtained by plotting the natural logarithm of R_S against the reciprocal value of absolute temperature ($1/T$). The intercept gives the value of ln A. The activation energy ΔE_a can be calculated by multiplying the slope of the regression line ($\Delta E_a/R$) by R. An analogous equation was used for description of the temperature dependence of the offload rate constant k_e.

The calculation of the activation energy ΔE_a using Eq. (13) was performed on three sets of calibration data, obtained at three levels of water turbulence. Because of a very low magnitude of sampling rates in stagnant water, evident temperature dependence was observed only for data obtained under conditions of turbulent water flow (40 and 70 min^{-1}).

The activation energies range between 20 and 208 kJ mol^{-1}. The average of all ΔE_a values was 93 kJ mol^{-1} with a standard deviation of 56 kJ mol^{-1}. This would correspond to an increase in sampling/offload rate by a factor 5.2 over the temperature range from 6 to 18 °C. For a comparison, Huckins et al. (in press) calculated from the literature data available for SPMDs an average activation energy of 37 kJ mol^{-1}. Thus, the effect of temperature on the Chemcatcher uptake kinetics appears to be more significant than that on SPMD sampling rates.

The activation energies calculated for uptake of acenaphthene, fluorene and phenanthrene were in line with the activation energies calculated for offload of D_{10}-acenaphthene, D_{10}-fluorene and D_{10}-phenanthrene. This is in agreement with isotropic exchange kinetics as well as with the assumptions that the temperature affects mainly the magnitude of the kinetic component of the sampling rate (k_e). Note that the calculation of ΔE_a was not performed for D_{10}-pyrene because of very low magnitude and a poor precision of the k_e values.

4.9. Effect of hydrodynamics

The sampling rates obtained for individual compounds under various flow conditions were compared. With exception of the moderately hydrophobic lindane (log $K_{OW} = 3.7$), a significant increase of sampling rate with increasing flow velocity was observed for all compounds under investigation. This corresponds well with the theory of diffusion through two films in series (Scheuplein, 1968; Flynn and Yalkowsky, 1972), which predicts a switch in the overall mass transfer to the aqueous phase control for hydrophobic compounds. A similar effect of hydrodynamics has been observed and explained also for SPMDs (Vrana and Schüürmann, 2002).

4.10. Method sensitivity

Minimum quantifiable TWA water concentrations were estimated by substituting the limits of quantification in the sampler extracts $m_{D(LOQ)}$ into Eq. (6). The calculated method

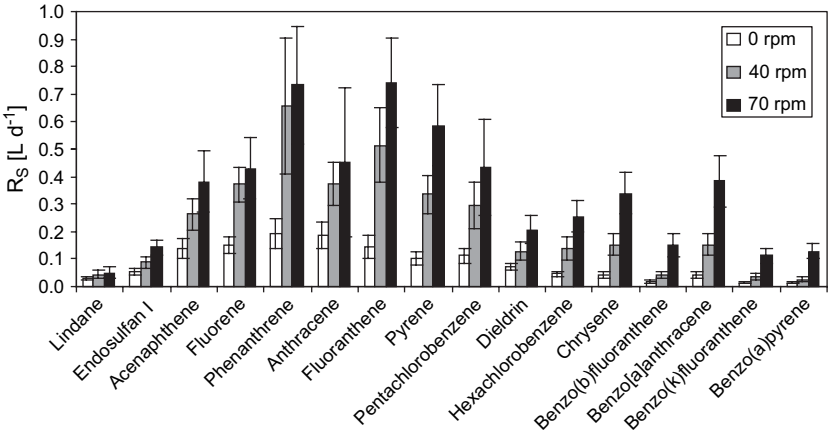

Fig. 9. Effect of hydrodynamics on the analyte sampling rate values. Data are presented from the flow-through exposure conducted at 11 °C and various carousel rotation speeds (0, 40 and 70 min^{-1}; experiments 4, 5 and 6, respectively; see Table 1). The compounds are sorted according to their increasing hydrophobicity.

Table 2
Sensitivity of the passive sampling device

Compound	MLD[a] (ng L^{-1})	MLQ[b] (ng L^{-1})
Acenaphthene	0.5–2.6	1.5–8.8
Fluorene	0.1–0.9	0.4–3.1
Phenanthrene	0.05–0.6	0.2–2.2
Anthracene	0.1–0.9	0.2–3.1
Fluoranthene	0.03–0.7	0.1–2.5
Pyrene	0.1–2.4	0.2–8.0
Benzo[*a*]antracene	0.4–25.2	1.3–83.3
Chrysene	0.2–7.7	0.7–25.2
Benzo[*b*]fluoranthene	0.6–20.6	2.1–68.2
Benzo[*k*]fluoranthene	1.8–21.1	6.1–69.9
Benzo[*a*]pyrene	1.3–18.1	4.3–59.7
Indeno[1,2,3-*cd*]pyrene	10.1	33.4
Dibenzo[*a*,*h*]antracene	2.0–8.5	6.7–27.8
Benzo[*g*,*h*,*i*]perylene	5.4–14.1	17.9–46.9
Pentachlorobenzene	0.1–0.9	0.4–2.9
Hexachlorobenzene	0.05–1.6	0.2–5.3
Lindane	2.2–12.0	7.3–40.1
Endosulfan I	0.6–9.1	2.0–30.5
Dieldrin	0.2–5.3	0.8–17.7

[a] MLD – method limit of detection, expressing the minimum TWA water concentration detectable by the sampler; the range of MLD was calculated for a typical 14 days sampler exposure and typical limits of detection for a GC/MS method using a splitless injection of 1 μL of sampler extract (0.5–6 ng/sampler).

[b] MLQ – method limit of quantification, expressing the minimum time-weighted average (TWA) water concentration quantifiable by the sampler; the range of MLQ was calculated for a typical 14 days sampler exposure and typical limits of quantification for a GC/MS method using a splitless injection of 1 μL of sampler extract (1.7–20 ng/sampler).

limits of quantification depend on the sampling rate R_S, and the method sensitivity increases with increasing sampler exposure period. Moreover, improved sensitivity can be achieved at elevated temperatures and turbulent hydrodynamic conditions. The calculated range of quantification limits for a typical 14-day sampler deployment is shown in Table 2.

5. Conclusions

The study provided a calibration database necessary for reliable integrative sampling of hydrophobic micropollutants, including polyaromatic hydrocarbons and organochlorine pesticides, in water. It characterised the effect of two main environmental variables, temperature and water turbulence, on the sampler performance. The implication of the experiment demonstrating the apparent isotropic exchange kinetics is that, by knowing the behaviour of either the absorption or desorption kinetics, the opposite one will also be understood. This finding can be used practically for in situ recalibration of the sampler, where it is difficult to measure the level of environmental variables (especially turbulence and biofouling), but it is possible to determine the offload kinetics of PRCs. Sampling rates can be calculated from the known offload rate constants k_e of PRCs and their correlations with the sampling rates R_S.

This study contributes to the growing pool of evidence indicating that the PRC concept is widely applicable for the determination of in situ sampling kinetics, required for more accurate measurement of TWA concentrations using integrative passive samplers. The successful application of the PRC approach with other designs of water samplers including SPMDs (Booij et al., 1998; Huckins et al., 2002), silicone strips (Booij et al., 2002) and with membrane-enclosed sorptive coating samplers that use polydimethylsiloxane as a receiving phase (Vrana et al., 2001; Vrana et al., unpublished data) has been demonstrated. In addition this concept has been recently applied to passive air samplers, e.g. tristearin-based samplers (Müller et al., 2000), SPMDs (Söderström and Bergqvist, 2004) and polyurethane foam samplers (Bartkow et al., 2004). Recently, Chen and Pawliszyn (2004) demonstrated the applicability of PRCs for rapid field sampling/sample preparation using solid-phase microextraction (SPME).

Nevertheless, more research is required to incorporate the PRC concept into sampler configurations with very strong analyte retention in the receiving phase, such as the polar organic chemical integrative sampler (POCIS; Alvarez et al., 2004), polar design of the Chemcatcher (Kingston et al., 2000) or samplers characterised by anisotropic analyte exchange kinetics (Persson et al., 2001).

Our future work will focus on demonstrating the practical application of the laboratory calibration data, obtained in this study, for the measurement of TWA water concentration of priority pollutants in the field. Empirical and mechanistic models relating the calibration data to physicochemical properties of the sampled compounds will enable to apply the calibration data for measurement of a broader range of pollutants. More research is necessary to provide on understanding the effect of biofouling on the sampler performance.

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Appendix A. Supplementary information

The supplementary information contains tables of selected physicochemical properties of test analytes; analyte sampling rates and PRC offload rate constants; apparent distribution coefficients between the sampler receiving phase and water and correlation coefficients between the sampling rates of analytes and offload rate constants of PRCs. Supplementary information for this manuscript can be downloaded at doi:10.1016/j.envpol.2005.10.033.

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Modelling and field application of the Chemcatcher passive sampler calibration data for the monitoring of hydrophobic organic pollutants in water

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The exchange kinetics of hydrophobic organic pollutants between passive sampler and water were modelled to enable the measurement of time weighted average concentrations of pollutants. The applicability of the model was tested in a field study.

Abstract

Passive sampling of dissolved pollutants in water has been gaining acceptance for environmental monitoring. Previously, an integrative passive sampler consisting of a C_{18} Empore® disk receiving phase saturated with *n*-octanol and fitted with low density polyethylene membrane, was developed and calibrated for the measurement of time weighted average (TWA) concentrations of hydrophobic pollutants in water. In this study, the exchange kinetics were modelled to obtain a better understanding of the mechanism of the accumulation process and to enable the measurement of TWA concentrations of hydrophobic pollutants in the field. An empirical relationship that enables the calculation of *in situ* sampling rates of chemicals using performance reference compounds was derived and its application was demonstrated in a field study in which TWA aqueous concentrations estimated from sampler data for target analytes were compared with TWA concentrations obtained from spot samples of water collected regularly during the sampler deployment period.
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Keywords: Chemcatcher; Hydrophobic organic pollutants; Passive sampling; Water monitoring

1. Introduction

Passive sampling of organic pollutants in water has been gaining acceptance for environmental monitoring. A range of passive sampling devices has been developed for monitoring organic pollutants in water. These include the lipid-filled semi-permeable membrane device (SPMD; Huckins et al., 1993) and the membrane enclosed sorptive coating (MESCO; Vrana et al., 2001) for non-polar compounds and the polar organic chemical integrative sampler (POCIS; Alvarez et al., 2004) for polar compounds. The design and field performance of a wide range of passive samplers suitable for monitoring organic pollutants have recently been reviewed (Namiesnik et al., 2005; Stuer-Lauridsen, 2005; Vrana et al., 2005a).

We previously developed a passive sampling device (Chemcatcher) for the measurement of time weighted average (TWA) concentrations of pollutants in aquatic environments

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(Kingston et al., 2000; Vrana et al., 2005b). The sampler is based on the diffusion of target compounds through a membrane and the subsequent accumulation of these pollutants in a sorbent-receiving phase. Accumulation rates and selectivity are regulated by the choice of both the membrane and a receiving phase material. One of the prototypes was designed for the sampling of non-polar organic compounds with log octanol/water partition coefficient (log K_{OW}) values greater than three (Kingston et al., 2000). This system used a 47 mm C_{18} Empore® disk as the receiving phase and a low density polyethylene (LDPE) membrane. The C_{18} Empore® disk has a high affinity and capacity for the sampled pollutants.

Despite the wide application of passive samplers, calibration data that relate absorbed amounts of chemicals to their aqueous concentrations are rare. As a result, field measurements using passive samplers are primarily reported in terms of absorbed amounts of chemicals, and only occasionally are the absorbed amounts translated into actual aqueous concentrations. To enable measurement of TWA water concentrations of non-polar organic pollutants, we calibrated the Chemcatcher sampler in a flow-through tank under controlled conditions. The calibration experiments were designed to characterize the effect of physicochemical properties (compound hydrophobicity), temperature and hydrodynamics on kinetic and thermodynamic parameters characterising the exchange of analytes between the sampler and water. The calibration data have been reported recently (Vrana et al., 2006).

In this study, the exchange kinetics of analytes between the sampler and water was modelled to obtain further insight into the mechanism of the accumulation process and to enable the measurement of TWA concentrations of non-polar priority pollutants in the field. An empirical relationship that enables the calculation of *in situ* sampling rates of non-polar chemicals using performance reference compounds (PRCs) was derived. Its application was demonstrated in a field study in which sampler data were compared with spot samples of water, collected regularly during the sampler deployment.

1.1. Theory

The theory of steady-state mass transfer of an analyte from water to the Chemcatcher passive sampler has been described (Vrana et al., 2006). The amount of the chemical accumulated from water in the receiving phase of the sampler with constant analyte concentration can be described by the equation:

$$m_D = m_{D0} + (C_W K_{DW} V_D - m_{D0})\left[1 - \exp\left(-\frac{k_o A}{K_{DW} V_D}\right)t\right] \quad (1)$$

where m_D [kg] is the mass of analyte in the receiving phase, m_{D0} [kg] is the analyte mass in the receiving phase at the start of exposure, C_W [kg m^{-3}] represents the water concentration during the deployment period, K_{DW} is the receiving phase/water distribution coefficient, V_D [m^3] is the volume of the receiving phase, k_o [m s^{-1}] is the overall mass transfer coefficient, A [m^2] is the membrane surface area, and t [s] equals time.

The overall mass transfer coefficient k_o is affected by the diffusion of analytes in the individual layers; i.e. aqueous boundary layer and LDPE membrane as well as by their partitioning into the membrane and receiving phase. The contribution of the receiving phase to the overall resistance is considered to be negligible (Vrana et al., 2005b). From theory (Scheuplein, 1968; Flynn and Yalkowsky, 1972), the overall mass transfer resistance to the uptake of a chemical is given by the sum of particular barrier resistances to mass transfer. The overall resistance ($1/k_o$) is then given by:

$$\frac{1}{k_o} = \frac{1}{k_W} + \frac{1}{k_M K_{MW}} = \frac{\delta_W}{D_W} + \frac{\delta_M}{D_M K_{MW}} \quad (2)$$

where k_W and k_M are mass transfer coefficients in the aqueous boundary layer and the membrane, respectively. Eq. (2) shows that resistance to mass transfer increases with the increasing thickness of the barrier δ and decreases in the diffusion and partition coefficients D and K, respectively.

The coefficient in the exponential function (Eq. (1)) is referred to as the overall exchange rate constant k_e.

$$k_e = \frac{k_o A}{K_{DW} V_D} \quad (3)$$

In the initial uptake phase, pollutant uptake is linear or integrative. For practical applications, Eq. (1) can be reduced and rewritten:

$$m_D = m_{D0} + C_W R_S t \quad (4)$$

where R_S [m^3 s^{-1}] is the sampling rate of the device, and represents the equivalent water volume sampled per unit of time.

$$R_S = k_o A = k_e K_{DW} V_D \quad (5)$$

Adding chemical standards called PRCs to the receiving phase of the passive sampler prior to exposure has been suggested as a means to calibrate the exchange rates *in situ* (Booij et al., 1998; Huckins et al., 2002a). The use of PRCs can be justified providing that analyte uptake and offload kinetics are governed by the same mass transfer law, and obey first order exchange kinetics. When PRCs are used that are not present in water ($C_W = 0$) and isotropic exchange kinetics applies, Eq. (1) reduces to:

$$m_D = m_{D0} \exp(-k_e t) \quad (6)$$

2. Materials and methods

2.1. Physicochemical properties of chemicals

Preferred or selected values of physicochemical properties, including octanol/water partition coefficients (log K_{OW}) and aqueous solubilities (S) were taken from Mackay et al. (1992a,b) and have been summarized previously (Vrana et al., 2006). Values of D_W were estimated using Hayduk and Laudie equation (Tucker and Nelken, 1982). The distribution coefficient between the receiving phase of the sampler and water log K_{DW} can be described by a linear empirical function of log K_{OW} (Vrana et al., 2006):

$$\log K_{DW} = 1.382 \log K_{OW} - 1.77 \quad (R = 0.97,\ s = 0.13,\ n = 31) \quad (7)$$

Booij et al. (2003) showed that the LDPE-membrane partition coefficient $\log K_{MW}$ can be described as a linear function of $\log K_{OW}$, with a temperature-dependent intercept. The intercept was reported to be close to zero for a temperature of approximately 10 °C and we used the predictive equation in form:

$$\log K_{MW} = 0.972 \log K_{OW} \quad (8)$$

2.2. Passive sampler design

The passive sampler construction and preparation have been described previously (Vrana et al., 2005b, 2006). Briefly, the sampler consists of a PTFE body containing a C_{18} Empore® disk (47 mm diameter) as a receiving phase. A 40 μm thick LDPE membrane (47 mm diameter) is placed on the top of the receiving phase. 450 μL of *n*-octanol is added to the interstitial space between the receiving sorbent phase and the membrane. The PTFE body supports both the receiving phase and the LDPE membrane and seals them in place. The calculated total volume of the receiving phase V_D is 600 μL (Vrana et al., 2006).

2.3. Calibration data

The calibration data were obtained in experiments designed to measure the uptake of target analytes and offloading of PRC at different combinations of temperature and hydrodynamic conditions in a full factorial design. The calibration data were gathered in order to determine the sampling parameters for uptake of target analytes (sampling rate; R_S) and for the offload of PRCs (overall exchange rate constants; k_e) and to observe how they are affected by environmental conditions. Briefly, in each experiment up to 14 passive samplers were exposed for up to 14 days in a constant concentration flow-through exposure system, under controlled conditions of temperature, water turbulence, and analyte concentration. Each factor (temperature, stirring speed) was tested at three levels, resulting in the total number of nine experiments. The experiments have been described in detail and the calibration data reported (Vrana et al., 2006).

2.4. Field performance test

To assess the performance of the Chemcatcher for monitoring the target analytes in the field, samplers were deployed in a river. The sampler data were compared with data obtained using spot sampling of water. The sampling site was located in Eijsden at the location of a water quality monitoring station (Rijksinstituut voor Zoetwaterbeheer Integraal Afvalwaterbehandeling – RIZA), near the entry of the River Meuse into The Netherlands. Three replicate Chemcatcher samplers were deployed for 14 days from 24th May to 6th June 2004. During the exposure, the water temperature at the sampling site varied from 18 to 21 °C. On the day of deployment, samplers were transported to the field in a portable coolbox. At the sampling site, transport lids were removed from the samplers and samplers were placed into a protective deployment cage made of a stainless steel perforated sheet with 5 mm square holes. The dimensions of the cage were 350 mm in length, 245 mm in width, 240 mm in height. Samplers were hung in the cage about 20 mm from the top with the membranes facing downwards. The cage was deployed at depth of approximately 1 m below the surface, and was secured to a barge using a rope. To prevent the cage from floating in the current, weights were attached under the cage to a rope 1 m long. On day 14, three replicate samplers were removed from the deployment cage, checked visually for mechanical damage and the extent of biofouling, photographed and sealed with their transportation lids. The samplers were transported to the analytical laboratory in a coolbox.

An additional field control sampler was exposed to air while samplers were being deployed and collected. The field control was processed as the deployed samplers and was used to measure contamination during transportation and handling. Three sampler fabrication controls were also analysed to determine contamination arising from the manufacturing process, sampler components, laboratory storage, processing and analytical procedures, but also to determine the initial concentration of PRCs in the samplers before exposure. The procedures of extraction and instrumental analysis by GC/MS of passive sampler extracts in *n*-octanol have been described (Vrana et al., 2005b). Analyte detection was performed using an MS detector with selected ion monitoring (SIM) of two or three characteristic ions for each compound in both detection and quantification. Detection limits of the method were calculated using the regression line of the chromatographic peak area against as the analyte amount in four external calibration standards in *n*-octanol with lowest concentrations. Detection limit corresponded to the analyte amount for which the peak area is equal to 3 times the standard deviation of the calibration curve intercept.

River water samples were taken by means of specially designed apparatus at the Eijsden monitoring station. This was a continuously running stainless steel tap, fed by a pump. The intake water pump was located at about the same level as the cages with samplers. Six 1-L water samples were taken at regular intervals during the exposure period. Spot samples were filtered through a glass fibre filter (Whatman, 0.7 μm pore size), extracted using three aliquots (100 mL) of dichloromethane. Extracts were reduced in volume using a gentle stream of nitrogen and dried by filtering through sodium sulphate. Quality control samples were also prepared by fortifying pure water with target analytes (added in 0.5 mL acetone solution) and processed as samples. The spiking concentration was 100 ng L^{-1} for each single component. Average percent recoveries of analytes from water ranged between 29% for pentachlorobenzene and 101% for benzo[*b*]fluoranthene, respectively. The concentrations of analytes determined in water extracts were corrected using procedural recovery rates. The final volume was adjusted to 200 μL and samples were analysed by GC/MS for contaminant content.

3. Results and discussion

3.1. Mechanism of analyte uptake

The mass transfer of a given chemical in a passive sampling device includes several diffusion and interfacial mass transport steps across the different barriers that may be present (Vrana et al., 2005a). To obtain a more detailed insight into the mechanism of the accumulation process, the contribution of aqueous and polymer film resistance to the overall mass transfer was characterised. The combination of Eqs. (2) and (3) enables the modelling of the contribution of the resistances of the aqueous boundary layer and the polyethylene membrane to the exchange rate constant k_e (or its reciprocal value $1/k_e$, which is the overall sampler residence time τ):

$$\frac{1}{k_e} = \frac{K_{DW} V_D}{A}\left(\frac{1}{k_W} + \frac{1}{k_M K_{MW}}\right) \quad (9)$$

where k_W and k_M are mass transfer coefficients in the aqueous boundary layer and the polyethylene membrane, respectively. For the purpose of the fit, k_e values of individual compounds in each experiment were calculated first using Eqs. (5) and (7). Eq. (9) was fitted to the data by nonlinear parameter estimation, adopting a log normal distribution of errors, and by estimating the mass transfer coefficients in the form $\log k$ rather than k, to speed up convergence. Details of the parameter estimation are given in supplementary information (Appendix A).

According to the two-resistance film theory, moderately hydrophobic compounds should be accumulated under membrane control. With the exception of lindane, a significant increase of sampling rate with increasing flow velocity was observed for all compounds under investigation. Therefore, a test was performed to determine whether the contribution

of the membrane to the overall resistance to mass transfer as estimated using Eq. (9) was significant. For this purpose the data were fitted to both the model including the membrane contribution and to a simple model in which this was neglected:

$$\frac{1}{k_e} = \frac{K_{DW} V_D}{A} \frac{1}{k_W} \quad (10)$$

The significance of the contribution of the membrane resistance to explaining the variation in overall resistance to mass transfer was then tested using the extra sum of squares principle as described in Booij et al. (1998). Inclusion of the extra parameter (k_M) did not yield a statistically significant reduction in variance and the simpler model was accepted. Thus, with the range of compounds used in our calibration studies it was not possible to calculate the contribution of membrane resistance to mass transfer. The fit results are summarized in Table 1 and shown in Fig. 1.

For hydrophobic compounds under investigation ($\log K_{OW} > 3.5$), the transport kinetics are governed by the aqueous boundary layer. This hypothesis is supported by the decrease in k_e values with increasing K_{OW} and also by the fact that k_W is a function of flow rate/turbulence.

Film theory (Cussler, 1984; Jeannot and Cantwell, 1997) hypothesizes a liquid boundary layer of thickness δ_W, which is postulated to be completely stagnant and non-convected, so that a solute molecule crosses it by only pure diffusion. At steady state, the aqueous phase mass transfer coefficient can be expressed as:

$$k_W = \frac{D_W}{\delta_W} \quad (11)$$

The film theory predicts an increase in k_W at faster flow rates that decrease δ_W.

Table 1
Values of mass transfer coefficients for the aqueous boundary layer (k_W) obtained as optimized parameters of the nonlinear regression analysis of the overall exchange rate constant $\log k_e$ as dependent on the octanol–water partition coefficient $\log K_{OW}$ using Eq. (10). Regression analysis was performed on data obtained at temperatures 6 °C (Fit 1), 11 °C (Fit 2) and 18 °C (Fit 3), respectively

Fit no.	Experiment no.	Temperature [°C]	Stirring speed [rpm]	$\log k_W$[a] [m s^{-1}]	R_S[b] [L d^{-1}]
1	1	6	0	-6.60 ± 0.11	0.04
1	2	6	40	-6.73 ± 0.11	0.03
1	3	6	70	-6.28 ± 0.11	0.08
2	4	11	0	-6.39 ± 0.10	0.06
2	5	11	40	-6.00 ± 0.10	0.15
2	6	11	70	-5.86 ± 0.10	0.21
3	7	18	0	-6.49 ± 0.19	0.05
3	8	18	40	-5.81 ± 0.12	0.23
3	9	18	70	-5.62 ± 0.14	0.36

[a] Statistical indices of the fits are the number of data points $n_1 = 45$, $n_2 = 51$, $n_3 = 38$; the correlation coefficients $r_1 = 0.95$, $r_2 = 0.96$ and $r_3 = 0.94$; and the standard deviations of the fits $s_1 = 0.18$, $s_2 = 0.18$, $s_3 = 0.26$.

[b] The apparent sampling rate R_S of compounds accumulated under aqueous boundary layer was calculated $k_w A$.

The calculations of diffusional flux in a fluid show that the mass transfer coefficient k_W should be a function of the fluid velocity u, in accordance with law u^n for a great variety of geometrical shapes of streamlined bodies and for different types of surface (Levich, 1962; Cussler, 1984). With the exception of the data measured at 6 °C (stirring rates 0 and 40 rpm), the k_W increases when the flow increases in agreement with the film theory (Fig. 2). Unfortunately, the hydrodynamics in the experimental setup used in our study are complicated, since sampler bodies are non-streamlined and affect the current profiles and turbulence in the system. Further, the sampler contains sharp edges that are expected to dramatically change the local hydrodynamic conditions. Therefore, a quantitative prediction of the dependence $k_w = f(u)$ using semi-empirical mass transfer calculations used in chemical engineering is difficult.

For compounds that are accumulated under aqueous boundary layer control, the apparent sampling rates can be calculated as $R_S = k_w A$ (Table 1). Our model does not predict large differences in sampling rates for compounds accumulated under aqueous boundary layer control. In reality, sampling rate decreases with increasing $\log K_{OW}$. One of the factors causing the decrease is that the diffusion coefficient decreases with the increasing molecular size. Huckins et al. (2006) reviewed the literature on mass transfer in fluids and found that the typical empirical relations between the mass transfer coefficient and the diffusion coefficient are of the form $k_W \sim D_W^{2/3}$. Based on this relation, the Chemcatcher sampling rates at $\log K_{OW} = 7$ are expected to be about 80% of the sampling rates at $\log K_{OW} = 4$. We observed that the decrease of sampling rate with increasing hydrophobicity was much sharper. Huckins et al. (2002b) observed a very similar trend for lipid-filled SPMDs and suggested several possible hypotheses to explain the drop in sampling rates for very hydrophobic compounds: (a) the sharp reduction in compound solubility in the polyethylene membrane; (b) potential formation of molecular dimers in the aqueous phase; and (c) the potential overestimation of dissolved aqueous concentrations due to sorption to dissolved organic carbon (DOC). Hypothesis (a) can be rejected, because the observed sampling rates for very hydrophobic compounds were flow-dependent, indicating aqueous boundary layer control over the mass transfer. The most likely explanation is the underestimation of laboratory-derived sampling rates due to analyte sorption to DOC. Unfortunately, the actual DOC concentration was not measured continuously in the calibration studies. Thus, apparently low sampling rates of very hydrophobic compounds can potentially be caused by artefacts in the measurement of the water concentrations of hydrophobic chemicals. Sampling of DOC-bound residues by solid phase extraction (method to analyse water from the exposure tank in the calibration study) cannot be ruled out. However, there seems to be no alternative sampling equipment that would be suitable for accurate routine measurements of dissolved concentrations at a reasonable cost. Further research is necessary to investigate the impact of DOC on calibration data for all passive sampler designs.

In order to estimate the thickness of the aqueous boundary layer (δ_W) at the surface membrane of sampler, aqueous

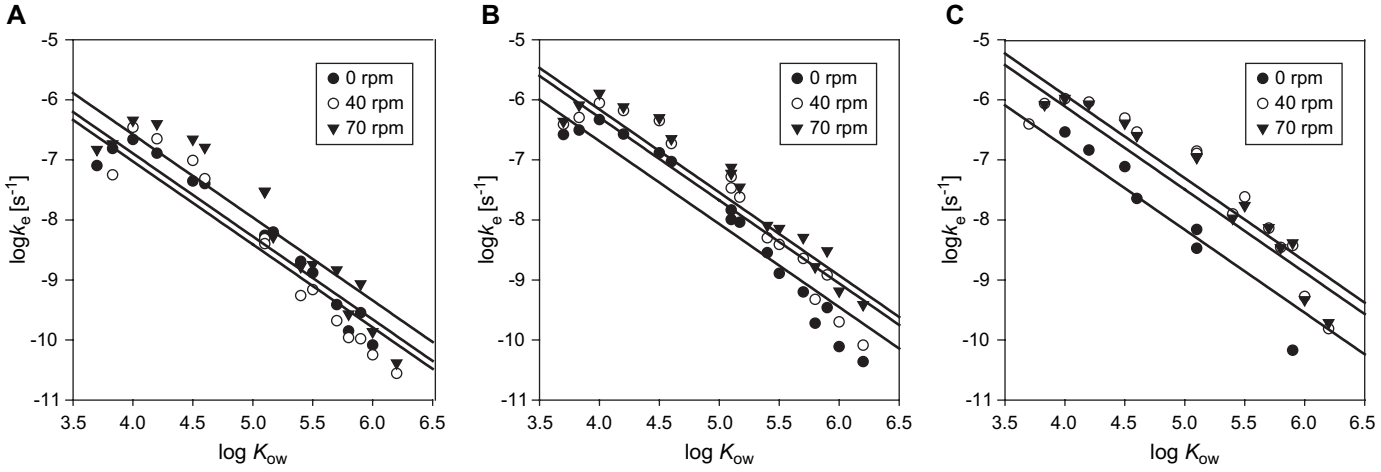

Fig. 1. Dependence of the exchange rate constant k_e on the octanol–water partition coefficient log K_{OW} at 6 °C (panel A), 11 °C (panel B) and 18 °C (panel C) at various calibration carousel rotation speeds. The lines correspond to Eq. (10) with the values of optimized parameters log k_W given in Table 1.

diffusion coefficients D_W of the test compounds at different temperatures were calculated using Hayduk and Laudie equation (Tucker and Nelken, 1982). The median D_W values (3.09, 3.67 and 4.96 × 10^{-6} cm^2 s^{-1} at 6, 11 and 18 °C, respectively) were then used to calculate δ_W from Eq. (11). In environmental situations the effective thickness of the aqueous boundary layer can vary from about 10 μm (extremely turbulent/high flow conditions) to more than 1000 μm (deep stratified lakes of deep seas) (Gale, 1998). The estimated boundary aqueous film thickness in this study decreases from more than 1000 μm to less than 200 μm with increasing flow turbulence. These thicknesses are higher than expected based on the highly turbulent flow conditions in the calibration tank. However, the calculated δ_W reflects the local hydrodynamic conditions in the immediate vicinity of the membrane, located inside a 20 mm deep depression in the sampler body. Thus, the sampler design seems to effectively reduce the convective transport of analytes to the sampler membrane. A modification of the Chemcatcher design that reduces the depth of the cavity in the sampler body would be likely to increase the sampling rates in flowing water, thus improving the sampler's sensitivity, but this would also increase the variation of sampling rates caused by fluctuations in hydrodynamic conditions.

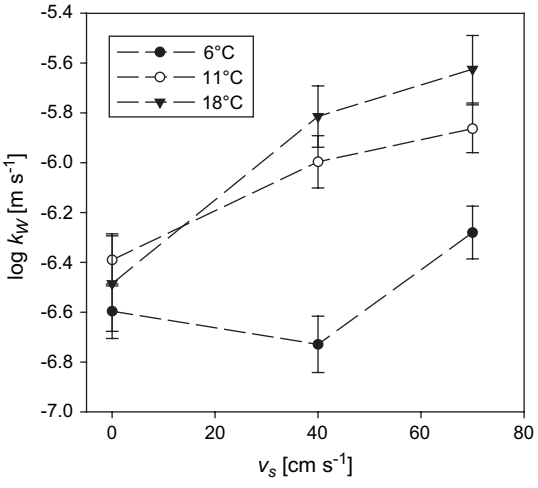

Fig. 2. The average mass transfer coefficient in the aqueous boundary layer k_W as dependent on the linear velocity u_S of the sampler in the flow-through exposure system at various temperatures. Linear velocity u_S was calculated as $2\pi rf$, where r is the radius between the centre of the calibration carousel and the centre of the sampler and f is the rotation frequency.

3.2. Empirical uptake rate model

The mechanistic model explains the differences in sampling rates among compounds and among exposure conditions and discriminates among compounds accumulated under membrane control and aqueous boundary layer control. For a practical application of the calibration data for interpretation of results obtained with the Chemcatcher passive sampler in field studies, it is more convenient to derive, and easier to use the empirical equation for *in situ* estimation of sampling rates.

Huckins et al. (2002b, 2006) showed that for SPMDs differences in exposure conditions cause sampling rates to be shifted by a constant factor for all compounds. In this study, a similar observation was made. The Chemcatcher log R_S vs. log K_{OW} plots have very similar shapes, but show a varying offset for the different experimental conditions. Therefore, a nonlinear regression was performed for all log-transformed sampling rates R_S from the nine calibration experiments using a third order polynomial function of log K_{OW}:

$$Y_{i,j} = P_i + aX_j + bX_j^2 + cX_j^3 \quad (12)$$

where $Y_{i,j}$ is the log R_s of compound j in experiment i, and X_j is the log K_{OW} value of compound j. The parameters a, b, and c characterize the shape of the hydrophobicity profile of the sampling rates, common for all calibration experiments, and the parameters P_1–P_9 represent the offsets for the individual

experiments caused by varying environmental conditions. Sampling rates could be described by:

$$\log R_S = P_i + 22.755\ \log K_{OW} - 4.061\ \log^2 K_{OW} + 0.2318\ \log^3 K_{OW} \quad (R = 0.92,\ s = 0.22,\ n = 134) \qquad (13)$$

Estimates of the optimised parameters a,b,c, and intercepts P_i are summarized in Table 2. A plot of ($\log R_S - P_i$) as a function of $\log K_{OW}$ is shown in Fig. 3. The standard deviation of the fit (0.22 log units) corresponds to an uncertainty factor of approximately 1.7, which is relatively good considering the large differences in exposure conditions tested (temperatures between 6 and 18 °C and a wide range of water turbulence) and the corresponding 172-fold difference in sampling rates. Information on concentrations that are accurate within a factor of two, is still highly relevant for environmental risk assessment purposes. Note that the empirical equation is applicable only for interpolation for compounds with $\log K_{OW}$ values within the range 3.7–6.8.

3.3. Application of the empirical model to estimate in situ TWA concentrations

To assess the applicability of the data obtained with Chemcatcher sampler for measuring TWA water concentrations of non-polar priority pollutants in the field, samplers were deployed for 14 days at a sampling site located at Eijsden in the River Meuse in The Netherlands. The sampler data were compared with spot water samples collected regularly during the sampler deployment period.

The amounts of analytes accumulated in the Chemcatcher during field deployment are shown in Table 3. The fabrication blanks and field blanks contained quantifiable levels of phenanthrene, pyrene and benzo[*a*]anthracene. Quantifiable levels of eight PAHs (acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene and chrysene) were found in samplers exposed in the field for 14 days.

Table 2
Values of optimized parameters of the nonlinear regression analysis of the sampling rate $\log R_S$ [L d^{-1}] as dependent on the octanol–water partition coefficient $\log K_{OW}$ using Eq. (13)

Experiment no.	Temperature [°C]	Stirring speed [rpm]	Parameter	Parameter value[a]
All experiments			a	22.7549 ± 2.4590
All experiments			b	−4.0611 ± 0.4762
All experiments			c	0.2318 ± 0.0302
1	6	0	P_1	−42.28 ± 4.16
2	6	40	P_2	−42.39 ± 4.16
3	6	70	P_3	−41.92 ± 4.16
4	11	0	P_4	−42.03 ± 4.16
5	11	40	P_5	−41.64 ± 4.16
6	11	70	P_6	−41.35 ± 4.16
7	18	0	P_7	−42.36 ± 4.17
8	18	40	P_8	−41.32 ± 4.16
9	18	70	P_9	−41.28 ± 4.16

[a] Statistical indices of the fit are the number of data points $n = 134$, the correlation coefficient $R = 0.92$, and the standard deviation of the fit $s = 0.22$.

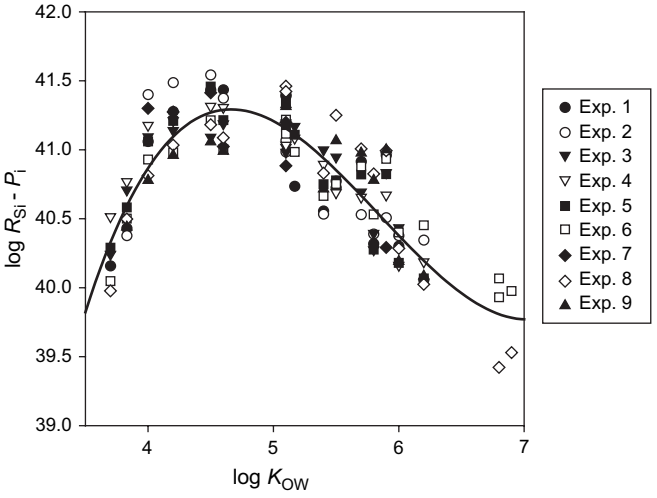

Fig. 3. Sampling rate as a function of compound hydrophobicity (expressed by $\log K_{OW}$). The curve represents the best fit of the experimental data with the empirical model (Eq. (13)). The effect of environmental variables temperature and water turbulence is expressed by the offset of the curve on the *Y*-axis (P_i) and is eliminated in this projection.

The levels of acenaphthene, anthracene and benzo[*a*] anthracene found in field samplers after a 14 day exposure were not significantly different from the fabrication blank values (*t*-test, $\alpha = 0.05$). The maximum coefficient of variation (or relative percent difference, where only duplicate samples were available) of samples with concentrations significantly elevated above the blank levels did not exceed 50%.

The following algorithm was applied to calculate TWA water concentrations from the amounts of analytes accumulated in samplers during field deployment.

3.3.1. Estimation of the in situ exchange kinetics

First, the *in situ* overall exchange rate constants k_e were calculated from the rearranged Eq. (6).

$$k_e = \frac{\ln(m_{D0}/m_D)}{t} \qquad (14)$$

Using the mean PRC concentrations (from triplicate samples) in the fabrication blanks m_{D0}, the mean concentrations in field samplers m_D, and an exposure time of 14 days.

To estimate a statistically significant k_e value, it is necessary to ensure that the PRC concentration found in field exposed samplers is significantly decreased in comparison with the concentration found in fabrication blanks. One of the options to test this is shown in Appendix A. The test showed that there was a significant offload of all PRC excepting D_{10}-pyrene; the D_{10}-pyrene data was not used in later calculations of sampling rates. The k_e values obtained during the field exposure are shown in Table 4.

3.3.2. Calculation of sampling rates of PRCs

Sampling rates R_S of the PRCs were calculated using Eqs. (5) and (7). The calculated R_S values are shown in Table 4.

Table 3
Mean amount of analytes found in passive samplers (ng per sampler) in fabrication blanks, in the field blank and at the sampling site in the River Meuse after 14 days of exposure

Compound	Fabrication blank	CV ($n=3$)[a]	Field blank ($n=1$)	14 days exposure	CV ($n=3$)
Acenaphthene	<2.4		n.d.[b]	n.d.	
Fluorene	<0.9		n.d.	21	29%
Phenanthrene	16	7%	n.d.	59	26%
Anthracene	<0.6		n.d.	n.d.	
Fluoranthene	<0.5		n.d.	34	31%
Pyrene	7	7%	n.d.	38	27%
Benzo[*a*]anthracene	24	7%	n.d.	n.d.	
Chrysene	<1.5		n.d.	4	16%
Benzo[*b*]fluoranthene	<2.9		n.d.	n.d.	
Benzo[*k*]fluoranthene	<2.9		n.d.	n.d.	
Benzo[*a*]pyrene	<2.3		n.d.	n.d.	
Indeno[1,2,3-*c*,*d*]pyrene	<5.4		n.d.	n.d.	
Dibenz[*a*,*h*]anthracene	<1.5		n.d.	n.d.	
Benzo[*g*,*h*,*i*]perylene	<3.2		n.d.	n.d.	
Pentachlorobenzene	<0.8		n.d.	n.d.	
Hexachlorobenzene	<0.5		n.d.	n.d.	
Lindane	<1.5		n.d.	n.d.	
Dieldrin	<1		n.d.	n.d.	

[a] Number of replicates.
[b] n.d. = Not detected.

3.3.3. Calculation of sampling rates of analytes

The PRC-derived sampling rates were fitted to Eq. (13), using the exposure specific effect P_i as the only adjustable parameter (Table 4). The sampling rates of individual compounds were then estimated from Eq. (13) with the optimized value of parameter P_i. This approach is illustrated in Fig. 4.

3.3.4. Applicability of the linear uptake model

The chemical uptake into the sampler remains linear and integrative in the initial period of the exposure until the sorbed amount approaches half of its equilibrium value ($t_{1/2} = \ln 2/k_e$). Our previous study demonstrated that the offload halftime $t_{1/2}$ of a PRC also characterizes the halftime of uptake saturation of an analogue compound (Vrana et al., 2006). In general, $t_{1/2}$ increases with increasing affinity to the receiving phase for the compound; in case of the non-polar Chemcatcher sampler it increases with increasing hydrophobicity of the analyte. The linear uptake model for calculation of TWA water concentrations can be applied only for compounds where the deployment period does not exceed the $t_{1/2}$ value. The $t_{1/2}$ values of PRCs used in the field study are reported in Table 4. The deployment period did not exceed the $t_{1/2}$ for any of the compounds. This indicates that the linear uptake model can be applied for all compounds with $\log K_{OW} > 4$.

3.3.5. Calculation of TWA water concentrations from passive sampler data

TWA concentrations of target analytes at the sampling site in the River Meuse were estimated from concentrations in the exposed passive samplers using the rearranged Eq. (4):

$$C_W = \frac{m_D - m_{Df}}{R_S t} \quad (15)$$

where C_W represents the TWA water concentration during the deployment period, m_D is the analyte mass found in the sampler after field exposure, m_{Df} is the average mass of analyte found in the field blank, R_S is the estimate of the *in situ* sampling rate derived as described above, and t equals exposure time. The TWA concentration was calculated as arithmetic average of the three estimates calculated from analyte amounts found in replicate samplers. The uncertainty level of this estimate was expressed as the standard error of the mean. TWA

Table 4
Summary of *in situ* PRC exchange kinetic parameters and distribution coefficients obtained from the 14-day field exposure in the River Meuse. Optimized parameter P_i of the empirical model (Eq. (13)) characterizes exposure specific conditions and can be used for calculating substance specific sampling rates R_S

PRCs	$\log K_{OW}$	$\log K_{DW}$	% PRC[a]	k_e [d^{-1}]	$t_{1/2}$ [d]	R_S [L d^{-1}]	P_i
D_{10}-Biphenyl	3.90	3.62	52	0.046	15	0.115	
D_{10}-Acenaphthene	3.92	3.65	61	0.036	19	0.095	
D_{10}-Fluorene	4.18	4.01	68	0.027	25	0.166	−41.78
D_{10}-Phenanthrene	4.57	4.55	82	0.014	48	0.301	
D_{10}-Pyrene	5.18	5.39	95	n.s.[b]	175	n.d.[c]	

[a] % of PRC remaining in the sampler after exposure.
[b] Not significant.
[c] Not determined.

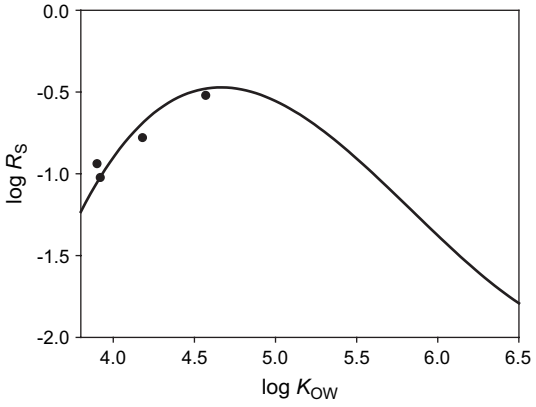

Fig. 4. Estimate of *in situ* sampling rates (log R_S) of PRCs (points) and target analytes (line) at the sampling site in the River Meuse in The Netherlands as a function log K_{OW}. The curve represents the best fit of the *in situ* PRC data with the Eq. (13).

concentrations are shown in Fig. 5. Note that the estimates of TWA water concentrations were calculated only for analytes in samples with concentrations significantly higher than those in the fabrication blanks. If no value is reported, the amount of the analyte found in the field exposed sampler was not significantly higher than that found in the fabrication blank.

3.3.6. Estimation of TWA concentrations from spot sample data

When using spot sampling it is difficult to estimate TWA concentrations in a water body such as a river where levels of the pollutant vary widely in time. An example of temporal changes in water concentrations of phenanthrene found in filtered spot samples is shown in Fig. 5. In order to achieve representative estimates of TWAs it is necessary to use composite samples or large numbers of individual spot samples. Alternative strategies include continuous online methods (e.g. SAMOS systems) or passive samplers. Currently the only method accepted by regulators is spot sampling, and for passive sampling to be accepted for monitoring in a regulatory context it is necessary to establish its reliability compared with spot sampling.

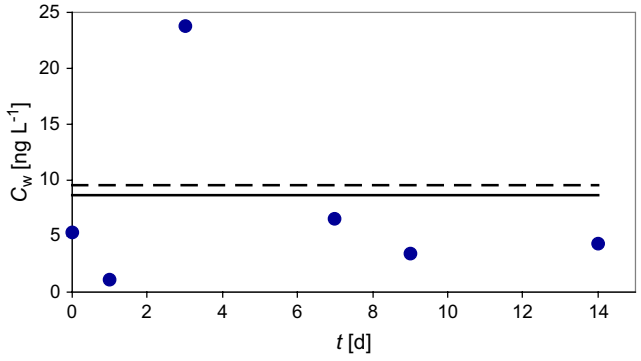

Fig. 5. Concentrations of phenanthrene in filtered spot samples (C_W) from the River Meuse. The full line represents the 14-day TWA concentrations. The dashed line represents the corresponding TWA concentrations estimated using Chemcatcher.

Six spot water samples were taken at regular intervals during the 14 days of sampler exposure. The arithmetic average of the six measurements was taken as the best estimate of the TWA concentration. The uncertainty level on this estimate was expressed as the standard error of the mean.

3.4. Comparison of TWA concentrations determined using passive samplers and spot samples

In the current work a comparison of passive sampling and spot sample TWA concentration data from the field study was possible for five PAHs: fluorene, phenanthrene, fluoranthene, pyrene and chrysene. For the remaining compounds, the levels found either in passive samplers or in spot samples were below the limits of quantification. TWA concentrations of pollutants over the 14-day sampling period, using both methods, are given in Fig. 6.

The maximum difference in TWA concentrations determined using both independent methods was for fluorene, where TWA concentration estimated from the passive sampler data was higher than that calculated from spot sample data. A good (a difference of less than 20%) agreement between the TWA concentrations calculated using both methods was observed for phenanthrene and fluoranthene. TWA concentrations of pyrene and chrysene estimated from passive sampler data were lower (approximately by a factor of two) than the corresponding values calculated from spot sample data.

When comparing the TWA concentrations calculated from spot samples and passive samplers, it is important to consider the differences in contaminant fractions in water that are measured using the two methods. TWA concentrations estimated using passive samplers do not account for the pollutants bound to particles and colloids in water. Water samples filtered through 0.45 μm pore size filters still contain a contaminant fraction that is bound to dissolved organic material (DOM) present in water. The truly dissolved fraction of hydrophobic analytes in water will depend on the level and quality of DOM, which may fluctuate during the sampling period (Burkhard, 2000). Huckins et al. (2006) estimated that a two-fold reduction of the freely dissolved concentration can be expected at DOC level as low as 1 mg L^{-1} for compounds with

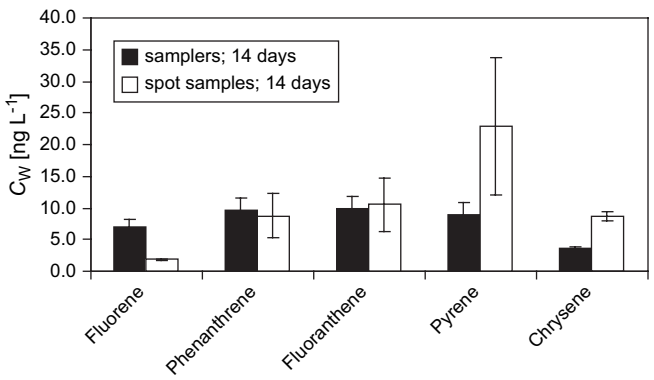

Fig. 6. TWA water concentrations (C_W) for a 14-day period estimated from the levels in Chemcatcher and those measured using spot samples at the sampling site in the River Meuse.

$\log K_{OW} = 7$. These authors also concluded that, because of the uncertainty associated with the calculations of the truly dissolved fraction using available models, this magnitude of reduction could occur for compounds with $\log K_{OW} > 6$ at this DOC level. This is in agreement with our observation of a twofold difference between TWA concentrations determined using spot sampling and passive samplers for pyrene and chrysene ($\log K_{OW} = 5.1$ and 5.7, respectively) at the average DOC level at the sampling site during deployment of 5.0 mg L^{-1}. Another reason for the differences observed between spot sampling and passive sampling may be that higher or lower than average concentrations may have been present during the sampling interval between the individual spot samples. Any change in ambient concentration during these intervals is undetected.

Despite the inherent difficulties, the current study demonstrates that a passive sampling technique delivers reasonable estimates of TWA concentrations for PAHs with $\log K_{OW} < 6$ when compared with the estimates based on repeat spot sampling.

4. Conclusions

This study demonstrated that a calculation of TWA concentrations of waterborne hydrophobic pollutants was possible using the laboratory-derived passive sampler calibration data.

Application of the mechanistic uptake model to the calibration data enabled the interpretation of differences in sampling rates among the test compounds and under varying exposure conditions. The model also permitted the classification of the compounds according to the mechanism of uptake, determined on the basis of its physicochemical properties of the compounds. Compounds with $\log K_{OW} > 3.5$ are accumulated in the Chemcatcher sampler under aqueous boundary layer control. Thus, their uptake kinetics is sensitive to both changes in temperature and water turbulence. Moreover, kinetic performance characteristics of the Chemcatcher sampler are likely to change with modifications to the geometry of the sampler body.

An empirical relationship was derived that enabled the laboratory-derived sampling rates to be corrected for variations in the *in situ* exposure conditions. The correction is made using the information on *in situ* exchange kinetics of PRCs. This study contributes to the growing pool of evidence that supports the validity of using PRCs for the determination of *in situ* sampling kinetics. This method increases the accuracy of estimates of TWA concentrations obtained using integrative passive samplers. The successful application of the PRC approach with other designs of passive sampler including SPMDs (Booij et al., 1998; Huckins et al., 2002a) and silicone strips (Booij, unpublished data) has been demonstrated.

The empirical equation is applicable for calculation of sampling rates of compounds with $\log K_{OW}$ values in the range from 3.7 to 6.8. This approach is of value for pollutants for which no calibration data exist. Correlation of the calibration data with molecular descriptors other than octanol/water partition coefficients may bring additional information on the uptake process (Abraham, 1993; Abraham et al., 2004).

The validity of this approach has been demonstrated by obtaining reasonable estimates of TWA concentrations for a range of PAHs in a field study. However, there are still a number of problems to be investigated when comparing data obtained from passive sampling with those obtained from spot samples. To improve the reliability of the data obtained with the two sampling methods, there is a need for equipment that can provide information on the concentrations of truly dissolved contaminants present in water at a reasonable cost. This would enable a more precise validation of the passive sampling technology.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.envpol.2006.04.030.

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Performance of the Chemcatcher® passive sampler when used to monitor 10 polar and semi-polar pesticides in 16 Central European streams, and comparison with two other sampling methods

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ABSTRACT

We investigated the performance of the Chemcatcher®, an aquatic passive sampling device consisting of a sampler body and an Empore® disk as receiving phase, when used to monitor acetochlor, alachlor, carbofuran, chlorfenvinphos, α-endosulfan, fenpropidin, linuron, oxadiazon, pirimicarb and tebuconazole in 16 Central European streams. The Chemcatcher®, equipped with an SDB-XC Empore® disk, detected seven of the aforementioned pesticides with a total of 54 detections. The time-weighted average (TWA) concentrations reached up to 1 μg/L for acetochlor and alachlor. Toxic units derived from these concentrations explained reasonably well the observed ecological effects of pesticide stress, measured with the SPEAR index. In a follow-up analysis, we compared the Chemcatcher® performance with those of two other sampling systems. The results obtained with the Chemcatcher® closely matched those of the event-driven water sampler. By contrast, the TWA concentrations were not significantly correlated with concentrations on suspended particles. We conclude that the Chemcatcher® is suitable for the monitoring of polar organic toxicants and presents an alternative to conventional spot sampling in the monitoring of episodically occurring pollutants.

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1. Introduction

The monitoring of pesticide concentrations in surface waters is an inevitable step for the environmental risk assessment of pesticides. For these compounds, field runoff represents a relevant input path into streams in agricultural areas (Liess et al., 1999; Neumann et al., 2002). Runoff events occur discontinuously in association with heavy precipitation, and runoff-related pesticide exposure may have adverse effects on invertebrate communities (Leonard et al., 2000; Liess and von der Ohe, 2005). Since most pesticide concentrations during runoff events decrease to

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background levels within hours to a few days, routine water monitoring which mainly relies on spot (bottle) sampling at fixed intervals is likely to miss a great proportion of relevant events (Richards and Baker, 1993; Leu et al., 2004). Hence, environmental monitoring techniques are needed that allow for detection of runoff-related peak exposure and that are labour- and cost-efficient at the same time.

Continuous water sampling represents an alternative to spot sampling. Throughout the last decade, passive sampling devices using various receiving phases have been employed successfully for continuous monitoring of various pollutants in surface waters (Stuer-Lauridsen, 2005; Vrana et al., 2005). The Chemcatcher® passive sampler with polar receiving phase and the polar organic chemical integrative sampler (POCIS) performed well in the monitoring of polar organic contaminants (Escher et al., 2006; Alvarez et al., 2007). Nevertheless, there is a paucity of studies addressing the monitoring of short-term pollution events with passive samplers (Greenwood et al., 2007). Furthermore, to our knowledge, only one study demonstrated a relationship between pesticide concentrations determined by passive samplers and effects on aquatic communities (Leonard et al., 2000). The establishment of such a relationship is hampered by the fact that time-weighted average (TWA) concentrations are obtained from passive sampling devices, whereas peak concentrations are required to assess potential acute ecotoxicological effects. In this study we present results of a field study at 16 sampling sites using the Chemcatcher® passive sampler to detect the polar and semi-polar pesticides acetochlor, alachlor, carbofuran, chlorfenvinphos, α-endosulfan, fenpropidin, linuron, oxadiazon, pirimicarb and tebuconazole. The compounds were chosen on the basis of their ecotoxicological relevance in the sampling region (Schäfer et al., 2007a). In addition, we examine the extent to which the TWA concentrations can be related to a community-based biotic index—the Species At Risk (SPEAR)-index—designed to detect effects of pesticides on benthic invertebrates (Liess and von der Ohe, 2005).

Since several sampling systems have been proposed to assess runoff-related pesticide exposure, there is also a need to compare the performance of different sampling systems. Therefore, another objective of this study was to compare the performance of the Chemcatcher® with the performances of two other sampling systems: an event-driven water sampler (EDS) and a suspended-particle sampler (SPS). (Technical drawings of all sampling methods can be found in the supplementary data.) Both methods have been proposed and used to catch runoff events in previous studies (Liess et al., 1996, 1999; Schulz et al., 2001; Liess and von der Ohe, 2005) and were deployed at the same sampling sites as the passive samplers in this study (Schäfer et al., 2007a, b). Comparison of the Chemcatcher® to these sampling methods comprised the following criteria: (1) number of pesticides detected and (2) the total number of detections above the limit of quantitation. Since sampling methods should deliver results that are relevant to assess effects on biota, we included as criteria also (3) the ability to explain variation in the SPEAR index.

2. Materials and methods

2.1. Study area

Brittany, located in northwestern France, was chosen as the sampling region since (1) agriculture is the predominant land-use type there with 23.5% of the area (27,510 km^2) being used for corn (19.2%), vegetable (2.6%), oil-seed (1.2%) and potato (0.5%) production and (2) in Western Europe pesticide usage is the highest globally in terms of expenditures per area (Oerke and Dehne, 2004). A total of 16 sampling sites in small agricultural streams (max. width: 5 m, max. depth: 0.8 m) were selected on the basis that they were expected to exhibit a gradient in pesticide contamination (Schäfer et al., 2007a).

2.2. Preparation, deployment and extraction of the passive sampler

The Chemcatcher® passive sampling device (University Portsmouth, UK; commercially available at Alcontrol AB, Linkoping, Sweden) was employed for continuous water monitoring as described by Kingston et al. (2000). The Chemcatcher® consists of a polytetrafluorethylene (PTFE) sampler body and, for the purpose of this study, was equipped with SDB-XC Empore® disks (3M, Neuss, Germany) as the receiving phase (47 mm diameter; 15.9 cm^2 surface area) containing polystyrene-divinylbenzene (PS-DVB) as sorbent.

Before use, the SDB-XC Empore® disk was conditioned with 10 mL acetone (HPLC-grade), 10 mL 2-propanol (analytical grade) and 10 mL methanol (HPLC-grade) obtained from Merck (Darmstadt, Germany). The conditioned disks were placed in the Chemcatcher® body, which was subsequently filled with purified water, closed and stored in zip-lock bags at 4 °C until exposure (<48 h). To obtain a rapid response to concentration changes, no diffusion-limiting membrane was used. Procedural blanks were stored non-exposed throughout the whole study period.

The Chemcatcher® devices were deployed at the 16 sampling sites on 9–11 May for 10–13 days (Fig. 1), prior to a period with expected heavy precipitation according to the local weather forecast (www.meteofrance.com). The samplers were fixed to steel bars approximately 15 cm below the water surface. The open side of the Chemcatcher® was sealed with a copper mesh (mesh size 5 mm) to prevent mechanical damage and suppress biofouling (Vrana et al., 2005). It was directed towards the stream bottom. Four sites were equipped in duplicate and one in triplicate to assess the variability of the pesticide uptake. A field blank was exposed to the air during deployment and retrieval of samplers to account for potential airborne pollution.

After exposure, the passive samplers were filled with stream water from the respective site, closed and stored in zip-lock bags at 4 °C in the dark. In the laboratory, the SDB-XC Empore® disks were carefully taken off the PTFE body, dried under vacuum using a vacuum manifold for about 15 min and subsequently eluted twice with 10 mL acetonitrile/methanol. The eluate was gently evaporated to dryness under nitrogen at 30 °C in a 200 mL evaporation vial using a TurboVap 2 concentration workstation (Zymark, Hopkington, USA) and

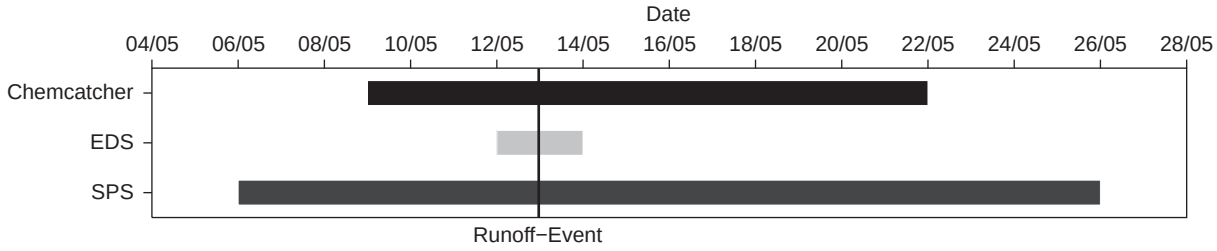

Fig. 1 – Sampling scheme for the three monitoring methods in 16 French streams. "Runoff-event" indicates a heavy precipitation event (>10 mm/day).

Table 1 – Physicochemical and analytical data for 10 measured pesticides

Compound	Type[a]	Class[a]	Log K_{ow}[b]	Log K_{oc}[b]	LOQ CC (ng/L)[c,d]	LOQ EDS (ng/L)[c]	LOQ SPS (μg/kg)[c,e]	LOQ calc. (μg/kg)[c,f]	LC50 (μg/L)[a,g]
Acetochlor	H	Chloroacetamide	2.39	2.32	5.1	25	12.5	0.26	9000
Alachlor	H	Chloroacetamide	3.52	2.28	5.4	25	12.5	0.24	10,000
α-Endosulfan	I	Organochlorine	3.83	4.13	3.6	25	12.5	16.86	75
Carbofuran	I	Carbamate	2.32	1.75	10.4	25	12.5	0.07	38.6
Chlorfenvinphos	I	Organic phosphorous acid	3.10	2.47	5.2	25	12.5	0.37	0.3
Fenpropidin	F	Piperidine	2.90[a]	3.20[i]	4.1	25	12.5	1.98	500
Linuron[h]	H	Urea derivative	3.20	2.70	4.3	25	12.5	0.63	120
Oxadiazon	H	Oxadiazole	4.80	3.51	3.5	25	12.5	4.04	2400
Pirimicarb	I	Carbamate	1.70	1.90	4.5	25	12.5	0.10	17
Tebuconazole	F	Triazole	3.70[a]	3.50[i]	6.1	25	12.5[j]	3.95	4200

[a] Taken from Tomlin (2003), I = insecticide, H = herbicide, F = fungicide.
[b] Taken from Sabljic et al. (1995).
[c] LOQ = limit of quantification for a sample obtained with the respective method.
[d] CC = Chemcatcher®; computed for 14-day exposure.
[e] For extraction of 10 g of suspended particles.
[f] Sample LOQ for suspended particles that would correspond to the level of the EDS LOQ assuming equilibrium partitioning, computed according to $LOQ_{calc.} = LOQ\ EDS \cdot K_{OC} \cdot f_{OC}$, where $f_{OC}$is the mass fraction of organic carbon (assuming $f_{OC} = 5\%$).
[g] LC50 for *Daphnia magna*.
[h] Quantificated as 3,4-dichloroaniline.
[i] Estimated with Chemprop 4.1 (http://www.ufz.de/index.php?en=6738).
[j] 25 and 100 for some samples with high matrix interference.

redissolved with 200 μL acetonitrile. Prior to analysis, 5 μL triphenyl phosphate (TPP) was added as internal standard (IS).

2.3. *Chemical analysis*

The selected compounds (Table 1) were quantified using an Agilent 6890N (Agilent Technologies Germany, Boeblingen, Germany) gas chromatograph (GC) equipped with a MPS2 autosampler, a CAS4 inlet (both from Gerstel, Mühlheim a.d. Ruhr, Germany) and an Agilent 5973 mass selective detector (MSD). The limit of quantification (LOQ) of the GC-MSD was 125 pg/μL for all compounds. The sample LOQs differed between the sampling methods and between compounds for the Chemcatcher (Table 1). Typical total ion chromatograms are given in Fig. 2.

2.4. *Calculation of passive sampler TWA concentrations*

From the field-exposed passive samplers, the accumulated mass of each compound per sampler is obtained. To calculate TWA concentrations, a substance-specific sampling rate R_s, expressed in equivalent volume of sampled water per day, is required. For the compounds of this study, the sampling rates were previously determined in a laboratory flow-through experiment and found to range from 0.1 to 0.5 L/day (Gunold et al., 2007). In addition, this calibration study showed that the Chemcatcher® remained in the linear integrative uptake regime for up to 14 days. Using the sampling rates of this study, the TWA concentrations for the sites in our study were calculated according to

$$C_w = \frac{m_s}{R_s t}, \quad (1)$$

where C_w is the TWA concentration of the respective analyte in the water phase in the dimension mass/volume and m_s is the accumulated mass after exposure time t. The procedural blank and the field blank yielded zero background contamination and had therefore not to be considered in Eq. (1).

The calculated TWA concentrations should be regarded as approximation only, because between-site variation in water

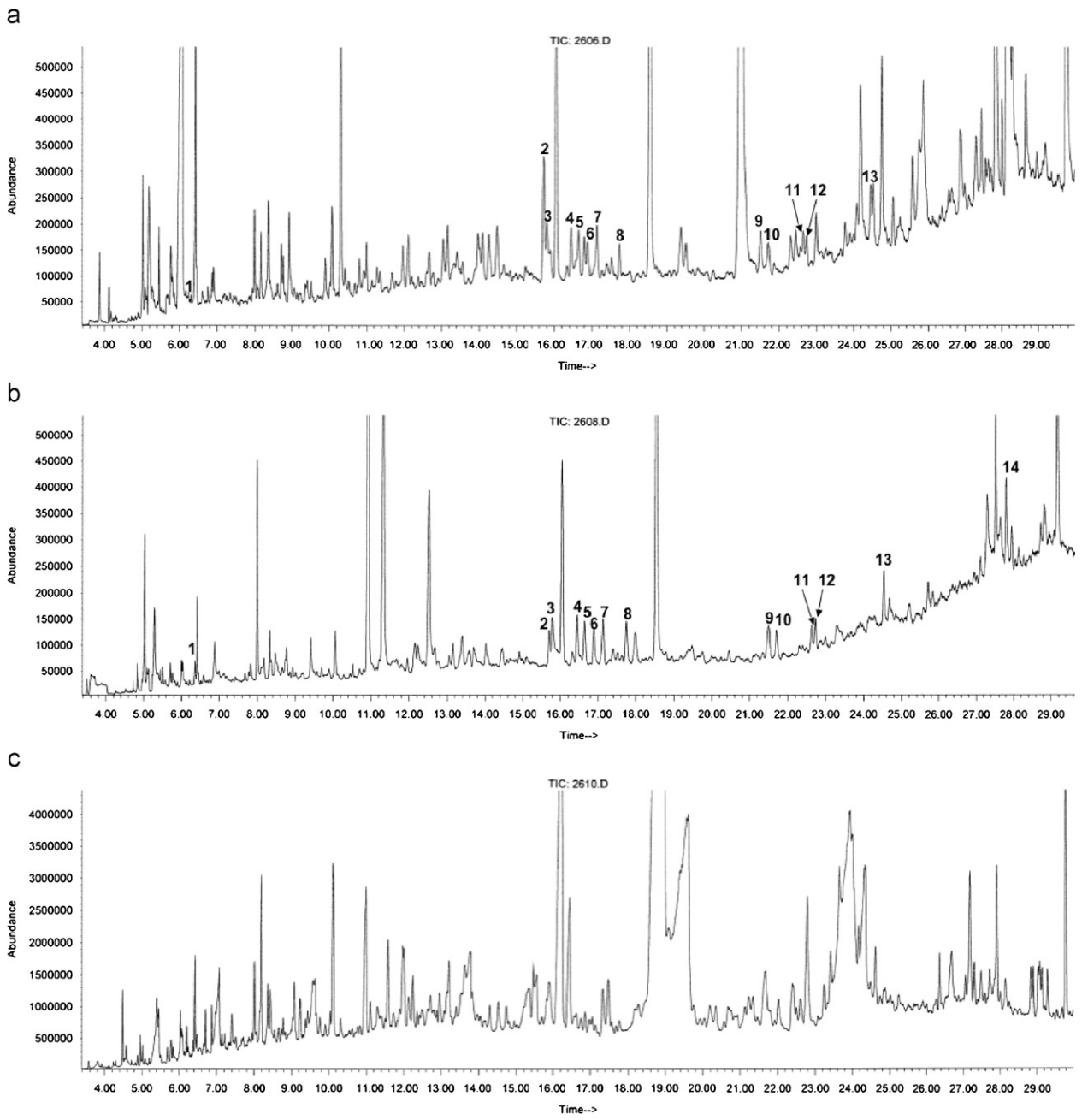

Fig. 2 – Typical total-ion chromatograms for (a) the event-driven water sampler (EDS), (b) the Chemcatcher®, and (c) the suspended-particle sampler (SPS). The samples were spiked with 1 μg/L (SPS 100 μg/kg) of pesticide standards. Deuterated internal standards were only used for comparison of the EDS and Chemcatcher®. Please note the different scaling of the y-axis for the SPS chromatogram. Analytes: 1: carbofuran, 2: pirimicarb D6, 3: pirimicarb, 4: acetochlor D11, 5: acetochlor, 6: alachlor D13, 7: alachlor, 8: fenpropidin, 9: chlorfenvinphos D10, 10: chlorfenvinphos, 11: α-endosulfan D4, 12: α-endosulfan, 13: oxadiazon, 14: tebuconazol.

temperature and biofouling were not taken into account, as the performance reference compound (PRC) concept (Huckins et al., 2002) was not applicable (Gunold et al., 2007).

2.5. *Linking exposure to the SPEAR index*

We examined the extent to which the TWA concentrations determined with the Chemcatcher® can explain variation in the SPEAR index. Briefly, the SPEAR index predicts the effects of organic toxicants on the invertebrate community of a site, based upon traits of benthic invertebrates such as voltinism, migration potential, emergence time and physiological sensitivity (Liess and von der Ohe, 2005). Practically, these traits are used to classify the observed macroinvertebrate community of each sampling site into taxa potentially sensitive or tolerant towards organic toxicants. Subsequently, the SPEAR index value for a respective site is derived by computing the relative abundance of sensitive species in a community.

Details on the sampling of the benthic invertebrates and on the computation of the SPEAR index are given in Schäfer et al. (2007a).

To assess and standardize the toxicity of the measured TWA concentrations, a log-transformed maximum toxic unit (TU) was computed using the 48-h acute median lethal concentration (LC50) for *Daphnia magna* (Table 1) as described by Schäfer et al. (2007a). A TU value of −5 was assigned to a site if no pesticide was found, corresponding to unpolluted sites in a previous study (Liess and von der Ohe, 2005).

2.6. Description of the EDS

The EDS was designed to catch peak concentrations during pesticide runoff. The sampling system set into the streams consisted of a 1-L glass bottle fixed to a steel bar and was mounted approximately 5 cm above normal water level (Liess et al., 2001; Schulz et al., 2001). After a heavy rain event (>10 mm precipitation/24 h) the filled sample bottles were retrieved and water samples were solid-phase-extracted using 6 mL Chromabond HR-P columns containing 500 mg of PS-DVB, purchased from Macherey-Nagel (Düren, Germany), according to the method described in Schäfer et al. (2007a). The eluates were treated as described for the Chemcatcher®. The EDS monitoring results reported here refer to a single heavy-rain event (>10 mm/day) during the study period that occurred between 12 and 13 May (Fig. 1). The TUs of this method were taken from Schäfer et al. (2007a).

2.7. Description of the SPS

The SPS was designed to sample suspended particles and consisted of a 3-L sedimentation vessel that was buried in the streambed. Suspended particles that entered therein could settle down (Liess et al., 1996). The sampled suspended material was collected at 2-week intervals, freeze-dried and passed through a 2-mm sieve to remove needles, sticks and leaf parts. Approximately 10 g (dry weight) of the sample was extracted using an accelerated solvent extraction (ASE 200 system from Dionex, Idstein, Germany; extraction parameters: two 6-min cycles with ethyl acetate–acetone (2:1) at 110 °C and 11 MPa) with subsequent size exclusion chromatography (SEC) cleanup (Biobeads S-X3 cleanup column from Antec GmbH, Sindelsdorf, Germany) as described by Schäfer et al. (2007b). Due to matrix interferences the collected fraction in SEC was not evaporated further than to 1000 μL and, subsequently, 50 μL TPP was added as IS. To obtain comparable data sets, we used the results of the sampling period between 6 and 23–26 May for this method (Fig. 1). A maximum sediment TU was computed from the suspended particle concentrations as described in Schäfer et al. (2007b). Log-transformed sediment TUs are referred to as STU.

2.8. Data analysis

Pearson's correlation coefficient r was calculated to indicate the similarity of two sampling methods followed by a t-test to detect significant correlations. Observations that were below LOQ for a compound at a certain site and for all sampling methods were excluded from analysis. In case an observation below LOQ corresponded to a measurement above LOQ in another sampling method, the observation below LOQ was replaced by half the LOQ. This substitution by a constant proved to be most reliable for small data sets in a comparative study (Clarke, 1998). Linear models were constituted (1) to analyse if the linear regression for two sampling methods differed significantly between sites or compounds which were included as covariate factors, and (2) to examine the explanatory power of TU (STU for SPS) for variation in the SPEAR index.

Due to the low number of replicates (2 and 3) we calculated the relative range (RR) as dispersion measure for the TWA concentrations:

$$\mathrm{RR}(\%) = \frac{(\max(X) - \min(X))}{\overline{X}}, \quad (2)$$

where X are the observations for the respective compound at a certain site and $\overline{X}$ is the mean of X. The RR is a more conservative estimate of the sample dispersion compared to the relative standard deviation (RSD). All statistical computations and graphics were created with the open-source software package R (www.r-project.org) using version 2.6 (for Mac OS X, 10.4.10).

3. Results

3.1. Pesticide monitoring with the Chemcatcher® passive sampler

At the 16 sites, seven of the 10 target pesticides were found with the Chemcatcher® passive sampler (Table 2); those not detected were chlorfenvinphos, α-endosulfan and fenpropidin. Both chloroacetamide herbicides—acetochlor and alachlor—were detected most frequently above the LOQ and had the highest TWA concentrations, reaching up to 1 μg/L. Tebuconazole and pirimicarb were found only occasionally and had the lowest TWA concentrations. The TWA concentrations exhibited high variation at three of the five sampling sites with up to 150% in terms of RR (Table 2). The other sites showed medium (<50% RR) and low (<30% RR) variation for the majority of the compounds.

The TUs for the sites ranged from −2.4, corresponding to 1/250 the LC50 of *D. magna*, to −5 (Table 2). The TU values explained reasonably well the variation in the SPEAR index ($r^2 = 0.5$, $p < 0.01$, $n = 16$) (Table 3), indicating effects of pesticides on the abundance of sensitive invertebrate taxa.

3.2. Comparison of the three sampling methods concerning pesticide monitoring

All pesticides of the monitoring program were found in the water samples of the EDS and this sampling method yielded also a slightly higher number of total detections compared to the Chemcatcher® (Table 3). Nevertheless, the pesticide concentrations found by the two water sampling methods were significantly correlated ($r = 0.79$, $p < 0.01$, $n = 75$). The concentrations determined with the EDS were in general a factor of 4–5 higher than the Chemcatchers' TWA concentrations (Fig. 3). The linear regression model, encompassing EDS'

Table 2 – Time-weighted average concentrations in ng/L (±relative range[a] where replicates available) of pesticides determined with the Chemcatcher® passive sampler as well as TUs and STUs for the three sampling methods[b]

Site	Acetochlor	Alachlor	Carbofuran	Linuron	Oxadiazon	Pirimicarb	Tebuconazole	TU CC[c]	TU EDS[c,d]	STU SPS[c,e]
1	1158	184	124	54	10	bq	bq	−2.5	−0.4	0.7
2	14	7	21	bq	bq	bq	bq	−3.3	−2.2	−5.0
3	18	198	bq	37	bq	bq	bq	−3.5	−2.7	2.5
4	196	40	36	9	7	bq	bq	−3.0	−2.5	−2.2
5	219	96	127	48	8	bq	6	−2.5	−2.0	1.1
6	60 (±148%)	12 (±99%)	bq	16 (±94%)	4 (±72%)	5 (±86%)	bq	−2.6	−2.5	−5.0
7	37	132	92	57	bq	8	bq	−3.5	−2.1	−5.0
8	454 (±102%)	681 (±99%)	159 (±27%)	41 (±116%)	9 (±103%)	bq	bq	−2.4	−0.8	0.9
9	486 (±29%)	1233 (±14%)	52 (±22%)	22 (±25%)	bq	bq	15 (±10%)	−2.9	−2.6	−2.0
10	388 (±55%)	182 (±44%)	20 (±13%)	66 (±48%)	26 (±95%)	6 (±26%)	11 (±33%)	−3.3	−2.8	−4.1
11	20	14	bq	bq	bq	12	bq	−3.2	−2.6	−5.0
12	bq	bq	bq	bq	bq	bq	bq	−5.0	−5.0	−5.0
13	16 (±120%)	24 (±139%)	bq	bq	bq	bq	bq	−5.0	−4.7	1.0
14	bq	bq	bq	bq	bq	bq	bq	−5.0	−5.0	−2.7
15	bq	bq	bq	bq	bq	bq	bq	−5.0	−5.0	−5.0
16	bq	bq	bq	bq	bq	bq	bq	−5.0	−5.0	1.2

[a] $n = 2$, except site 8 ($n = 3$). Calculated using Eq. (2).
[b] bq = below limit of quantification; chlorfenvinphos, α-endosulfan and fenpropidine are not displayed because all observations were below limit of quantification.
[c] Calculated with LC50 values taken from Tomlin (2003), see Table 1.
[d] Calculated from data given in Schäfer et al. (2007a).
[e] Calculated from data given in Schäfer et al. (2007b).

Table 3 – Comparison of the three sampling systems in 16 French sites

Sampling method	Number of different pesticides detected	Total detections above the LOQ	Explanatory power for the SPEAR index[a]
Chemcatcher®	7	54	$r^2 = 0.50$ ($p < 0.01$)
EDS	10	66	$r^2 = 0.38$ ($p = 0.01$)
SPS	5	22[b]	$r^2 = 0.01$ ($p > 0.05$)

[a] Linear regression with the respective TUs/STUs as explanatory variable and SPEAR as response variable.
[b] Significantly lower than the total detections by the other methods in multiple comparison tests (χ^2-test with Bonferroni correction, $p < 0.05$).

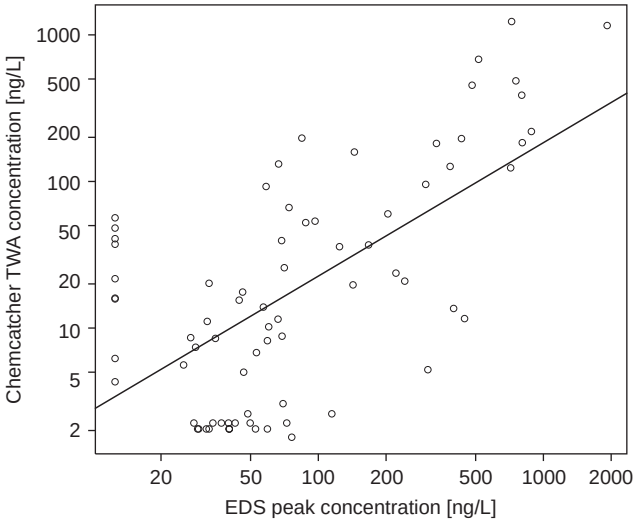

Fig. 3 – Relationship between the Chemcatcher® TWA concentrations and the EDS peak concentrations in 16 agricultural streams, on a double logarithmic scale. Observations that were below LOQ for both sampling methods were excluded from analysis. Model parameters: $r^2 = 0.4$, $p < 0.01$, $n = 75$. Model parameters for non log-transformed concentration: $r^2 = 0.62$, $p < 0.01$, $n = 75$.

concentrations as explanatory variable and the Chemcatchers' concentrations as response variable, was not significantly different between sites or compounds (analysis of variance of the models with and without the covariate factors, *F*-test, $p > 0.05$). For the log-transformed pesticide concentrations inclusion of the covariate compounds in the linear model did increase the amount of explained variance significantly (analysis of variance, *F*-test, $p < 0.01$). However, separate linear regression models for each compound yielded only two significant relationships (*t*-test, $p < 0.05$) (Fig. 4).

In the suspended particles sampled with the SPS, only 5 of the 10 pesticides were observed; any of the compounds alachlor, carbofuran, linuron, oxadiazon and pirimicarb was found. The total number of pesticide detections (22) in the particulate phase was significantly reduced (χ^2-test with Bonferroni correction, $p < 0.05$) compared to both water phase methods (Table 3). No significant correlations were observed between water concentrations derived from the EDS and the Chemcatcher® on the one hand and the suspended particle concentrations monitored with the SPS on the other hand ($r = 0.05$ and 0.08, $p > 0.05$, $n = 76$ and 72, respectively).

3.3. *Comparison of the three sampling methods concerning effects assessment*

The STUs calculated on the basis of suspended particle concentrations were higher than the TUs based on water concentrations, with a maximum STU value of 2.5 corresponding to 321 times the LC50 for *D. magna*. For water concentrations, the TUs peaked at −0.42, equivalent to 1/2.5 the LC50 value for *D. magna* (Table 2). The TUs of the two water sampling methods were very similar, indicated by an *r* of 0.94 ($p < 0.01$, $n = 16$). The SPEAR index was reasonably well explained by the TUs of the EDS and the Chemcatcher®, whereas no significant linear relationship was observed between STUs and SPEAR (Table 3).

4. Discussion

4.1. *Using the Chemcatcher® for the monitoring of polar and semi-polar pesticides*

The Chemcatcher® passive sampler equipped with a SDB-XC Empore® disk detected all compounds included in the monitoring program except fenpropidin, chlorfenvinphos and α-endosulfan, although these compounds were found in samples obtained by the other sampling methods. In general, the Chemcatcher® should be suitable for detecting these substances, as they showed above average uptake rates in the samplers' receiving phase in a calibration study (Gunold et al., 2007). The non-detections with the Chemcatcher® are not likely to result from too low concentrations because in the EDS samples the concentrations of fenpropidin, chlorfenvinphos and α-endosulfan were not lower than those of the other monitored compounds. An explanation for the non-detection with the Chemcatcher® is that the period of exposure to these pesticides was shorter than in the case of the other compounds detected, resulting in a TWA concentration below LOQ. Since we have no temporal resolution of the water concentrations over the course of the runoff event, this issue remains unresolved.

The levels of the TWA concentrations observed with the Chemcatcher® are in good agreement with another field study on 7 sites in southern England using the POCIS passive sampler, where concentrations up to 1 μg/L were reported for

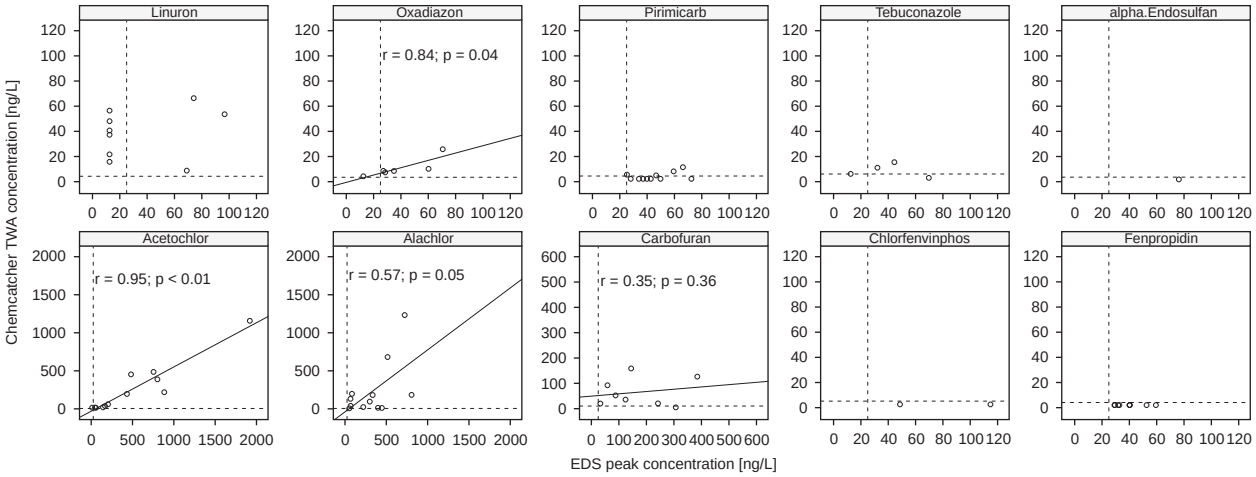

Fig. 4 – Relationship between the Chemcatcher® TWA concentrations and the EDS peak concentrations in 16 agricultural streams, for single compounds. Observations that were below LOQ for both sampling methods were excluded from analysis. Dashed lines indicate LOQ, *r* = Pearson's correlation coefficient. Regression lines are shown for >3 observations above LOQ for both methods.

Diuron (Alvarez et al., 2004). Concerning variation in TWA concentrations for replicate deployments of passive samplers, some studies reported similar findings (Stuer-Lauridsen, 2005; Alvarez et al., 2007), while another study with the Chemcatcher® found lower variability (RSD<20%, $n = 2$), though the exposure time was 3-fold reduced compared to our study (Escher et al., 2006). Variation in the rate of uptake into the receiving phase may result from differences in biofouling and environmental conditions such as temperature or current velocity. Since environmental conditions are nearly identical within a single sampling point, we suggest that the variation in our study resulted from the high biofouling that was observed on the samplers after deployment (Greenwood et al., 2007). Therefore, new techniques are needed for polar passive samplers that help to reduce variability during field exposure, such as the PRC approach for non-polar compounds (Alvarez et al., 2007).

The derived TUs could reasonably well explain variation in the SPEAR index (Table 3). This suggests that variation in the composition of the invertebrate community could partly be attributed to pesticide stress and hence that the relative abundance of taxa classified as sensitive according to the SPEAR approach is reduced due to pesticides. A link between TWA concentrations and ecological effects was also found in two other studies (Leonard et al., 2000; Escher et al., 2006). Firstly, runoff-related endosulfan concentrations in passive samplers deployed in the Namoi river in Australia could be linked to the decline in invertebrate population densities (Leonard et al., 2000). Moreover, the Chemcatcher® was successfully employed to monitor herbicides and assess phytotoxicity in a small-scale field study in Australia (Escher et al., 2006). However, caution should be taken when relating TWA concentrations to effects on biota because no distinction can be made between a low-level chronic contamination and a short-term peak contamination on the basis of TWA concentrations. In a situation in which both chronic contamination and peak contamination are present, no link may be found between TWA concentrations and ecological effects. Furthermore, the relationship between TWA concentrations and biotic metrics will most likely not hold in situations in which more than one peak event occurs during the exposure time. Nevertheless, passive samplers with a polar receiving phase may constitute a labour- and cost-efficient tool for field monitoring of polar organic toxicants when the exposure characteristics are known and episodic events are rare.

4.2. *Comparison of the Chemcatcher® with the EDS*

The Chemcatcher® passive sampler had a slightly lower number of total detections than the EDS (Table 3), but the concentrations were closely related ($r = 0.79$, $p<0.01$, $n = 75$). Since the EDS sampled only one precipitation-driven runoff event (Fig. 1), the similarity of the TWA and EDS concentrations suggests that this event was the most relevant source of the pesticides sampled with the Chemcatcher®. Thus, our findings emphasize the relevance of field runoff as input path for pesticides in aquatic ecosystems and hence are in accordance with the results of previous studies in streams of Germany (Liess et al., 1999; Neumann et al., 2002). On average, the TWA concentrations were 4- to 5-fold lower than the EDS concentrations (Fig. 3). The concentrations determined with the EDS were assumed to represent peak concentrations during runoff (Liess et al., 2001; Schulz et al., 2001). Assuming that concentrations following runoff events drop to below 10% of the peak water concentration within 1–4 days (Richards and Baker, 1993; Leu et al., 2004), one would expect the TWA water concentrations to be in the range of $\frac{1}{12}-\frac{4}{12}$ of the EDS concentrations, based on an average exposure time of 12 days (Eq. (1)). Furthermore, this should be dependent on physicochemical properties of investigated pesticides and thus lead to significant differences between compounds. Indeed, we observed a significant difference in the relationship between TWA and peak concentrations for different compounds, though only for log-transformed concentrations. Furthermore, the slopes of the regression lines were different in separate linear regressions for the various

compounds (Fig. 4). Nevertheless, we are aware that more extensive data are needed to prove these differences between compounds.

4.3. *Comparison of the Chemcatcher® with the suspended-particles sampler*

Only five pesticides were detected on the suspended particles sampled with the SPS, and the total number of detections was significantly lower compared to the Chemcatcher® (Table 3). This may be explained by the polarity of the study compounds in view of the fact that the pesticides not detected had a log K_{ow} <3.1 except for oxadiazon (Table 1). Moreover, the smaller number of observations related to the SPS samples may be partly due to the LOQ, because it was a factor of 3–180 higher than the corresponding LOQs of the water samplers except for α-endosulfan, when assuming equilibrium partitioning between water and particulate phase (see LOQ calc., Table 1). The LOQ for the SPS could only be improved by stronger preconcentration of the eluate or by extracting an increased mass of suspended particles. Besides the fact that the amount of sample material from SPS was rather limited, both possibilities were hampered by the high magnitude of matrix coextraction masking the analyte peaks (Fig. 2). Thus, a more efficient SEC or solid phase extraction cleanup method for polar pesticides would be needed to achieve a lower LOQ (Dabrowska et al., 2003; Schäfer et al., 2007b).

Consequently, the particle-associated pesticide concentrations exhibited no significant correlation with the TWA concentrations or the EDS peak concentrations which refer to the dissolved water phase. This low similarity was also expressed by the proportion of cases $(\frac{18}{22})$ in which pesticides were found on suspended particles but not in samples collected by either the Chemcatcher® or the EDS. Similarly, no clear relationship between particle-associated contaminants and water concentrations was found in a 1-year monitoring study of 30 organic pesticides in six rivers in the UK (Long et al., 1998). Furthermore, high variability of the pesticide distribution between particulate and water phase was observed in tributaries of the Mississippi river (Pereira and Rostad, 1990) and in a field experiment on the release of six organic pesticides from a heavy clay soil during precipitation events (Brown et al., 1995). The contaminant distribution between particulate and water phase is influenced by environmental conditions, physicochemical properties and site-specific conditions that may explain the observed variation: (1) size of suspended particles, (2) composition and structure of organic matter in the particles (Zhou et al., 1995), (3) runoff-water flow rate (Gouy et al., 1999) and (4) lag time between pesticide application and runoff event. This variation in the pesticide partitioning between particulate and dissolved phase (Brown et al., 1995; Long et al., 1998) along with the high LOQ can explain why the results of the sampling with the SPS and the Chemcatcher® were very different.

Although the SPS samples indicated much higher pesticide stress in terms of STU compared to the TUs derived from the TWA and peak concentrations, no significant relationship could be established to the SPEAR index. By contrast, other studies demonstrated significant linear relationships between STUs derived from bed sediments and the benthic community tolerance metrics (Wildhaber and Schmitt, 1998) or macroinvertebrate community composition (Friberg et al., 2003).

The differing results of our study most likely result from monitoring suspended particle concentrations instead of bed-sediment concentrations. Suspended particles in field runoff usually have much higher contaminant concentrations than bed sediments and are rarely in equilibrium with the water phase, rendering questionable the application of the STU approach (Liess et al., 1996; Long et al., 1998). In the present study, results from passive sampling and event-driven water sampling were more informative when used to explain variation in the invertebrate community. We propose that water concentrations are more likely to explain effects of episodic events with polar toxicants, whereas the effects of chronic exposure to hydrophobic compounds may be predicted from analysis of the sediment phase. However, this should be tested in future studies, and passive samplers in different configurations can be useful tools for such studies.

5. Conclusions

- The Chemcatcher® can be employed for continuous water sampling of polar organic toxicants for up to 14 days.
- The Chemcatcher® configured with a SDB-XC Empore® and without diffusion-limiting membrane represents a promising method for the monitoring of short-term exposure that conventional spot water sampling is likely to miss.
- Given the increasing attention that is paid to polar substances, a method similar to the performance reference compound concept is needed to account for variation in the passive sampling of polar compounds.
- Exposure assessment with the Chemcatcher® passive sampler yields results similar to water sampling but differs from suspended-particles sampling.
- In large-scale studies with frequently recurring pollution events, the Chemcatcher® is more labour- and cost-efficient than event-driven water sampling.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.watres.2008.01.023.

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Príloha 13

Lobpreis T., **Vrana B.**, Dominiak E., Dercová K., Mills G. A., and Greenwood R., Effect of housing geometry on the performance of ChemcatcherTM passive sampler for the monitoring of hydrophobic organic pollutants in water, ***Environ. Pollut*., 2008, 153, 706–710.**

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Short communication

Effect of housing geometry on the performance of Chemcatcher™ passive sampler for the monitoring of hydrophobic organic pollutants in water

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The effect of passive sampler geometry on accumulation kinetics of organic pollutants from water was evaluated.

Abstract

Passive sampling of pollutants in water has been gaining acceptance for environmental monitoring. Previously, an integrative passive sampler (the Chemcatcher™) was developed and calibrated for the measurement of time weighted average concentrations of hydrophobic pollutants in water. Effects of physicochemical properties and environmental variables (water temperature and turbulence) on kinetic and thermodynamic parameters characterising the exchange of analytes between the sampler and water have been published. In this study, the effect of modification in sampler housing geometry on these calibration parameters was studied. The results obtained for polycyclic aromatic hydrocarbons show that reducing the depth of the cavity in the sampler body geometry increased the exchange kinetics by approximately twofold, whilst having no effect on the correlation between the uptake and offload kinetics of analytes. The use of performance reference compounds thus avoids the need for extensive re-calibration when the sampler body geometry is modified.
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Keywords: Chemcatcher™; Passive sampling; Water monitoring; Hydrophobic organic pollutants; Polycyclic aromatic hydrocarbons

1. Introduction

Passive sampling devices are gaining acceptance as tools that can be used in monitoring programmes to measure concentrations of pollutants dissolved in water (Vrana et al., 2005a). One of these, the Chemcatcher™ passive sampler, was developed to measure time weighted average (TWA) concentrations of a range pollutants (including non-polar organic, polar organic and metals) in aquatic environments (Kingston et al., 2000). The sampler is based on the diffusion of compounds through a membrane and their subsequent accumulation in a sorbent receiving phase. The prototype designed to sample non-polar organic compounds (log octanol/water partition coefficient (log K_{OW}) greater than four) has a C_{18} Empore® disk saturated with *n*-octanol as the receiving phase and this is overlaid with a low density polyethylene (LDPE) membrane (Vrana et al., 2005b). The sampler has been calibrated for the measurement of TWA concentrations of hydrophobic pollutants in water (Vrana et al., 2006). In the calibration experiments the effect of physicochemical properties (e.g. compound hydrophobicity), water temperature and hydrodynamics on kinetic and thermodynamic parameters characterising the exchange of analytes between the sampler

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and water were investigated. It was found that the rate of uptake of test analytes from water to the sampler receiving phase is related to the rate at which they offload to the water. This enables the use of off-loading rates of performance reference compounds (PRCs) preloaded on to the receiving phase to be used to adjust uptake rates for the effects of temperature and hydrodynamic conditions in the field. The calibration procedures and data have been reported (Vrana et al., 2006, 2007).

The rate of diffusion from the bulk water to the receiving phase is proportional to the surface area over which diffusion takes place and inversely proportional to the diffusion path length. Therefore, the physical dimensions of the sampler body will significantly affect the sampling rate for different analytes. The body of the Chemcatcher™ was optimised in terms of both materials of construction and geometry. PTFE was selected for the sampler body as it has a low sorption capacity for most environmental pollutants (Kingston et al., 2000; Vrana et al., 2005b, 2006, 2007). The housing was constructed to fit a 47 mm Empore® disk receiving phase, having an active sampling area of 17.5 cm^2.

Uptake kinetics of many hydrophobic analytes have been shown to be controlled by diffusion in the aqueous boundary layer at the surface of the LDPE membrane (Vrana et al., 2006). The resistance to mass transfer of the boundary layer depends on hydrodynamic conditions in the vicinity of the membrane, and these are significantly affected by the sampler geometry. The membrane and receiving phase of the first generation Chemcatcher™ (*old design*) were located inside a 20 mm deep depression in the front of the sampler body. This well effectively buffers the effect of fluctuating flow on sampler performance. It effectively reduces convective transport of analytes to the sampler membrane, thus reducing sampling rates (i.e. the rate at which the sampler accumulates chemicals). The depth of cavity in the Chemcatcher™ body (*new design*) was reduced to 7 mm (Fig. 1) in order to increase sampling rates; this is particularly important for hydrophobic chemicals that are present in only low dissolved concentrations in the aquatic environment.

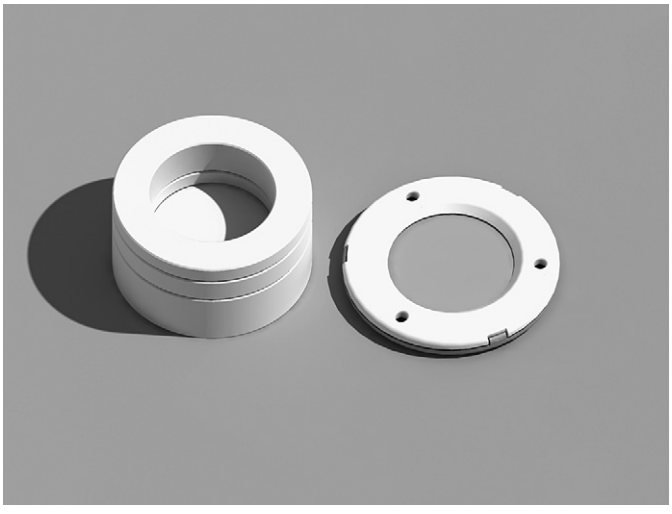

Fig. 1. Views of the old (left) and the new (right) designs of the Chemcatcher™ sampler body.

The aim of this study was to compare the performance of the old and new designs in monitoring hydrophobic organic pollutants and to determine whether calibration data obtained with the old design could be used for the new design. The uptake kinetics of polycyclic aromatic hydrocarbons (PAHs) to and release kinetics of PRCs from the new design were measured in a flow-through system under conditions identical to those used by Vrana et al. (2006) with the old design.

2. Theory

Mass transfer of an analyte from water to the Chemcatcher™ sampler has been described (Vrana et al., 2006), and accumulation of a chemical in the receiving phase of the sampler from water can be described by:

$$m_D(t) = m_{D0} + (C_W K_{DW} V_D - m_{D0})[1 - \exp(-k_e t)] \quad (1)$$

where m_D [kg] is the mass of analyte in the receiving phase, m_{D0} [kg] is the analyte mass in the receiving phase at the start of exposure, C_W [kg m^{-3}] is the concentration in the water during the deployment period, K_{DW} is the receiving phase/water distribution coefficient, V_D [m^3] is the volume of the receiving phase, k_e [s^{-1}] is the exchange rate constant and t [s] equals time.

The initial uptake phase is approximately linear or integrative. Here the amount of a chemical in the receiving phase is directly proportional to the product of the concentration in the surrounding water (C_W) and the exposure time (t). Eq. (1) can be rewritten as:

$$m_D(t) = m_{D0} + C_W R_S t \quad (2)$$

where R_S is the substance specific sampling rate (L day^{-1}), which can be determined experimentally. When PRCs are used and exchange kinetics are isotropic, Eq. (1) reduces to a single parameter equation:

$$m_D(t) = m_{D0}\exp(-k_e t) \quad (3)$$

where the amount of PRC added to the sampler (m_{D0}) is known.

Mass transfer is affected by the diffusion of analytes in the individual layers (i.e. aqueous boundary layer, diffusion limiting membrane and the receiving phase) and by their partitioning into the LDPE membrane and receiving phase. Compounds with log $K_{OW} > 4$ are accumulated in the Chemcatcher™ under aqueous boundary layer control (Vrana et al., 2006), and their uptake kinetics is therefore sensitive to changes in the boundary layer thickness, and this depends on hydrodynamic conditions at the sampling surface. For compounds with log $K_{OW} > 4$, the kinetic performance characteristics of the Chemcatcher™ are likely to be highly dependent on the geometry of the sampler body. The new design effectively decreases the thickness of the boundary layer and

hence results in faster mass transfer of such compounds that are accumulated under boundary layer control.

3. Materials and methods

3.1. Materials and chemicals

C_{18} Empore® disks (47 mm diameter) were from Varian Inc., Walton-on-Thames, UK. LDPE membrane (40 μm thick) was from Fisher Scientific, Loughborough, UK. The solvents (HPLC grade), acetone, ethyl acetate, methanol, *n*-hexane, *n*-octanol, *n*-nonane, 2,2,4-trimethylpentane and water were from Fisher Scientific. Certified (purity > 98%) reference standards of the test PAHs, internal standards, PRCs [perdeuterated PAHs: $^2H_{10}$-biphenyl (D_{10}-BIP), $^2H_{10}$-fluorene (D_{10}-FLU), $^2H_{10}$-phenanthrene (D_{10}-PHE), $^2H_{10}$-acenaphthene (D_{10}-ACE), $^2H_{10}$-pyrene (D_{10}-PYR) and $^2H_{12}$-benz(a)anthracene (D_{12}-BaA)], and, certified external calibration solutions (10 μg mL^{-1} in cyclohexane) were from Qmx Laboratories, Saffron Walden, UK.

3.2. Passive sampler construction

The passive sampler preparation has been described (Vrana et al., 2006): the sampler body houses a C_{18} Empore® disk receiving phase overlaid with a 40 μm thick LDPE membrane (47 mm diameter). *n*-Octanol (450 μL) is added to the interstitial space between the receiving phase and membrane. The new design sampler (Fig. 1) consists of three components (two body parts and a lid for storage and transport), which are clipped together. This makes the sampler cheaper and assembly and disassembly faster than with the old design, where screw threads were used. The new sampler is designed as a disposable device for a single field deployment, thus eliminating the need for cleaning and accompanying quality control measures required for trace analysis. The new design is made of moulded polycarbonate and can be recycled.

3.3. Calibration experiment

The exposure conditions were identical with those used for the calibration of the old design (Vrana et al., 2006). Twelve passive samplers (new design) were exposed for up to 7 days in a flow-through exposure system with a constant analyte concentration (nominally set to 100 ng L^{-1}), under controlled temperature (18 °C), water turbulence (carousel rotation speed 40 rpm). Samplers were removed from the exposure tank at regular time intervals, and PAHs and PRCs extracted from the receiving phases. PAHs from water samples taken regularly during the calibration, instrumental conditions and data processing were performed according to Vrana et al. (2006).

4. Results and discussion

The effects of body geometry on compound specific sampling rate (R_S) of target PAHs and the offload rates (overall exchange rate constants; k_e) of PRCs were determined by comparing the calibration data with those obtained for the old design.

4.1. Uptake of analytes

Concentrations of the test PAHs in water (C_W) in the test tank remained constant over the exposure period. Satisfactory linear regression fits of Eq. (2) for the uptake analytes from water to the sampler receiving phase disks were obtained for all test compounds. The sampling rates (R_S) ranged from 0.23 L day^{-1} for benzo(k)fluoranthene to 1.14 L day^{-1} for pyrene. The error (expressed as standard deviation) of R_S combines the error in the measurement of the chemical accumulated in the disk with that in the measurement of aqueous concentration in the calibration system. The latter represents the main source of uncertainty in R_S.

4.2. Offload of PRCs

The offload rate of PRCs from the C_{18} Empore® disks was fitted by non-linear regression analysis using Eq. (3) with m_{D0} and k_e as adjustable parameters. Characteristic PRC offload curves are shown in Fig. 2. Satisfactory first order decay fits were obtained for D_{10}-BIP, D_{10}-ACE, D_{10}-FLU and D_{10}-PHE, but the rate of release of D_{10}-PYR and D_{12}-BaA from the disk was too slow to be measured reliably and the k_e values were not significantly different from 0 ($P > 0.05$).

4.3. Effect of sampler geometry on the analyte uptake

In line with theoretical expectations, higher (up to a factor of 2.5) sampling rates (R_S) of PAHs were obtained with the new design. This applied to all of the test compounds except fluoranthene and pyrene, for which no significant difference in R_S between designs was observed. The latter can be attributed to the errors associated with the determination of R_S being greater than the effect investigated.

4.4. Effect of sampler geometry on the PRC elimination

The effect of body design on the elimination rate of the PRCs under constant exposure conditions was measured as the first order elimination rate constant (k_e) that is independent of concentration. The uncertainty associated with k_e is much lower than that associated with the estimation of R_S since the former is based solely on the measurement of the amount of analyte remaining in the Empore® disks, and unlike the measurement of the latter does not involve the measurement of the concentration in the calibration water. For the PRCs (D_{10}-BIP, D_{10}-FLU, D_{10}-ACE and D_{10}-PHE) with measurable

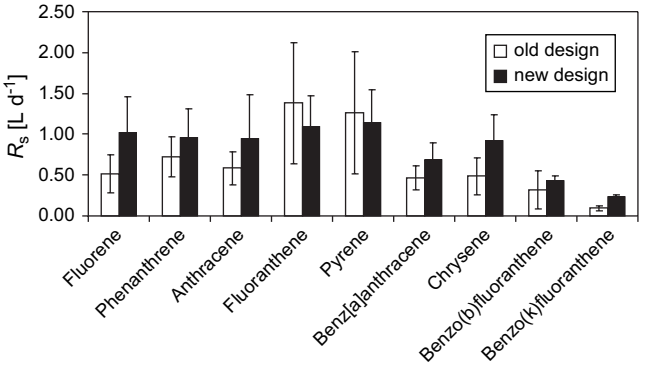

Fig. 2. Comparison of sampling uptake rates (R_S) for different polycyclic aromatic hydrocarbons for old and new Chemcatcher™ sampler designs. Uptake rates were measured in a flow-through test tank with constant analyte concentration (nominal concentration 100 ng L^{-1}) with a water temperature of 18 °C and a carousel rotation speed of 40 rpm.

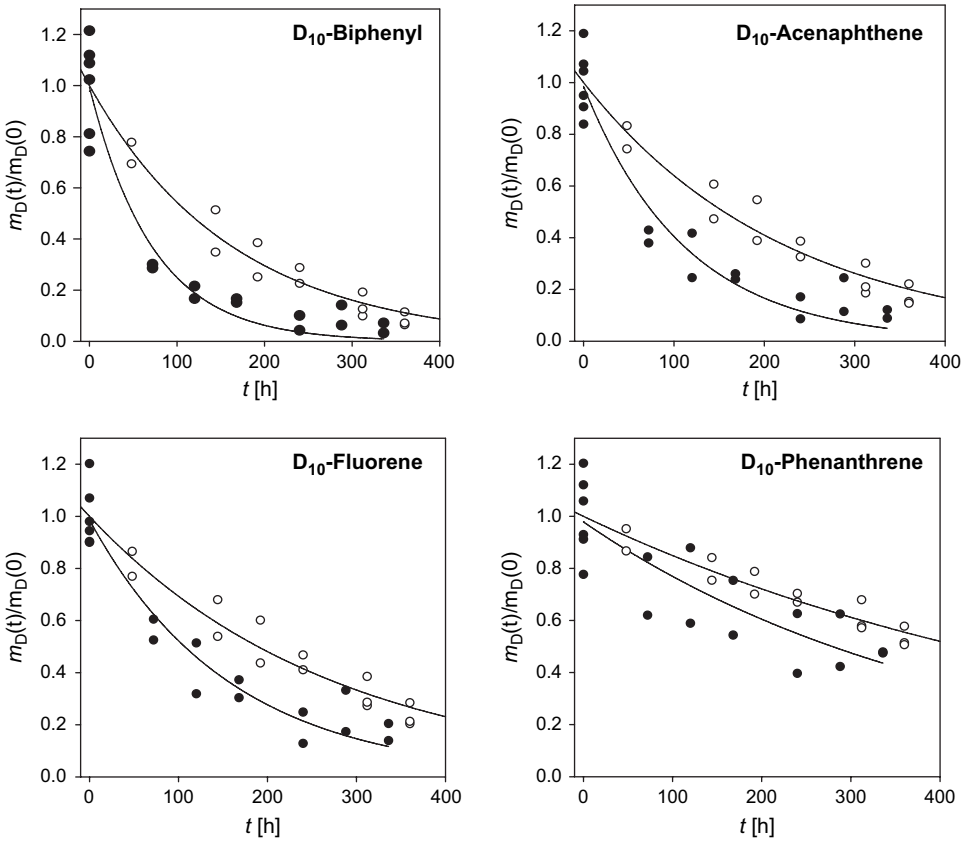

Fig. 3. Release of performance reference compounds (expressed as the mass fraction of the initial amount remaining in the sampler) from the C_{18} Empore® receiving phase disks fitted in the two different Chemcatcher™ sampler body designs. Dark and white dots represent experiments with the new and old sampler body design, respectively. The lines represent best fits of the data using first order decay equation. The flow-through exposures were conducted at water temperature of 18 °C and a carousel rotation speed of 40 rpm.

elimination kinetics, a significant difference ($P > 0.05$) was observed between k_e values for the two sampler body designs. The off-loading of PRCs is 1.5 (D_{10}-PHE) to 2.3 (D_{10}-BIP) times faster with the new sampler design as shown in PRC offload curves (Fig. 3) and calculated values of k_e (Fig. 4).

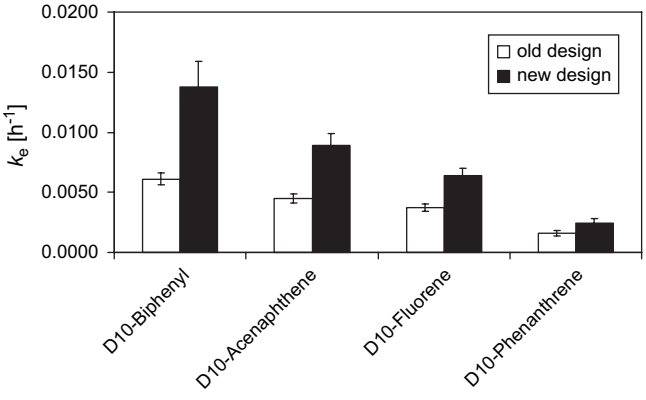

Fig. 4. Comparison of exchange rate constant k_e values for old and new Chemcatcher™ sampler designs. Calibration experiments were conducted at water temperature of 18 °C and a carousel rotation speed of 40 rpm.

4.5. Calibration data for the new Chemcatcher™ design

Exchange kinetics of hydrophobic organic pollutants ($\log K_{OW} > 4$) between sampler and water were faster with the new than with the old design of the non-polar Chemcatcher™, and this is likely to be due to the shallower cavity in the new design reducing the thickness of the aqueous boundary layer at the diffusion limiting membrane surface. In order to avoid a lot of extra work it is important to determine whether the extensive calibration data set for the old design can be used with the new design.

Previously Vrana et al. (2006) demonstrated a strong correlation between uptake and offload kinetic parameters for non-polar analytes and their deuterated analogues over a wide range of temperatures and flow rates:

$$R_S = k_e V_D K_{DW} \quad (4)$$

The correlations between R_S and k_e for phenanthrene and fluorene are shown in Fig. 5. The data are based on nine flow-through experiments performed with the old design under various exposure conditions (Vrana et al., 2006) together with calibration data obtained with the new design under one set of exposure conditions in this study. The linear regression lines for the old sampler can be extrapolated to fit the observed

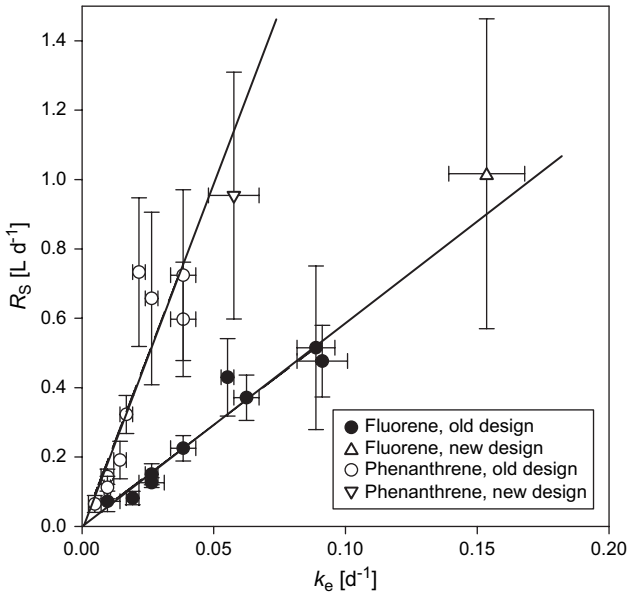

Fig. 5. Correlation between sampling rates R_S of fluorene and phenanthrene and offload rate constants k_e of their perdeuterated analogues (PRCs). The data represents nine flow-through experiments at various exposure conditions, performed with the old design of sampler body (Vrana et al., 2006) and one exposure experiment with the new sampler body. The lines demonstrate that the good correlation derived for the old design can be extrapolated for the new design.

data for the new sampler design. Thus, R_S values for new sampler design can be accurately extrapolated from the $R_S = f(k_e)$ curve obtained using the old design.

5. Conclusions

This study shows that PRCs can compensate uptake rates of non-polar pollutants for changes in local hydrodynamic conditions at the surface of the diffusion membrane caused by modification of the sampler body geometry. Since these compounds ($\log K_{OW} > 4$) are accumulated under aqueous boundary layer control, sampling rates are increased, and hence sensitivity is improved, by reducing the thickness of the stagnant layer associated with the cavity of the sampler. The sampler accumulates chemicals under aqueous boundary layer control, and the thickness of this will fluctuate with water turbulence. In the new design the thickness of the boundary layer will be smaller and hence both the sensitivity and the effect of turbulence will be proportionately greater. A balance has to be made between sensitivity and reducing the impact of turbulence on sampling rates. It is unlikely that a flow-insensitive passive sampler can be developed that has sufficiently high sampling rates for use in all environments (Booij et al., 2007). Nevertheless, where PRCs are used the need for extensive, time-consuming re-calibration is avoided when sampler body geometry is altered. This result has general consequences for all samplers (such as semipermeable membrane devices [SPMD] and membrane enclosed sorptive coating [MESCO]) used for non-polar organic pollutants where sampling rates are under boundary layer control (Huckins et al., 1993; Vrana et al., 2001). However, extension of this approach to samplers for polar organic compounds has proved problematic (Alvarez et al., 2007).

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Review

Potential applications of passive sampling for monitoring non-polar industrial pollutants in the aqueous environment in support of REACH

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ABSTRACT

Possible roles of passive sampling within the context of the European REACH legislation are discussed. Passive samplers can provide information on environmental concentrations, fate and behaviour of substances of concern. They can potentially replace biota in the assessment of bioavailability, having advantages including lower cost and variability, and greater repeatability and acceptability on ethical grounds. Where remedial actions (e.g., product withdrawal, replacement or redesign) may be required, wrong decisions are potentially very costly. Against this background it may be possible to develop strategies based on passive sampling that will protect the environment from potential damage whilst minimising operational costs.

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Contents

1. Introduction

The European Union (EU) has introduced new legislation (enacted in June 2007) that aims to manage all anthropogenic chemicals (manufactured in Europe or imported) that are used in significant quantities in order to protect human health and the environment. The legislation is called Registration, Evaluation, Authorisation and Restriction of Chemical Substances (REACH—Regulation (EC) No. 1907/2006) and replaces more than 40 existing European Directives and Regulations. Details are given in Corrigendum to Regulation (EC) No. 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals [1]. A European Chemicals Agency has been established in Helsinki (Finland) to deal with the routine management of this legislation. REACH has removed the distinction between existing and new substances that was present in the old legislation, and has thus increased dramatically the number of chemicals that require registration. A further marked change is that the burden of proof that chemicals placed on the market are safe has been shifted from the regulatory authorities to the applicant for registration. There is a great incentive to register compounds since unregistered substances cannot be manufactured or placed on the European market, and it is expected that in the region of 180,000 substances will be pre-registered during 2008. Whilst the legislation will be phased in by tonnage to spread the burden, the process will continue, and by 2018 it will be necessary to register all compounds produced in quantities of 1 tonne or more per year. Some substances

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(e.g., pharmaceuticals) that are covered by other legislation are exempt from REACH. A tighter time scale and higher priority apply to substances (e.g., carcinogens, persistent and bioaccumulative substances, and potential endocrine disruptors) that are recognised as hazardous. Registration is compulsory for compounds that are released into the environment during use. This legislation will require risk assessments of this large range of substances based on predicted environmental exposure. In some cases, especially for potentially hazardous chemicals, and those released into the environment during use, environmental monitoring will be required to provide the evidence to support registration. This may involve measurements in a range of compartments including water, sediment, suspended solids, and air for volatile substances. In order to measure environmental fate it will be necessary to use robust and representative monitoring data. The cost of obtaining this information is potentially high, and any methods that can reduce this will be helpful to a wide range of industries. A variety of approaches to monitoring has been developed to replace the current regulatory practice of intermittent grab sampling combined with classical laboratory analysis in order to reduce costs and increase representativeness and reliability of the data obtained [2]. This paper will not attempt a comprehensive review of passive sampling since in recent years there have been several exhaustive reviews of the available literature [3–7]. Instead this paper will identify areas where passive sampling could provide reliable information to support applications for registration under the REACH legislation in a cost effective manner, and focus on these after a brief overview of passive sampling technology.

2. Current monitoring practice

Current regulatory monitoring practice has been used for many years, and has become accepted for legislative purposes because of the significant developments and improvements in laboratory-based analytical chemical methods over the last two decades. These have reduced levels of detection for a wide range of analytes, and provide increased confidence in measurements made. This has been helped by the introduction of quality control protocols and associated quality assurance procedures that are underpinned by the provision of good quality reference materials and inter-laboratory trials. Until recently relatively little attention has been paid to the sampling step that precedes the laboratory analysis [8]. Sampling is particularly problematic for many of the industrial chemicals of concern, many of which are classified as priority pollutants in the aquatic environment. This is particularly marked for compounds which are present at only trace levels, and for highly lipophillic compounds of which only a small fraction is truly dissolved, and most is bound to either dissolved or suspended organic matter. For many years sampling of the aquatic environment has relied on the collection of spot (bottle or grab) samples that are transported to a laboratory for qualitative and/or quantitative analysis. Although this apparently simple procedure is commonly used to underpin legislation, there are problems associated with it, and significant errors can arise, particularly where pollutants are present at only low levels. For some analytes it is necessary to take steps (e.g., the addition of a preservative such as a biocide, or for metals an acid) to ensure the integrity of the sample during transport and storage [9]. Even so the sample can become modified by processes such as adsorption to the walls of the sample container, volatilisation, and either chemical and/or microbial degradation. A further drawback of spot sampling is that it provides information on water quality only at the instant that the sample is taken. This may not be representative of average water quality, especially where concentrations of pollutants fluctuate in time due to factors such as run-off associated with seasonal application of pesticides, sporadic industrial discharges and rain events [10]. In order to overcome this latter problem, methods such as automated sampling equipment that collect samples at regular intervals to give a more representative sample of the water body over periods of time from hours to days have been used (e.g., composite sampling devices and on-line analytical systems). However, in these systems there is a large potential for contamination from, and adsorption to components such as sampling tubes, valves and pumps. For compounds present at only trace levels these losses can represent a significant proportion of the chemical originally present and this can introduce large uncertainties where either spot or automated sampling methods are used; and these will reduce confidence in any subsequent modelling or risk assessment procedures. The sampling stage is even more problematic for other environmental compartments such as sediment, suspended material, and sludge, despite recent improvements in the extraction methods available for these difficult matrices.

Interpretation of the biological relevance of the levels of pollutants (particularly non-polar compounds) measured by current sampling, sample preparation, and analytical procedures is difficult. This is particularly important for substances identified as potentially persistent and bioaccumulative. In an attempt to obtain more toxicologically relevant information, living organisms, typically caged fish or caged sessile species such as bivalve molluscs, have been used as monitors. Organisms are deployed over extended periods and changes in the levels of pollutants of interest are measured in body tissues at the beginning and end of the trial. This approach can give an estimate of the average environmental concentrations of pollutants over the deployment period (up to several months). This bioaccumulation gives a qualitative indication of levels of pollutants and can be used in a comparative way between sites and between times to measure spatial and temporal variation, respectively [11]. However, this method has some limitations. It is not possible to expose organisms in harsh environments such as in some industrial and domestic discharges where concentrations of pollutants exceed toxic levels. A further difficulty is that the test species, even when taken from apparently uncontaminated sites, may contain measurable levels of some pollutants before deployment and it is necessary to depurate before use, and take large, representative control samples at the start of the monitoring campaign. The analysis of tissue samples from biota is expensive and time consuming because of the complex sample preparation step that is necessary. It is not possible in many cases to assume that because a particular chemical is not bioaccumulated it is not present in the water column. Some pollutants are eliminated by the test animals, and this can occur at rates ranging from negligible to matching or exceeding the uptake rates. Passive samplers have been developed to overcome some of the shortcomings of both spot sampling and biomonitoring procedures. Some forms of these devices have been designed to mimic the uptake of pollutants by living organisms, and as such may be particularly useful in preparing REACH registration applications for some classes of potentially bioaccumulative or toxic compounds.

3. Passive samplers

Passive samplers have been used in environmental monitoring since the beginning of the 1970s. The early designs were used to measure concentrations of gaseous pollutants in air [12], and this technology is now widely used in monitoring ambient air quality and workplace exposures to potentially harmful compounds such as volatile organic solvents. These air samplers are now commercially available, and standards and official methods (e.g., ASTM, EPA,

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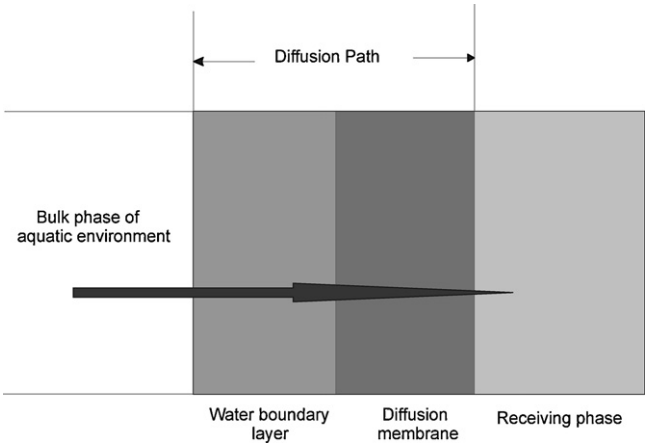

Fig. 1. Schematic diagram showing the components of passive samplers that in kinetic mode maintain a low concentration at the surface of the receiving phase so that the rate of diffusion of substances across the water boundary layer and/or diffusion-limiting membrane is proportional to the concentration in the bulk water phase.

NIOSH, CEN and ISO protocols) have been developed for use with these devices. A number of global networks of passive samplers has been established to map the movement of persistent anthropogenic organic pollutants across the world. More recently passive samplers have been developed for monitoring concentrations of pollutants in water, soils and sediments. However, this technology has not gained similar acceptance within the water regulatory context. Several designs of device are available either as experimental prototypes or as commercial products [4].

The same principles of operation apply to all passive sampler devices, both for use in air and water. Uptake of a chemical from the environment is by passive diffusion. The samplers comprise a receiving phase that accumulates contaminants, and has a very high affinity for them so that the concentration at its surface is maintained close to zero, and a diffusion-limiting layer that separates the receiving phase from the bulk water environment (Fig. 1). Hence the mass of a contaminant accumulated is determined by its concentration in the water, the length of exposure, and the sampling rate (R_s) of the sampler. The latter is determined by a number of factors including the area of sampler available for diffusion, the properties of the diffusion-limiting layer (e.g., thickness and resistivity), and the properties (e.g., size and polarity) of the chemical. R_s can be interpreted as the apparent volume of water cleared of pollutant per unit of time. For kinetic samplers, operating in the linear uptake mode, far from the thermodynamic equilibrium between sampler and water, R_s is independent of the concentration of the pollutant in the water. For long exposure times that exceed the linear uptake phase the extracted volume is constrained by the sorption capacity of the passive sampler. When thermodynamic equilibrium between sampler and water is approached, sampling is no longer integrative, and the accumulated amount of analyte no longer reflects the time-weighted average concentration. Most passive samplers measure only concentrations of freely dissolved analytes and not the total amount of analyte present in the water column. Fractions that are bound to suspended particulate matter or to dissolve organic carbon (DOC) are not measured due to either their exclusion by the diffusion-limiting layer, or poor uptake by the receiving phase. In all passive samplers the mass accumulated is used to determine the external concentration, but depending on sampler design and mode of operation this can reflect either the equilibrium concentration or the time-weighted average (TWA) concentration over the deployment period (days to months). Where environmental concentrations fluctuate in time then the kinetic samplers are used, but in more constant or slowly changing conditions the equilibrium samplers are deployed. Since the samplers accumulate substances over a prolonged period the analytes are effectively preconcentrated, and this can bring them above the level of detection of the analytical method. It would be necessary to collect and extract large volumes of water in order to achieve a comparable sensitivity with spot sampling.

Passive samplers have been developed for monitoring environmental pollutants from a range of chemical classes including metals, polar organics, non-polar organics, organo-metallics, and volatile organics [7]. Samplers have been used in both equilibrium and kinetic modes for some of these classes. Equilibrium samplers have been mostly used to measure concentrations of pollutants in ground water and in sediment pore water [13,14]. A number of designs is available, and one has been used to monitor volatile organic compounds in ground water [15]. A much wider range of kinetic samplers (Fig. 2) is available, and these have been used for all chemical classes of pollutant [16]. For metals two main designs of kinetic samplers are available for the measurement of TWA concentrations of the labile fraction of metals. In the diffusive gradients in thin films (DGT) sampler a thin hydrogel layer forms the diffusion-limiting membrane, and this overlays a chelating agent receiving phase. The Chemcatcher® (metals version) uses a similar receiving phase (in this case in the form of a commercially available Empore™ disk) and the diffusion-limiting layer is provided by a cellulose acetate membrane [17]. The DGT has an established record in the monitoring of metals such as cadmium, chromium, copper, lead, and zinc in a wide range of aquatic environments [18,19]. Information on the relative concentrations of labile and bound species of metal present in the water can be obtained by simultaneous deployment of DGTs with hydrogels of different porosities. This is important since some species of metals are far more toxic than others.

The Chemcatcher® (polar organic version) and polar organic integrative sampler (POCIS) are designed to monitor concentrations of polar ($\log K_{ow} < 4$) organic pollutants [20,21]. In both samplers the diffusion-limiting membrane is a polyethersulphone sheet with water-filled micropores, and the receiving phases comprise a range of adsorbent materials, either bound in an Empore™ disk, or in a free particulate form. These have been used for measuring the TWA concentrations of a range of polar herbicides, pharmaceuticals, and personal care products, and are described more fully in another paper in this issue [22].

A much wider range of passive samplers is available for monitoring non-polar organic substances ($3 < \log K_{ow} < 8$). The semi-permeable membrane device (SPMD) consists of a lay-flat low density polyethylene (LDPE) tube (the diffusion-limiting layer) containing a small quantity (up to 1 mL depending on the size of sampler) of triolein (the receiving phase) [23]. This lipid was originally incorporated in order to allow the sampler to mimic a biological organism. The Chemcatcher® (non-polar organic version) also has a LDPE diffusion-limiting membrane, but the receiving phase consists of an Empore™ disk containing a C_{18} chromatographic adsorbent saturated with *n*-octanol [24,25]. In this sampler the receiving phase and membrane are supported and held by a watertight PTFE body. The membrane-enclosed sorptive coating (MESCO) sampler is a miniaturised sampler with a receiving phase that comprises a small rod or tube coated with a polydimethylsiloxane or silicone layer [26]. This is housed in bag made of either cellulose or LDPE that acts as the diffusion-limiting membrane. Other samplers that have been widely studied include LDPE strips and silicone rubber sheets [11,27]. For both of these the sampler material acts as the receiving phase and the water boundary layer at the surface provides the diffusion-limiting layer.

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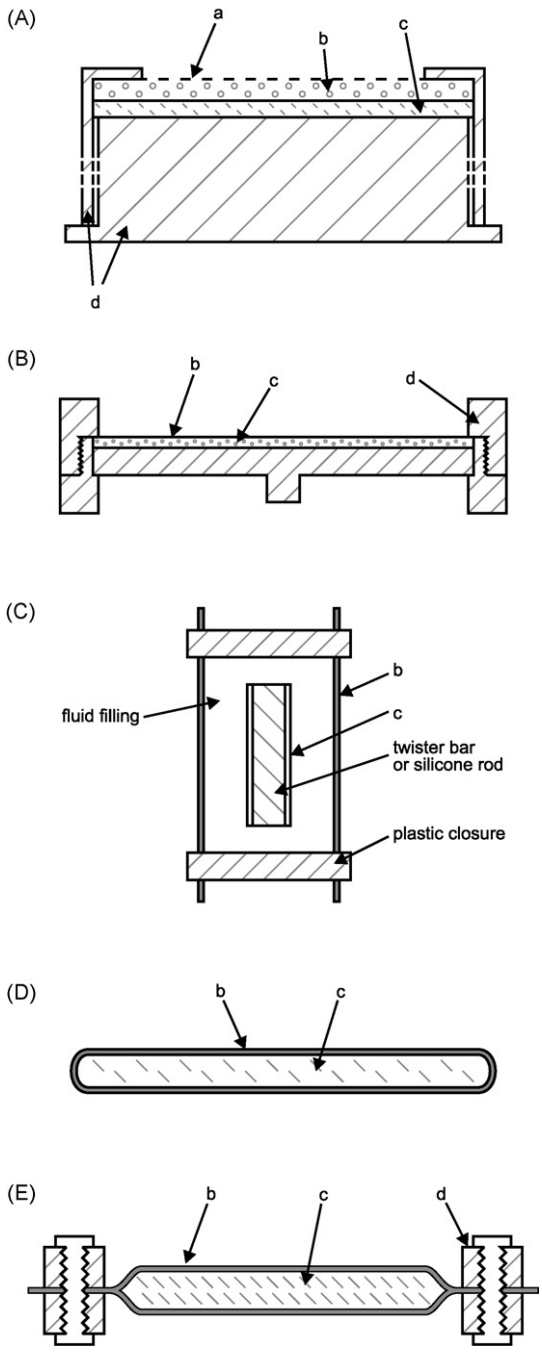

Fig. 2. Schematic diagrams of the main designs of passive sampler showing the components. Key: (a) protective membrane, (b) diffusion membrane, (c) receiving phase, and (d) sampler body. (A) Diffusive gradients in thin films (DGT), (a) prefilter, e.g., cellulose nitrate, (b) hydrogel, (c) gel containing chelating agent, and (d) plastic; (B) Chemcatcher®, (b) low density polyethylene, polyethersulphone, or cellulose acetate, (c) Empore™ disk, e.g., C_{18}, poly(styrenedivinylbenzene) copolymer or chelating resin, and (d) PTFE; (C) membrane-enclosed sorptive coating (MESCO), (b) dialysis membrane, or low density polyethylene, and (c) polydimethylsiloxane or silicone; (D) semi-permeable membrane device (SPMD), (b) low density polyethylene, and (c) triolein; (E) polar organic integrative sampler (POCIS), (b) polyethersulphone, (c) chromatographic phase, e.g., Oasis, and (d) stainless steel flanges.

Whilst these samplers all have the same basic components, their structural configurations, handling properties, ease of use and performance are widely different. They all have strengths and weaknesses, and it is important to select the sampler most appropriate for each particular problem to be investigated. The SPMD has the largest base of published data to support its field application [28]. It has a large surface area and since the rate of diffusion is proportional to this, it can achieve very high sampling rates (R_s values in excess of 1 L h^{-1}) for some compounds. This device is particularly well suited for measuring analytes present at trace levels. The extraction of the pollutants from the triolein, and preparation of the sample for analysis can be time consuming and use large volumes of high purity solvents (usually hexane). Recently a number of techniques have been developed to reduce the time and volumes of solvent necessary to achieve efficient extraction of pollutants from deployed SPMDs. These methods include pressurised fluid, microwave assisted and ultrasonic extraction techniques [29]. The recovery of sequestered chemicals from the Chemcatcher® is more straightforward as the receiving phase can be directly extracted with small volumes of solvent [24]. Preparation for analysis requires only a concentration step. However, this sampler has a smaller surface area (17.5 cm^2) than the standard SPMD (450 cm^2), and hence proportionally lower (≈26-fold) R_s values. The MESCO has a small surface area and hence low sampling rates [30]. However, for this sampler solvent extraction is not necessary prior to analysis since pollutants on the sorbent coated bar can be desorbed directly in the modified injection port of a gas chromatograph. This increases analytical sensitivity since all of the analyte is introduced into the instrument, and there is no interfering solvent peak, but it is not possible to have repeat injections (single shot analysis). The LDPE and silicone strips are similar to the SPMD but here there is no lipid phase and the polymer acts as the receiving phase, whilst a boundary layer of water provides the diffusion-limiting layer [31,32]. These can have large surface areas, and associated high sensitivities, but require large volumes of solvent to extract the pollutants. In addition, for the silicone rubber it is necessary to extract (e.g., using Soxhlet extraction) the sheets before deployment in order to remove any interfering monomers and other contaminants to ensure low background levels. However, after deployment the preparation of the extract for analysis is simpler and less expensive than for the SPMD since steps to separate substances from lipid are eliminated. One problem common to all passive samplers is that to a greater or lesser extent, depending on design, the uptake rates are dependent on temperature and turbulence of the water [27,33]. The rate of uptake can also be deleteriously affected by the growth of microorganisms (biofouling) on the surface of the diffusion-limiting membrane [34,35].

3.1. Calibration

Calibration of equilibrium samplers depends on estimating the sampler/water partition coefficients for the compounds of interest. In some cases this parameter can be predicted by quantitative models on the basis of physicochemical properties. However, bias can be introduced into the estimation of the partition coefficients for highly non-polar compounds. Since these can bind to the walls of the calibration tank, and to DOC and to any suspended organic matter these can lead to an overestimation of the freely dissolved fraction in the water phase. This problem has been addressed by the application of a co-solvent method using a range of concentrations of methanol in the external water phase [11,36].

For kinetic samplers a range of approaches has been adopted to estimate the calibration parameters [16,37]. For these samplers the kinetics of uptake can be described as an exponential approach to equilibrium, and although different models with varying degrees of complexity have been developed, the key parameter for all of them is the apparent water sampling rate (R_s) that has units of volume per unit time. Laboratory experiments are needed to estimate this parameter, and several methods have been used, including static exposure, static exposure with renewal, and continuous flow [38].

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Ideally these should provide estimates that cover a range of water temperatures and turbulence conditions that would be found in field exposures. The range of turbulences is usually achieved by varying the stirring rate in the calibration tank [25]. The problems of bias for very hydrophobic compounds are similar to those described for the equilibrium samplers, where the presence of dissolved or suspended organic carbon can reduce the effective (freely dissolved) concentration of analytes in the calibration tank [16].

Biofouling of the sampler membrane can have an effect on the value of R_s [34,35], but is difficult to model since the development of a biofilm can vary widely at one site at different times of the year and between sites depending on the diversity of fouling organisms present, and the rate of settlement and growth. Despite the difficulties surrounding the calibration process, a lot of data have been collected for the various designs of passive samplers for non-polar analytes.

One approach to solving the problems associated with the determination of R_s values for use in a wide range of environmental conditions has been to use performance reference compounds (PRCs) [39,40]. These are compounds (typically deuterated analogues of the compounds to be measured) that are loaded onto the receiving phase of the sampler prior to deployment, and that offload at a measurable rate. If the kinetics of uptake and offloading are isotropic, that is the rates of offloading of the PRCs are affected by temperature, turbulence and biofouling in a manner similar to the uptake rates of pollutants, then the rates of loss of PRCs from the sampler can be used to correct the uptake rates of pollutants for the effects of those environmental variables. This approach can effectively provide *in situ* calibration of the samplers, and has been widely used for most of the range of samplers used for non-polar pollutants. This has the advantage of removing the necessity of monitoring water turbulence that is difficult to measure, and does not necessarily reflect conditions prevailing at the face of the diffusion membrane. There is also some evidence that this approach to calibration can compensate for some of the impact of biofouling on uptake [40,41]. The use of PRCs can increase confidence in the field measurements, and provides a way of introducing quality control measures into the sampling process.

4. Applications of passive sampling in monitoring industrial chemicals

4.1. Measurement of time-weighted average concentrations of substances in water

Passive sampling was developed in part as a response to a need to monitor levels of high volume industrial chemicals and their derivatives like the PAHs [42–45], organo-chlorinated pollutants, polychlorinated dibenzo-p-dioxin, polychlorinated dibenzo-p-furan [46], chlorinated and alkylated phenols [47,48] and PCBs [49,50], and persistent non-polar pesticides such as the cyclodienes, and DDT [51]. SPMDs have proved useful in this area because of their high sampling rates for non-polar substances ($\log K_{ow} > 4$) that are dissolved in water at only trace levels (low ng L^{-1} to pg L^{-1}). Large volumes of water would need to be processed in order to measure these compounds using bottle samples linked to conventional analytical methods. The applications have been extended to cover new and emerging compounds of concern including organo-metals used in wood preservation and in antifouling preparations (e.g., tributyl tin) [52,53]; polycyclic musk xylene, musk ketone used in domestic products [54], and polychlorinated naphthalenes [55].

Passive sampling has the potential to contribute the REACH registration process in a number of ways. A decision on the approval of a registration of a substance under the REACH regulations will be based on a number of factors including volume of use, predicted environmental concentration (PEC), toxicological properties, exposure of aquatic organisms and bioavailability. For existing and new compounds initial assessments will be based, where possible, on a modelling approach. More work will be needed to evaluate substances that are lipophillic and stable, and that will potentially be released into the environment, either directly or indirectly. Compounds falling into this category will include some substances that are components of personal care and household products that will enter the environment via the waste water system. In order to estimate any environmental risk associated with individual substances, it is necessary to estimate the movement of compounds of interest to the aquatic environment. This must take into account the various possible sources, and in particular inputs from waste water effluent. For existing substances of concern it may be necessary to monitor concentrations of compounds in domestic effluents and surface waters in order to obtain data to estimate the degree of environmental risk. This is not straightforward where inputs into sewage treatment plants (STPs) and effluents from them fluctuate widely over a diurnal period, and vary between seasons. In addition, they can be markedly affected by sporadic weather events. Planning a monitoring programme is further complicated by a lack of spatial homogeneity following a discharge of effluent to a river. It is not uncommon for a plume of effluent to remain close to one bank of a river for many kilometres, and mixing is rarely instantaneous [56]. This situation can be even more complicated in tidal waters. There is a need for mapping the distribution of effluent in mixing/dilution zones in order to obtain a representative picture of dispersion and dilution of the substances of interest. Whilst monitoring in perceived 'hotspots' can provide a worst case scenario, it may be very misleading, and this will not provide representative information on average and/or maximum values of environmental concentrations. Such maximum environmental concentrations (MECs) may skew modelling and lead to unrealistic risk assessments. Appropriate sampling frequency, sampling period and pattern are prerequisites for representative sampling to be achieved. Castiglioni et al. [57] found a difference of a factor of two between maximum day time and minimum night time influent loads in an STP. Such a variation may introduce bias when using time-proportional sampling methods, in this case with an estimated underestimation of influent load of 5–15%. In order to obtain representative information that will give the necessary level of confidence in a risk assessment it would be necessary to use a high frequency of spot sampling, or flow-weighted composite sampling. This would be very expensive, particularly where there was marked local spatial variation. Costs could be reduced by using passive samplers deployed over a period of weeks at a range of sites to provide TWA concentrations of the substances of interest.

An example of where the utility of passive sampling has been demonstrated is provided by the monitoring of polybrominated diphenyl ethers (PBDE) that are used as flame retardants in a wide range of goods and products for use in the home. These compounds are extremely hydrophobic ($\log K_{ow}$ from 4 up to as high as 10), and are present in surface waters at sub-ppb levels; but are of concern because they are very persistent and have been shown to bioaccumulate, and have been included in regulatory monitoring programmes in water and sediments. One particularly interesting monitoring campaign for the substances that illustrates the potential utility of passive sampling in this context was that of Booij et al. in the Scheldt estuary and along the North Sea coast of the Netherlands [58]. Using SPMDs this group was able to measure a series of PBDE congeners present at very low concentrations (0.1–5 pg L^{-1}). However, this is because of the large factor of preconcentration exhibited by these devices. There are problems when dealing with the extremely hydrophobic congeners in this series

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Table 1
Time-weighted average (TWA) water concentrations for a 14-day period estimated from the levels in the Chemcatcher® and those measured using filtered spot samples at the sampling site in the River Meuse.

Compound	log K_{ow}	TWA concentration (ng L^{-1})	
		Passive sampler[a]	Filtered spot samples[b]
Fluorene	4.2	7.5 (±1.2)	1.6 (±0.1)
Phenanthrene	4.5	10.2 (±2.0)	8.4 (±3.5)
Pyrene	5.1	9.6 (±1.8)	22.9 (±10.8)
Fluoranthene	5.1	10.5 (±1.8)	11.7 (±4.1)
Chrysene	5.7	3.7 (±0.3)	8.7 (±0.8)

[a] The TWA concentration was calculated as arithmetic average of the three estimates calculated from analyte amounts found in replicate samplers. The uncertainty level of this estimate was expressed as the standard error of the mean (in parentheses).

[b] The arithmetic average of the six measurements of spot samples at regular intervals during 14 days of sampler exposure was taken as the best estimate of the TWA concentration. The uncertainty level on this estimate was expressed as the standard error of the mean (in parentheses).

since as discussed above calibration procedures can give underestimates of uptake rates because of the tendency of these compounds to associate with DOC, suspended solids, and components of the calibration rig.

Another application that demonstrates the utility of passive sampling is provided by the field trials carried out by Vrana et al. in a stream (the Spittelwasser) that flows through a highly polluted industrial area (Bitterfeld in Saxony-Anhalt, Germany) using the MESCO device [30]. They measured TWA concentrations of PAHs, PCBs, and some cyclodienes using 20-day exposures of the samplers alongside grab samples taken at the beginning and end of the deployment period. Some compounds (hexachlorobenzene, acenapthenene, fluorene, benzo[a]anthracene and chrysene) were measured quantitatively in the MESCO samplers but were not recovered from grab samples. Others (γ-hexachlorohexane, anthracene, phenanthrene, fluoranthene and pyrene) were measured in both samplers and grab samples, and the estimates of concentrations differed by up to a factor of two between the two methods. These differences could have been due to fluctuations in the concentrations in the period between grab sampling events. The variability between duplicate MESCO samplers was small (relative percentage difference in the range 6–15%).

A field trial in the River Meuse (at Eijsden in the Netherlands) using the Chemcatcher® passive sampler to monitor PAHs and using the PRC approach demonstrated the utility of the samplers to provide measures of TWA concentrations where there are fluctuations in concentration with time, and enabled a comparison of spot and passive sampling for compounds covering a limited range of polarity [59]. In this trial six equally spaced spot samples were taken over a 14-day deployment period, and the average concentrations of five PAHs (chrysene, fluoranthene, fluorene, phenanthrene and pyrene) that were quantifiable in both spot samples and passive samplers were calculated. The estimates of TWA concentrations based on passive sampling and spot sampling are presented in Table 1. For fluoranthene and phenanthrene there was a reasonable agreement (<20% difference) between the estimates of concentration derived from spot and passive sampling. However, for chrysene and pyrene the passive sample-based estimates were markedly less than the estimates based on spot sampling. The concentration of fluorene estimated by passive sampling was higher than that measured in spot samples. There was a marked increase (approximately a factor of 10) in the concentration of phenanthrene measured in spot samples during the first week of the trial. However, the TWA concentrations estimated by the two sampling methods were very similar. This indicates that most of the phenanthrene in the filtered fraction was in the freely dissolved form, and demonstrates the

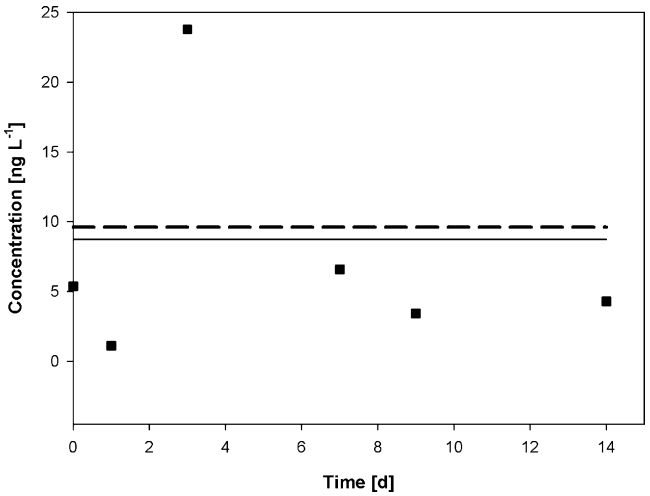

Fig. 3. Concentrations of phenanthrene in six spot samples (filtered at 0.45 μm) taken at regular intervals during a 14-day deployment of three replicate Chemcatcher® samplers in the River Meuse (Netherlands). The water temperature varied between 18 and 21 °C, and the samplers were maintained at a depth of 1 m. The solid line represents the time-weighted average (TWA) based on the spot samples, and the dashed line the TWA estimated from the passive samplers.

potential for passive sampling to provide TWA concentrations even where the concentration in the water fluctuates in time (Fig. 3). It is, however, difficult to compare estimates of concentrations of substances obtained by spot and passive sampling. The fractions of contaminants measured by the two methods can be different, especially in a regulatory context where for organics unfiltered spot samples are used for analysis. Any of the substance bound to particulate material or DOC will not be available for uptake by passive sampling. Even, as in this comparative study, where spot samples were filtered through 0.45 μm filters prior to analysis, there can still be differences between the data from the two methods since some of the compound can be bound to DOC. The concentration of the truly dissolved fraction of hydrophobic analytes in water will depend on the level and quality of the DOC present, and this may change with time. It may change rapidly in, for example, a weather event such as heavy rainfall followed by run-off from surrounding land. The impact of the concentration of DOC on the freely dissolved fraction of organic compounds available for uptake by passive samplers will increase with increasing hydrophobicity of the pollutant. A further factor that can lead to apparent differences between the concentrations estimated by the two methods is the occurrence of fluctuations in concentration not detected by the frequency of spot sampling used. It will be particularly difficult to compare the values from the two methods where spot sampling is infrequent, for instance where spot samples are taken, for convenience, only at the beginning and end of the deployment period. This needs to be kept in mind when interpreting data from the monthly samples used in regulatory compliance monitoring under the WFD.

The applications outlined above illustrate the potential utility of passive sampling for providing robust and representative information on concentrations of freely dissolved (biologically significant) fractions of non-polar chemicals in various divisions of the aquatic environment. This could be particularly useful within the context of the registration of existing substances of concern within the remit of the REACH legislation. These methods can provide representative data to underpin studies of the environmental fate and distribution of substances in waste, surface and ground waters, even where inputs fluctuate diurnally, seasonally or sporadically. In most cases the use of passive sampling would be less expensive than using high frequency spot sampling to obtain this information.

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4.2. Use of passive samplers to assess the potential for bioaccumulation

It is important to assess the potential for bioaccumulation for substances identified as potentially persistent and bioaccumulative. Passive samplers could provide an alternative to the use of biota in this context. The information from passive sampling could more representative of general bioavailability particularly where the substance of interest is metabolised by the test species. Since there is marked inter-specific variation in metabolic capability, the information from a single test species (usually selected on the basis of availability and ease of deployment) may not be representative of other organisms within the ecosystem under consideration.

The potential of passive samplers for providing sound information to underpin registration packages under the REACH legislation is illustrated in a number of recent studies in which passive samplers were deployed alongside biomonitoring organisms. A detailed and rigorous study of the bioavailable fractions of PAHs, PCBs, and organo-chlorine pesticides at fresh water sites in the Amsterdam (Netherlands) area was carried out by Verweij et al. [60]. This group examined levels of compounds from these families of non-polar pollutants in the muscle tissue of caged carp, SPMDs, and sediments. The sampling sites covered a wide range from lakes that were thought to be relatively uncontaminated to sites that receive significant inputs from domestic effluent, dredging activities, and major organic chemical plants (including a coal tar refinery plant). SPMDs (loaded with PRCs) were deployed alongside caged carp at each site, and sediment samples were taken during the exposure period. Since for highly hydrophobic substances the concentrations in the water are generally very low, and typically below the level of detection of standard analytical methods, the concentrations were estimated on the basis of their SPMD-water partition coefficients. For some of the groups of pollutants investigated in this study the control levels in unexposed fish were relatively high, and the variation between individuals was large. This reduced their utility as indicators of exposure, though tissue levels of pollutants were elevated in fish exposed at heavily polluted sites compared with those in animals deployed at cleaner sites. In contrast the variation between individual SPMDs at each site was small (<10%). The water concentrations calculated on the basis of both SPMD and carp data were generally predicted to fall below the level of detection of the analytical method. The SPMD method does not assume equilibrium conditions and the fish model does. Since the data indicated that the fish tissues were not in equilibrium with the external medium, the concentrations of most substances found in this trial in water were more reliably estimated using the passive samplers. The use of concentrations of pollutants in sediments to estimate concentrations of highly hydrophobic materials in water proved to be less reliable than the use of SPMDs. The authors indicated that this could be due to a lack of homogeneity in sediments in terms of both the nature and distribution of organic matter present. However, the overall levels of pollutants present in the sediment gave a useful indication of exposure of a site to non-polar pollutants. The striking conclusions of this study were that levels of substances in sediments and fish tissues do not provide a reliable estimate of bioavailability. Since the extraction and analysis of animal tissues and sediments are more complex than for passive samplers, and deployment of fish is far more expensive, and ethically questionable, passive sampling provides an attractive, cost effective alternative to biomonitoring. This approach has potential to provide the reliable and robust information required to support registration applications within REACH.

Some of the general conclusions of the above study were supported by the work of Smedes who deployed silicone rubber passive samplers alongside mussels (*Mytilus edulis*) at a range of coastal (North Sea and Wadden Sea) and estuarine sites (River Scheldt) in the Netherlands [11]. All eight sites had sufficiently high salinities to enable the marine mussels to survive. In this study, measurements of non-polar pollutants in both mussels and passive samplers spanned 4 years, and enabled seasonal effects to be measured. Uptake by the mussels was calculated as the difference between the concentrations in control animals at the beginning of the exposure period and those in deployed animals after exposure. For most compounds the ranges of concentrations found in mussels were consistent with ranges of freely dissolved concentrations in the water calculated from the passive samplers. Seasonal fluctuations in estimated concentrations of pyrene in the water were reflected in the seasonal changes in concentrations in the mussel tissues. However, there were a few exceptions, for example, phenanthrene where the relative range in concentrations in the water derived from sampler data was more than three times higher than that for the estimates based on mussels.

Laboratory investigations to assess the utility of passive samplers (in this case SPMDs) in measuring the bioavailability of PAHs to a commonly used test organism, *Daphnia magna*, took into account the effects of DOC in the external medium [61]. A range of concentrations of DOC was produced using commercially available humic acids, or DOC extracted from river water, or an artificial mixture of meat and vegetable extracts and sugars. The latter was used in most studies and the authors found a reasonable correspondence between the fractions of the test PAHs available to the *D. magna*, and those available to the SPMDs. There was a slight bias with the SPMD available fraction tending to be smaller than the bioavailable fraction, and therefore the former slightly underestimates the latter. This bias increases with increasing concentrations of DOC, but is less than 50% where DOC levels are in the range found in most rivers in temperate regions. Since the variation between bioaccumulation assays is large, the observed deviation between the *in vitro* and *in vivo* systems is in practice relatively unimportant.

These examples illustrate a number of the issues that need to be considered when comparing accumulation by passive samplers with that by biota. Whereas the uptake by samplers is based purely on thermodynamic factors, albeit affected by environmental factors such as temperature, turbulence and biofouling, uptake by living organisms is also affected by biological factors that are more difficult to control or measure. The bioaccumulation factor (the ratio between the concentration in the water and the concentration in the biota) will depend on amongst other things the size, behaviour and metabolic capability of the species used, the amount of growth over the deployment, and the reproductive status. The latter can have a marked effect where a large proportion of an animal's resources is exported in the form of gametes. Additionally some animals that feed on detritus either from the sediment or from suspended particles may absorb pollutants from both dissolved fractions (primarily over the respiratory surface) and from the food. Thus concentrations in test organisms do not always give a good reflection of concentrations in the water phase, and the reliability will vary from compound to compound. In the above studies there was a reasonable agreement between the concentrations in animals and the predicted concentrations in water, but there were important exceptions. The estimates of concentrations in water based on passive sampling may be more representative of levels of pollutants in the water column and general bioavailability than measurements based on a single test species that may be exposed internally to a pollutant, but fail to accumulate it to detectable levels because of rapid elimination. Increased confidence in the estimates of bioavailability based on passive samplers would result from comparisons with multiple species.

Passive samplers could provide a low cost and robust means of predicting the bioaccumulation of substances by means of laboratory-based assays for both existing and substances. Where

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field data are required, this technology could provide, representative measurements of bioavailability in a range of environments, including some where organisms could not be deployed (e.g., industrial and domestic effluents). Since most test organisms are limited to either fresh water or saline water, it is not possible to deploy them in a wide range of environmental conditions, and so it is difficult to use biomonitoring to obtain comparable data in all regions of a river and its estuary.

Passive samplers have been used in combination with toxicity assays either to determine total toxicity of the pollutants in a water body, or in combination with a bioassay-directed chemical analysis approach to identify the toxic fractions amongst the many compounds accumulated during deployment. This approach has been applied by Rastall et al. to detect substances with estrogenic activity in a number of rivers in Germany and the UK [62]. SPMDs were used to accumulate hydrophobic compounds, and the extracts from the samplers were fractionated using reverse-phase HPLC. This method also provided estimates of the hydrophobicity of the various fractions. The estrogenic activity of each fraction was then measured using the yeast estrogen screen (YES) assay. Fractions that showed high estrogenic activity in this assay were then analysed by GC–MS to obtain a tentative identification of the active components. A similar study has been undertaken using the POCIS sampler to accumulate polar estrogenic agonists. In this case the extracts were tested using the YES assay, and the results compared with accumulation of these compounds in caged fish [63]. The results from spot sampling, passive sampling, and bioaccumulation in the fish were correlated, and the profile of estrogenic substances accumulated by the passive samplers was similar to that found in the fish. In the context of REACH the level of a substance of interest and its toxicity in standard tests could be separated from the impact of the many other pollutants present in the water.

5. Conclusions

Passive samplers have the potential to help in providing robust information on which decisions to approve registration applications can be based. Where information on environmental levels, behaviour, and fate are needed passive samplers can provide representative measurements of average concentrations that could be obtained by spot sampling only when used at a prohibitively expensive high frequency. Another advantage is that the masses of hydrophobic substances accumulated during deployment can ensure that the analytes fall within the range of quantification. For many non-polar compounds it would be necessary to transport and process large volumes of water in order to achieve this. Moreover, this technology provides a measure of the freely dissolved and biologically available fraction of the substance. This is more ecotoxicologically relevant information than either total concentration in unfiltered spot samples, or filtered concentrations. The latter are to a large extent defined by the filtration process used. Where measurements of bioavailability and bioaccumulation are required for registration packages, the costs of obtaining the data for these would be increased significantly. Laboratory-based studies using passive samplers to assess the potential for bioaccumulation could provide robust, reliable information at relatively low cost compared with the use of biota. Data obtained during registration could be used to develop and prove quantitative structure–activity relationships for bioavailability. Laboratory data obtained using passive samplers could be related to accumulation under field conditions where field assessments are required, again providing more reliable information than could be obtained using biomonitoring. Passive samplers have the potential to replace the use of living organisms in assessing bioavailability since they have a number of advantages including lower cost, greater repeatability, smaller variability, and greater acceptability on ethical grounds.

Where remedial actions (e.g., product withdrawal or replacement, or redesign) may be required it will be necessary to take the cost/benefit ratio into account. Part of this evaluation will be to assess the utility of the substance, and this will be balanced against the potential risk to environmental health. It is important that the information on which a decision is based is fit for purpose since the cost of a wrong decision is potentially very high. Against this background it may be possible to develop strategies based on passive sampling that will provide protection from possible environmental damage whilst minimising operational costs.

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Príloha 15

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Field Performance of Seven Passive Sampling Devices for Monitoring of Hydrophobic Substances

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The performance of seven passive sampling devices for the monitoring of dissolved concentrations of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), hexachlorobenzene, and *p,p′*-DDE was evaluated through simultaneous field exposures of 7−28 days in the River Meuse (The Netherlands). Data from the Chemcatcher, low density polyethylene membranes, two versions of the membrane-enclosed sorptive coating (MESCO) sampler, silicone rods, silicone strips and semipermeable membrane devices (SPMD) was assessed through rate of dissipation of performance reference compounds (PRCs), mass of analyte absorbed by the samplers and time-weighted average concentration (C_{TWA}) data. Consistent PRC data throughout the range of samplers tested here confirmed the transition from membrane- to boundary layer-controlled exchange at log K_{OW} 4.5−5.0. The comparison of sampler surface area-normalized masses absorbed for analytes under boundary layer-control showed some variability between samplers that can be attributed to the conformation and deployment of the various samplers and to the uncertainty associated with the analysis conducted in different laboratories. Despite different modes of calculation, relatively consistent C_{TWA} were obtained for the different samplers. The observed variability is likely to be due to the uncertainty of sampler-water partition coefficients and the extrapolation of analyte uptake rates at the high log K_{OW} range (under boundary layer-controlled exchange) from a narrow PRC data range, and these issues require further work. Finally, the usefulness of passive sampler-generated contaminant concentrations is demonstrated through the comparison with institutional monitoring and with European Water Framework Directive Environmental Quality Standards (EQS).

Introduction

Many nonpolar organic substances such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) may cause adverse effects in aquatic environments (*1*). Since these hydrophobic contaminants readily sorb to bottom sediments, concentrations in surface waters are generally in the low ng L^{-1} to pg L^{-1} range. Consequently, the regulatory monitoring and risk assessment of hydrophobic contaminants in surface waters is generally hampered by the inability to measure reliably these low (and sometimes fluctuating) concentrations (*2*). Under the Water Framework Directive (WFD) currently in force across the European Union, environmental quality standards (EQS) are defined for a set of hydrophobic priority substances that include, for example, PAHs, organochlorine pesticides and brominated flame retardants (*2*). Bottle sampling for the measurement of contaminant concentrations in water can become particularly challenging depending on sample pretreatment such as filtration or storage, the extraction technique used and levels of suspended solids or dissolved organic matter present in the water. The reporting of values below poor limits of detection (LOD) is unlikely to support current legislation.

Since the introduction of passive sampling two decades ago, the focus has increasingly been on the determination of time-weighted average concentrations (C_{TWA}) of hydrophobic contaminants dissolved in water (*3*−*5*). Contaminant accumulation into passive sampling devices is a diffusive process resulting from the difference in chemical activity of the contaminant dissolved in water and that in the sampler. These integrative samplers are generally composed of a receiving phase for contaminant accumulation and a membrane to limit mass transfer. Mass transfer itself depends on the characteristics of the contaminant of interest such as the size of the molecule, its affinity for the membrane/receiving phase material, and transport across phases, namely the membrane layer, the diffusive boundary layer and any biofilm layer developing at the surface of the sampler during extended exposures. Calibration experiments are generally conducted in the laboratory to determine contaminant uptake rates (R_S) by exposing samplers under constant conditions of contaminant concentration, water temperature and turbulences at the surface of the sampler. Since the application of laboratory-determined R_S to field situations is unreliable, the dissipation of performance reference compounds (PRCs), non-naturally occurring chemicals spiked into the sampler prior to deployment, allows R_S calibration in situ (*6*, *7*). This is only possible when there is an isotropic exchange of chemicals between the sampler and water.

The intercomparison of sampling procedures in the wider context of quality control schemes is often overlooked. Nonetheless, such intercomparisons when applied to passive sampling can address the reproducibility of sampler preparation, extraction and analysis, field deployment procedures by different teams and the accuracy and precision of C_{TWA}. While a range of passive samplers at various stages of their development are available and have been the subject of much testing separately, they have seldom been evaluated alongside each other. Here, the simultaneous deployment of seven passive sampling devices was undertaken in the River Meuse

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(The Netherlands) for exposures of 7−28 days to evaluate (i) the legitimacy of PRC-based in situ R_S calibration across the range of samplers, (ii) the effects of factors such as the method used to calculate concentrations, and (iii) the influence of the exposure time on C_{TWA} generated by the various samplers. The extraction and analysis of passive samplers for PAHs and PCBs in three different laboratories provides an additional dimension to this study.

Materials and Methods

Field Site. Passive samplers were deployed between 12th April and 10th May 2005 at a monitoring station on the River Meuse (The Netherlands) situated downstream of the border with Belgium (50°46′46.1 "N; 5°41′58.9"E). The Meuse river water is classified as hard ($CaCO_3 \sim 250$ mg L^{-1}) and during this field study, values of temperature, pH, and total/dissolved organic carbon (TOC/DOC) were in the range 14−17 °C, 7.7−7.9, 4−7 mg L^{-1}, and 2−4 mg L^{-1}, respectively (more detailed data is provided in the Supporting Information (SI)).

Passive Sampling Devices. The seven passive samplers tested included semipermeable membrane devices (SPMDs), a version of the Chemcatcher designed for sampling hydrophobic compounds, low-density polyethylene membranes (LDPEs), silicone strips, two types of membrane-enclosed sorptive coating samplers (MESCOs) and silicone rods (*7*−*11*). While both SPMDs and the Chemcatcher use an LDPE membrane, their receiving phases are a thin film of triolein and a C_{18} Empore disk loaded with 1-octanol, respectively. LDPE membrane, silicone strip, and silicone rod samplers are single-phase samplers. The original MESCO (referred to as MESCO I (m) with m for modified) uses a cellulose acetate dialysis membrane filled with water, however, it differs from the original design as a result of the replacement of the Gerstel Twister by a silicone rod (*10*). MESCO II is based on an LDPE envelope around a silicone rod with an additional air layer separating the two phases (*11*). Characteristics of the samplers are given in Table 1. Chemcatcher, SPMD, LDPE membrane, silicone strip and rod, and MESCO II devices were all spiked with PRCs with log K_{OW} values in the range 3.9−7.3 to allow the estimation of contaminant exchange kinetics between water and the sampler (see Table 1 for PRCs used for each sampler).

Sampler Preparation, Processing and Analysis for PAHs and PCBs. Chemcatcher devices with a Teflon sampler body (University of Portsmouth, UK) were prepared, extracted and analyzed for PAHs by gas chromatography−mass spectrometry (GC-MS) as described previously (*9*). Standard size SPMDs (92 cm long; 2.5 cm wide) were purchased from Exposmeter AB (Tavelsjo, Sweden) and extracted following published procedures (*12*). Briefly, SPMDs were dialyzed (2 × 24 h in *n*-hexane) and the triolein removed from the extract through a size-exclusion chromatographic column with dichloromethane as mobile phase. Finally, the solvent was exchanged to *n*-hexane and extracts reduced and analyzed by GC-MS for PAHs and PCBs (*8*). LDPE membranes (64.4 cm long; 2.5 cm wide) were prepared from lay-flat tubing purchased from Brentwood Plastics Inc. (St Louis, MO), pre-extracted with *n*-pentane overnight before spiking with a series of PRCs by incubating them in a PRC methanol−water solution (80/20 v/v) (*8*). Silicone strips were made from 0.5 mm thick sheets (Rubber BV, Hilversum, The Netherlands) and were of a similar dimension to LDPE membranes. These were precleaned by Soxhlet extraction with ethyl acetate (16 h) and methanol (2 h), and a similar procedure to that used for LDPE membranes was employed to spike PRCs into silicone strips. Following exposure both types of sampler were wiped with a damp paper tissue to remove biofilms and then extracted in 100 mL *n*-pentane (once for LDPE membranes and twice for silicone strips). Extracts were reduced, cleaned-up with silica (2 g, deactivated with 6%

TABLE 1. Characteristics of the Passive Sampling Devices Tested

	passive sampling devices[a]						
	SPMD[b]	Chemcatcher,[b]	LDPE[c]	silicone strip[c]	MESCO I (m)[d]	MESCO II[d]	silicone rod[d]
membrane material	LDPE (70 μm)	LDPE (40 μm)	LDPE (112 μm)	silicone (500 μm)	cellulose acetate	LDPE (100 μm)	silicone
receiving phase material	Triolein	C_{18} Empore disk/octanol			silicone	silicone	
surface area (cm^2)	460	17	324	321	0.33	1	0.64
sampler volume, V_S (cm^3)	4.95	0.6	1.77	8.02	0.016	0.047	0.031
performance reference compounds[e,f]	*ACE-d_{10} FLUE-d_{10} PHE-d_{10} CHRY-d_{12}*[g] B[*a*]A- d_{12}	*BIP-d_{10} ACE-d_{10} FLUE-d_{10} PHE-d_{10}* PYR-d_{10} B[*a*]A-d_{12}	ACE-d_{10} PHE-d_{10} *FLUO-d_{10} CHRY-d_{12}* CB004 CB155 CB204	*ACE-d_{10} PHE-d_{10} FLUO-d_{10}* CHRY-d_{12} CB004 CB155 CB204		*PHE-d_{10} ANT-d_{10}* FLUO-d_{10} PYR-d_{10} B[*a*]A-d_{12}	PHE-d_{10} ANT-d_{10} *FLUO-d_{10}* PYR-d_{10} B[*a*]A-d_{12}

[a] See the Materials and Methods section for full names of samplers. [b] GC-MS at the University of Portsmouth. [c] GC-MS for PAHs and GC-ECD for PCBs at NIOZ. [d] Thermal desorption-GC-MS at UFZ, Leipzig. [e] PRC for which elimination rates could be used for further data interpretation are in italic. [f] BIP: biphenyl; ACE: acenaphthene; FLUE: fluorene; PHE: phenanthrene; ANT: anthracene; PYR: pyrene; FLUO: fluoranthene; CHRY: chrysene; B[*a*]A: benzo[*a*]anthracene. [g] PRC elimination rate significant only for the 28 day exposure.

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water; elution with *n*-pentane) and analyzed by GC-MS for PAHs. An electron capture detector was used for the detection and quantification of PCBs, hexachlorobenzene and *p,p′*-DDE. MESCO I (m) was prepared by inserting a precleaned silicone rod (1 cm long; 2 mm diameter, Goodfellow Ltd., UK) into a dialysis membrane bag (18 mm flat width and 30 mm long) made from regenerated cellulose (Spectra/Por 6, molecular weight cutoff 600 Da) filled with Milli-Q water (*10*). Diffusion-limiting envelopes of MESCO II were composed of air-filled nonporous LDPE membrane (purchased from Polymer-Synthesewerk, Rheinberg, Germany) containing a 1.5 cm long silicone rod (from Goodfellow GmbH, Bad Nauheim, Germany) of 2 mm diameter as receiving phase spiked with PRCs (*11*). The bare silicone rods used were 8 cm long and 2 mm diameter. Following sampler retrieval, silicone rods were removed from the MESCO membranes and stored in glass vials at −20 °C until analysis. Bare silicone rods were quickly washed under tap water and dried with tissue paper before storage at −20 °C. The combined processing and analysis of silicone rods (1.5 cm long from the MESCOs and 1 cm pieces cut from silicone rods) consisted of a thermal desorption step followed by GC-MS analysis. A thermo-desorption unit (TDU) from Gerstel (Mülheim a.R., Germany) was placed on top of an Agilent 6890 GC (Agilent Technologies, Palo Alto, CA) equipped with a cold injection system CIS-4 (Gerstel) and a mass spectrometric detector (MSD) 5973N (Agilent). Full details of the analysis can be found elsewhere (*11*). In all cases, quality assurance procedures such as the use of internal standards for the extraction and analytical steps and the assessment of analyte recoveries were conducted.

Sampler Deployment and Retrieval. All prepared samplers were stored at −20 °C and the temperature maintained below 0−4 °C during transport to and from the field site. Preparation and trip control samplers were prepared and transported in a similar way to exposed samplers and opened to the air during deployment and retrieval procedures. During deployment, controls were stored in closed containers at −20 °C. Samplers were mounted onto stainless steel cages, and moorings kept them 1 m below the surface of the water. In most cases, triplicate passive sampling devices of each type were exposed for a period of 7 days, two consecutive 14 day periods (14 days (1) and 14 days (2), respectively), and an overlapping 28 day exposure (further details on replication in SI). In addition, silicone strips, were deployed for four consecutive 7 day exposures. The 7 day sampling period for Chemcatcher, SPMDs and LDPE membranes was not undertaken in cages and samplers were therefore exposed to higher water turbulences.

Results and Discussion

Adequacy of the Performance Reference Compound Approach. The measurement of PRC dissipation provides information on contaminant exchange kinetics between water and the sampler and allows the estimation of R_S values in situ (*6*). Analytes for which the concentration in the sampler approaches equilibrium with the concentration in the water are characterized by significant or even complete elimination of PRC with similar log K_{OW}. However, negligible or little PRC dissipation is indicative of rates in the linear phase of uptake. The threshold between these two regimes is generally found for PRCs with log K_{OW} of 4.5−5 for exposure periods of several weeks (*13, 14*). In addition, using multiple PRCs with a range of log K_{OW} makes it possible to establish when kinetics of uptake into the sampler are membrane- or boundary layer-controlled. The overall resistance to mass transfer ($1/k_O$) into the samplers can be expressed as the sum of the water (δ_W/D_W) and membrane-side ($\delta_M/K_{MW}D_M$) resistances:

$$\frac{1}{k_O} = \frac{\delta_W}{D_W} + \frac{\delta_M}{K_{MW}D_M} \quad (1)$$

with K_{MW} the membrane−water partition coefficient, δ_W and δ_M the boundary and membrane layer thicknesses (m), and D_W and D_M ($m^2\ s^{-1}$) analyte diffusion coefficients in water and the membrane, respectively.

Amounts of analytes absorbed by the samplers follow a first-order approach to equilibrium:

$$N = K_{SW}VC_{TWA}[1 - \exp(-k_e t)] \quad (2)$$

where N is the amount of analyte absorbed (ng), K_{SW} the sampler−water partition coefficient ($L\ L^{-1}$), V the volume of the sampler (L), k_e the exchange rate constant (h^{-1}), t the exposure time (h), and C_{TWA} is in ng L^{-1}. PRC dissipation also follows first-order kinetics:

$$N_{PRC} = N_{0,PRC} \exp(-k_e t) \quad (3)$$

where $N_{O,PRC}$ and N_{PRC} are PRC masses in the samplers prior to and following exposure, respectively and where k_e is given by

$$k_e = \frac{k_O A}{K_{SW}V} = \frac{R_S}{K_{SW}V} \quad (4)$$

where k_O is the overall mass transfer coefficient (see eq 1), A the surface area of the sampler (m^2), V the volume of the sampler (L) and R_S the analyte uptake rates ($L\ d^{-1}$).

PRC elimination rates, k_e, were calculated for the various exposures and samplers and their statistical significance tested using a procedure described previously (*15*). Overall, it was possible to use most PRC data; however, data were not used when release was either close to 100% or insignificant, or when amounts remaining in trip controls were significantly lower than in fabrication controls (see SI for further details).

Since configurations of the devices differ widely (Table 1) and k_e is proportional to A/V (eq 4), elimination rates were normalized to this ratio. The relationship between k_eV/A values for 14 and 28 day exposures and log K_{OW} is presented in Figure 1A. The spread of the data across the range of samplers is less than one log unit and the apparent plateau for PRCs with log K_{OW} < 5 is indicative of membrane-controlled mass transfer (*13*). The overlap of Chemcatcher and SPMD (both using LDPE membrane material) data and generally higher k_eV/A values for silicone strips and MESCO II for PRCs with log K_{OW} < 5 reflects higher diffusion coefficients in the silicone material compared with LDPE (*16*).

Overall mass transfer coefficients (k_O) determined as the product of k_eV/A and K_{SW} (eq 4), were plotted as a function of log K_{OW} (Figure 1B). K_{SW} for nondeuterated PRC analogues were used (see following section for a detailed list of references). The transition between membrane-controlled mass transfer, where k_O increases with increasing PRC hydrophobicity, to boundary layer-control becomes more apparent with the bell-shaped relationship between log k_O and log K_{OW} (Figure 1B). Under boundary layer-controlled mass transfer, R_S is expected to decrease with increasing hydrophobicity. Here, a decrease can be observed for silicone strips (phenanthrene-d_{10} and fluoranthene-d_{10}) and LDPE membranes (fluoranthene-d_{10} and chrysene-d_{12}).

The transition between membrane- and water-side-control of mass transfer appears to occur for compounds with log K_{OW} between 4.5 and 5.0 (Figure 1B) and confirms previously observed cutoff points (*13, 14*). One would expect similar k_O values for fluoranthene-d_{10} under boundary layer-controlled exchange for LDPE membranes and silicone strips since both types of samplers have a similar configuration

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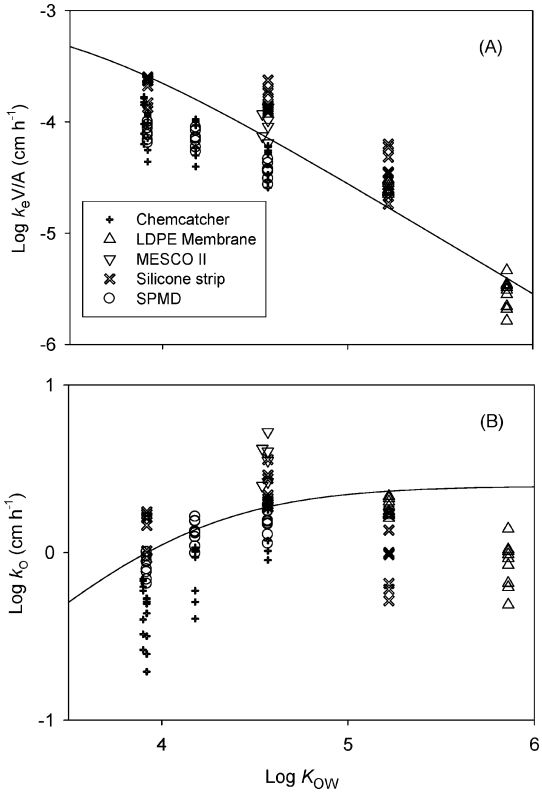

FIGURE 1. (A) First-order performance reference compound elimination rates, k_e, normalized to the sampler surface to volume ratio (A/V) for five different passive samplers. (B) Mass transfer coefficients, k_0, as the product of k_eV/A and sampler-water partition coefficients, K_{SW}. Data are for 14 (1st and 2nd successive exposures) and 28 day exposures. Lines are intended as a guide to the eye only.

and were disposed randomly in the same cages during exposure. Accounting for an uncertainty of log K_{SW} of around 0.3 log units, differences observed here are not likely to be significant (*16*).

PRC mass transfer coefficients were regressed (using Minitab version 14) against log K_{OW} for those under membrane layer-controlled kinetics and molecular weight (MW) for those under boundary layer-limited exchange (Table 2). The observation of similar slopes for log k_O versus log K_{OW} regressions for Chemcatcher and SPMDs is not unexpected since both samplers use an LDPE membrane. The steeper slopes observed for both samplers for the 7 day exposure under higher water turbulences indicate that resistance to mass transfer in the boundary layer is of a similar order of magnitude to that in the membrane for analytes with log K_{OW} near 4.5. According to eq 1, k_O is influenced by both K_{SW} and the analyte diffusion coefficient D_M for the membrane material when mass transfer is membrane-controlled. With slopes of log K_{SW}-log K_{OW} relationships close to unity, observed log k_O-log K_{OW} slopes of 0.7−0.95 as shown in Table 2 are plausible. Slopes for silicone strips, however, are significantly lower. It is likely that resistance to mass transfer in the boundary layer is not negligible and contributes to the overall resistance to mass transfer of PRCs with higher log K_{OW} used in these regressions. This is important since with an accurate knowledge of K_{SW} and D_M values, estimates of k_W (D_W/δ_W) may be obtained from PRCs under "membrane-controlled uptake". PRC-based information on boundary layer-controlled uptake is available only for LDPE membranes and silicone strips (Table 2). A linear regression of log k_O on log MW gave values in the range −3 to −8.9 which are over an order of magnitude higher than the slope of −0.35 predicted if the reduction in mass transfer coefficients was solely the result of a decrease in analyte diffusion coefficients in water with increasing molecular weight (*14*). These slopes are, however, similar to those from log k_O-log MW regressions obtained in sediment slurries (*17*). This sharp decrease in k_O values has been observed previously during sampler calibration experiments (*13, 15*) and attributed to (i) the transfer in the membrane of the Chemcatcher or SPMD becoming rate-limiting again owing to an increasing difficulty for larger molecules to diffuse in the LDPE, or (ii) contaminant sorption to DOC that reduces the fraction available to the samplers and results in the underestimation of R_S values of large molecular weight PAHs for example. Since the present data is based on PRC elimination rather than analyte uptake, log k_O-log MW relationships suggest that a significant reduction in analyte diffusion coefficients in the membrane materials tested here is possible and contributes the strong decrease in uptake rates for compounds with log $K_{OW} > 5$.

Calculation of TWA Concentrations. Concentrations of dissolved contaminants in the Meuse river water were calculated using the following equation (combination of equations 2 and 4):

$$C_{TWA} = \frac{N}{K_{SW}V\left[1 - \exp\left(-\frac{R_S t}{K_{SW}V}\right)\right]} \quad (5)$$

Further details of the calculation of C_{TWA} are available in the SI. Literature values for K_{SW} for each sampler are needed and exposure-specific R_S have to be determined. K_{SW} values for the Chemcatcher, LDPE membranes, MESCO I (m), MESCO II, silicone strips, silicone rods and SPMDs were obtained from refs *15, 14, 18−21* (using the experimental design as described in ref *22*), and *13*, respectively. R_S for the PRCs were calculated from $R_S = k_{e,PRC}\ K_{SW}\ V$. Since PRC-based R_S are for a limited log K_{OW} range, models relating R_S to analyte properties were used to estimate R_S for compounds outside the PRC range. A full description of the calculation of R_S values is provided in the SI. Briefly, sampling rates of the PRCs were fitted to the empirical log R_S-log K_{OW} relationships reported for the Chemcatcher (*15*) and SPMDs (*13*). For all other samplers, these relationships are not available and sampler-specific methods were used. For silicone strips, the PRC-based linear relationship between $k_{e,PRC}$ and K_{SW}^{-1} was used to extrapolate the R_S value for analytes with log $K_{OW} < 4.6$. For those above this threshold, boundary layer-controlled uptake was assumed and $R_{S\text{-}PRC}$ for fluoranthene-d_{10} was used to extrapolate uptake rates for the remaining compounds according to $R_S \sim (V_m)^{-0.39}$ where V_m is the analyte molar volume at boiling point (*13*). For LDPE membranes, the empirical K_{OW}-R_S model developed by Booij and co-workers (*14*) based on SPMD/LDPE membrane experimental calibration data was used to estimate R_S for all analytes (see SI). Offloading of fluoranthene-d_{10} and chrysene-d_{12} and literature data were used to estimate two empirical parameters B_W and B_m representative of mass transfer in the boundary and membrane layers, respectively. The product of the mass transfer coefficient obtained and the surface area of the sampler is R_S. For MESCO I (m), no PRC data was available. Instead mean values of laboratory-based R_S were used. These were corrected according to eq 4 to account for the use of a different receiving phase (with different V and K_{SW}) (*10, 23*). For MESCO II, the overall mass transfer coefficients were calculated from the sum of theoretical mass transfer coefficients for the various layers of the sampler as previously undertaken (*19*). Water-side mass transfer was adjusted using available PRC data. Finally, analyte R_S for silicone rods were also estimated from semiempirical mass transfer coefficients calculated

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TABLE 2. Slopes of Linear Regressions of Log k_0 on Log K_{OW} and Log k_0 on Log MW for Each of the Samplers and Exposure Period of 7, 14, and 28 Days

	membrane-controlled uptake ($(\Delta\log k_0)/(\Delta\log K_{OW})$), (SE)[a]				boundary layer-controlled uptake ($(\Delta\log k_0)/(\Delta\log MW)$), (SE)[a]			
exposure (days)	7	14 (1)	14 (2)	28	7	14 (1)	14 (2)	28
Chemcatcher	0.95[b] (*0.07*)	0.91 (*0.08*)	0.79 (*0.06*)	0.85 (*0.10*)				
SPMD	0.93[b] (*0.29*)	0.71 (*0.17*)	0.78 (*0.05*)	0.78 (*0.17*)				
LDPE					−8.5 (*2.6*)	−5.6 (*2.0*)	−8.9 (*1.8*)	−4.8 (*0.5*)
silicone strip	−[c]	0.18 (*0.04*)	0.39 (*0.05*)	0.47 (*0.03*)	−[c]	−8.8 (*1.6*)	−8.5 (*2.4*)	−3.1 (*1.2*)

[a] SE = standard error of the slope. [b] Deployment outside the cage resulting in higher mass transfer for PRC with log K_{OW} ~ 5. [c] Insufficient replication available.

for the membrane and boundary layer according to eq 1. A 10 μm boundary layer thickness based on k_e for fluoranthene-d_{10} was adopted. Interestingly, this value is similar to that obtained for MESCO II.

In order to evaluate the performance of the various samplers, we compared (i) masses of analytes absorbed (normalized to the respective sampler surface areas) for all analytes that were in the linear phase of uptake, (ii) calculated C_{TWA}, and (iii) the precision of these C_{TWA} estimates.

To compare surface area-normalized amounts of analytes, we first calculated the average amounts for each analyte and each sampler for the 7 day exposure. This was repeated for the 14 and 28 day exposures. These values were then divided by the corresponding values obtained for the LDPE membrane samplers. LDPE membrane samplers were selected based on the fact that the largest number of analytes was detected with this sampler. The size of data sets used to create the box-plots (Figure 2A) is indicative both of the number of analytes in the linear phase of uptake for the various samplers and of the relative method quantification limits (MQLs) of the various methods. These show that MQLs generally increase in the order LDPE membrane ~ silicone strip ~ SPMD < silicone rod ~ MESCO II < MESCO I (m) ~ Chemcatcher. Generally samplers with large surface areas such as LDPE membranes, silicone strips and SPMDs enabled the quantification of all target compounds. The very similar mean analyte masses accumulated in silicone strips and in LDPE membranes result from the analysis being conducted in the same laboratory and the samplers having almost identical sizes and similar mounting in deployment cages. The uncertainty in the normalized mean ratio for SPMDs combines that associated with the analysis being conducted in a different laboratory with those due to differences in turbulences around the samplers resulting from their larger dimensions. Similar factors influence the data obtained for the other samplers. Some variability can be observed for these samplers though the significantly smaller size of data sets is likely to affect these results. The particularly small data set for MESCO I (m) is the result of membrane rupture in exposures of over 14 days.

To compare C_{TWA} values, we first calculated the geometric mean of C_{TWA} for each compound and each exposure taken over all seven samplers. Ratios of individual C_{TWA} estimates over the geometric mean were then calculated. Dissolved contaminant concentrations varied over 3 orders of magnitude with low molecular weight PAHs at the ng L^{-1} level down to PCBs found at concentrations of tens of pg L^{-1}. Marked differences in C_{TWA} generated by the various samplers can be observed in Figure 2B. C_{TWA} estimated by LDPE membranes, MESCO II and SPMDs are closest to respective mean concentrations. Concentrations measured by the Chemcatcher appear generally higher than mean concentrations. This could be explained by a reduction in uptake rates (as shown by PRC elimination rates) with increasing exposure time. Data obtained with MESCO I (m) and the silicone rods consistently under predict mean concentrations and appear much lower than those generated by the Chemcatcher, LDPE membrane or silicone strips. This could be the result of possible bias induced by the method used to calculate TWA concentrations from analyte masses accumulated or uncertainty in the PRC data for the silicone rods. Since the uptake of many of the analytes detected and quantified by these two samplers had reached a significant degree of equilibrium, most of the variability in C_{TWA} may be linked to the variability of K_{SW} values (*16*). An uncertainty (or bias) of 0.3 log units is not impossible and would result in error equivalent to a factor of 2 when calculating C_{TWA} for analytes close to equilibrium. It should be noted here that Figure 2B reflects the variability among samplers and among laboratories.

Finally, to compare the precision of C_{TWA} values, C_{TWA} for each analyte and each sampler were log-transformed before calculating standard deviations. The antilog of these standard deviations can be interpreted as an uncertainty factor and provides a comparison of the overall precision of the different passive sampling methods used here (Figure 2C). The observed variability for all samplers was in the range 1.2−1.5. The smallest variability is generally exhibited by the Chemcatcher and LDPE membranes. The precision of analytical measurements decreases with decreasing analyte concentration. Concentrations of these analytes in passive sampler extracts are closest to analytical LODs where analytical precision is worst. In contrast with the less hydrophobic PAHs (close to equilibrium), the calculation of C_{TWA} for analytes in the linear phase of uptake relies significantly more on PRC elimination rates. Therefore, the precision of C_{TWA} for these compounds cumulates errors from more sources since it includes differences in the physical preparation of the samplers, in masses accumulated by the samplers, in the PRC elimination rates and finally in the extraction and analytical measurements (generally close to analytical LODs) conducted in two different laboratories. Interestingly, here the spread of the LDPE membrane data is much lower than for silicone strips and SPMDs.

Effect of Sampler Exposure Time. Sampler exposure time has an impact not only on PRC dissipation but also on masses of analyte accumulated. Longer deployments generally result in the accumulation of higher masses of contaminants that are in the linear phase of uptake (i.e., far from equilibrium) facilitating their analytical measurement while bringing sampler concentrations of less hydrophobic ones closer to equilibrium with the water phase. However, membrane fouling by biofilm-forming microorganisms or accumulation of suspended matter on the sampler surface may affect the exchange of analytes and PRCs between water and passive sampler when samplers are exposed long enough for these phenomena to occur. Exposures of 14 and 28 days resulted in significant biofouling comprising a large proportion of sediment particles. This may be due to a combination of relatively small openings on the cages used for deployment and the "zigzag" mounting of samplers within the cages that facilitates sediment particles settlement inside the cage.

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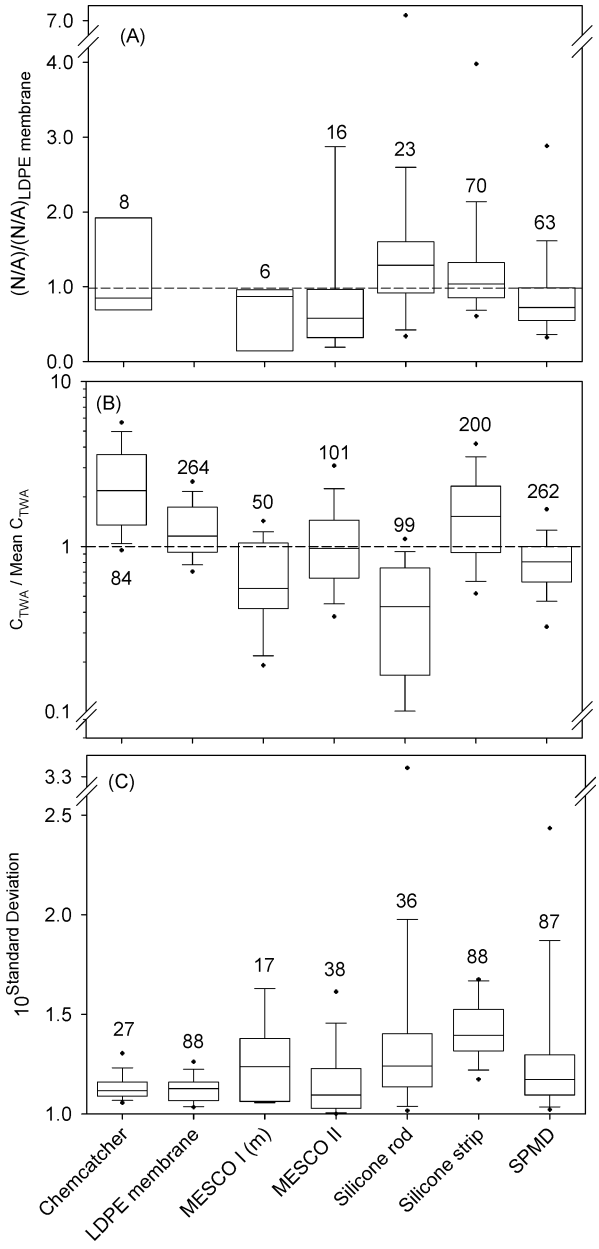

FIGURE 2. (A) Box-plots of sampler surface area-normalized amounts absorbed for analytes under boundary layer controlled uptake (N/A). These were normalized with respect to those for LDPE membrane samplers ($(N/A)_{LDPE\ membrane}$) and calculated for each analyte and each exposure. (B) Ratios of time-weighted average concentrations (C_{TWA}) measured by the different samplers to the geometric mean concentration (from all sampler replicates) for each analyte and exposure time. (C) Box-plot of standard deviations of log-transformed sampler-specific C_{TWA} calculated for each analyte and exposure. Values on the box-plots represent the sample size on which the box-plot is based. Dots are 5/95 percentiles.

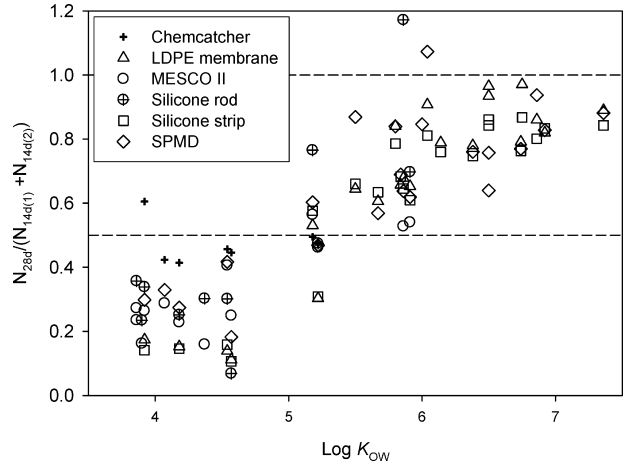

FIGURE 3. Ratio of analyte masses accumulated over 28 days to the sum of masses accumulated during the two successive 14 day exposures. Reference lines at $y = 1$ and 0.5 indicate ideally compounds for which uptake is linear over the 28 days and those that have reached equilibrium, respectively.

Significantly less fouling of the samplers was observed for the 7 day exposure outside the cages.

Our approach here was to compare masses of analytes accumulated and this was possible for the 28 day or consecutive 14 day deployments since sampler-specific exposure conditions were identical. Figure 4 shows the ratio of the mass of contaminant accumulated over 28 days to the sum of masses accumulated over the two successive 14 day exposures. In the case of compounds in the linear phase of uptake (generally with log $K_{OW} > 5$) during these 28 days, a ratio of one would be expected. However, for those close to reaching equilibrium, a ratio of 0.5 should be obtained if the dissolved analyte concentration in the water phase did not change noticeably during the field test. For analytes with log $K_{OW} > 5$, ratios are in the range 0.5−1.0 with most values in the range 0.6−0.95 (Figure 3). Since PRC data demonstrated that most of these compounds were in the linear phase of uptake during the 28 days, ratios of one should be observed. The lower values seen here may result from increasing fouling of the samplers over time during exposure. When considering analytes that have neared equilibrium, most ratios are well below 0.5. While this could be explained by radical changes in dissolved analyte concentrations during exposures, contaminant masses accumulated during four successive 7-day exposures of silicone strips did not demonstrate such changes in concentration (data not shown). Masses of contaminants with log $K_{OW} < 5.2$ accumulated in all samplers appear to decrease with increasing exposure time and increasing membrane fouling, possibly as a result of degradation of the less hydrophobic PAHs. However, (photo-) degradation of analytes sorbed onto the receiving phase of the samplers is unlikely.

Concerns can be raised when estimating C_{TWA} of the more mobile and degradable compounds when heavy membrane fouling is observed during long passive sampler deployment. Additional work is required to understand such a process and to estimate its overall importance in the determination of C_{TWA}. For the more hydrophobic contaminants, generally linear uptake was observed and exposure time/heavy fouling induced only minor changes in estimates of C_{TWA}. While minimal effects of biofouling have previously been observed (*24*), changes in uptake rates during exposure can be compensated since biofouling is expected to affect PRC release in a similar manner to analyte uptake (*13*). Here, only the PRC elimination data for the Chemcatcher showed a reduction in uptake rates when increasing sampler exposure from 14 to 28 days.

Regulatory Use of Passive Sampling Data. Clear objectives and readily available methods with adequate limits of detection, precision and accuracy are required for regulatory monitoring. Water quality monitoring of hydrophobic organic contaminants as defined in the European WFD is based on the comparison of samples with "whole water" EQS. Since passive sampling measures the truly dissolved fraction of contaminants in water data generated by this method cannot be compared directly

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with currently set WFD EQS, even though the fraction sampled is more toxicologically relevant. Nevertheless, comparisons with "whole water" EQS values are possible after a further data manipulation to account for sorption to DOC and suspended particulate matter data (see SI). DOC-water (K_{DOC}) and OC-water (K_{OC}), partition coefficients (*25, 26*) may be used to calculate "whole water" concentrations from passive sampler-based C_{TWA}. Despite the high uncertainty of K_{OC} and K_{DOC}, the use of conservative values will result in an overestimation of "whole water" concentrations. If these are still well below EQS, compliance may be demonstrated. Passive sampling-based whole water concentrations were compared with those obtained using bottle sampling collected during the field trial and with monthly institutional monitoring data for the period 2002−2005 (Table S5). Additionally, "whole water" concentrations were estimated from data obtained from monitoring of suspended particulate matter and of the fraction of organic carbon for the same 2002−2005 period. Bottle sampling was characterized by many measurements below limits of detection (LODs) that varied by a factor of 2−7. When comparing concentrations measured by bottle sampling with EQS values (Table S5), it is important to take account of limits of quantification, particularly for larger molecular weight PAHs (e.g., for benzo[*ghi*]perylene) since for a method to be considered fit-for-purpose these values should not exceed one-third of the EQS. Mean whole water concentrations of benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene estimated from passive sampling are very close to proposed WFD annual average EQS. Most mean concentrations estimated from suspended particulate matter monitoring for 2002−2005 were variable and close to or above EQS (*2*).

Passive samplers generally provide data that is less variable than that from "whole water" sampling since the latter may be strongly influenced by levels of suspended particulate matter. This lower variability is an attractive characteristic in the monitoring of water quality and the detection of temporal trends in concentrations. The present study showed that the C_{TWA} estimated by the different samplers varied by a factor of 2 on average while short-term within-sampler variability was a factor of 1.3. Efforts should focus on quantifying the long-term within-sampler variability and understanding and reducing the variability between different types of samplers. LODs of passive samplers with large surface area are likely to be well below typical concentrations encountered across Europe for analytes with log $K_{OW} < 7.5$, and this enables their use for monitoring tasks such as comparison with EQS or the monitoring of trends (*4, 27*). For other samplers such as Chemcatcher and MESCO, screening for larger molecular weights PAHs can be undertaken with "field" LODs in a similar range to EQS levels. Investigative monitoring tasks or monitoring at sensitive sites or where elevated concentrations are expected (e.g., sewage/stormwater effluents) are therefore most appropriate applications for these devices.

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Supporting Information Available

Additional details on water quality, sampler replication data, lists of chemicals analyzed and detected by the various samplers, and details of the calculation of time-weighted average concentrations.This material is available free of charge via the Internet at http://pubs.acs.org.

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Príloha 16

Lobpreis T., **Vrana B.**, and Dercová K., Innovative approach to monitoring organic contaminants in aqueous environment using passive sampling devices , Inovatívne prístupy k monitorovaniu organických kontaminantov vo vodnom prostredí použitím pasívneho vzorkovania, *Chemicke Listy* 2009, 103, 548–558.

Chem. Listy *103*, 548−558 (2009) Referát

INOVATÍVNE PRÍSTUPY K MONITOROVANIU ORGANICKÝCH KONTAMINANTOV VO VODNOM PROSTREDÍ POUŽITÍM PASÍVNEHO VZORKOVANIA

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Kľúčové slová: pasívne vzorkovanie, organické kontaminanty, monitorovanie životného prostredia, biomonitoring

Obsah

1. Úvod

Problematika monitorovania kontaminantov vo vodnom prostredí je aktuálna najmä v prípade stopových organických látok. Mnohé z nich patria medzi ťažko degradovateľné zlúčeniny, pričom u mnohých z nich dochádza k bioakumulácii v organických tkanivách. Do životného prostredia bolo uvoľnené antropogénnou činnosťou veľké množstvo chemických látok s rôznymi fyzikálno-chemickými vlastnosťami, preto aj celkový vplyv týchto látok na ekosystém nie je jednoduché popísať. Tieto polutanty zahŕňajú pesticídy, organické rozpúšťadlá, priemyselné chemikálie, liečivá, látky z priemyselného a domáceho odpadu a degradačné produkty týchto látok. Osud kontaminantu v životnom prostredí je často neznámy, mnohé z nich prechádzajú dokonca procesom čistenia odpadových vôd bez zmeny. Problematikou perzistencie organických kontaminantov pri úprave pitnej vody sa zaoberal napr. Stackelberg a spol.[1]

Vzorkovanie[2] patrí medzi najdôležitejšie kroky každého analytického postupu, pretože chyby, ktoré vzniknú pri odbere vzoriek už nie je možné neskôr odstrániť[3] a tým výrazne vplývajú na celkovú nepresnosť merania[4]. Málokedy je možné odobratú vzorku analyzovať priamo, vo väčšine prípadov je nevyhnutné, aby finálnej analýze predchádzali rôzne úpravy. Zahŕňajú extrakciu analytu z vodného prostredia, aby sa odstránili prípadné interferencie a zakoncentrovanie vzorky z dôvodu zvýšenia citlivosti metódy. Tieto postupy, najmä analýza stopových koncentrácií kontaminantov, sú časovo veľmi náročné a nezriedka predstavujú 70–90 % z celkového času analýzy[5]. Preto trendy v tejto oblasti smerujú k zjednodušeniu analýzy, napríklad spojením vzorkovania a zakoncentrovania do jedného kroku, alebo k zníženiu objemov použitých rozpúšťadiel, čo je efektívnejšie z ekonomického, ale aj ekologického hľadiska.

Pod pojmom pasívne vzorkovanie rozumieme techniku, ktorá je založená na voľnom prestupe analyzovanej látky z vodného prostredia do prijímajúcej fázy pasívneho vzorkovača ako výsledok rozdielov chemického potenciálu analytu medzi oboma fázami. Prestup látky sa riadi kinetikou 1. Fickovho difúzneho zákona a prebieha až do vytvorenia termodynamickej rovnováhy v systéme. Predstavuje rýchlu, efektívnu a jednoduchú metódu na monitorovanie širokého spektra organických aj anorganických kontaminantov v prostredí. Jej výhoda spočíva v znížení nákladov, znížení objemov rozpúšťadiel, vo vysokej citlivosti a v poskytnutí informácie o časovo váženej koncentrácii (time-weighted average; TWA). Keďže ide o *in situ* metódu, nedochádza v porovnaní s bodovými odbermi k zmenám zloženia vzorky (napr. pH, teplota, obsah kyslíka) počas transportu[6]. Pasívne vzorkovače je možné okrem vodného prostredia použiť aj na analýzu kontaminantov vo vzduchu a pôde. Po prvýkrát boli patentované a použité v roku 1927 na sledovanie koncentrácie oxidu uhoľnatého vo vzduchu[7]. Odvtedy došlo k výraznému vývoju a rozšíreniu oblasti využitia, čo dokumentuje aj množstvo publikácií a literárnych prehľadov uverejnených na tému pasívneho vzorkovania. Najvýznamnejšie z rešerší sú uvedené v tabuľke I.

Tabuľka I
Zoznam prehľadových prác k problematike pasívneho vzorkovania

Rok	Meno autora	Predmet prehľadovej práce
1981	Fowler[8]	Teória a základy pasívneho vzorkovania vo vzduchu vrátane vplyvu teploty, tlaku a odozvy vzorkovača
2000	Kot a spol.[9]	Dlhodobé monitorovanie vo vodnom prostredí
2000	Lu a spol.[10]	Teória a aplikácia semipermeabilných membrán (SPMD)
2002	Gorecki a spol.[5]	Použitie pasívnych vzorkovačov v pôde, vo vzduchu a vo vode a biomonitorovanie
2003	Mayer a spol.[11]	Vzorkovanie v rovnovážnej oblasti
2005	Stuer-Laudrisen[12]	Monitorovanie organických mikropolutantov
2005	Namiesnik a spol.[13]	Pasívne vzorkovanie s dôrazom na mikroextrakciu na tuhej fáze (SPME)
2005	Vrana a spol.[14]	Metódy pasívneho vzorkovania vo vodnom prostredí
2007	Mills a spol.[15]	Monitorovanie farmaceutických látok
2007	Vrana a spol.[16]	Pasívne vzorkovanie na monitorovanie znečistenia životného prostredia
2008	Seethapathy a spol.[17]	Techniky pasívneho vzorkovania v environmentálnej analýze vo vodách, pôdach a vzduchu

2. Monitorovanie kontaminantov

2.1. Bodové odbery

Najčastejšie používaným spôsobom vzorkovania je bodový odber vzoriek, pri ktorom sa vzorka odoberá v určitom okamihu a na konkrétnom mieste, pričom jeho voľba by mala reprezentovať vzorkovanú oblasť ako celok[18]. Problematická zostáva interpretácia bodových odberov, keď sú údaje získané zo vzoriek v jednom mieste a v jednom okamihu používané na charakterizáciu stavu celej lokality. Pri dodržiavaní európskej rámcovej smernice o vodách (WFD) je nevyhnutné zabezpečiť porovnateľnosť jednotlivých dát nameraných rôznymi členskými štátmi[19]. Na dosiahnutie tohto cieľa budú potrebné nové analytické metódy a prístupy[20], výber vhodných certifikovaných referenčných materiálov a interlaboratórne experimenty[21].

Konvenčný postup pri monitorovaní znečistených alebo odpadových vôd pozostáva z odberu väčšieho množstva vody, zakoncentrovania vzorky v laboratóriu rôznymi extrakčnými technikami, vyčistenia vzorky od potenciálne interferujúcich prímesí a následnej inštrumentálnej analýzy. Monitorovanie vo vode komplikuje viacero problémov, najmä veľmi nízka hladina kontaminantov a jej premenlivosť. Pre dosiahnutie požadovanej medze detekcie je často nutné spracovať veľký objem vzorky, čo je v prípade ultrastopových koncentrácií veľmi zložité. Veľkým problémom je predovšetkým stanovenie kontaminantov rozpustených vo vodnej fáze, teda biologicky dostupných[22]. Rovnako komplikované je stanovenie toxických účinkov polutantov v nízkych koncentráciách pomocou biotestov. Akútne testy toxicity spravidla nezaznamenajú odozvu a chronické testy sú omnoho náročnejšie a drahšie, aj keď umožňujú sledovať dlhodobé účinky aj nízkych koncentrácií. Takýto systém síce dokáže simulovať vplyv dlhodobej expozície polutantov na organizmus, ale opäť ide o vzorku odobranú v jednom okamihu[23]. Nevýhody bodových odberov možno zhrnúť nasledovne:

- Analýzy vzoriek získaných z bodových odberov reprezentujú iba zloženie vzorky v momente odberu a nemusia zachytiť náhodnú kontamináciu v inom čase.
- Nastávajú problémy pri kontrole kvality pri manipulácii s veľkými objemami vody potrebnými na analýzu stopových koncentrácií.
- Bežnými analytickými postupmi sa nedá stanoviť koncentrácia skutočne rozpustených a biodostupných polutantov.
- Toxikologické dáta a chemické kritériá kvality vody sú často založené iba na koncentrácii rozpustených látok a nie na celkovom množstve polutantov vo vodnom prostredí.
- Konvenčné postupy bývajú často neúspešné pri stanovení ultrastopových množstiev bioakumulujúcich kontaminantov.

Obmedzenia bodových odberov sa dajú čiastočne eliminovať použitím opakovaných odberov, ktoré sú však fyzicky, logisticky a ekonomicky náročné, predovšetkým pri monitorovaní vzdialenejších oblastí. Bez dostatočne opakovaných odberov nie je možné vyjadriť časovo priemernú koncentráciu sledovaných látok[24]. Na prekonanie nedostatkov monitorovania pomocou bodových odberov bolo vyvinutých viacero metód, ako napr. biomonitoring, on-line monitoring, *in situ* kontinuálny odber vzoriek, alebo pasívne vzorkovanie[25].

2.2. Biomonitoring

Meranie koncentrácie polutantov v tkanivách živých vodných organizmov, najmä rýb, je obvyklou metódou používanou na monitorovanie úrovne kontaminácie vôd polutantmi. Táto metóda je založená na jave bioakumulácie, t.j. zakoncentrovaní hydrofóbnych látok (napr. polychlórované bifenyly (PCB), polycyklické aromatické uhľovodíky (PAH) a organochlórované pesticídy (OCP)) v tukových tkanivách organizmov. Proces aktívnej a pasívnej akumulácie umožňuje merať koncentrácie skúmaného analytu, ktoré mnohonásobne prevyšujú jeho koncentráciu v prostredí a ktoré by nebolo možné detegovať konvenčnými analytickými postupmi. Využitie živých organizmov pri monitorovaní znečistenia životného prostredia eliminuje niektoré nedostatky bodových odberov. Takto získané dáta reprezentujú odozvu na skutočne biodostupnú frakciu kontaminantu a je možné priamo sledovať toxický vplyv na organizmus. Biomonitoring patrí medzi integrálne techniky, čo predstavuje výhodu oproti bodovým odberom, keďže dochádza ku kontinuálnej akumulácii analytu[26]. Takto získané údaje poskytujú informáciu o časovo spriemernenej koncentrácii polutantu. Využitie živých organizmov ako vzorkovačov má viacero výhod: odzrkadľujú skutočný vplyv stavu životného prostredia na živočíchy, vo väčšine prípadov sa využívajú natívne druhy, čiže odpadá potreba ich transportu na skúmanú lokalitu a aj ekonomický aspekt je nezanedbateľný[27]. Mali by však spĺňať isté kritériá[28]: a) nemalo by dochádzať k ich migrácii, b) musia byť rozšírené v celej sledovanej lokalite, c) pri dlhodobom monitoringu by mala byť zabezpečená stabilná populácia a d) na rôznych miestach by mala platiť rovnaká korelácia medzi koncentráciou v prostredí a tkanive. Všeobecne môžu byť živé organizmy použité v procese monitorovania životného prostredia dvoma spôsobmi: ako biomonitory a ako bioindikátory. Patria medzi ne organizmy alebo spoločenstvá organizmov, ktoré poskytujú informácie o kvalitatívnych alebo kvantitatívnych zmenách polutantov v životnom prostredí, resp. pri bioindikátoroch sa sledujú morfologické a histologické zmeny, často na bunkovej úrovni, ako aj metabolicko-biochemické procesy. Biomonitorovanie je možné použiť aj pre ťažké kovy[29].

Použitie živých organizmov na *in situ* monitorovanie kontaminantov v životnom prostredí je sprevádzané s viacerými problémami a obmedzeniami. Výsledná miera expozície je viazaná na druh, zdravotný stav a pohlavie organizmu, ako aj na konkrétnu oblasť, povahu vody a teplotu. Z dôvodu charakteristickej schopnosti metabolizácie určitého typu látok u niektorých zo sledovaných kontaminantov nemusí dochádzať k bioakumulácii, navyše je táto schopnosť závislá od veku a pohlavia organizmu. Významným obmedzením je migrácia druhov v závislosti na teplote, množstve a druhu potravy, nezohľadňuje sa ani výška hladiny toku. V konečnom dôsledku je obtiažne s istotou vzťahovať ryby k danému miestu odberu. Práve vyššie spomenuté podmienky môžu predstavovať nevýhody použitia živých organizmov pri monitorovaní znečistenia. Problematická zostáva aj interpretácia výsledkov, ako aj ich porovnanie z rôznych odberových oblastí. Rovnako ich nie je možné použiť v prostredí s vysokou koncentráciou kontaminantov (napr. čistiarne odpadových vôd).

Živé organizmy je možné použiť aj ako biologické systémy skorého varovania, ktoré využívajú toxikologickú odozvu organizmu na prítomnosť kontaminantu v prostredí[30]. Ako indikátorové organizmy slúžia najčastejšie rôzne druhy rýb, larvy komárov, dafnie[31], mikroorganizmy[32], ustrice a iné mäkkýše. Systémy skorého varovania sa najčastejšie používajú pri monitorovaní pitnej vody a jej rozvodov[33] a pri čistiarňach odpadových vôd.

Polutanty sa v organizme zakoncentrujú z rozpustenej fázy vo vode (biokoncentrácia), ako aj príjmom týchto látok z ich potravinového reťazca (bioakumulácia). Živé organizmy teda nemôžu spoľahlivo plniť úlohu pre identifikáciu zdroja kontaminácie z dôvodu nedostatočnej proporcionality medzi koncentráciou v tukovom tkanive a vo vodnom prostredí. V prípade spracovania vzoriek živých organizmov (napr. rýb) nie je určená jednotná metóda spracovania vzoriek. Na analýzu sa používa tzv. jedlý podiel, ten však nie je jednoznačne definovaný. Tým je znížená porovnateľnosť dát, pretože niektoré sú generované len z čistej svalovej hmoty rýb a iné aj zo zhomogenizovanej svaloviny a kože. Namerané výsledky sa síce nemusia výrazne odlišovať, neposkytujú však opakovateľné údaje. Biomonitoringu sa bližšie venoval vo svojich prácach napr. Mora a spol.[34] Pre porovnanie, postup odberu a spracovania vzoriek s použitím pasívnych vzorkovačov je jednoznačne daný a spracovaný do podrobného návodu.

Biomonitorovanie bolo použité napríklad v rámcovom programe EU (WorkPackage 3, WP3) pri monitorovaní kvality vôd Stredozemného mora[35], kde boli ako živé organizmy použité mušle[36] a ryby[37].

2.3. Pasívne vzorkovanie

Pasívne vzorkovače fungujú vo vodnom prostredí na integratívnom princípe, t.j. počas expozície dochádza ku kontinuálnej extrakcii sledovaných látok z vody (akumuluje sa len rozpustný, ľahko bioprístupný podiel) bez toho, aby sa dosiahla termodynamická rovnováha medzi organickou fázou vo vzorkovači a vodou. Rýchlosť akumulácie látky do vzorkovača je priamo úmerná jej vodnej koncentrácii. Po ukončení expozície je možné z akumulovaného množstva analytu pomocou vzorkovacej rýchlosti odhadnúť hodnotu časovo váženého priemeru vodnej koncentrácie (TWA, time-weighted average concentration) aj periodicky sa opakujúceho znečistenia počas expozície. Meraniu TWA koncentrácie v prostredí sa bližšie venoval napr. Zhao a spol.[38] Týmto spôsobom je možné znížiť nutný interval vzorkovania a tým dosiahnuť aj zníženie nákladov. Metódy pasívneho vzorkovania ďalej umožňujú eliminovať viaceré nevýhody bodových odberov, ako napríklad zachytenie výkyvov koncentrácie kontaminantov vo vode, zjednodušeniu analytických postupov, alebo detekciu aj ultrastopových množstiev látok,

ktoré bežnými postupmi nie je možné detegovať. Výhodou je aj monitorovanie biodostupnej frakcie, ktorá je relevantná pre predikciu osudu látok v životnom prostredí, keďže metóda pasívneho vzorkovania je analogická s javom biokoncentrácie kontaminantu z vody do živých organizmov.

Základnou prednosťou tejto metódy je model expozície, ktorý je možné opísať fyzikálno-chemickými parametrami[39]. Nakoľko akumulačné schopnosti tohto modelu sú podobné ako u vodných živočíchov (s výnimkou vplyvu faktorov charakteristických pre živý organizmus: nezávislosť na druhu, pohlaví, bez metabolizácie, akumulácia nie je prahová pre prežitie organizmu), označuje sa model často ako „virtual fish“[40]. Technika pasívneho vzorkovania umožňuje prepočet koncentrácie kontaminantov na základe kalibračných dát a tým aj stanovenie koncentrácie sledovaných polutantov vo vode.

Kontaminanty sú pri pasívnom vzorkovaní zachytené a viazané do vhodného média obsiahnutého vo vzorkovači, ktoré označujeme ako prijímajúca fáza. Môže ňou byť rozpúšťadlo, chemické činidlo alebo porózny adsorbent. Prijímajúca fáza je vystavená expozícii vo vodnom prostredí, ale nedochádza ku kvantitatívnej extrakcii, ako je tomu pri vsádzkovej extrakcii. Koncentrácia kontaminantu vo vodnom prostredí sa nemení vplyvom extrakčného procesu[41]. Princípom extrakcie je prestup analyzovanej látky z vodného prostredia cez fázové rozhrania do prijímajúcej fázy. Limitujúcou vrstvou prestupu by mala byť membrána, ale často, najmä pri nízkych hodnotách konvekcie, sa limitnou stáva laminárna difúzna vrstva vody na povrchu membrány. Adsorpcia alebo absorpcia kontaminantov z vodného prostredia sa u väčšiny vzorkovačov riadi podľa modelu, ktorý odvodil Huckins a spol[42].

Kinetika akumulácie je riadená difúziou a dá sa opísať nasledovným vzťahom

$$C_S(t) = C_S(0) + (C_W . K_{DW} - C_S(0)).\left(1 - exp\left[-\frac{k_0 . K_{MW} . A}{K_{DW} . V_D}\right].t\right)$$

kde $C_S(t)$ je koncentrácia analytu v vzorkovači v čase t; $C_S(0)$ koncentrácia analytu vo vzorkovači v čase 0; C_W koncentrácia analytu vo vodnom prostredí; K_{DW} rovnovážny rozdeľovací koeficient systému prijímajúca fáza/voda; k_0 celkový koeficient prestupu látky; K_{MW} rovnovážny rozdeľovací koeficient systému membrána/voda; A plocha povrchu vzorkovača; t čas; V_D objem prijímajúcej fázy.

Priebeh akumulácie kontaminantu z prostredia do prijímajúcej fázy sa dá rozdeliť na dva režimy – kinetický (lineárny) a rovnovážny. Pri rovnovážnom vzorkovaní je doba expozície vzorkovača v prostredí dostatočne dlhá na to, aby došlo k ustáleniu termodynamickej rovnováhy medzi koncentráciou látky vo vode a v prijímajúcej fáze. Rovnovážnemu vzorkovaniu sa venovali viacerí autori[11,43]. Pri vzorkovaní v kinetickej oblasti akumulácie je tok látky priamo úmerný rozdielu chemickej aktivity vo vodnej a v prijímajúcej fáze. V počiatočnej fáze expozície vzorkovača v prostredí je hodnota desorpcie analytu z prijímajúcej fázy zanedbateľná a vzorkovač pracuje v lineárnej (t.j. integrálnej) oblasti.

Popri nesporných výhodách spojených s pasívnym vzorkovaním je potrebné spomenúť aj limitácie týchto postupov. Nie sú vhodné ako systémy skorého varovania, ale predovšetkým na dlhodobejší monitoring. Technológia je stále vo vývoji, doteraz neboli schválené referenčné štandardizované sústavy a chýba aj zakotvenie v legislatíve. Monitorovanie pasívnymi vzorkovačmi vyžaduje rozsiahly systém kalibračných dát a problematickým zostáva aj porovnanie s výsledkami získanými konvenčným spôsobom. Špecifickým problémom je aj znečistenie povrchu vzorkovačov mikroflórou (tzv. bioznečistenie), ktoré pri dlhodobejšom monitorovaní vytvára dodatočnú bariéru voči prestupu látok cez fázové rozhrania. V neposlednom rade je to aj riziko odcudzenia počas expozície.

2.4. Porovnanie biomonitoringu a pasívneho vzorkovania

Koncentrácie perzistentných polutantov extrahovaných z pasívnych vzorkovačov sú proporcionálne ku koncentráciám týchto látok rozpustených vo vode. Naproti tomu polutanty v živých organizmoch sú viac ako na vodnej koncentrácii závislé na polčase vylučovania a dochádza aj ku skresleniu profilu kontaminácie vplyvom metabolizmu. Niektoré kontaminanty (napr. PAH) vzhľadom k ich rýchlej premene v organizme často nie sú v rybách detegovateľné. Táto skutočnosť platí všeobecne pre látky s nízkym rozdeľovacím koeficientom systému *n*-oktanol/voda (log K_{OW}). Pri porovnávaní výsledkov merania z expozície pomocou pasívnych vzorkovačov a živých organizmov môže dôjsť ku zhode, čo platí najmä pri interpretácii látok, ktoré sa z tela organizmu prakticky nevylučujú a bioakumulujú sa. Štúdie v rôznych krajinách na rôzne kontaminanty (napr. PAH[44], OCP a PCB[45], ťažké kovy a hydrofóbne organické kontaminanty[46]) naznačujú, že použitie pasívnych vzorkovačov na monitorovanie stopových koncentrácií je efektívnejšie ako u živých organizmov a vďaka štandardizovaným postupom poskytujú porovnateľné údaje z rôznych lokalít. Výborná korelácia medzi metódami pasívneho vzorkovania a bodovými odbermi bola dosiahnutá aj pre endokrinné disruptory[47] a vybrané aromatické uhľovodíky[48]. Výhodou pasívnych vzorkovačov je aj možnosť ich použitia vo vysokokontaminovanom prostredí, napr. v čistiarňach odpadových vôd, kde by biomonitorovacie organizmy neboli schopné prežiť.

2.5. Faktory ovplyvňujúce pasívne vzorkovanie

Pri pasívnom vzorkovaní je potrebné zohľadňovať mechanizmus výmeny sledovaného analytu medzi vodnou a prijímajúcou fázou. Na kompenzovanie environmentálnych vplyvov pri pasívnom vzorkovaní bolo vyvinutých viacero metód. Jednou z nich je použitie vnútorných štandardov, tzv. PRCs (Performance Reference Compounds)[49]. Ako vnútorný štandard slúžia štruktúrne, najčastejšie deuterované analógy skúmaného kontaminantu. Sú to analy-

ticky neinterferujúce látky, ktoré sa v prostredí prirodzene nevyskytujú. Vnútorné štandardy sa pridávajú do prijímajúcej fázy ešte pred expozíciou v presne známej koncentrácii a táto metóda je založená na skúmaní vyplavovania štandardu z pasívneho vzorkovača. Mechanizmus akumulácie môže byť ovplyvnený viacerými faktormi.

Rýchlosť prestupu látky je limitovaná difúziou cez semipermeabilnú membránu, alebo vodnou laminárnou difúznou vrstvou, ktorá vzniká na rozhraní membrána – voda. Laminárna difúzna vrstva predstavuje nepremiešavanú vodnú vrstvu v tesnej blízkosti membrány, hrúbka tejto vrstvy, a následne aj odpor voči prestupu analytu, je silne závislá od turbulencií v okolí pasívneho vzorkovača. Pri posudzovaní difúzie limitujúcej vrstvy je potrebné zohľadniť typ a vlastnosti membrány, vlastnosti prostredia počas vzorkovania, ako aj vlastnosti monitorovaného analytu. Vo všeobecnosti platí, že vzorkovacia rýchlosť R_S, ako aj akumulované množstvo monitorovaného analytu vo vzorkovači, sa so stúpajúcou turbulenciou výrazne zvyšuje, ak difúziu limituje laminárna difúzna vrstva vody na povrchu vzorkovača. Štúdie skúmajúce vplyv hydrodynamických podmienok na prestup látky dokázali, že redukovanie turbulencií v okolí SPMD malo v prípade organochlórovaných zlúčenín (log K_{OW} 4–8) za následok až 4-násobné spomalenie prestupu látky, prípadne 1,5-násobné zvýšenie pri stúpajúcej rýchlosti prúdenia kvapaliny (v rozpätí 0,004–0,2 m s^{-1}, cit.[50]). Niektoré typy vzorkovačov, ako napríklad vlákna SPME, sú však hydrodynamickými podmienkami ovplyvňované v menšej miere[51]. Vplyvu hydrodynamických podmienok na prestup látky cez fázové rozhrania sa venovali Vrana a Schüürmann[52].

Ďalším významným faktorom, ktorý ovplyvňuje prestup látky do prijímajúcej fázy, je teplota. Vo všeobecnosti platí, že so zvyšujúcou sa teplotou rastie aj prestup látky do prijímajúcej fázy. Pre závislosť teploty od R_S platí rovnica Arrheniovho typu. Napríklad, pre vzorkovač typu Chemcatcher, vyvinutý pre vzorkovanie hydrofóbnych látok, zmena teploty zo 6 na 18 °C spôsobí až vyše 5-násobné zvýšenie vzorkovacej rýchlosti[53].

Charakteristickým problémom pri použití pasívnych vzorkovačov vo vodnom prostredí je tvorba biofilmu. Nechránený povrch vzorkovača ponoreného do vody je vystavený riziku kolonizovania baktériami a rôznou mikroflórou a faunou prirodzene sa vyskytujúcich vo vodnom prostredí. To môže viesť k vytvoreniu biofilmu na povrchu membrány, ktorý svojimi vlastnosťami znižuje celkový koeficient prestupu látky, najmä zvýšením hrúbky difúznej vrstvy a blokovaním pórov semipermeabilnej membrány. Hrúbka vrstvy biofilmu môže byť rozdielna aj medzi jednotlivými vzorkami vzorkovačov pochádzajúcich z toho istého experimentu. Zloženie biofilmu je závislé od mikrobiologického zloženia a vlastností vodného systému.

Kolonizujúce mikroorganizmy môžu dokonca poškodiť povrch membrány, ak je vyrobená z biodegradovateľného materiálu. Huckins a spol.[54] zistili vo viacerých prípadoch 20–70% zníženie akumulácie polycyklických aromatických uhľovodíkov pri použití pasívnych vzorkovačov SPMD znečistených biofilmom. Model použitý na opis prestupu látky cez biofilm naznačuje, že v ideálnom prípade sa správa ako imobilizovaná vodná vrstva, s odporom voči prestupu látky nezávislým od rozdeľovacieho koeficientu biofilm-voda. To znamená, že látky difundujú cez biofilm takmer rovnakou rýchlosťou, bez ohľadu na ich hydrofóbnosť. Toto bolo potvrdené aj ďalšou štúdiou[55] pri monitorovaní PAH, kde bol zistený 50% pokles akumulácie v porovnaní s neznečistenými vzorkami, avšak vhodnou voľbou vnútorných štandardov bolo možné tento problém eliminovať.

3. Prehľad typov pasívnych vzorkovačov

3.1. Chemcatcher

Pasívny vzorkovač Chemcatcher pracuje vo vodnom prostredí na integratívnom princípe, t.j. počas expozície dochádza ku kontinuálnej extrakcii sledovaných látok z vody bez toho, aby sa dosiahla termodynamická rovnováha medzi organickou fázou vo vzorkovači a vodou. Chemcatcher je zložený z viacerých častí. Podporný disk slúži na umiestnenie membrány a prijímajúcej fázy, predná a zadná časť pomocou vodotesného závitu tento disk upevnia. Pri transporte sa používa aj uzáver, ktorý zabraňuje mechanickému poškodeniu povrchu membrány. Voliteľne sa môže použiť aj ochranná mriežka vyrobená z nehrdzavejúcej ocele, bronzu alebo medi. Celkový priemer predstavuje 70 mm a efektívna vzorkovacia plocha priemer 45 mm. Schránka vzorkovača je vyrobená z polytetrafluoroetylénu (PTFE; Teflon), ktorý je vhodný najmä kvôli veľmi nízkej schopnosti adsorbovať sledované analyty na svojom povrchu. Pri expozícii v prostredí sa vzorkovače umiestňujú horizontálne membránou smerujúcou nadol, aby sa eliminovala akumulácia sedimentujúcich častíc na povrchu disku.

Základom je difúzno-limitná membrána a viazaná tuhá prijímajúca fáza. Ich vhodnou kombináciou sa dá Chemcatcher použiť na monitorovanie širokého spektra látok, ako napr. vysoko nepolárnych látok (DDT, DDE)[56], organociničitých zlúčenín (MBT, TBT)[57], polárnych a semipolárnych pesticídov[58] alebo farmaceutík[59]. Na vzorkovanie nepolárnych organických kontaminantov s hodnotou log K_{OW} väčšou ako 4 sa používa polyetylénová (LDPE; low density polyethylene) membrána a ako prijímajúca fáza slúži C_{18} Empore™ disk. Táto fáza je založená na tuhom sorbente imobilizovanom do polymérnej matice (90 % sorbent : 10 % PTFE hm.) vo forme disku a prekonáva viaceré problémy spojené s používaním kvapalných prijímajúcich fáz, ako napríklad vyplavenie do vodného prostredia. Takýto systém je aj odolnejší voči poškodeniu a naviac je možné vhodnou voľbou komerčne dostupných diskov zvýšiť spektrum analyzovaných látok, alebo naopak, selektívne zvoliť fázu zachytávajúcu úzku skupinu kontaminantov. Pre polárnejšie látky sa používa polyétersulfónová membrána (PES) a taktiež Empore™ disk, ktorý sa vyznačuje dostatočnou afinitou aj kapacitou pre väčšinu relevantných kontaminantov. Medzi ďalšie

používané mikroporózne limitno-difúzne membrány patria membrány zo sklenených vlákien, polykarbonátu, teflónu, polyvinylidéndifluoridu (PVDF), acetátu celulózy (CA), polysulfónu (PS) a regenerovanej celulózy. Membrána slúži ako semipermeabilná bariéra redukujúca prestup látky medzi vodným prostredím a prijímajúcou fázou a takisto zabraňuje prestupu molekúl väčších ako veľkosť pórov membrány, ako napr. znečiťujúce anorganické častice, makromolekuly alebo mikroorganizmy[16]. Pre polárnejšie látky (log K_{OW} < 3) sa používa fáza vyrobená zo sulfónovaného polystyréndivinylbenzénu (SDB-RPS, alebo SDB-XC Empore™ disk)[60]. Ak sa zvolí ako prijímajúca fáza chelatačný disk, je možné pomocou vzorkovačov Chemcatcher monitorovať vo vodnom prostredí aj obsah toxických a ťažkých kovov (Cu, Cd, Co, Mn, Ba, Ca, Sr, Zn, Al, Cr, Sn, Pb, Fe, Ni, Mg)[61].

Pasívne vzorkovače Chemcatcher prešli od ich prvého použitia v praxi[62] vývojom, čo vyústilo do prípravy vzorkovačov Chemcatcher II. generácie. Sú vyrobené z lisovaného plastu (polykarbonát), skladajú sa z troch častí a membrána s prijímajúcou fázou sa upevňuje jednoduchým „zacvaknutím“. Cieľom vývoja bolo zefektívnenie činnosti vzorkovača, zníženie hmotnosti, zjednodušenie manipulácie a v neposlednom rade zredukovanie nákladov potrebných na výrobu. Táto optimalizácia, najmä zníženie profilu z 30 na 7 mm, viedla k zlepšenej kinetike vzorkovania a zníženiu vnútorného odporu vzorkovača voči prestupu hydrofóbnych organických látok s log K_{OW} väčším ako 5 (cit.[63]). Toto bolo docielené pridaním malého množstva *n*-oktanolu do priestoru medzi prijímajúcu fázu a polyetylénovú membránu. *n*-oktanol je rozpúšťadlo s vysokou afinitou k sledovaným látkam[64].

3.2. Semipermeabilné membránové zariadenie

Ďalším typom pasívnych vzorkovačov sú semipermeabilné membrány (SPMDs, Semipermeable Membrane Devices) plnené trioleínom, syntetickým rybím tukom. Vzorkovací systém bol vyvinutý Huckinsom a spol.[65] a jeho usporiadanie sa ustálilo v štandardne používanej konfigurácii. Vzorkovač SPMD sa skladá z polopriepustnej membrány (hrúbky 75–95 μm) rozmerov 94 × 2,5 cm s pórmi špecifického rozmeru do $1 \cdot 10^{-9}$ m, čo je základné priblíženie k veľkosti molekúl, ktoré môžu difundovať cez biomembrány. Vnútri membrány je uzavretý syntetický lipid trioleín (1,2,3-tri-[*cis*-9-octadecenoyl] glycerol). Pri expozícii dochádza k akumulácii lipofilných kontaminantov do prostredia trioleínu.

Kapacita SPMD je daná jej rovnovážnym rozdeľovacím koeficientom K_{TW} (systém trioleín/voda) a objemom trioleínu. Schopnosť vzorkovania je určená veľkosťou tohto parametra. Uspokojivo sa dajú vzorkovať látky s hodnotou log K_{OW} < 6,5, avšak kvôli hydrofóbnej membráne nie je tento systém vhodný na monitorovanie látok s log K_{OW} < 3. Monitorovanie pomocou SPMD bolo overené pre rôzne analyty, ako napr. polychlórované dibenzodioxíny a furány (PCDD, PCDF)[66], pesticídy (DDT, DDE, DDD)[67], polycyklické aromatické uhľovodíky (PAH)[68], organochlórované pesticídy[69] alebo polychlórované bifenyly (PCB)[70].

Výhodou SPMD je možnosť expozície priamo v sedimentoch ako kontaktný priamy test a tieto výsledky sa môžu použiť pre odhad rizika pre bentické organizmy. Rovnako ako vzorkovače Chemcatcher, aj vzorkovače SPMD vyžadujú súbor kalibračných dát na elimináciu charakteristických environmentálnych podmienok[71]. Systém potom na základe zistených kinetických parametrov umožňuje prepočet koncentrácie kontaminantov a tým stanovenie výslednej koncentrácie sledovaných polutantov vo vode. Po expozícii v prostredí sú membrány extrahované *n*-hexánom alebo dichlórmetánom a následne je dialyzát analyzovaný chemicky alebo toxikologicky[72]. Chemická analýza prebieha metódami kvapalinovej chromatografie (HPLC), plynovej chromatografie, alebo plynovej chromatografie s hmotnostnou spektrometriou (GC/MS).

Použitie SPMD dobre simuluje proces difúzie cez biomembrány (napr. epitel rybích žiabrov). Difúzia cez biomembrány je považovaná za rozhodujúcu pri biokoncentrácii polutantov. SPMD naplnené syntetickým rybím tukom dokážu simulovať proces biokoncentrácie v živom organizme. Toto bolo potvrdené aj štúdiou[73], v ktorej boli porovnávané koncentrácie PCB, PAH a OCP vo vode, rybách a sedimentoch. SPMD sú vyrábané zo syntetických materiálov, ktoré zaisťujú väčšiu jednotnosť a reprodukovateľnosť ako živé organizmy. Vďaka svojej vysokej citlivosti zachytia širokú škálu chemikálií aj v stopových koncentráciách, vrátane takých, ktoré sú organizmami metabolizované. Môžu byť exponované nielen vo vodnom prostredí, ale aj v sedimentoch[74]. SPMD patria v súčasnosti medzi najpoužívanejšie typy pasívnych vzorkovačov a detailne sa im venoval vo svojej práci napr. Esteve-Turrillas[75].

3.3. Polárne organické chemické integračné vzorkovače

Pasívne vzorkovače POCIS (Polar Organic Chemical Integrative Sampler) sú v princípe podobné vzorkovačom SPMD, používajú sa však na monitorovanie hydrofilných kontaminantov, ako sú napr. pesticídy, liečivá[76], steroidné hormóny, herbicídy[77] alebo antibiotiká. Tieto zlúčeniny sa dostávajú do vodného prostredia celosvetovo a u mnohých z nich bol pozorovaný efekt chronickej toxicity.

Vzorkovač POCIS pozostáva z prijímajúcej fázy (sorbentu), ktorá je z oboch strán obklopená hydrofilnou mikroporóznou polyétersulfónovou membránou (pre vzorkovanie polárnych organických látok). Tá je upevnená medzi dvoma podpornými kruhmi. Zloženie prijímajúcej fázy (sorbentu) sa volí na základe charakteru látok, ktoré chceme monitorovať. Efektívna vzorkovacia plocha štandardne používaného systému POCIS predstavuje 41 cm^2 na jeden vzorkovač o približnom priemere 10 cm (cit.[78]). Vzorkovanie prebieha iba z rozpustenej fázy, a teda umožňuje zistenie skutočne biologicky dostupného podielu. Tieto vzorkovače tiež pracujú na princípe integratívneho vzorkovania, sú v prostredí exponované počas viacerých

týždňov a poskytujú informáciu o časovo priemernej koncentrácii kontaminantu vo vodnom prostredí.[79]

3.4. Vzorkovače s membránou uzavretým sorpčným potahom

Pasívne vzorkovače MESCO (Membrane-Enclosed Sorptive Coating) sa používajú na monitorovanie hydrofóbnych organických polutantov. Medzi hlavné výhody patrí: malý rozmer, extrakcia a prekoncentrácia z vodného prostredia bez použitia rozpúšťadiel, bezstratová separácia prijímajúcej fázy a jednoduchá analýza v termodesorpčnej jednotke.

Základ vzorkovača tvorí malá, približne 1,5 cm dlhá tyčinka pokrytá tenkou vrstvou polydimetylsiloxánu (PDMS), ktorá je umiestnená v dialyzačnom vrecku vyrobenom z regenerovanej celulózy, prípadne LDPE. Použitie PDMS ako prijímajúcej fázy je vhodné kvôli afinite k polutantom, inertným vlastnostiam ako aj stabilite pri termodesorpcii[80]. Princípom vzorkovania je selektívny prestup látky z vodného prostredia a následná absorpcia na prijímajúcu fázu. Dialyzačná membrána je naplnená destilovanou vodou a uzatvorená na oboch koncoch. Pri expozícii sa používajú viaceré vzorkovače zoradené za sebou. Pri spracovaní vzoriek MESCO sa prijímajúca fáza vyberie z membrány, opláchne destilovanou vodou, vysuší a následne sa analyzuje obsah naakumulovaných látok pomocou termodesorpčnej GC/MS[81]. Táto metóda je kvôli nízkym stratám vhodná práve na stanovenie stopových koncentrácií vo vodnom prostredí.

Podobne ako väčšina pasívnych vzorkovačov, aj vzorkovače MESCO prešli optimalizáciou. Prvý prototyp sa skladal z LDPE membrány uzavretej na oboch koncoch s vloženým SPME vláknom pokrytým PDMS, ktoré je vhodné pri monitorovaní nepolárnych látok z vodného prostredia[82]. V ďalšej generácii, označovanej ako MESCO I (cit.[83]), bolo ako prijímajúca fáza použité miešadlo Twister™ (Gerstel, Mülheim/Ruhr, Germany) pokryté vrstvou PDMS, ktoré je používané na bezrozpúšťadlovú mikroextrakciu. Zakladá sa na rovnakom princípe ako vlákno SPME, má však vyššiu extrakčnú kapacitu. Membrána je vyrobená z regenerovanej celulózy. Posledný typ, MESCO II, spája výhody vysokej kapacity prijímajúcej fázy druhej generácie so stabilitou LDPE membrány pôvodného typu vzorkovača[84]. Navyše bol pomerne drahý a krehký Twister™ nahradený silikónovou tyčinkou.

Napriek malým rozmerom povrchu prijímajúcej fázy a objemu vzorkovača, citlivosť MESCO je porovnateľná s inými druhmi pasívnych vzorkovačov, pretože celé množstvo analytu obsiahnutého v PDMS sa prenesie do GC, kde je následne analyzované. Komplexnejšie je problematika vzorkovačov MESCO diskutovaná v literatúre[16], ako aj príklady aplikácie v prostredí[85].

3.5. Keramický dozimeter

Keramický dozimeter patrí medzi pasívne vzorkovače, ktoré sú obzvlášť vhodné na dlhodobé monitorovanie kontaminantov vo vodnom prostredí a najčastejšie sa používajú na sledovanie kvality podzemných vôd. Skladá sa z keramickej tuby, ktorá predstavuje limitno-difúznu membránu a tuhého sorbentu vo forme guličiek (napr. Dowex Optipore L-493) ako prijímajúcej fázy. Tvarom pripomína rúrku s priemerom 15 mm, hrúbkou stien 1,5 mm o dĺžke najčastejšie 5−10 cm a pórmi 5−100 nm. Časovo vážené spriemernené koncentrácie namerané v podzemných vodách pomocou keramických dozimetrov veľmi dobre korelujú s hodnotami získanými často opakovanými bodovými odbermi[86].

Na monitorovanie stopových koncentrácií nepolárnych látok, ako napr. PAH, sa používa ako prijímajúca fáza Amberlite IRA-743. Ide o iónovýmennú živicu na polystyrénovej báze s dostatočnou kapacitou viazať kontaminanty a dobrou zmáčavosťou. Výhodou tohto typu vzorkovača je možnosť dlhodobého použitia (90 dní) aj bez predchádzajúcej časovo náročnej kalibrácie[87]. Bolo dokázané[88], že uvedená prijímajúca fáza (Amberlite IRA-743) je schopná udržať naakumulovaný kontaminant aj po premiestnení keramického dozimetra do deionizovanej vody na dobu 100 dní prakticky bez strát.

Nedávno bol predstavený nový typ pasívneho vzorkovača, ktorý kombinuje jednoduchosť keramického dozimetra a možnosť biostanovenia. Bol označený ako „keramický toximeter“[89] a obsahuje špeciálnu prijímajúcu fázu, Biosilon. Je upravená tak, aby bolo po naakumulovaní kontaminantu umožnené priľnúť bunkám stavovcov k jej povrchu a vyvolať biologickú odozvu. Na biostanovenie sa využíva indukcia 7-etoxyresorufín-*O*-deetylázy v prítomnosti PAH. Táto metóda však nebola doteraz dostatočne preskúmaná a vyžaduje ďalšiu optimalizáciu. Monitorovaniu kontaminantov pomocou keramických dozimetrov sa bližšie venuje kapitola v knihe Passive Sampling Techniques in Environmental Monitoring[16].

3.6. Pasívny difúzny vak

PDB (Passive Diffusion Bag) patrí medzi pasívne vzorkovače pracujúce v rovnovážnej oblasti, pričom rovnováha je dosiahnutá do 24 h v prípade vzduchom plnených vzorkovačov (PVD, Passive Vapour Diffusion) a do 48 h v prípade vodou plnených vzorkovačov[90]. Približný rozmer štandardného PDB je 61 cm na dĺžku o priemere 32 mm. Primárne sa používa na získavanie informácií o koncentrácii nepolárnych prchavých zlúčeninách (VOC) v podzemných vodách. Práve pri monitorovaní prchavých zlúčenín treba postupovať veľmi opatrne, keďže už aj pri samotnom odbere dochádza k stratám. PDB sú taktiež vhodné na dlhodobý monitoring nálezísk podzemnej vody a sledovanie prítomnosti predovšetkým trichlóreténu (TCE), benzénu, toluénu, etylbenzénu a xylénu (BTEX).

Základ zariadenia tvorí semipermeabilná membrána, ktorá obsahuje deionizovanú vodu (prípadne vzduch). Ak je daný pasívny vzorkovač v kontakte so vzorkovacím médiom, nastáva difúzia kontaminantov cez semipermeabilnú membránu do deionizovanej vody. Po ukončení expozície sa voda spolu s polutantmi, ktorá sa dostala cez

polopriepustnú membránu do vzorkovača, vypustí do nádoby na neskoršiu analýzu. PDB sa týmto úkonom regeneruje a vzorkovač je pripravený na ďalšiu expozíciu. Vhodnosť aplikácie PDB pri monitorovaní kontaminantov v podzemných vodách a porovnanie s klasickými technikami bola potvrdená experimentálne[91].

Semipermeabilná membrána slúži zároveň aj ako limitno-difúzna bariéra voči prestupu látky z vodného prostredia. Vhodnou voľbou materiálu je možné dosiahnuť selektivitu vzhľadom na monitorovanú skupinu kontaminantov a dokonca je možné sledovať prítomnosť anorganických zložiek[92]. Medzi najčastejšie používané patria dialyzačné membrány z regenerovanej celulózy a LDPE (Low Density Polyethylene) membrány.

3.7. Mikroextrakcia na tuhú fázu

Pri mikroextrakcii na tuhú fázu (SPME, Solid phase microextraction)[93] ide o jednoduchú extrakčnú metódu. V tomto prípade je extrakčným médiom tenké kremenné vlákno potiahnuté tenkou vrstvou polyméru, často PDMS (polydimetylsiloxán). Extrakčnú rovnováhu možno dosiahnuť, v závislosti od fyzikálno-chemických vlastností látok, už v priebehu tridsiatich minút a množstvo analytu, ktoré je naviazané na vlákne sa analyzuje plynovou alebo vysokoúčinnou kvapalinovou chromatografiou. Napriek krátkemu času potrebnému na dosiahnutie rovnováhy, je možné zaradiť metódy SPME medzi pasívne vzorkovanie, najmä kvôli rovnakému princípu voľného prestupu látky z prostredia do prijímajúcej fázy. Táto metóda umožňuje monitorovanie hydrofóbnych chemikálií, vrátane PAH, PCB, chlórovaných pesticídov a fenolov. SPME je možné použiť aj na monitorovanie pôdy. Priame porovnanie s koncentráciou analytu (PAH) v dažďovkách dokázalo, že pri technike SPME skutočne dochádza k akumulácii voľne dostupnej frakcie[94]. Výhoda SPME spočíva v rýchlom dosiahnutí rovnováhy, relatívne jednoduchej analýze, nízkych nákladoch, dobrej korelácii so živými organizmami a nenáročnej manipulácii. Vlákna SPME pokryté vrstvou polyakrylátu je tiež možné použiť na simuláciu javu bioakumulácie a odhad akútnej toxicity na živý organizmus[95].

Zatiaľčo mnoho aplikácií SPME sa usiluje o najvyššiu možnú efektívnosť extrakcie, nd-SPME (negligible depletion SPME – mikroextrakcia na tuhú fázu so zanedbateľným večerpaniem) predstavuje špecifickú aplikáciu na merania voľnej koncentrácie testovanej vzorky, pričom sa extrahuje len nepatrné množstvo analytu, čo môže predstavovať problém pri celkovej kvantifikácii. Ide o novú metódu, ktorá umožňuje stanovovať voľne dostupnú frakciu kontaminantu, ako aj zisťovanie rozdeľovacích koeficientov. To sa dá využiť pri skríningu a identifikácii bioakumulujúcich zlúčenín v prostredí[96]. Technika nd-SPME je detailnejšie opísaná v literatúre[97].

Metóda SPME sa často používa aj pri sledovaní úrovne znečistenia sedimentov, pričom ich toxické vlastnosti sú priamo vztiahnuteľné na množstvo biodostupnéhu podielu kontaminantu obsiahnutého v pórovej vode[98]. Pri monitorovaní v sedimentoch sa používa termín matrix-SPME (matricová SPME)[99], pretože pri extrakcii z prostredia sa na dosiahnutí rovnováhy zúčastňuje matrica sedimentu ako celok a výsledky je možné použiť na výpočet fugacitných koeficientov[11]. Sklenené vlákno je pokryté 15 μm hrubou vrstvou PDMS, umiestni sa do prostredia až po dosiahnutie rovnováhy (podľa charakteru analytu 1 až 30 dní) a následne analyzuje plynovou chromatografiou.

4. Záver

Technológia pasívneho vzorkovania, uvedené možnosti použitia a jej implementácia do praxe poukazujú na značný potenciál tejto inovatívnej metódy pri monitorovaní kvality životného prostredia. Napriek tomu, že prešla dlhoročným vývojom, metóda pasívneho vzorkovania sa stále rozvíja a zdokonaľuje. Výskum sa v tejto oblasti sústreďuje na elimináciu možných environmentálnych faktorov ovplyvňujúcich kinetické parametre vzorkovačov (teplota, hydrodynamické podmienky, bioznečistenie), hľadanie materiálov vhodných pre vzorkovanie nových skupín látok a spojenie chemickej a toxikologickej odozvy na prítomnosť kontaminantu v prostredí. Medzi významné výhody v porovnaní s konvenčnými prístupmi vzorkovania patrí jednoduchosť, nízka ekonomická náročnosť, možnosť použitia bez vonkajšieho zdroja energie, poskytovanie informácie o časovo váženom priemere koncentrácie a detekcia aj ultrastopových hladín kontaminantu. Samotným cieľom pasívneho vzorkovania nie je nahradiť klasické bodové odbery, ale poskytnúť dodatočné informácie ku stavu znečistenia životného prostredia.

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([a]Department of Biochemical Technology, Faculty of Chemical and Food Technology, Slovak University of Technology, Bratislava, [b] Water Research Institute, Slovak National Water Reference Laboratory, Bratislava, Slovak Republic): **Innovative Approach to Monitoring Organic Contaminants in Aqueous Environment Using Passive Sampling Devices**

The aim of this review is to introduce new methods of monitoring organic contaminants in aqueous environment. Passive sampling devices are able to overcome many of the limitations associated with conventional spot sampling of waters. They work in the integrative mode allowing the estimation of time-weighted average concentrations of contaminants in water, soil, sediments or air. Unlike most monitoring methods, passive samplers measure the dissolved, i.e. bioavailable fraction of water pollutants. In addition, they are able to effectively concentrate the pollutants that are present in trace amounts. The passive sampling devices should not replace conventional sampling; they provide additional information on the environment pollution at a reasonable cost.

61. ZJAZD CHEMIKOV

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Príloha 17

Allan I. J., Booij K., Paschke A., **Vrana B.**, Mills G. a, and Greenwood R., Short-term exposure testing of six different passive samplers for the monitoring of hydrophobic contaminants in water., ***J. Environ. Monit.*, 2010, 12, 696–703.**

Short-term exposure testing of six different passive samplers for the monitoring of hydrophobic contaminants in water†

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Passive sampling devices are increasingly relied upon for monitoring non-polar organic contaminants in water. While many types of devices are available they have seldom been evaluated alongside each other. We tested six passive sampling devices namely: Chemcatcher, two modified versions of the membrane enclosed sorptive coating (MESCO I (m) and MESCO II), silicone rod and strip and semipermeable membrane device (SPMD). Samplers spiked with a range of performance reference compounds (PRCs) were exposed (5 days) in a continuous flow-through tank using Meuse river water fortified with fluctuating concentrations (20–700 ng L^{-1}) of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, hexachlorobenzene and *p*,*p*′-DDE. Dissipation rates of PRCs appeared to provide reliable information on exchange kinetics even under these short-term exposure conditions. They accounted for differences between masses of contaminants accumulated by replicate samplers, indicating that the variability between replicates was in part due to differences in water turbulences and hence boundary layer thickness. In this system, resistances in the membrane and boundary layers are likely to be in the same order of magnitude for PRCs. Sampler performance was evaluated by comparing masses accumulated in the devices only for analytes for which uptake was linear (integrative) and limited by transport across the boundary layer. Consistent data were obtained across the range of samplers despite their different configurations, and the analysis being conducted in three separate laboratories. The pattern in analyte masses accumulated by Chemcatcher and MESCO II data could be explained by the extraction and analysis being conducted only on the receiving phase of the samplers and a significant impact of the lag-phase prior to obtaining a steady flux of contaminants across the polyethylene membranes.

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Introduction

Passive sampling is a monitoring technique that is increasingly being used to measure dissolved concentrations of hydrophobic contaminants in water.[1–3] Accumulation of contaminants relies on diffusion of chemicals present in the water phase into the device as a result of a difference in chemical activity of the contaminant in water and that in the sampler. Devices may be simple polymeric membranes such as low density polyethylene (LDPE) membrane or silicone strips,[4] or more complex designs such as the Chemcatcher[5] composed of a LDPE membrane superimposed onto a receiving phase (*n*-octanol-loaded C_{18} Empore® disk), SPMD[6] with triolein-filled LDPE tubing or the MESCO samplers with a silicone rod or Gerstel Twister bar

Environmental impact

Passive sampling devices have the potential to respond to many of the challenges set by legislative texts such as the EU Water Framework Directive regarding the monitoring of aquatic micropollutants. Advantages include measurement of the freely dissolved concentration of contaminants in water and continuous monitoring over periods of time. Since different types of devices exist, the equivalence of the data they provide must be demonstrated and their working principle understood before they can be widely applied within monitoring programmes. This paper is one of few studies comparing the performances of number of passive samplers for organic compounds and demonstrating the consistency of the data they provide. Useful insights in the working principles of the some of the samplers are also given.

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receiving phase enclosed in various types of membrane.[7–9] The mass transfer of contaminants into these samplers is dependent on both the characteristics of the device and the physico-chemical properties of the analytes being sequestered.[1] Mass transfer of pollutants into the samplers is a multi-step phenomenon involving (i) transport of the chemical across the water boundary layer present at the surface of the sampler, (ii) transfer across the membrane and/or receiving phase layer of the sampler and in some cases (iii) transport across the biofilm layer that develops as a result of extended exposure in natural waters.[1] The overall resistance to mass transfer ($1/k_O$) into a sampler can be described as the sum of resistances in the water (δ_W/D_W), membrane ($\delta_M/K_{MW}D_M$) and biofilm ($\delta_B/K_{BW}D_B$):

$$\frac{1}{k_O} = \frac{\delta_W}{D_W} + \frac{\delta_M}{K_{MW}D_M} + \frac{\delta_B}{K_{BW}D_B} \quad (1)$$

with k_O the overall mass transfer coefficient (m s^{-1}), K_{MW} (L L^{-1}) the membrane–water (or sampler–water when using single-phase polymeric samplers) partition coefficient, K_{BW} the biofilm–water partition coefficient, δ_W, δ_M and δ_B the boundary, membrane and biofilm layer thicknesses (m), and D_W, D_M and D_B (m^2 s^{-1}) analyte diffusion coefficients in water, membrane and biofilm layers, respectively. It has been shown that, depending on exposure conditions (water temperature and turbulence), resistance to mass transfer is generally influenced more by membrane-side processes for analytes with relatively low log K_{OW} and more by transport across the boundary layer for those with high log K_{OW} values.[10,11] The threshold partition coefficient separating these two mass transfer processes is typically in the region of log K_{OW} 3.5–5.0.[10–12]

Integrative monitoring can be achieved if the exposure duration is kept well below the time required for the concentration in the sampler to reach equilibrium with the dissolved concentration in water.[1] The amount of analyte absorbed by passive samplers may be represented by a first-order kinetic approach to equilibrium:

$$m = K_{SW}VC_W[1 - \exp(-k_e t)] \quad (2)$$

where m is the amount of analyte absorbed (ng), K_{SW} the sampler–water partition coefficient (L L^{-1}), V the volume of the sampler (L), k_e the exchange rate constant (d^{-1}), t the exposure time (d) and C_W the analyte concentration (ng L^{-1}). k_e is given by:

$$k_e = \frac{k_O A}{K_{SW}V} = \frac{R_S}{K_{SW}V} \quad (3)$$

where A is the surface area of the sampler (cm^2), k_O the overall mass transfer coefficient (m s^{-1}) and R_S the analyte uptake rate (L d^{-1}). R_S is the analyte specific equivalent volume of water cleared by the sampler per unit of time, and is needed to calculate analyte concentrations in the water column. First-order dissipation kinetics of PRCs, non-naturally occurring chemicals spiked into the sampler prior to deployment, can be used to estimate k_e, the exchange rate constant (eqn (4)):

$$m_{PRC} = m_{0,PRC} \exp(-k_e t) \quad (4)$$

where $m_{0,PRC}$ and m_{PRC} are masses of PRC in the sampler prior to and following exposure, respectively. When PRC dissipation is complete (or close to), then equilibrium between the concentration of analytes with similar log K_{OW} in the sampler and that in water may be assumed. However, little (or negligible) PRC dissipation indicates that the uptake is in the linear phase. The boundary between these two regimes is generally found for PRCs with log K_{OW} of 4.0–5.0 for typical exposures of up to several weeks.

Many sources of error contribute to the uncertainties in the measurement of C_W obtained using integrative passive samplers. These arise from the reproducibility in sampler fabrication, PRC spiking, the accuracy of K_{SW} values (eqn (2)), the accuracy of PRC measurements and potential effects of biofouling and DOC.[13,14] For highly hydrophobic compounds whose uptake is generally under boundary layer-control and for which data on dissipation of PRC analogues are not commonly available, further uncertainty arises from the extrapolation of their uptake rates from data for less hydrophobic PRCs.[6,11,15] The application of a range of different passive sampling devices with distinctly different working principles, and inter-laboratory variation in sampler processing and analysis are likely to increase the overall uncertainty in these measurements.[10] Further variability may also result from the quantification of analyte masses in extracts from passive samplers close to the analytical limits of detection.

The present study assessed the performance of six different passive samplers for the measurement of hydrophobic organic contaminant concentrations in water. Samplers were exposed over a short period (five days) in a tank with a through flow of natural Meuse river water fortified with a range of PAHs, PCBs and pesticides. The concentrations used were made to fluctuate over the exposure period, reaching high levels at the peaks, in order to simulate a pollution event. Contaminant concentrations higher than those commonly found in surface waters were used in order to extend the number of analytes that were accumulated by all of the types of samplers tested. The evaluation of the performances of the different sampler designs compared dissipation rates of PRCs from the various samplers, and masses of analytes absorbed by the samplers normalised to sampler surface area. As this comparative study involved a number of laboratories, it provided a realistic evaluation of the performance of the samplers since in normal practice the overall uncertainty of measurements will include inter-laboratory variability.

Materials and methods

Experimental procedure for sampler exposure

The study was undertaken in Eijsden (The Netherlands) for a period of 5 days in April 2005. This experiment was designed to expose simultaneously six different types of passive sampling device to Meuse river water fortified with various PAHs, PCBs, hexachlorobenzene and *p,p′*-DDE (standards purchased from Qmx Ltd, UK). A full list of compounds spiked into the river water for this test and/or analysed for can be found in the ESI† (Table SI-1). The system consisted of a custom-made stainless steel tank designed to hold 200 L of river water and to house a 27 cm diameter Teflon® carousel composed of five platforms for exposure of the various passive sampling devices (Fig. 1). The carousel was operated using an electrical overhead stirrer with a rotation speed set to 30 rpm for the entire duration of the experiment. This system allowed uniform contaminant

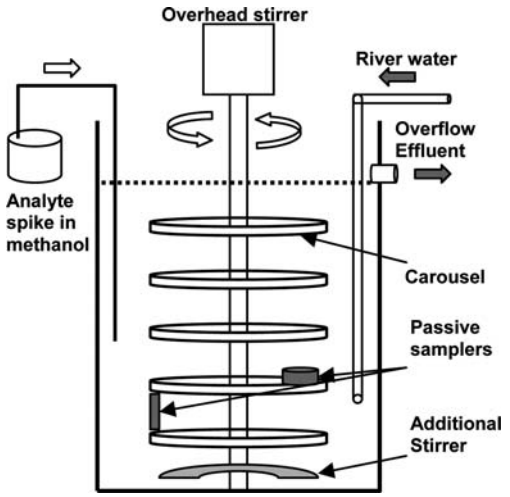

Fig. 1 Diagram of the test tank used for the exposure of the various types of passive sampling devices.

concentrations in water throughout the container for the duration of the experiment. Samplers were exposed using a flow-through system and fresh Meuse river water was pumped into the tank at the rate of 10 L h^{-1} to ensure that the overall removal of test analytes from the water phase by the samplers was negligible. The spiking solution was prepared by dissolving PAHs, PCBs, hexachlorobenzene and *p*,*p*′-DDE into methanol. A Watson-Marlow peristaltic pump and pre-cleaned silicone tubing were used to deliver the methanolic solution to the test tank (0.7 mL h^{-1}). The volumetric flow of methanol was kept low so that the concentration of methanol in water was negligible ($\ll$1%). The effluent solution from the tank was treated as chemical waste.

Meuse river water is classified as hard with $CaCO_3$ close to 250 mg L^{-1}. The water temperature during sampler exposure varied between 16 and 18 °C. Dissolved and total organic carbon levels were 2.5 and 3.5 mg L^{-1}, respectively. Two artificial peaks in the contaminant concentrations in water were simulated during this five day long experiment (Fig. 2). Five different

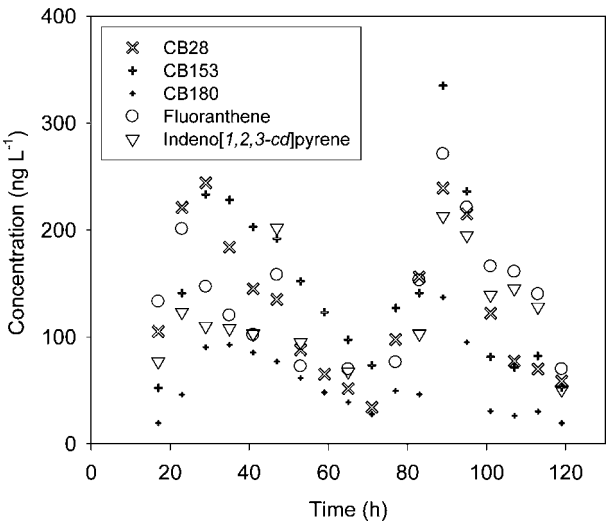

Fig. 2 Variation in total concentration (ng L^{-1}) for selected PCBs and PAHs measured in water during the five day tank test.

spiking solutions containing similar analytes but at different concentrations were prepared so that contaminant concentrations in the tank could vary without addition of significant amounts of methanol to the water. Measured total concentration of single PAH and PCB compounds in water varied in the range <50 to 500 and 20–400 ng L^{-1}, respectively. Total concentrations of hexachlorobenzene and *p*,*p*′-DDE in water reached a maximum of 700 and 500 ng L^{-1}, respectively. High contaminant concentrations were selected and simulated in order to enable significant accumulation of most analytes in most types of samplers during this short exposure period.[10]

Passive sampling devices

Six passive samplers were tested: SPMDs, a version of the Chemcatcher designed for sampling hydrophobic compounds, silicone rods and strips and two types of MESCOs. Small-sized SPMDs (Exposmeter AB, Tavelsjo, Sweden) (5 cm long, 2.5 cm wide and filled with 0.055 mL of triolein) were used. The Chemcatcher was made of a Teflon® body holding a 40 μm thick LDPE membrane superimposed onto a C_{18} Empore® disk loaded with 1-octanol (450 μL). Silicone strips (Rubber BV, Hilversum, The Netherlands) were made from 500 μm thick silicone (64.4 cm long and 2.5 cm wide). Silicone rod samplers are single-phase samplers (total length of 8.0 cm and diameter 0.2 cm). The original version of MESCO (referred to as MESCO I (m) with m for modified) was produced by inserting a pre-cleaned silicone rod (Goodfellow Ltd, UK) (1 cm long and 2 mm diameter) into a dialysis membrane bag (18 mm flat width and 30 mm long) made from regenerated cellulose (Spectra/Por 6, molecular weight cutoff 600 Da) filled with MilliQ water. A silicone rod was used as receiving phase instead of the Gerstel Twister bar used in the original version of the sampler. The MESCO II comprised a silicone rod enclosed into a LDPE envelope with an additional air layer separating the two phases.[16] Lay-flat LDPE membrane (Polymer-Synthesewerk, Rheinberg, Germany) (100 μm thick) and pre-conditioned silicone rod (Goodfellow GmbH, Bad Nauheim, Germany) were used. The ends of the tube were heat sealed to form a bag (3 cm long and 2 cm wide). SPMD, Chemcatcher, silicone strip and rod and MESCO II devices were all spiked with PRCs with log K_{OW} values in the range 3.9–7.3 to allow the estimation of contaminant exchange kinetics between the sampler and water.[10]

Samplers were stored at −20 °C until deployment. Preparation and trip controls were treated in a similar fashion to exposed samplers. Trip controls were opened to the air during deployment and retrieval procedures. Triplicate samplers of each type were randomly mounted onto the carousel close to the edge of the carousel plates (see Fig. 1).

Sampler preparation, processing and analysis

Chemcatchers were prepared, extracted and then analysed for PAHs by gas chromatography-mass spectrometry (GC-MS) following procedures described previously.[5,10,17] Small-sized PRC-spiked SPMDs were extracted in a similar way to that undertaken for standard size samplers following published procedures.[18] Briefly, SPMDs were dialysed (2 × 24 h in hexane), and the triolein removed from the extract using a size-exclusion

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chromatographic column with dichloromethane as mobile phase.[18] Finally, the solvent was exchanged to hexane and extracts reduced in volume and analysed by GC-MS for hexachlorobenzene, *p*,*p*′-DDE, PAHs and PCBs.[10] Silicone strips were spiked with a series of PRCs by exposing the samplers to a PRC methanol–water solution (80 : 20 v/v).[4] The strips were cleaned by soaking in ethyl acetate prior to spiking with PRCs. This step ensures the quality of blanks and removes possible oligomers that may interfere with the analytical step. Following exposure, samplers were wiped with a damp paper tissue before being extracted twice (2 × 100 mL) with pentane. Extracts were reduced in volume, cleaned-up with silica (2 g, deactivated with 6% water; elution with pentane) and analysed by GC-MS for PAHs. An electron capture detector was used for the detection and quantification of PCBs, hexachlorobenzene and *p*,*p*′-DDE. The combined processing and analysis of silicone rods (1.5 cm long from the MESCOs and 1 cm pieces cut from silicone rods) consisted of a thermal desorption step followed by GC-MS analysis. A thermodesorption unit (TDU) (Gerstel, Mülheim a.R., Germany) was placed on top of an Agilent 6890 GC (Agilent Technologies, Palo Alto, CA, USA) equipped with a cold injection system CIS-4 (Gerstel) and a mass spectrometric detector (MSD) 5973N (Agilent). Details of the analysis can be found elsewhere.[7,16,19] A detailed list of PRCs used with each sampler can also be found in ESI† (Table SI-2) and elsewhere[10] and only PRCs for which dissipation was significant when compared with control samplers (one-sided t-test according to Vrana and co-workers[15]) were included in the data analysis.

Results and discussion

Performance reference compounds

Where the offloading kinetics of PRCs are isotropic with the kinetics of uptake, then PRCs can be used for the *in situ* estimation of the exchange rate parameter (k_e) for the movement of contaminant between water and sampler. Since the passive sampling devices have very different geometries, in order to compare their relative performances it was necessary to normalise PRC elimination rates to the surface area (A) to volume (V) ratio (eqn (3)). Resulting log k_eV/A values were plotted as a function of compound hydrophobicity (log K_{OW}) (Fig. 3A). The spread of k_eV/A values across the five sampler designs is generally less than 0.4 log unit. The product of normalised k_e values and K_{SW} (eqn (3)), is the overall mass transfer coefficient (k_O) and is plotted in Fig. 3B as a function of log K_{OW}. Log K_{OW} and sampler-specific K_{SW} values used here to prepare Fig. 3 are detailed in previous work.[10] The spread of log k_O is approximately 0.5 of a log unit. One factor that contributes to this overall variability is the inherent difference in water turbulence around the various samplers due to their shape and positioning on the carousel. A further contribution to the uncertainty comes from the involvement of three laboratories in the extraction and chemical analysis steps and the uncertainty associated with K_{SW} values. The observed variability is slightly lower than the spread of PRC data observed for the same samplers deployed for longer periods of time in the field.[10] The variability within type of sampler does not appear much smaller than that across sampler type. This indicates the validity of using PRCs with the

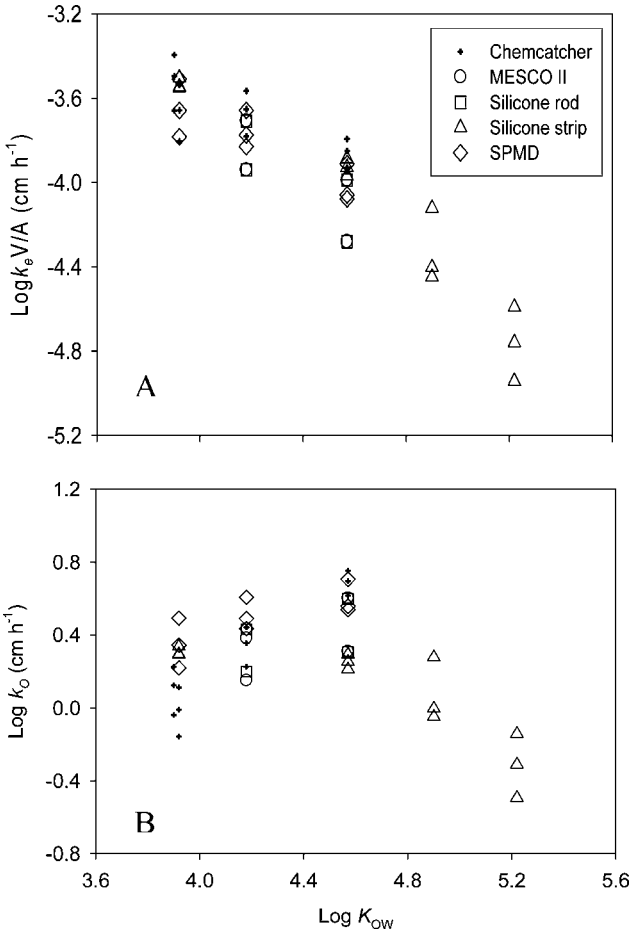

Fig. 3 First-order PRC dissipation rates normalised to sampler volume to surface area ratio (k_eV/A) for five samplers (A) and overall mass transfer coefficients, k_O, for PRCs (B). Note: no PRCs were used with MESCO I (m) samplers.

samplers for hydrophobic organic compounds, and the robustness of the approach since all of the devices are functioning in a similar manner and yielding comparable results. However, the range of polarity of pollutants for which the various samplers can be used in an integrative manner in practice varies, and is determined by the time taken to approach equilibrium in relation to the required length of field deployment.

Half-time to equilibrium (t_{50}) was calculated to estimate thresholds between linear and non-linear uptake phases. t_{50} values for analytes with log K_{OW} < 4.5–4.6 were under 7 days for most samplers (based on PRC data). Half-time to equilibrium increased in the order silicone rod < SPMD < silicone strip < chemcatcher < MESCO II. In this range, t_{50}s as low as 1–4 days were found for SPMDs and silicone rods. Those for the Chemcatcher were in the range 2 to 8 days for analytes with log K_{OW} below 5. Based on limited PRC data, t_{50}s for MESCO II were between 7 and 22 days. Therefore, masses of the least non-polar analytes absorbed by these samplers may not be representative of the whole five days of exposure. This has been exemplified previously in simulations of deviations between true and measured C_{TWA} in relation to the timing of the occurrence of peaks under conditions of fluctuating concentrations of the

analyte of interest and the t_{50} for that particular compound.[20] Linear uptake is, however, expected for all samplers and analytes with log K_{OW} > 5. The t_{50} for MESCO I (m) exposure is likely to be >10 days for most analytes studied here.[7] For MESCO II, the t_{50} calculated here for low molecular weight PAHs is in agreement with the one week estimate by a previous study.[9]

Increases in overall mass transfer with increasing PRC hydrophobicity can be seen for analytes with log K_{OW} between 3.9 and 4.5 in the Chemcatcher, silicone rod, and SPMD. This positive slope indicates that resistance to mass transfer in the membrane for analytes with log K_{OW} < 4.8 cannot be neglected. However, it does not appear as steep as expected under fully membrane-controlled exchange for SPMDs[11] and Chemcatcher.[15] PRC dissipation data for silicone strip samplers clearly show a decrease in overall mass transfer coefficient with increasing PRC hydrophobicity and this is indicative of boundary layer-controlled contaminant exchange between sampler and water for analytes with log K_{OW} > 4.5.

Analyte masses absorbed

A number of different criteria can be used for the comparison of the performance of different types of passive sampling devices. These can include the measurement of analyte masses absorbed normalised to sampler volume or area depending on whether analyte concentrations in the sampler have reached equilibrium or if uptake remains in the kinetic sampling stage.[6,10,11]

In the present system, measured total water concentrations (including bound and dissolved material) are likely to be higher than dissolved concentrations driving the uptake by the samplers. It is possible to calculate and compare TWA concentrations of pollutants for all samplers. However, uncertainty in the estimates obtained with the several types of sampler may be introduced by the different methods of calculation (*e.g.* use of empirical log R_S–log K_{OW} models[6]), uncertainties in the PRC dissipation rates and the values used for parameters such as sampler–water partition coefficients (K_{SW}). Hence it is challenging to make direct comparisons between estimates of dissolved concentrations of pollutants based on passive sampling and measurements based on analysis of spot water samples.

Despite the short exposure time of five days, the spiking of the matrix with relatively high concentrations of contaminants resulted in the detection of a higher number of compounds with higher limits of detection than were found in a previous study in the field. The full list of compounds analysed for in extracts from each type of passive samplers was published previously.[10] In the latter the same range of devices was deployed but for much longer times (up to 28 days).[10] It is possible to assess the performance of the different sampler designs by comparing masses of analytes accumulated by the samplers, assuming linear uptake and boundary layer-control. In this case, masses are normalised to the surface area (A) of the sampler (eqn (3)).

In order to aid interpretation of the data, normalised masses for each analyte from each sampler were further divided by the mean of analyte masses absorbed into SPMD samplers. These were plotted on a log scale against log K_{OW} for each sampler (Fig. 4). A ratio of 1 implies a negligible effect of the differences in sampler configuration, sampler placement in relation to water turbulences in the tank and variability in the analysis in different laboratories. In this case based on PRC data, normalised masses for analytes with log K_{OW} > 4.6 would be expected to be similar and independent of the material used for the preparation of the sampler.

MESCO I (m), silicone rod and strip samplers (and SPMD) appeared to be generally consistent for analytes with log K_{OW} > 4.5 with values reasonably close to one within the observed variability. Normalised masses as a proportion of masses absorbed into SPMDs are generally within a factor of 2. Based on the masses accumulated, the transition to boundary layer-controlled uptake does appear to occur at a log $K_{OW} \approx 4.6$. Below this threshold, ratios are far from the reference value of one. This indicates that for these analytes uptake is affected by the volume of the sampler and the sensitivity of the sampler to fluctuations in concentration.

The within-sampler variability for MESCO I (m), MESCO II, silicone rod and silicone strip samplers is smaller than that observed for the SPMD and Chemcatcher. However, for both of the latter, a good relationship was observed between the relative masses of analyte absorbed in the different replicate samplers (with log K_{OW} > 4.6) and respective PRC dissipation data. This also indicates that despite PRCs being under "membrane-controlled" exchange kinetics, they appear to be representative of boundary layer resistance. In this system resistances in the membrane and boundary layers are likely to be in the same order of magnitude. This is further confirmed by comparing the relative standard deviations for PAH masses accumulated by triplicate SPMDs and the resulting C_W calculated using d_{10}-phenanthrene R_S values for respective replicates. As shown in Fig. 5, the within-sampler variability reduces when PRC-based uptake rates are taken into account. While a similar picture can be seen for the Chemcatcher data, it is further complicated by the lag-phase effect.

Replicate MESCO I (m), MESCO II and silicone rod samplers were exposed in a very similar fashion (since samplers are physically linked in a strip or rod) resulting in very low variability between replicate samplers. Although silicone strips are not joined together, the three replicates were deployed in a similar way, and this contributes to the low variability between replicates. Further, silicone strips and rods are made of a single polymer/membrane material and the entire sampler is generally extracted following exposure. Although the SPMD has a more complicated design, the whole sampler (including the LDPE membrane) is commonly extracted for analysis. However, for Chemcatcher and MESCO samplers, only the receiving phase, and not the LDPE layer, is extracted, and both Chemcatcher and MESCO II exhibit a decrease in the ratio of normalised masses with increasing analyte log K_{OW} (Fig. 4). This is particularly marked for MESCO II where ratios close to or below 0.1 (a factor of ten or more below the expected value of 1) are found for the largest PAH and PCB compounds. It is likely that this behaviour results from the analysis of only analytes accumulated in the receiving phase, and a lag-phase in the accumulation of analytes in the receiving phase. This lag-phase can be considered as the time required for a steady state flux to be established across barriers of the sampler.[6] Ratios for largest PAHs and PCBs are lower for MESCO II than those found for the Chemcatcher and this may be due to the additional air layer present in MESCO II. Wennrich *et al.*[9] estimated MESCO II lag times in the range of 5–30 h and values as high as 48 h for PCBs.

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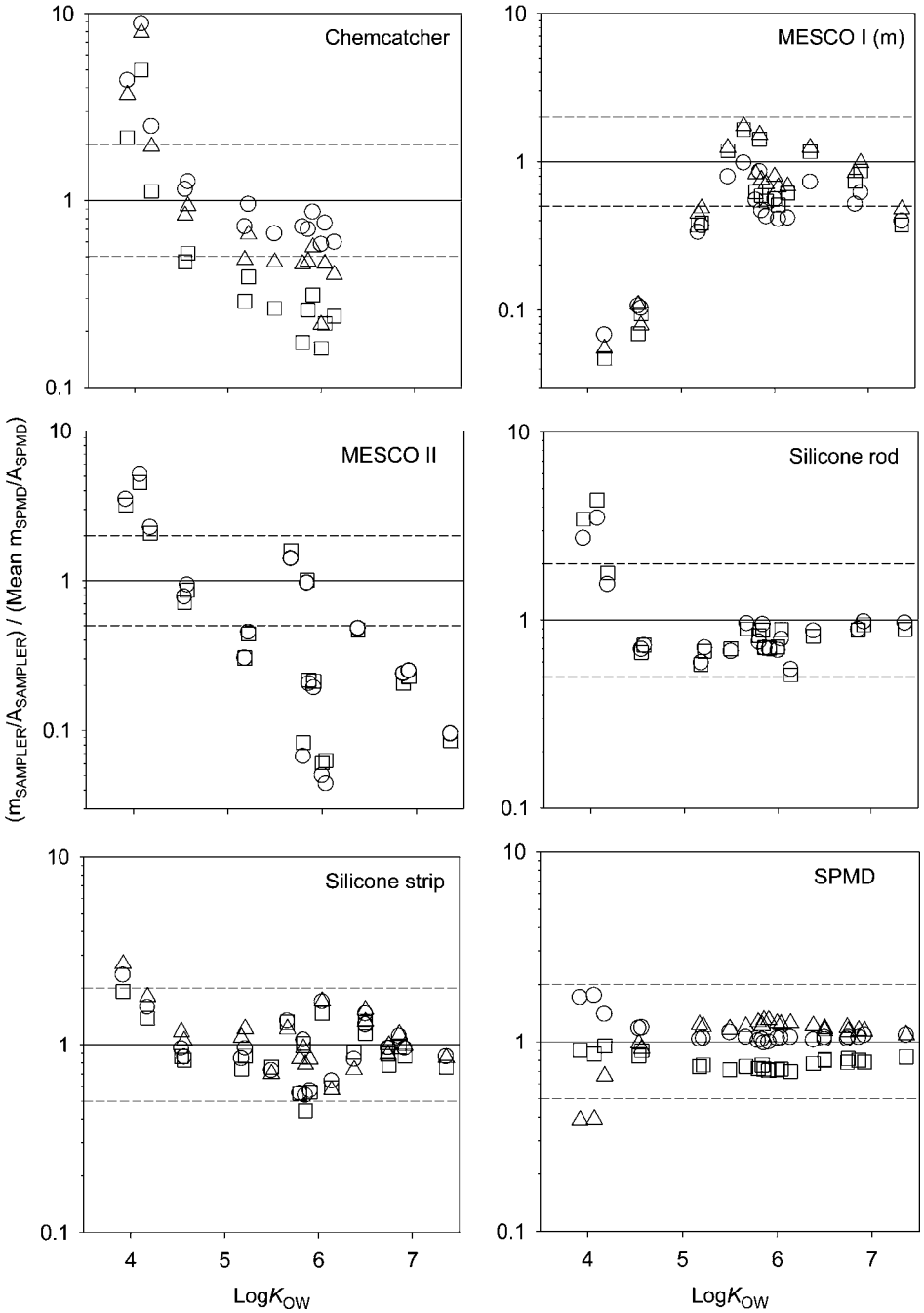

Fig. 4 Masses, m, of PAHs, PCBs, p,p'-DDE and HCB absorbed in the six different samplers normalised to the surface area of the samplers ($m_{SAMPLER}/A_{SAMPLER}$) and divided by the mean of triplicates measurements of normalised masses absorbed by SPMDs (m_{SPMD}/A_{SPMD}). On the plot of MESCO II data, white and grey symbols are for PAHs and PCBs, respectively. Different symbols represent replicates.

Estimates of membrane-based lag time[6] ($t_L = \delta_M^2/6D_M$), using published D_M values,[21,22] ranged between <1 h and 26 h for MESCO II (not accounting for the air layer), and between 20 min and 4 h for Chemcatcher. The lower values for the latter are due to the thinner LDPE membrane used in this sampler.[5]

Interestingly, MESCO II data for PAHs and PCBs appeared to follow two distinct trends (Fig. 4). Rather than plotting ratios as a function of log K_{OW}, these are shown in Fig. 6 as a function of analyte diffusion coefficient in LDPE polymer.[21] Improved agreement between ratios of PAHs and PCBs can be observed. This confirms that processes occurring in the LDPE membrane of MESCO II affect the overall uptake into this sampler under the present conditions.

Implications for the use of passive sampling devices

This study generally confirms and furthers our understanding of the principles of contaminant uptake into six types of passive sampling devices for monitoring non-polar organic contaminants. The ability to select test compounds and to use relatively

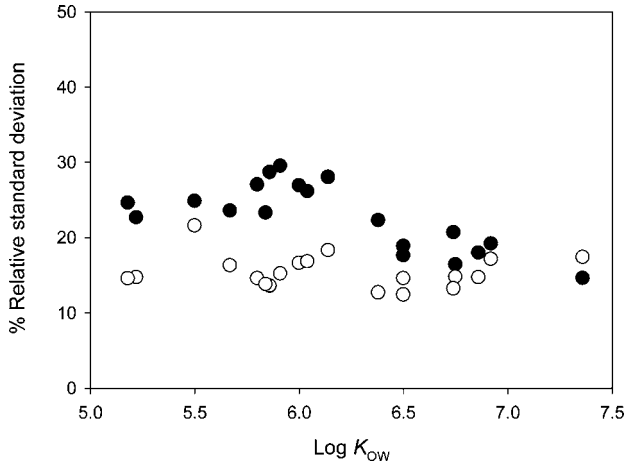

Fig. 5 Relative standard deviations (%) of triplicates measurements of PAH masses absorbed by SPMDs (●) and resulting triplicate C_W calculated using respective d_{10}-phenanthrene R_S (○) for analytes whose uptake is expected to be linear and under boundary layer-control.

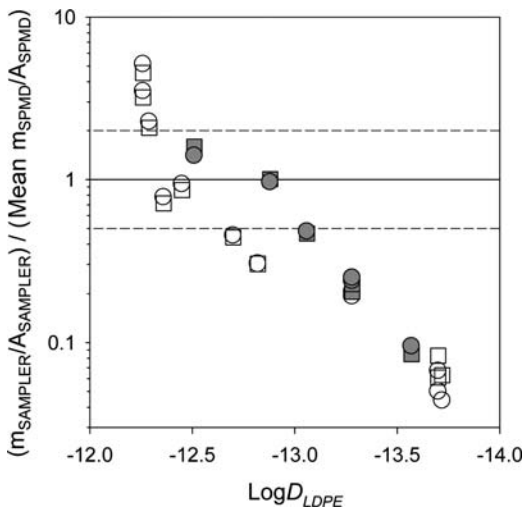

Fig. 6 Masses of PAHs, PCBs, *p*,*p*′-DDE and HCB absorbed in MESCO II normalised to the surface area of the samplers ($m_{SAMPLER}/A_{SAMPLER}$) and divided by the mean of triplicates measurements of normalised masses absorbed by SPMDs (m_{SPMD}/A_{SPMD}) plotted against log diffusion coefficient in the LDPE membrane.[21] White and grey symbols are for PAHs and PCBs, respectively.

high contaminant concentrations in the exposure tank allowed the evaluation to be effected across a wider range of compounds (and properties) than was possible in a previous comparative field study.[10] This was particularly important for samplers (*e.g.*, Chemcatcher) with relatively low uptake rates, and allowed a more thorough comparison of the devices. In addition, with higher contaminant masses accumulated in the samplers (further away from limits of detection), the inter-laboratory variability in the analysis is likely to be lower. These masses were used to compare the performance of the various samplers, where the overall variability included that due to analysis being conducted in three different laboratories. PRC dissipation data are consistent across the range of samplers and the transition between membrane- and boundary layer-controlled uptake is in agreement with masses of contaminants accumulated under boundary layer-controlled uptake. The variability exhibited by certain sampler replicates could be explained by their positioning in the tank and differences in water turbulences around the replicates and this was demonstrated by the PRC dissipation rates. This work underlines the utility of the PRC approach since in natural waters conditions at the sampler surface can vary over short distances and in time. This *in situ* calibration method increases the robustness of applications of passive sampling in monitoring water quality.

Devices tested in this trial had a range of properties, and some are better suited for use for compounds of lower log K_{OW} and at higher concentrations (*e.g.* Chemcatcher), whilst others (*e.g.* SPMD, silicone strips and rods) are well suited for monitoring very non-polar compounds of which the dissolved concentration will be low. The latter samplers have high uptake rates and equilibrium is approached over short exposure times for compounds with log K_{OW} < 4.6, when sampling ceases to be integrative, and information on TWA concentration is lost. Another significant property that needs to be considered is the occurrence of a lag-phase for Chemcatcher and MESCO II where only the receiving phase is extracted. This reduces their utility for very short deployment times.

The comparison of sampler performance for analytes with log K_{OW} < 4.6 is more complex since under present conditions, sampling was not truly integrative for all analytes and all samplers and contaminant concentrations in water varied significantly during the exposure. Uncertainties associated with samplers with very different configurations, possibly exhibiting lag phases, or different receiving phase volumes and those with sampler–water partition coefficients, K_{SW} values needed for the comparison, render such comparison futile here.

Together with the use of reference sites, one way forward for the intercomparison of passive sampling technologies is the use of laboratory or pilot scale tank tests using either ultra pure, distilled or natural waters. Such trials have proved to be useful for conducting comparisons of the performance of passive sampling devices in measuring dissolved concentrations of metals[23] and, in the present study, non-polar organics. This can help reduce uncertainties in the measurement of the concentration of pollutants present and improve control over environmental variables such as temperature and turbulence.

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SSPI-CT-2003-502492; http://www.swift-wfd.com). Views presented here are those of the authors alone.

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Príloha 18

Prokeš R., **Vrana B.**, Klánová J., and Kupec J., Calibration of three passive samplers of hydrophobic organic compounds in water: Assessment of critical issues in experimental design data interpretation and field application, ***Fresenius Environ. Bull.*, 2010, 19, 2812–2822.**

CALIBRATION OF THREE PASSIVE SAMPLERS OF HYDROPHOBIC ORGANIC COMPOUNDS IN WATER: ASSESSMENT OF CRITICAL ISSUES IN EXPERIMENTAL DESIGN, DATA INTERPRETATION AND FIELD APPLICATION

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ABSTRACT

Three types of passive sampling devices (two samplers based on a silicone polymer sheet and semipermeable membrane devices) were calibrated for the measurement of time-weighted average (TWA) concentrations of hydrophobic micropollutants, including polycyclic aromatic hydrocarbons and organochlorine pesticides, in water. During a 28 day exposure to constant analyte concentrations, linear uptake was observed into silicone rubber sheets for compounds with log K_{ow} > 4.5. With exception of compounds with log K_{ow} < 4 in SPMDs, uptake into all passive samplers was controlled by the water boundary layer (WBL). Thus, sampling rates are expected to vary widely depending on hydrodynamic conditions during field exposure. Sampling rates of highly hydrophobic polycyclic aromatic hydrocarbons (log K_{ow} > 6) in all calibrations were significantly underestimated in comparison with the theoretical model that is based on diffusion of analytes in WBL. The difference could be explained by the effect of sorption to colloids present in water in the calibration tank. Since an independent measurement of analyte exchange kinetics using performance reference compounds was not performed, sampling rates in the field were calculated for anthracene using its concentrations in collected spot samples. Field sampling rates for the rest of compounds with log K_{ow} > 4.5 were estimated using laboratory-derived calibration data adjusted for field exposure conditions. Application of this approach is demonstrated in a field study in which TWA aqueous concentrations from sampler data for target analytes correlated well with concentrations obtained from spot samples of water collected during the sampler deployment.

KEYWORDS: calibration, passive sampling, persistent organic pollutants, semipermeable membrane devices, silicone rubber

INTRODUCTION

Passive sampling techniques are widely applied to assess exposure and contamination in water, air and soils. These techniques allow determination of the time-weighted average concentration of freely dissolved pollutant fraction over extended periods of time. Passive samplers are cheaper than conventional methods, their manipulation is simple, no power is needed and they can be used in harsh conditions. Diffusion of organic pollutants from sampled media to the sampler is driven by a difference in the chemical potentials. One of the most common applications of the passive sampling devices is the estimation of time weighted average (TWA) concentrations of pollutants for environmental risk assessment. The concentration found in a passive sampler can be used for estimation of TWA water concentration in field situations providing accurate calibration data is available.

The accumulation of chemicals by passive samplers is characterized by an initial linear uptake stage followed by curvilinear and equilibrium partitioning stages. The exchange process between a passive sampler and water is described as follows [1]:

$$N = m_s K_{sw} C_w (1 - e^{-k_e t}) \quad (1)$$

where N is the mass of a target compound in the sampler at time t, k_e is the exchange rate coefficient, K_{SW} is the sampler/water partition coefficient, m_S is the mass of the sampler and C_w is the concentration of a target analyte in water. In the initial uptake phase, when the exponential term is very small (<< 1), chemical uptake is linear or integrative. Then, in the linear region Eq. 1 can be reduced:

$$N = R_S C_W t \quad (2)$$

where R_S is the sampling rate of the system, representing the equivalent extracted water volume per unit of time. A model for estimation of R_S that combines the resis-

tance to transport in both the water phase and the sampler is often applied in the passive sampling literature [2-4]:

$$R_S = k_o A = A \Big/ \left(\frac{1}{k_w} + \frac{1}{k_s K_{sw}} \right) \quad (3)$$

where k_o is the overall mass transfer coefficient, A is a surface area of the sampler, k_w and k_S are the mass transfer coefficients through the water boundary layer (WBL) and the sampler, respectively.

The sampling rate R_S is dependent on a variety of factors including water flow velocity, water temperature and biofouling [2, 5-7]. Correction for this variability can be achieved by estimation of R_S from the dissipation rates of performance reference compounds (PRCs) spiked into the passive sampler prior to exposure. The dissipation rate is equal to the rate of the uptake process, and it is equally affected by variability in environmental factors [1, 8].

Laboratory-derived calibration data are necessary to establish the relationship between R_S and K_{ow} in order to apply R_S estimated for compounds with moderate hydrophobicity (e.g. PRCs) to compounds in a higher K_{ow} range. In this study, the relationship between R_S and log K_{ow} was investigated for three different passive samplers (two silicone polymer sheets and semipermeable membrane devices, SPMDs) for a range of polychlorinated biphenyls [9], organochlorine pesticides [10] and polycyclic aromatic hydrocarbons [6] in a flow-through system. Application of calibration data in a field exposure without the use of PRCs is demonstrated.

MATERIALS AND METHODS

Materials and chemicals

Organic solvents dichloromethane, methanol, *n*-hexane, cyclohexane and chloroform were obtained from Lab-Scan, Ireland and Sigma-Aldrich, Czech Republic. Standards of 16 polyaromatic hydrocarbons (PAHs), 6 polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and internal standards (*p*-terphenyl, PCB 121) were obtained from Sigma-Aldrich, Czech Republic. Physicochemical properties of test analytes are given in Table 1.

TABLE 1 - Selected physicochemical properties of test analytes at 25°C.

Compound	MW[a] (g mol^{-1})	log K_{ow}[b]	log K_{SW}[c] Altesil	log K_{SW}[c] LDPE	R_S (L d^{-1}) Altesil	R_S (L d^{-1}) SPMD
Naphthalene	128.2	3.37	3.03	2.81	Eq.[g]	n.d.[h]
Acenaphthylene	154.2	3.92	3.02	3.16	Eq.[g]	n.d.[h]
Acenaphthene	152.2	4.00	3.25	3.62	Eq.[g]	Eq.[g]
Fluorene	166.2	4.18	3.79	3.77	0.98	2.19
Anthracene	178.2	4.54	4.21	4.33	1.53	15.59
Phenanthrene	178.2	4.57	4.11	4.22	4.83	3.07
Fluoranthene	202.3	5.18	4.62	4.93	1.22	10.76
Pyrene	202.3	5.22	4.67	5.10	1.66	7.29
Benzo(a)anthracene	252.3	5.90	5.32	5.73	0.48	5.83
Chrysene	228.3	5.86	5.25	5.78	1.14	7.01
Benzo(b)fluoranthene	228.3	5.91	5.74	6.66	0.82	5.36
Benzo(k)fluoranthene	252.3	5.90	5.74	6.66	0.84	4.70
Benzo(a)pyrene	252.3	6.04	5.70	6.75	0.56	2.55
Indeno(1,2,3-cd)pyrene	276.6	6.50	6.06	7.40	0.35	2.84
Dibenzo(a,h)anthracene	278.4	6.75	6.24	7.32	0.12	2.35
Benzo(g,h,i)perylene	276.3	6.50	6.02	7.27	0.33	2.45
PCB28	257.6	5.67	5.53	5.40	1.79	6.62
PCB52	292.0	5.84	5.80	5.55	1.89	6.17
PCB101	326.4	6.38	6.28	6.18	1.66	4.80
PCB138	326.4	6.74	6.77	6.82	1.75	4.94
PCB153	360.9	6.83	6.72	6.81	1.37	3.34
PCB180	360.9	6.92	6.98	7.24	1.42	3.89
p,p´-DDE	318.0	5.70	5.67[d]	-	1.92	5.20
p,p´-DDD	320.1	5.50	5.48[d]	-	1.52	7.71
p,p´-DDT	354.5	6.19	6.14[d]	-	0.53[f]	3.04
α-HCH	290.8	3.70	2.60[e]	-	0.87	1.01[g]
β-HCH	290.8	3.80	2.60[e]	-	Eq.[g]	0.33[g]
γ-HCH	290.8	3.80	2.60[e]	-	0.84	1.87[g]
δ-HCH	290.8	4.10	2.60[e]	-	Eq.[g]	0.54[g]

[a]Molecular weight (MW)
[b]Octanol-water partition coefficient [17, 18].
[c]Silicone rubber-water and LDPE-water partition coefficients [19]
[d]Data interpolated from the log K_{ow}- log K_{sw} correlation
[e]Data from Paschke and Popp [20]
[g] Partitioning equilibrium has been likely achieved during 28-days exposure.
[h]not determined

Sampler preparation

SPMDs were prepared according to the procedure described by Huckins et al. [11]. The layflat low density polyethylene (LDPE) tubing was purchased from Polymer Institute Brno, Czech Republic. The LDPE tubing (width 3 cm, thickness 80 μm) was cut into 83 cm pieces and thermosealed at one end with a heat sealer (ETA 0762, Czech Republic). To remove monomers and other impurities the LDPE was extracted in *n*-hexane for 48 h with solvent exchange after 24 h. The tubing was filled with 1ml of triolein (≥97% purity, Sigma-Aldrich, Czech Republic) configured as a thin film and thermo-sealed at the other end. SPMDs had surface area of ≈ 460 cm^2.

Silicone rubber (SR) sheets from two producers Rubena (Rubena, Czech Republic) and Altesil (Altec, Great Britain) were used in this study. The wall thickness of SR Rubena and SR Altesil was 0.1 and 0.5 mm, respectively. Two types of SR were prepared using the procedure described by Rusina et al. [4, 12]. SR sheets were cut into pieces of size 25 × 9.3 cm with surface area of ≈460 cm^2. Two cleaning steps were applied to remove oligomers, other impurities and talcum powder from the surface. At first, SR was shaken in ethyl acetate for 1 d, and then Soxhlet-extracted in methanol for 12 h, wiped with a paper tissue and air dried in a fume-hood overnight.

Calibration experiments

In each experiment up to 9 passive samplers of each type were exposed in a constant concentration flow-through exposure system. This system was devised to allow calibration of the sampling devices to be made under controlled conditions of temperature (22°C), water turbulence, and analyte concentration (Fig. 1). It was operated in a temperature-controlled dark room. The system consisted of two glass tanks with an overflow to waste. Sterilised (using an UV lamp) and degassed (using helium) tap water and the solution of test analytes dissolved in methanol were mixed using a magnetic stirrer in a mixing tank at known and controlled rates and pumped into the exposure tank. Uncontaminated tap water was pumped into the second, control tank. Water was fed to the exposure tank using a peristaltic pump at a constant flow of 3-5 L h^{-1}, allowing a complete renewal of water in the tank every 4-6 h. Test chemicals were dissolved in methanol (667 μg L^{-1}) and the appropriate amounts of stock solution (1.5 - 2 μL min^{-1}) were delivered into exposure tank using a second peristaltic pump. A nominal concentration of 15-35 ng L^{-1} for each analyte was maintained throughout the experiments. The resulting methanol concentration in the exposure water did not exceed 0.0001 % (v/v). The effective flow velocity in both exposure tanks was 4 cm s^{-1}.

Prior to each exposure, the apparatus was operated for a minimum of 4-6 h without samplers to allow for stabilization of the water concentration of analytes. To ensure uniform hydrodynamic conditions in the vicinity of samplers, samplers were placed on stainless steel holders inside exposure tank. Two different orientations of sampler holders were used for exposure of SR and SPMDs, respectively. The control tank contained three samplers and the exposure tank up to 9 samplers.

The exposures of SR lasted up to 28 days, during which triplicate samplers were removed at set time intervals and analysed to determine the concentrations of accumulated test chemicals. Following exposure, the devices were removed and the samplers were extracted to determine the mass of each analyte present in the sampler.

In the first experiment with SPMDs, five samplers were exposed for 28d. The average concentration of pollutants in the exposure tank was 33.5 ng/l and the flow rate was 3.05 l/h. In the second experiment, two types of SR (Altesil and Rubena) were exposed in the same exposure tank. Nine sheets of each type were installed and triplicate sheets from each type were collected after 7, 20 and 28 d, respectively. The average concentration of pollutants was 15 ng/l and the flow rate was 5 l/h.

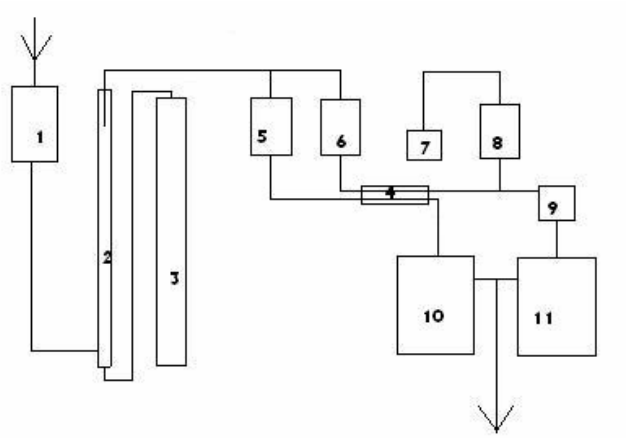

FIGURE 1 - Exposure apparatus used in flow-through calibration of passive sampling devices: 1-tap water inlet, 2-vertical tube, 3-helium cylinder, 4-UV tube for water disinfection, 5, 6, 8-peristaltic pumps, 7-solution of analytes in methanol, 9-mixing tank, 10- tank for exposure of samplers to uncontaminated water, 11- tank for exposure of samplers to contaminated water.

Extraction and analysis

Following exposure, SPMDs were rinsed with tap water and distilled water and then wiped with a paper tissue. For a better analyte recovery, the cleaned SPMDs were perforated with scissors and SPMDs (membrane with triolein) placed into a vial and extracted by dichloromethane for 3 d according to Lebo et al. [13]. The extract was reduced in volume to about 2 ml using gentle stream of high purity nitrogen. To remove polyethylene waxes and triolein the extract was cleaned by gel permeation chromatography (GPC) using BioBeads S-X3 200-400 mesh according to Luellen and Shea [14]. The flow rate of chloroform was 0.6 ml/min and sample collected between 25 and 42 min. The cleanup for analysis of PAHs was performed on a silica gel column, a sulphuric acid modified silica gel column was used for PCB/OCP analysis in samples [2]. Extracts were reduced under a stream of nitrogen. Terphenyl and PCB 121 were used as internal standards for

analysis of PAHs and PCBs, respectively. Samples were analysed using GC/MS.

The surface of SRs was cleaned before extraction in the same way as SPMDs. SRs were Soxhlet-extracted for 12 h in methanol. The extracts were reduced in volume to 15 ml using Kuderna Danish concentrator. The final evaporation was provided with a gentle stream of high purity nitrogen to about 2 ml. The samples were cleaned up using silica gel column, reduced and internal standards were added. Samples were analysed by GC/MS [4, 15].

The extracts were analyzed by GC/MS on an Agilent 6890 equipped with a DB-5MS column (60 m × 0.25 mm i.d., film thickness 0.25 μm, carried gas He). The sample was injected in splitless mode. The temperature program was 80°C (hold 4 min) increase at 15°C/min to 180°C (hold 15 min), increase at 5°C/min to 310°C (hold 20 min).

The MS parameters for both GC methods were: interface temperature 280°C, ion source temperature 250°C, electron impact (EI) ionization mode at 70 eV. Analysis was performed by selected ion monitoring (SIM) applying two or three characteristic ions for each compound in both detection and quantification.

Field study

The field study was performed at the sampling site Spytihněv (WGS84: 49°08'08,7" N, 17°30'11,9" E, altitude 188 m) in the Morava river (south-eastern part of the Czech Republic). This area is an industrial and agricultural region with 10 cities and 72 villages [16]. SRs were transported to the field in a cool box. SRs were placed in a stainless steel holder and exposed for 28 days. After period of sampling SRs were packed in two layers of aluminium foil, put in a polyethylene zip-lock bag and transported to the laboratory. Until analysis samples were stored in a freezer at -18°C.

RESULTS AND DISCUSSION

Data analysis

The experimentally determined time courses of the amounts of individual test substances in the Altesil sampler were fitted by linear regression analysis using modified Eq. 2 in form

$$\frac{N(t)}{C_W} = CF(t) = R_S t \qquad (4)$$

Where *CF*(t) is the concentration factor obtained by dividing the accumulated amount of analyte after defined time period *t* (0, 7, 20 and 28 days, respectively) by the average concentration in the exposure tank for a given time period (0 to *t*). CF presents equivalent volume of water extracted by sampler for a given period of time. Characteristic analyte uptake curves for the sampler are shown in Figures 2 and 3.

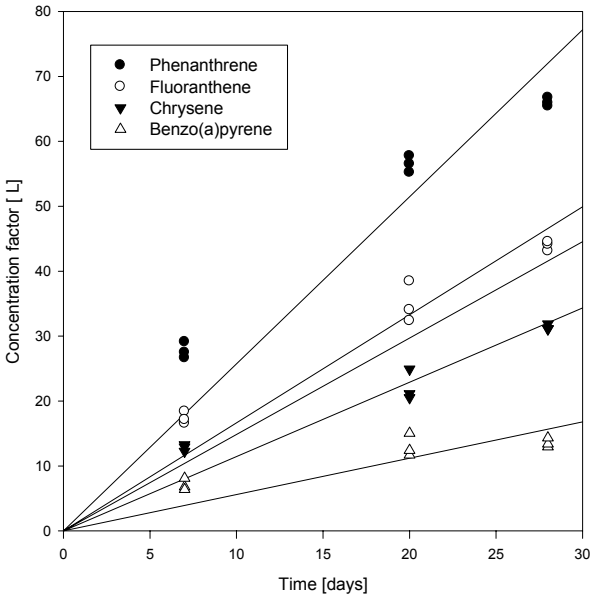

FIGURE 2 - Uptake of selected PAHs in the Altesil sampler in a flow-through exposure at nominal water concentration of analytes 15 ng L^{-1}. The drawn lines show the linear fits of the data using Eq. 4.

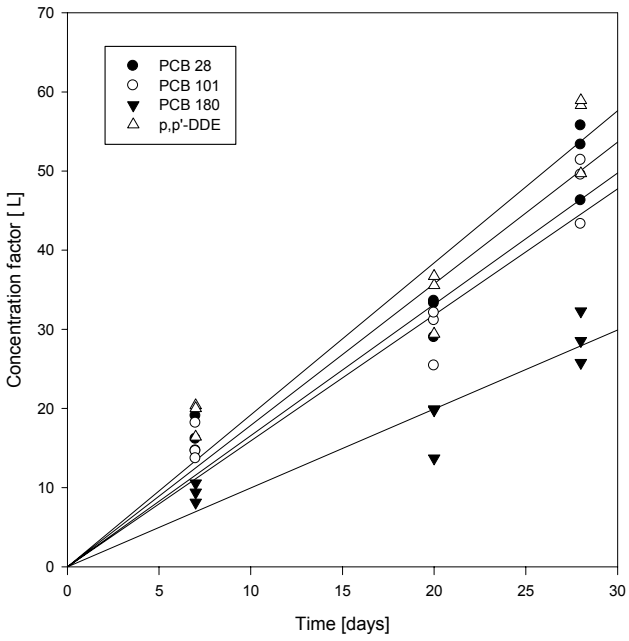

FIGURE 3 - Uptake of selected PCBs and organochlorinated pesticides in the Altesil sampler in a flow-through exposure at nominal water concentration of analytes 15 ng L^{-1}. The drawn lines show the linear fits of the data using Eq. 4.

Because an independent measurement of analyte exchange kinetics using PRC was not performed, an alternative check was performed that the uptake of analytes was linear and integrative during the whole exposure period. Uptake remains essentially linear until 50% of equilibrium concentration is reached. The time it takes to reach the equilibrium concentration ($t_{1/2}$) is related to the elimination rate constant and can be estimated:

$$t_{1/2} = \ln 2/k_e \approx \ln 2\, K_{SW}\, m_s / R_s \quad (5)$$

where K_{SW} is the sampler/water equilibrium partitioning coefficient. K_{SW} values published recently by Smedes et al. [17] were used. For HCH isomers, K_{SW} values for bulk silicone material were not available and log K_{SW} =2.6, obtained using solid phase microextraction fibre coated with polydimethylsiloxane was used [20]. The estimate shows that, with exception of HCHs (excepting δ-HCH), naphthalene and acenaphthylene ($t_{1/2}$ = 5, 10 and 18 days, respectively) with low values of partition coefficient (log K_{sw} < 3.7) compounds should accumulate into samplers in linear uptake mode during the whole exposure period of 28 days.

For SPMDs, uptake kinetics were not measured. Thus, sampling rates were estimated using a single point calculation from amounts accumulated after 28 days of exposure. Linear uptake regime during this exposure time was also checked for individual analytes using Eq. 5 and K_{SW} data available from literature [21]. Calculated sampling rates are shown in Table 1.

Comparison of two silicone rubber samplers

In the experiment with SR, identical exposure conditions were applied by the use of samplers with exactly the same surface area and geometry. They were also positioned in the exposure chamber in the same position. When uptake is linear (integrative) and WBL controlled and samplers are exposed in the flow through system under the same hydrodynamic conditions, masses of analytes absorbed by the samplers should be the same. Moreover, because both samplers are made of silicone rubber with similar properties (diffusion and partition coefficients of analytes), absorbed masses of analytes in the linear uptake phase are expected to be very similar even for compounds accumulated under membrane control (less hydrophobic compounds). The only difference in absorbed mass is expected for compounds that reach partition equilibrium during exposure (some of those with lowest K_{SW} values), for which the ratio of accumulated amounts in both samplers should be:

$$\frac{N_{1\infty}}{N_{2\infty}} = \frac{K_{sw1} m_{s1}}{K_{sw2} m_{s2}} \quad (6)$$

where $N_{i\infty}$ is the amount in a sampler accumulated at equilibrium. When equality of partition coefficients K_{sw} in both polymers is assumed, m_{s1}= 14 g (Altesil) and m_{s2} = 12 g (Rubena), the expected ratio of N_1/N_2 at equilibrium is 1.17. Considering the average variation in the experimental data of cca 10%, it seems unlikely that a significant difference in accumulated masses could be observed for compounds that reached partitioning equilibrium.

In agreement with theoretical considerations, the 28 day exposure resulted in the measurement of similar masses of all analytes for both SR polymers (Figs. 4 and 5). In comparison with Rubena, Altesil contained slightly higher amounts of PAHs and lower concentrations of PCBs and organochlorine pesticides. The same pattern was obtained for data from 7 and 20 day exposures. Because these differences were small, it cannot be unambiguously judged whether the differences originate in differences of SR material properties or in the bias of methods used for analyte quantification. In linear uptake phase, Rubena shows a comparable performance with Altesil and calibration data obtained for Altesil can be applied for both polymers. Po-

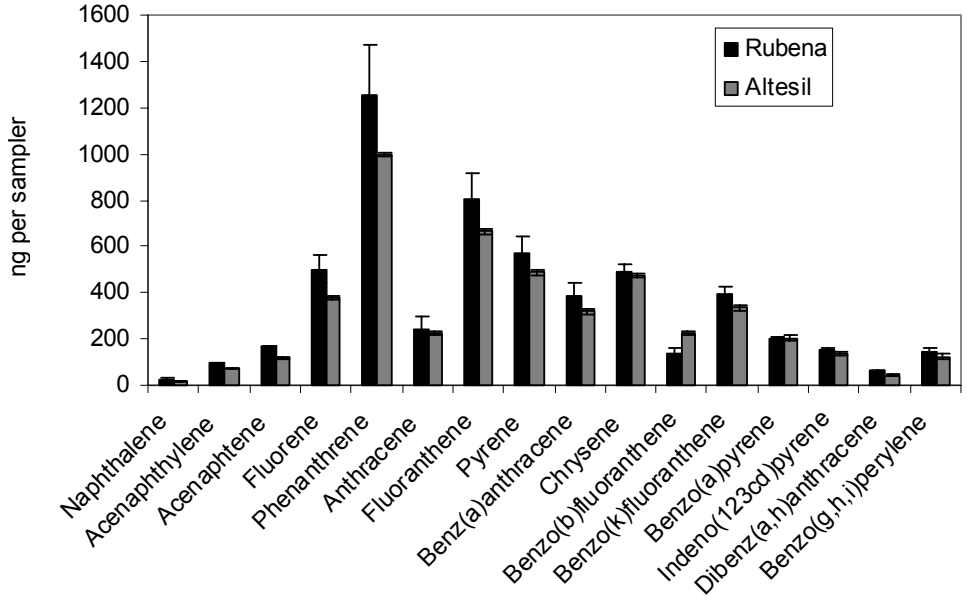

FIGURE 4 - Mean amounts of PAHs accumulated in two different SR samplers after 28 days of exposure at 15 ng L^{-1}.

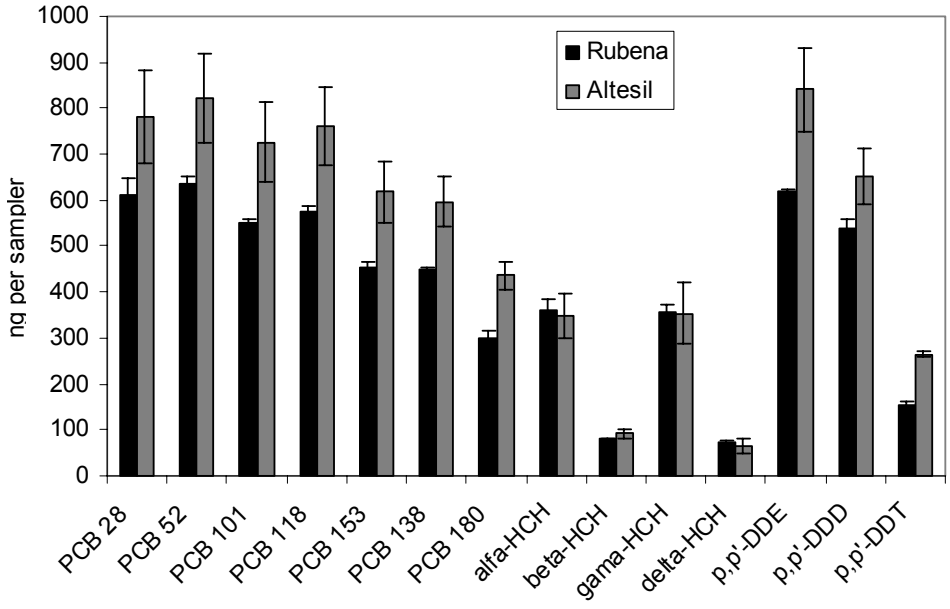

FIGURE 5 - Mean amounts of PCBs and organochlorine pesticides accumulated in two different SR samplers after 28 days of exposure at 15 ng L^{-1}.

tential differences in partition coefficients require further investigation. However, practical experience with Rubena shows that the polymer contains some components that complicate sample extraction, cleanup and instrumental analysis. Rubena is a type of industrial silicone that is surface treated with coating of chalk and we recommend Altesil as a better choice.

Comparison of Altesil and SPMD

As stated earlier, when a) uptake is linear (integrative) and WBL controlled and b) samplers with the same surface area are exposed in the flow through system under the same hydrodynamic conditions, masses of analytes absorbed by the samplers should be the same and independent of the sampler material. When comparing data obtained from SPMD and Altesil exposures, it is necessary to consider that the condition b) was not fulfilled. Although the samplers had the same surface area, their geometry was different. SPMDs are stripes 83×3 cm and Altesil sheets were rectangles 25×9 cm. Although the linear flow velocity in the calibration apparatus was maintained the same (4 cm s^{-1}), the difference of sampler orientation in the exposure chamber can cause significant differences in local hydrodynamic conditions. These result in differences in the thickness of the WBL at the surface of the sampler and consequently in the sampling rates of compounds accumulated under WBL control. Indeed, sampling rates of analytes accumulated in integrative regime in SPMDs were on average 5.8 times higher than those obtained for SR. Prolonged linear uptake is favoured in samplers with high accumulation capacity, given as a product $m_s \times K_{SW}$. High capacity of the Altesil sampler used in this study is achieved by the use of higher amount of sorptive material (14 g) in comparison with other samplers, e.g. the standard SPMD (5 g).

Theoretical model of analyte uptake

To obtain information on the processes that affect the sampling rates obtained in calibration studies, data were compared with the theoretical model for estimation of R_S that combines the resistance to transport in both the water phase and the sampler (Eq. 3).

Membrane control

The value of mass transfer coefficient in sampler material k_S (Eq. 3) can be calculated from the diffusion coefficient in the sampler material (D_S) and the half-thickness of the sampler δ_S:

$$k_S = \frac{D_S}{\delta_S} \tag{7}$$

The corresponding sampling rate of compounds accumulated fully under membrane control with negligible resistance to mass transfer in WBL ($1/k_w << 1/(k_S K_{SW})$ is given:

$$R_S = k_S K_{SW} A = \frac{D_S K_{SW} A}{\delta_S} \tag{8}$$

Diffusion coefficients of analytes of interest in SR were reported recently [12]. At laboratory temperature, for analytes of interest they range from 10^{-9} to 10^{-11} m^2 s^{-1} and they decrease with molecular volume. Diffusion coefficients in LDPE are 2 to 4 orders of magnitude lower than those in SR, ranging from 10^{-12} to 10^{-15} m^2 s^{-1} at 25°C [12]. Partition coefficients between various polymers including silicone rubber, LDPE and water were published, too [19]. Application of these values, δ_S = 2.5 and 0.08 mm for Altesil and SPMD, respectively, yields the estimate of sampling rates that can be potentially achieved if the resis-

tance of the WBL was negligible and compounds were accumulated completely under sampler control. For Altesil, estimated maximum achievable sampling rates are more than three orders of magnitude higher than those determined in our experiment. For SPMDs, calculation yields sampling rates for compounds with log K_{ow} > 4 that are more than two orders of magnitude higher than those determined in our experiment. This indicates that all compounds with log K_{ow} > 4 were accumulated under WBL and the resistance to mass transfer in the sampler material can be neglected. Less hydrophobic compounds (e.g. HCH isomers, and some less hydrophobic PAHs) may be accumulated under membrane control in SPMD [7].

Water boundary layer control

We demonstrated that most compounds under investigation were accumulated under WBL control. When neglecting the resistance to mass transfer in the sampler, sampling rates that are controlled by the WBL can be modeled as

$$R_S = k_w A \tag{9}$$

where k_w is the mass transfer coefficient in the WBL. In general, k_w increases when flow rates and turbulence intensities increase. The typical relation between k_w and the diffusion coefficient can then be summarized as [22]

$$k_w \approx D_w^{2/3} \tag{10}$$

Because sampling rates are commonly given as a function of log K_{ow}, Booij et al. [2] expressed log D_w for PCBs, PAHs and chlorobenzenes as a function of log K_{ow}, and obtained

$$R_S = AB_W K_{ow}^{-0.044} \tag{11}$$

where B_w is a constant for a given exposure, but may vary among exposures according to differences in hydrodynamic conditions and sampler geometry. AB_w has the same units as R_S and the value equals the hypothetical sampling rate for K_{ow} = 1. The equation predicts the sampling rates to weakly decrease with increasing log K_{ow} in the high log K_{ow} range. Depending on models used for estimation of diffusion coefficients, the dependence may vary from $R_S \approx K_{ow}^{-0.02}$ - $K_{ow}^{-0.06}$ [4]. Rusina et al. [4] confirmed this theory; in a calibration of silicone strips for PAHs and PCBs that experimental R_s was proportional to $K_{ow}^{-0.08}$.

In contrast to the theoretical model, steeper decrease of sampling rates of SR with increasing hydrophobicity was observed in our study. In the range where uptake is WBL controlled (log K_{ow} > 4.5), our data show that $R_s \approx K_{ow}^{-0.13}$, however, with a low correlation coefficient (R^2 = 0.09). Much better correlations where obtained when R_s were related to K_{ow} for individual classes of compounds. Dependences $R_s \approx K_{ow}^{-0.62}$ (R^2 = 0.90) and $R_s \approx K_{ow}^{-0.10}$ (R^2 = 0.56) were obtained for PAHs and organochlorine pesticides, respectively. Similar dependencies have been shown in experimental data obtained in other calibration studies, e.g. $R_s \approx K_{ow}^{-0.26}$ and $\approx K_{ow}^{-0.85}$ for SPMD [23] and Chemcatcher [24], respectively.

Analytes adsorbed on colloids or particles are not directly available for sampling with passive samplers. A possible reason for a large drop in measured sampling rates of very hydrophobic compounds may be the overestimation of dissolved aqueous concentrations due to sorption of analytes to dissolved organic carbon (DOC). Burkhard [25] reviewed contaminant sorption by dissolved organic matter. Using several hundreds of DOC-water partition coefficients (K_{DOC}) reported in these studies, he found that DOC-water partition coefficients for naturally occurring DOC (humic and fulvic acids, sediment pore water, soil pore water, groundwater, and surface water) was best described by

$$\log K_{DOC} = \log K_{ow} - 1.11 \tag{12}$$

The 95% confidence interval amounted to 1.3 log units, which corresponds to a scatter in the K_{DOC} values by a factor of 20.

Adopting Eq. 11 for the sampling rate of truly dissolved analytes, and the Burkhard relationship for sorption to DOC, the apparent sampling rate ($R_{S,app}$) is given by

$$R_{S,app} = \frac{R_S}{1+[DOC]K_{DOC}} = \frac{AB_W K_{ow}^{-0.044}}{1+[DOC]K_{DOC}} = \frac{AB_W K_{ow}^{-0.044}}{1+[DOC]QK_{ow}} \tag{13}$$

where Q is dependent on DOC quality (Q = $10^{-1.11}$ ≈ 0.078 for DOC of average quality; see Eq. 11).

In order to check if Eq. 13 sufficiently describes the experimental sampling rates, this model was fitted to the calibration data for compounds accumulated under WBL (with log K_{ow} > 4.5) and assuming a log normal distribution of errors.

$$\log R_S = \log AB_W - 0.044 \log K_{OW} - \sum_{i=1}^{2} z_i \log(1+[DOC]Q_i K_{OW}) \tag{14}$$

where log K_{ow} is the independent variable; z_i are indicator variables taking the value z_i = 1 for experimental data for the i-th group of compounds (i= 1 for PAHs and i=2 for organochlorine compounds, respectively), for the rest of the data, z_i= 0; and log R_S is the dependent variable. log AB_w and log Q_i [DOC] are adjustable parameters. Sampling rates of DDT were excluded from the calculation, because they seemed underestimated due to a measurement error of water concentration that was taken for calculation. Results of the fit are shown in Figure 6 and in Table 2. Inclusion of a DOC-sorption term in the model significantly improved the log R_S − log K_{ow} fit for the calibration data.

Unfortunately, DOC concentrations in water from the calibration apparatus were not measured. Thus, the DOC quality could be only roughly estimated, assuming a hypothetical concentration of DOC of 0.5 mg L^{-1}. Values of log Q fall within the 95% confidence range of log Q values (−2.4 to +0.2) reported by Burkhard [25]. Although the evidence is indirect, sorption to DOC probably caused an underestimation of the sampling rates of highly hydrophobic compounds in this study. The applied model indicates that different decrease of apparent sampling rate with

TABLE 2 - Nonlinear regression analysis results of log R_S to log K_{ow} using Eq. 14.[a]

Sampler	n	r	s	log AB_w (L d^{-1})	log Q_{PAH} [DOC]	log Q_{PCB} [DOC]	log Q_{PAH}[a] (cm^3 g^{-1})	log Q_{PCB}[a] (cm^3 g^{-1})
Altesil	21	0.94	0.13	0.54 ± 0.04	- 5.74 ± 0.09	-7.55 ± 0.33	-0.4	-2.3
SPMD	21	0.86	0.13	1.16 ± 0.05	-6.24± 0.12	-6.94± 0.16	-0.5	-1.2

[a]nonlinear regression was performed using SigmaPlot for Windows Version 11.0
[b]assuming [DOC] = 0.5 mg L^{-1}

increasing hydrophobicity for both groups of compounds may be explained by stronger adsorption of PAHs to colloidal matter in the experimental system than was the case for PCBs and organochlorine pesticides included in the datasets.

An underestimation of the sampling rate by a factor of 2 occurs when Q [DOC] K_{ow} = 1. Inspection of the data shows that sampling rates of compounds with log K_{ow} values greater than 5.7 for PAHs and 7.55 for organochlorinated pesticides and PCBs, respectively, may have been underestimated. Experimental data for PCBs seem to be less affected by sorption phenomena than data for PAHs. For SPMD data, where only a single point in time calculation of R_S was performed, similar results were obtained (Table 2).

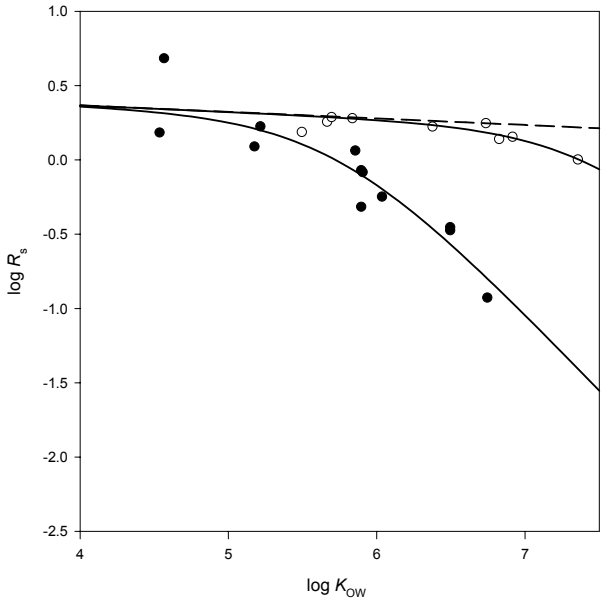

FIGURE 6 - Dependence of the sampling rate log *R*s in Altesil on the octanol/water partition coefficient log K_{ow} for PAHs (full dots), PCBs and OCPs (empty dots). The lines correspond to Eq. 14 with the values of optimized parameters given in Table 2. The dashed line shows the theoretical model of diffusion in WBL [2], Eq. 11.

The the difference of log AB_w in the two experiments is 0.62 which means that sampling rates determined in the experiment with SPMDs were on average four times higher than those in experiment with SR. This corresponds well with the mean value of sampling rate ratio of 5.8 for compounds accumulated in integrative regime. Data corrected for the effect of adsorption do not contradict the validity of the theoretical model ($k_w \approx D_w^{2/3}$).

Methods for independently measuring the extent of sorption to DOC should be included in future calibration experiments. Alternatively, methods of calibration, based on distribution of analytes between dosing and acceptor sheets that do not require measurement of analytes in the water phase should be applied [4].

Application of calibration data in field situations

Evaluation of calibration data obtained with the two passive samplers indicates WBL control over accumulation of all analytes with log K_{ow} > 4. Because of WBL control over the mass transfer, sampling rates are expected to vary widely depending on hydrodynamic conditions during exposure. Without the availability of information on *in situ* exchange kinetics from performance reference compounds (PRC), the error in estimate of sampling rates in a real situation can reach several orders of magnitude, depending on the difference of the hydrodynamic conditions between laboratory and the field. Without the availability of data from PRC elimination, an alternative method for minimizing the error in *in situ* R_S estimate is essential. In situ sampling rates can be estimated using Eq. 11. The value of B_W is variable in field conditions and it depends on local hydrodynamic conditions, sampler geometry and temperature. Thus, it has to be determined for each field exposure. For this purpose, it is necessary to determine the sampling rate for at least one compound under investigation. Preferably, it should be a) a compound that can be found both in the passive sampler and in the water phase at quantifiable concentration; b) a compound that is accumulated under WBL control and remains in linear uptake phase during the whole sampler exposure; c) the compound should be present in the sampled water predominantly in the dissolved phase. These conditions are fulfilled for moderately hydrophobic compounds with log $K_{ow} \approx 4.5$, e.g. phenanthrene or anthracene. For such compound, *in situ* R_S can be estimated using rearranged Eq. 2:

$$R_S = \frac{N}{C_W t} \tag{15}$$

where C_W is the mean value of anthracene concentration in spot samples of water taken during sampler exposure. Concentration of anthracene should not fluctuate widely during exposure, otherwise the calculation may be biased. A check has to be performed using Eq. 5 that the compound does not equilibrate during exposure. In the next step, value of log AB_W is calculated by substituting the calculated R_S value of anthracene into Eq. 11. Sampling rates of compounds with log K_{ow} > 4.5 are then extrapolated using Eq. 11 with adjusted exposure specific log AB_W value.

This approach was tested on data from a field study performed in the River Morava at the sampling site

Spytihněv in July 2007. Analyte concentrations obtained using passive sampling with Altesil (C_{TWA}) and spot samples taken before and after sampler exposure (C_b) are shown in Table 3. For anthracene, site specific value of log AB_W of 0.74 was calculated. This means that sampling rates at the sampling site were less than factor two higher than in the calibration study with Altesil. Nevertheless, this similarity in exposure conditions is likely only a coincidence. The mean calculated ratio of C_{TWA}/C_b of 2.8 is acceptable, considering possible fluctuation of water concentrations at the sampling site during exposure, which is not reflected in data from spot samples. A good correlation was obtained between concentrations obtained from Altesil SR and those obtained from spot sampling, assuming log normal data distribution.

$$\log C_b = -0.263 + 0.868 \log C_{TWA} \quad (16)$$

N= 21, R = 0.861, s = 0.40

Passive sampling data slightly overestimate data obtained using spot sampling. From theory, elevated difference between spot and passive sampling is expected for very hydrophobic compounds (log $K_{ow} > 6$) that adsorb on colloids and particles present in the water phase. Our limited dataset does not show any trend of difference increasing with hydrophobicity. For compounds that likely achieved partition equilibrium during exposure, concentration in water was calculated as $C_w = N/K_{sw}/m_s$. However, this concentration does not does not represent a TWA value.

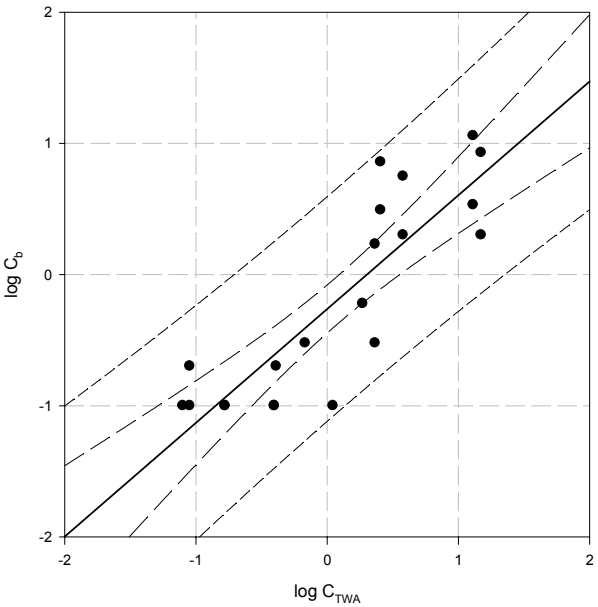

FIGURE 7 - Correlation between the TWA analyte concentrations determined using Altesil sampers (log C_{TWA}) and those determined in two spot samples taken before and following passive sampler exposure (log C_b) at the sampling site Spytihněv. Dashed lines present 95% confidence and prediction intervals, respectively.

TABLE 3 - Mean concentrations of PAHs, PCBs and OCPs found in Altesil (ng per sampler; n=2), calculated sampling rates R_S, estimates of TWAconcentrations from Altesil C_{TWA}, and concentrations measured in bulk water samples C_b collected at the beginning and the end of a 28 day sampler exposure at the sampling site Spytihněv in July 2007.

Compound	N [ng]	Sampling mode	R_s [L d^{-1}]	C_{twa} [ng L^{-1}]	C_{b1} [ng L^{-1}]	C_{b1} [ng L^{-1}]
Naphthalene	17	eq.[a]	n.e.[b]	1.2[d]	4.7	7.8
Acenaphthylene	9	eq.	n.e.	0.6[d]	0.3	0.1
Acenaphthene	29	eq.	n.e.	1.2[d]	2.1	1.2
Fluorene	66	eq.	n.e.	0.8[d]	2.3	1.2
Phenanthrene	260	Linear	3.5	2.6	7.2	3.1
Anthracene	385	Linear	3.5	3.8	5.6	2.0
Fluoranthene	1236	Linear	3.3	13.0	11.4	3.4
Pyrene	1416	Linear	3.3	14.9	8.5	2.0
Benz(a)anthracene	165	Linear	3.1	1.9	0.6	n.d.
Chrysene	206	Linear	3.1	2.3	1.7	0.3
Benzo(b)fluoranthene	60	Linear	3.0	0.7	0.3	n.d.
Benzo(k)fluoranthene	36	Linear	3.1	0.4	0.2	n.d.
Benzo(a)pyrene	97	Linear	3.0	1.1	0.1	n.d.
Indeno(1,2,3cd)pyrene	5	Linear	2.9	0.1	n.d.	n.d.
Dibenz(a,h)anthracene	n.d.	Linear	2.8	n.d.	n.d.	n.d.
Benzo(g,h,i)perylene	6	Linear	2.9	0.1	n.d.	n.d.
PCB 28	16	Linear	3.1	0.2	n.d.	n.d.
PCB 52	7	Linear	3.1	0.1	0.1	n.d.
PCB 101	4	Linear	2.9	0.1	n.d.	n.d.
PCB 118	1	Linear	2.8	n.d.	n.d.	n.d.
PCB 153	7	Linear	2.8	0.1	0.1	0.2
PCB 138	4	Linear	2.8	0.1	n.d.	n.d.
PCB 180	n.d.	Linear	2.6	n.d.	n.d.	n.d.
p,p'-DDE	36	Linear	3.1	0.4	0.1	0.1
p,p'-DDD	15	Linear	3.2	0.2	0.1	0.1
p,p'-DDT	n.d.	Linear	3.0	n.d.	n.d.	n.d.
α-HCH	32	eq.	n.e.	5.7[d]	0.3	0.7
β-HCH	n.d.[c]	eq.	n.e.	n.d.	n.d.	n.d.
γ-HCH	19	eq.	n.e.	3.4[d]	0.6	0.5
δ-HCH	n.d.	eq.	n.e.	n.d.	n.d.	n.d.

[a]eq. - partitioning equilibrium between sampler and water has likely been achieved
[b]n.e. – not estimated; [c]n.d. – not detected; [d]estimated using equilibrium partitioning model

CONCLUSIONS

The data confirms that for compounds accumulated under WBL control differences in water flow velocities can cause sampling rates to vary several orders of magnitude. Because of the complexity of the hydrodynamics involved, there is little hope that sampling rates can be expressed as a simple function of ambient flow rates [22]. Therefore, estimation of in situ sampling rates by measuring the dissipation rates of performance reference compounds should be mandatory. In their absence, alternative method must be applied that allows reliable estimate of *in situ* sampling rate of at least one compound under investigation. An option is the measurement of this compound using spot regular spot sampling during sampler exposure. Sampling rates for compounds that cannot be easily detected by spot sampling because of their very low concentrations can then be estimated from laboratory-derived relationships between R_S and log K_{ow} or other properties (diffusion coefficients, molecular mass etc.).

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Príloha 19

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Passive samplers for chemical substance monitoring and associated toxicity assessment in water

N. Tapie, M. H. Devier, C. Soulier, N. Creusot, K. Le Menach, S. Aït-Aïssa, B. Vrana and H. Budzinski

ABSTRACT

The European legislation, and in particular the Water Framework Directive requires the development of cost efficient monitoring tools that can provide the required information for the assessment of water contamination. Passive sampling methods represent one of the novel tools that have a potential to be used in various regulatory monitoring programmes aimed at assessing the levels of chemical pollutants. These methods are particularly interesting for sampling polar organic pollutants in water because they provide representative information of the water quality over extended time periods (days to weeks) in environments with fluctuating contaminant concentrations. This is achieved by integrative sampling of pollutants over the whole sampler deployment period. These tools can be coupled to toxicity testing using bioassays that give information on toxic and ecotoxic hazards associated to substances that are present, these substances being identified or not. In this study the polar organic chemical integrative sampler (POCIS) was used in surface water to evaluate the water contamination by polar organic compounds and their potential toxicity.

Key words | Biotests, hormones, passive sampling, pesticides, pharmaceuticals, POCIS

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INTRODUCTION

The restoration of good ecological and chemical status of all water bodies in Europe by 2015 as requested in the Water Framework Directive (WFD, Directive 2000/60/EC) is an important stake. One of the goals of this directive is to improve the water quality by reversing, when necessary, the degradation trend of underground and surface waters by gradually reducing the discharges of substances that have been classified as priority pollutants. Discharges should even be stopped for substances classified as hazardous priority compounds. To achieve this goal, the WFD requires the development of cost efficient monitoring tools that can provide the required information for the assessment of water contamination.

Checking water quality compliance with regulatory provisions is usually based on the chemical analysis of spot (bottle) samples of water taken at a defined frequency. This approach suffers from several drawbacks. Spot samples provide concentrations of pollutants only at the moment of sampling. Thus, in water bodies characterized by marked temporal and spatial variability there is an increased risk of a false classification of the chemical status. Further, the laboratory methods commonly used for the analysis of spot samples of water are often not sensitive enough to fulfil the required minimum performance criteria associated with the current environmental quality standards for pollutants (Commission Directive 2009/90/EC).

A promising alternative for monitoring pollutants in aquatic systems is based on the use passive sampling techniques. In comparison to spot sampling techniques, passive samplers provide a more representative picture of the water quality. This is achieved by the integrative sampling of contaminants during sampler deployment periods up to several weeks. Passive samplers can be used alongside spot sampling in order to corroborate or contradict the data obtained. This

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approach can provide additional 'weight-of-evidence' in water bodies where concentrations of contaminants are expected to fluctuate widely with time. The measurement of time-weighted average (TWA) concentrations over periods of weeks to months using passive sampling seems to be a promising approach.

A range of passive samplers has been developed for monitoring organic pollutants in water. Their different designs and field performance have been reviewed (Namiesnik *et al*. 2005; Stuer-Lauridsen 2005; Vrana *et al*. 2005). Among available passive sampling techniques polar organic chemical integrative sampler (POCIS) has shown a potential to be used in various monitoring programmes aimed at assessing the levels of polar organic compounds in the aquatic environment.

In addition to instrumental analysis of pollutants in sampler extracts, these can be subjected to toxicity testing using bioassays that give information on toxic and ecotoxic risks associated with the sampled substances (substances being identified or not (Alvarez *et al*. 2007)).

In this study field trials were carried out to assess the performance of the POCIS alongside spot sampling for monitoring a wide range of polar organic pollutants in surface water. Moreover, toxicity of the extracts from the field exposed samplers was evaluated to identify potential environmental hazards from compounds accumulated in the samplers during exposure, by using *in vitro* bioassays that detect endocrine-like and dioxin-like compounds.

MATERIALS AND METHODS

Materials

POCIS samplers (version for sampling pharmaceuticals) were provided by Exposmeter AB (Tavelsjö, Sweden). Acetonitrile, dichloromethane, isooctane and methanol (HPLC reagent grade, Scharlau) were purchased from ICS (Instrument Consommable Service, Belin Beliet, France). Glass solid phase extraction (SPE) cartridges of 6 mL with PTFE frits (20 µm porosity) and Oasis HLB bulk sorbent (60 µm) were purchased from Supelco (Saint Quentin-Fallavier, France) and Waters (Guyancourt, France), respectively. Pharmaceuticals and hormones were provided by Sigma Aldrich (Saint Quentin Fallavier, France), polycyclic aromatic hydrocarbons (PAH) by LGC Standard (Molsheim, France), Alkylphenols and pesticides by Cluzeau (Sainte Foy La Grande, France). The studied compounds were:

Pharmaceuticals (PHARM): amitryptiline, aspirin, caffeine, carbamazepine, diazepam, doxepin, gemfibrozil, ibuprofen, imipramine, ketoprofen, naproxen, nordiazepam, paracetamol, theophylline.

Polycyclic aromatic hydrocarbons (PAHs): acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(g,h,i)perylene, chrysene, dibenzo(a)anthracene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, naphthalene, perylene, phenanthrene, pyrene.

Hormones (HORM): 17α-ethynylestradiol, 17ß-estradiol, levonorgestrel, mestranol, norethindrone, estrone, progesterone.

Pesticides (PEST): alachlore, atrazine, desethyl atrazine (DEA), desisopropyl atrazine (DIA), bifenthrin, chlorfenvinphos, chlortoluron, methyl chlorpyrifos, chlorpyrifos, chlorsulfuron, cyanazine, cyfluthrine, cypermethrin, cyromazine, 1-(3,4dichlorophenyl)-3 methyl-urea (DCPMU), 1-(3,4dichlorophenyl)-urea (DCPU), 1-(2,4dichlorophenyl)-urea, dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethylene (DDE), dichlorodiphenyldichloroethane (DDD), deltamethrin, diazinon, dichlorvos, dimethachlor, dimethoate, diuron, esfenvalerate, ethroprophos, fenithrothion, fenvalerate, irgarol, isoproturon, lindane, linuron, malathion, metazachlor, metoxuron, nicosulfuron, permethrin, phosmet, prometryn, propachlor, propazine, pymetrozine, simazine, s-metolachlor, temephos, terbutryn, terbuthylazine, methyl tolclofos.

Phenols (AKP): 4-nonylphenol (NP), 4-ter-octylphenol (OP), nonylphenol ethoxyacetic acid (NP1EC), 4-nonylphenol monoethoxylate (NP1EO), 4-nonylphenol diethoxylate (NP2EO), bisphenol A.

Field experiments

POCIS (pharmaceutical version) were exposed in Nerac in the surface water in the Baïse River (Garonne basin, south west of France) (Figure 1). Two triplicates of POCIS (3 for chemical analysis and 3 *in vitro* bioassays, respectively) were deployed in May 2007 over a period of one month.

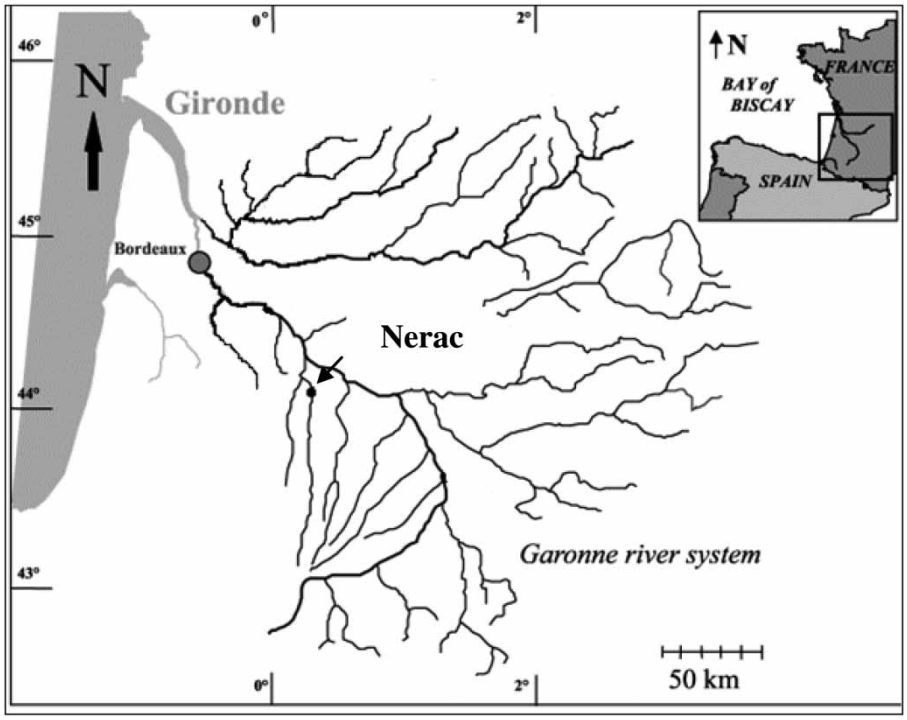

Figure 1 | Sampling site in Nérac in the Baise River (Garonne River Basin, South West of France).

During exposure POCIS were placed in a perforated canister made of high quality stainless steel to protect them from mechanical damage. Field control POCIS were used to follow an eventual contamination during transport and manipulation with samplers during deployment and retrieval. They were taken to the sampling site and exposed to the air during the immersion and the withdrawal of POCIS. Control POCIS were processed simultaneously and equally to the exposed samplers.

Spot water samples were also collected at the beginning, in the middle and at the end of the one month exposure period, to compare with the data obtained with passive sampling for several groups of compounds (PAHs, pharmaceuticals, alkylphenols, hormones, organophosphate pesticides, organochlorine pesticides, pyrethroid pesticides, triazines, phenylurea herbicides).

Chemical analysis

POCIS: After exposure, each POCIS was rinsed with ultra pure water to remove particles and biofilms present on the outer surface of the membranes. Control POCIS were processed using the same procedure. The metal disks were disassembled and the membranes were detached from the disks. The sorbent was carefully transferred into an empty glass solid phase extraction (SPE) tube by rinsing it with ultrapure water. The sorbent was dried by applying vacuum for 1 h. Analytes were eluted by 30 mL of dichloromethane/methanol mixture (50:50 v/v). The extract was concentrated first by using a rapidvap vaccum evaporation system (25 min), then by a gentle stream of nitrogen and finally dissolved in 150 µL of a solvent suitable for injection to an analytical instrument.

Water: Spot samples of water were collected during POCIS exposure. Water samples were collected to 4 L amber glass bottles. Before use, the bottles were detergent washed, acid rinsed and heated at 450 °C for 6 h. Immediately after collection, the samples were filtered through a glass fibre filter (GF/F 0.7 µm pore size). The analytes were measured in the filtrate.

Pharmaceuticals, alkylphenols, and phenylurea herbicides were analysed by LC/MS/MS. PAHs, hormones and remaining pesticides (triazines, organophosphate pesticides, pyrethroid pesticides) were analysed by GC/MS. The analytical procedures were adapted from Togola & Budzinski

(2008) for the pharmaceuticals, from Labadie & Budzinski (2005) for the hormones, from Budzinski *et al.* (2000) for the PAHs, from Alder *et al.* (2006) for the pesticides analysis and from Cailleaud *et al.* (2007) for the alkylphenols.

Procedural blanks were also regularly performed during the sample extraction process and all the results presented are corrected by taking the blank levels into account. The performance of analytical methods was checked by the extraction of a spiked sample in each series of analyses.

Analysed compounds were quantified using internal standard calibration. The response factors of the various compounds were measured by injecting a mixture of standard reference solutions.

Extraction recoveries

POCIS sampler contains 200 mg of Oasis HLB sorbent enclosed between two polyethersulfone (PES) membranes. The membranes which confine the sorbent are compressed between two metal disks (5.4 cm ID). The total exchanging surface area of the membranes is about 46 cm^2. The ratio surface area to mass of sorbent is 230 cm^2g^{-1}.

To determine the extraction recovery of analytes from the Oasis HLB sorbent empty glass solid phase extraction tubes with PTFE frits were packed with 200 mg of Oasis HLB sorbent and triplicate solide phase extraction cartridges were placed on a Visiprep vacuum manifold (Supelco). Each cartridge was spiked with a mixed standard solution of pharmaceuticals, pesticides, alkylphenols, hormones and PAHs by adding 50 µL of a standard solution in ethyl acetate to the sorbent. The analytes were eluted from the sorbent by 30 mL of dichloromethane/methanol mixture (50:50 v/v), which is quite a large volume that has been optimized to maximize extraction recoveries. The extract was concentrated first by using a rapidvap vaccum evaporation system (25 min) and then by using a gentle stream of nitrogen. These stages of evaporation require about 45 min. The losses of compounds have been tested during the development of the extraction method; no significant losses were observed (less than 5%). After the evaporation steps, the extract was dissolved into a solvent suitable for instrumental analysis.

Morover the validity of the methods analysis was confirmed by the extraction of a spiked sample for each series of analyses.

Table 1 | Extraction recoveries of some compounds from the Oasis HLB sorbent ($n = 3$)

Compound		Recovery (%) ($n = 3$)	
		Mean	rsd
PAH	Acenaphthene	79	±7
	Acenaphthylene	92	±12
	Anthracene	99	±4
	Benzo(a)anthracene	86	±11
	Benzo(a)pyrene	99	±3
	Benzo(b,j,k)fluoranthene	88	±8
	Benzo(e)pyrene	101	±5
	Benzo(g,h,i)perylene	104	±2
	Chrysene	100	±8
	Dibenzo(a,c)anthracene	104	±4
	Fluoranthene	105	±6
	Fluorene	84	±6
	Indeno(1,2,3-c,d)pyrene	109	±8
	Naphthalene	108	±13
	Perylene	83	±5
	Phenanthrene	99	±10
	Pyrene	102	±7
PHARM	Amitryptiline	97	±3
	Aspirin	66	±19
	Caffeine	77	±34
	Carbamazepine	71	±5
	Diazepam	105	±2
	Doxepin	58	±12
	Gemfibrozil	97	±7
	Ibuprofen	71	±9
	Imipramine	82	±11
	Ketoprofen	64	±12
	Naproxen	61	±17
	Nordiazepam	99	±1
	Paracetamol	63	±3
	Theophylline	81	±16
AKP	NP	96	±5
	OP	75	±2
	NP1EC	78	±3
	NP1EO	97	±6
	NP2EO	85	±9
	BPA	92	±9
HORM	17α-Ethynylestradiol	103	±15
	17ß-Estradiol	99	±17

(*continued*)

Table 1 | continued

Compound		Recovery (%) ($n = 3$) Mean	rsd
	Levonorgestrel	94	±16
	Mestranol	92	±19
	Norethindrone	93	±20
	Estrone	108	±18
	Progesterone	98	±15
PEST	Alachlore	104	±4
	Atrazine	87	±5
	Desethyl atrazine	92	±3
	Desisopropyl atrazine	106	±5
	Bifenthrin	70	±27
	Chlorfenvinphos	133	±19
	Chlorotoluron	100	±1
	Methyl chlorpyrifos	94	±2
	Chlorpyrifos	100	±1
	Chlorsulfuron	128	±1
	Cyanazine	70	±36
	Cyfluthrine	72	±22
	Cypermethrin	73	±20
	Cyromazine	85	±4
	DCPMU	71	±1
	DCPU	73	±2
	124-Dichlorodiphenylurea	72	±2
	DDT+DDE+DDD	53	±9
	Deltamethrine	61	±23
	Diazinon	117	±5
	Dichlorvos	74	±30
	Dimethachlor	148	±7
	Dimethoate	104	±14
	Diuron	94	±1
	Esfenvalerate	71	±24
	Ethroprophos	151	±23
	Fenithrothion	115	±14
	Fenvalerate	80	±18
	Irgarol	113	±10
	Isoproturon	107	±1
	Lindane	59	±6
	Linuron	70	±1
	Malathion	108	±2
	Metazachlor	132	±11
	Metoxuron	102	±1
	Nicosulfuron	131	±3
	Permethrin	74	±21
	Phosmet	95	±25
	Prometryn	112	±9
	Propachlor	108	±15
	Propazine	97	±4
	Pymetrozine	76	±37
	Simazine	93	±4
	s-Metolachlor	123	±5
	Temephos	83	±22
	Terbutryn	96	±9
	Terbuthylazine	134	±11
	Methyl tolclofos	97	±1

Coupling of passive sampling with *in vitro* bioassays

In addition to the chemicals analysis, POCIS were also used for toxicity testing using bioassays. After exposure, the sorbent was transferred into glass solid phase extraction tube for extraction. The organic compounds were eluted in 3 fractions: the first fraction (F1) with 10 ml of dichloromethane, the second fraction (F2) with 10 ml of dichloromethane/methanol mixture (50:50 v/v) and the final fraction (F3) with 10 ml of methanol. Each fraction was analysed for all selected compounds. Toxicity tests were performed on each fraction. The estrogenic, (anti-)androgenic and dioxin-like activities of the extracts were assessed by using three *in vitro* bioassays based on MELN (MCF-7 cells stably transformed with the firefly luciferase gene under the control of endogenous estrogen receptor; Balaguer *et al.* 2001), MDA-kb2 (MDA-MB-453 cells stably transformed with the firefly luciferase gene driven by a promoter regulated by endogenous androgen receptor; Wilson *et al.* 2002) and PLHC-1 (fish hepatoma derived cells; Louiz *et al.* 2008) cell lines, respectively. Description of cell lines and protocols for routine cell culture and environmental sample assessment has been reported in details previously (Louiz *et al.* 2008; Creusot *et al.* 2010). In brief, cells were seeded in 96-wells plates and left to grow up

to confluence before being exposed to carrier solvent (negative control) and serial dilutions of reference ligand (positive control) and POCIS extracts (test sample). In the MELN and MDA-kb2 assays, cells were exposed for 16 h and processed for luciferase activity assay. In the PLHC-1 assay, cells were exposed for 4 h (PAH-like activity) and 24 h (dioxin-like activity) and then were processed for 7-ethoxyresorufin-O-deethylase (EROD) activity assessment in intact cells. Toxic-equivalent quantities relative to reference compounds in samples were determined by comparing modelled dose–response curves of samples and reference compounds, as previously described (Louiz *et al.* 2008).

RESULTS AND DISCUSSION

Extraction of POCIS and recoveries

To determine the extraction recovery of analytes from the Oasis HLB sorbent, elution of analytes from spiked sorbent was performed. The percentage recoveries ($n = 3$) were higher than 70% for most of the compounds (Table 1). Only 9 compounds showed low extraction recovery. These were bifenthrin ($70 \pm 27\%$), cyanazine ($70 \pm 36\%$), aspirin ($66 \pm 19\%$), ketoprofen ($64 \pm 12\%$), paracetamol ($63 \pm 3\%$), naproxen ($61 \pm 17\%$), deltamethrin ($61 \pm 23\%$), lindane (59 ± 6) and DDT + DDE + DDD (53 ± 9).

The applied extraction protocol is efficient for 91 compounds belonging to 5 classes including PAHs, pharmaceuticals, alkylphenols, hormones and pesticides. For each set of analysed samples, a spiked sample was processed in order to monitor the performance of the extraction protocol.

Field exposures

POCIS samplers were deployed in May 2007 in the Baïse River (South West of France) during a period of one month. After exposure, sorbent was extracted to determine the mass of compounds (M_s) accumulated in POCIS. Only compounds found in POCIS are presented (Table 2).

Assuming linear uptake of all contaminants in the sampler during field exposure, TWA concentrations of studied compounds in water were calculated from the amount of analytes accumulated in POCIS (M_s) using laboratory-derived sampling rates R_s:

$$C_w = \frac{M_s(t)}{R_s \times t} \quad (1)$$

where, C_w is the TWA concentration in water over the sampler deployment period, $M_s(t)$ is the mass of analyte

Table 2 | Mass of analyte accumulated in the sorbent after an exposure time (M_s) and sampling rates (R_s) used for the calculation of the TWA concentration of sampled analytes (only compounds detected in field exposed samplers are shown)

	M_s (ng)	R_s (L.J^{-1})	References
Atrazine désisopropyl (DIA)	6	0.06	Mazzella *et al.* (2007)
Atrazine déséthyl (DEA)	18	0.12	Mazzella *et al.* (2007)
Simazine	Nd	0.31	Budzinski *et al.* (2009)
Atrazine	2	0.33	Budzinski *et al.* (2009)
Terbuthylazine	2	0.25	Mazzella *et al.* (2007)
Promethryn	2	0.36	Personal data
Terbuthryn	1	0.34	Personal data
Lindane	2	0.09	Alvarez *et al.* (2007)
Σ DDT	1	0.02	Alvarez *et al.* (2007)
Diuron	23	0.25	Mazzella *et al.* (2007)
Isoproturon	6	0.22	Mazzella *et al.* (2007)
Metoxuron	35	0.20	Mazzella *et al.* (2007)
Linuron	12	0.24	Mazzella *et al.* (2007)
Chlorsulfuron	5	0.11	Alvarez *et al.* (2007)
Nicosulfuron	119	0.04	Mazzella *et al.* (2007)
Caféïne	13	0.08	Togola & Budzinski (2007)
Carbamazépine	2	0.40	Togola & Budzinski (2007)
Aspirine	15	0.01	Togola & Budzinski (2007)
Paracétamol	18	0.02	Togola & Budzinski (2007)
Gemfibrozil	3	0.05	Togola & Budzinski (2007)
Diclofénac	2	0.17	Togola & Budzinski (2007)
Nonylphénol	26	0.02	Budzinski *et al.* (2009)
NP1EC	9	0.28	Personal data
17-Oestradiol (E2)	2	0.04	Zhang *et al.* (2008)
Testostérone (T)	2	–	No R_s data availabe

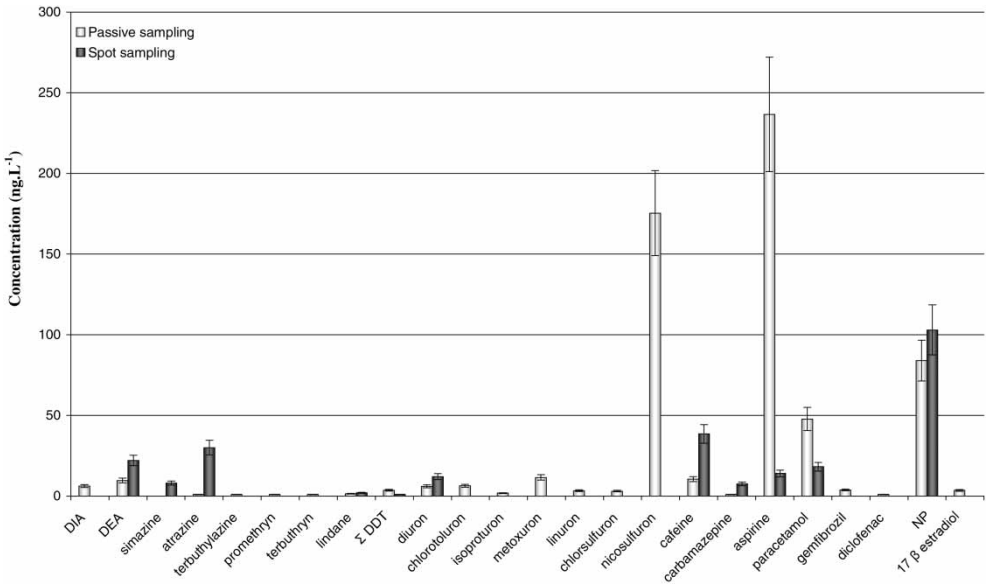

Figure 2 | Comparison of water concentrations determined by spot sampling and by passive sampling ($n = 3$).

accumulated in the sorbent after an exposure time (t) and R_s is the sampling rate. Data (R_s and M_s) used for the calculation are shown in Table 2, unfortunately no R_s data are available for testosterone.

The concentrations in water obtained by POCIS were compared to the water concentrations determined by spot sampling (Figure 2). Both sampling techniques are not fully comparable because spot sampling gives only a snapshot of contamination while POCIS provides an integrated concentration (the TWA value). Moreover, the filtering threshold used for water filtration is 0.7 µm, while the pores of the membranes of POCIS are 0.1 µm. Nevertheless, a good correlation between the concentration of water obtained by spot sampling and that obtained by passive sampling can be observed if the compounds are in sufficient concentration to be detected by passive sampling and if the concentration in water is constant over time. This was the case for DEA, lindane, diuron and NP (Figure 2).

On the contrary several phenylurea pesticides, like nicosulfuron, chlorotoluron, isoproturon, metoxuron, linuron, chlorsulfuron were detected by POCIS whereas they were not found in spot samples. This was also the case for pharmaceuticals gemfibrosil and diclofenac which were present in POCIS, but not detected in water samples. POCIS are able to accumulate quantifiable amounts compounds that were below the detection limit of the spot sampling method. Significant preconcentration of analytes from water together with integrative sampling that allows retention of episodic concentration peaks (normally not detected by low frequency spot sampling) enable POCIS to provide a better (more sensitive and more representative) information on the pollution of the sampled environment by polar organic compounds in comparison with spot sampling.

Coupling of passive sampling with *in vitro* bioassays

After exposures in the Baïse River, some POCIS were fractionated and each fraction was tested for estrogenic, (anti) androgenic, PAH-like, and dioxin-like activities using *in vitro* bioassays. Estrogenic activity was detected in the F1 fraction and to a lesser extent in F2 (Table 3). The most abundant compounds in fraction F1 were alkylphenols and pesticides, including estrogenic ones like 4-tert-octylphenol, bisphenol A and DDT metabolites (Table 4). Unexpectedly, the F3 fraction, which contained trace levels of steroid hormones, was not estrogenic in the MELN bioassay. The two fractions (F1 and F2) exhibited PAH-like activity of 47.5 and 15.8 ng of BaP-EQ per POCIS, respectively. Accordingly, PAHs were mainly detected in F1 but not in F2. So the activity detected in F2 could be due either to a higher sensitivity of the bioassay

Table 3 | Estrogenic, PAH-like, dioxin-like and androgenic activities detected in POCIS fraction using *in vitro* bioassays

POCIS fractions	E2-EQ[a] (ng/POCIS)	BaP-EQ[b] (ng/POCIS)	TCDD-EQ[c] (ng/POCIS)	DHT-EQ[d] (ng/POCIS)
F1	0.44	47.5	<0.6	<0.2
F2	0.06	15.8	<0.6	<0.2
F3	<0.02	<1.1	<0.6	<0.2

[a]E2-EQ: 17bestradiol-equivalents.
[b]BaP-EQ: benzo(a)pyrene-equivalents.
[c]TCDD-EQ: dioxin-equivalent.
[d]DHT-EQ: dihydrotestosterone-equivalent.

Table 4 | Quantity of studied compounds in POCIS Fraction (ng)

	Fraction 1 (ng)	Fraction 2 (ng)	Fraction 3 (ng)
Pharmaceuticals	20	14	Nd
PAHs	128	1	Nd
Alkylphenols + BPA	36	12	3
Hormones	nd	nd	4
Triazine	31	nd	Nd
Pyrethroids	nd	nd	Nd
Organophosphate pesticides	nd	nd	Nd
Phenyl urea pesticide	212	5	7

or to compounds that were not targeted in this study, such as transformation product of PAHs. Finally, no dioxin-like or (anti)androgenic activity could be detected in these samples.

CONCLUSIONS

Field studies in which the results obtained with passive samplers are compared to those obtained with conventional sampling techniques increase the body of evidence that is available to underpin acceptance of the validity of passive sampling. The data sets obtained in this study show the effectiveness of the POCIS in integrative sampling of a broad range of organic chemicals in the surface water. Moreover, the potential of coupling chemical and toxicological characterization of water quality using passive samplers was demonstrated. However, the detection of biological activities that could not be explained by chemical analyses supports further investigation to identify biologically active substances sampled by POCIS.

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Levels and distribution of dissolved hydrophobic organic contaminants in the Morava river in Zlín district, Czech Republic as derived from their accumulation in silicone rubber passive samplers

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ABSTRACT

Dissolved waterborne polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) were assessed over a period of one year at five sampling sites in a model industrial region in the Czech Republic using silicone rubber passive samplers. The spatial variability of POPs in the studied region in water was small and diffusive pollution sources predominate. Concentrations of the most volatile PAHs decreased with increasing water temperature in the whole region, which reflects the seasonality in atmospheric deposition. The dissolved concentrations of more hydrophobic PAHs, PCBs and OCPs in and downstream the industrial zone are related to desorption from suspended particles. Upstream the industrial area, a positive correlation of dissolved and particle-bound contamination was observed only for DDT metabolites and hexachlorobenzene. Calculated fugacities in water and bottom sediment indicated a fair degree of equilibrium between these compartments for OCPs and PCBs, whereas sediment represented a potential source of PAHs.

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1. Introduction

The freely dissolved concentration of persistent organic pollutants (POPs) in water is one of the important parameters for the assessment of their bioavailability and fate in the aquatic environment. It is generally assumed that particle and colloid-bound compounds cannot cross biological membranes, bioconcentrate and cause biological effects (Landrum et al., 1985). The freely dissolved concentration of POPs in the water column is directly proportional to their fugacity in the water phase (Mayer et al., 2003). Pollution monitoring based on direct water measurement of dissolved concentrations of POPs by bottle sampling is not reliable, as the individual spot samples of water collected at the sampling sites reflect only the pollution situation at the moment of sampling. Determination of extremely low (but toxicologically relevant) dissolved concentrations of hydrophobic compounds (levels below 1 ng L^{-1}) is complicated since the loss of such trace amounts of analytes through volatilization, glassware adsorption and degradation during transport and sample processing steps (filtration and extraction). Moreover, measurement of truly dissolved concentration of these compounds in water cannot be easily achieved by conventional liquid/liquid or solid phase extraction techniques because of potential bias of these methods introduced by co-extraction of analytes bound to colloids present in water samples.

Passive sampling techniques are widely applied to assess exposure and contamination in water, air and soils (Greenwood et al., 2007). Diffusion of organic pollutants from sampled media to the sampler is driven by the high affinity of analysed compounds to the sorbent material of the receiving phase in the sampler. The concentration found in a passive sampler can be used for calculation of time weighted average (TWA) water concentration over extended periods of time for environmental risk assessment, providing accurate calibration data is available.

In this study, passive samplers made from polydimethylsiloxane (PDMS) sheets, better known as silicon rubber (SR), were deployed to characterize the spatial and temporal distribution of the hydrophobic organic pollutants including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorinated pesticides (OCPs) and hexachlorobenzene (HCB) and their dynamics in the dissolved phase in the water column of the Morava river and its tributary Dřevnice in a model industrial area of Zlín in the Czech Republic (Fig. 1). Previous studies conducted in the Zlín region evaluated the risk related to POPs contamination of river sediments and alluvial soils (Hilscherova et al., 2007). A long-term monitoring showed different dynamics of PAHs and PCBs during

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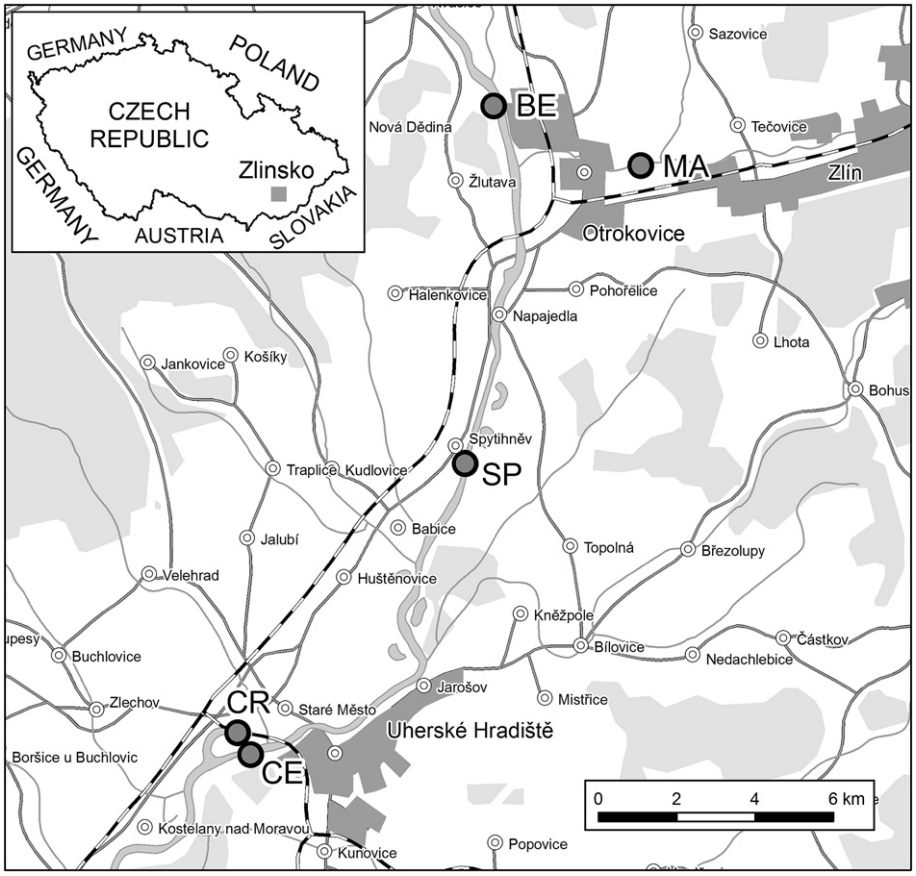

Fig. 1. Map of the sampling sites in the Zlín area, Czech Republic.

floods when PAHs were redistributed from the sediments to alluvial soils while PCBs have been washed out of the study region.

This paper presents particular results of a larger study aimed at characterization of contaminant distribution and dynamics in a fine temporal resolution between various aquatic compartments (surficial and suspended sediments, water) in the Zlín region.

2. Materials and methods

2.1. Materials and chemicals

Organic solvents dichloromethane, methanol, *n*-hexane, cyclohexane and chloroform were obtained from Lab-Scan, Ireland and Sigma–Aldrich, Czech Republic. Standards of 16 polyaromatic hydrocarbons (PAHs), 6 polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), HCB and internal standards (*p*-terphenyl, PCB 121) were obtained from Sigma–Aldrich, Czech Republic. Physicochemical properties of analytes are given in Supplementary information.

2.2. Sampling sites

A one year study was conducted from July 2007 to July 2008 at 5 sampling sites in the river Morava and its tributaries in the model impacted area close to the town of Zlín in south-eastern part of the Czech Republic (Fig. 1). It belongs to the basin of the river Danube and it includes a part of the major river Morava with its tributary Dřevnice. This area is an industrial and agricultural region with 10 cities and 72 villages, with the largest industrial city Zlín, it has high economic and cultural significance and is noted for its industrial and agricultural activities. Water and sediment in this area has been historically impacted by extensive industrial activities as well as agriculture. The five sites have been previously shown (based on analysis of contaminants in sediments and alluvial soils) to represent three regions within this area according to their location and contamination characteristics and the division into regions has been previously validated by cluster analysis (Hilscherova et al., 2007). Table 1 describes the sampling site locations. Actual water temperature and volume discharge data were obtained from Czech Hydrometeorological Institute.

2.3. Passive samplers

Silicone rubber (SR) sheets from Altesil (Altec, Great Britain) were applied as passive samplers. The application was first time described by Smedes (2007). Rusina et al. (2007) characterized the polymer properties used for sampler construction. Among the materials tested, PDMS-based polymer Altesil showed the best overall performance including low release of oligomers, moderate swelling in solvents, fast diffusion coefficients of nonpolar compounds in the PDMS materials and high partition coefficients of hydrophobic compounds between the polymer and water. Rusina et al. (2010) calibrated the silicone rubber passive samplers and derived relations between the calibration parameters (sampling rates) and physicochemical properties of sampled compounds. Recently, Smedes et al. (2009) reported for a number of hydrophobic organic compounds (PAHs and PCBs) reliable partition coefficient data between silicone rubber polymer and water using a co-solvent method. The knowledge of sampling rates and polymer/water partition coefficients of hydrophobic organic compounds in combination with site specific exchange kinetics of contaminants between the sampler and water allow for the application of silicone rubber based passive samplers in quantitative measurement of these compounds dissolved in water.

The wall thickness SR Altesil was 0.5 mm. SR were prepared using the procedure described by Rusina et al. (2007, 2010). SR sheets were cut into pieces of size 25 × 9.3 cm with surface area of ≈460 cm^2. Two cleaning steps were applied to remove oligomers, other impurities and talcum powder from the surface. At first, SR was shaken in ethyl acetate for 1 d, and then Soxhlet-extracted in methanol for 12 h, wiped with a paper tissue and air dried in a fume-hood overnight.

2.4. Sampling campaign

Before and after each passive sampler exposure, bottom sediment, suspended sediment and water samples were collected for analysis of target compounds. Temperature, pH, conductivity, oxygen content and water flow were also measured during each visit at the sampling site. SRs were transported to the sampling site in a cool box, wrapped in two layers of aluminium foil, and a polyethylene zip-lock bag. At the sampling site, two replicate samplers were placed in a stainless steel wire holder that was then suspended at depth of approximately 1 m below the water surface on a rope with a buoy, and secured to the shore using a rope. Weights were

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Table 1
Description of sampling sites in the model study area.

No.	Sampling site	Symbol	Water body	WGS84	WGS84	Altitude [m]	Mean annual discharge[a] [m^3/s]
1.	Bělov	BE	Morava river	49,21811	17,50136	185	44.74
2.	Malenovice	MA	Dřevnice river	49,20772	17,55469	199	1.67
3.	Spytihněv	SP	Morava river	49,13581	17,50211	182	49.92
4.	Čerťák – Morava	CE	Morava river	49,06719	17,43628	177	49.92
5.	Čerťák – branch	CR	Oxbow lake of the Morava river	49,06844	17,43561	181	–[b]

[a] Calculated from volume discharge data available for the period July 2007–July 2008.
[b] Volume discharge was not measured at this sampling site located in an oxbow lake.

attached (using a rope) under the cage to prevent the cage from floating up in the current. Passive samplers were exposed to water column in 28-day deployment periods. Following exposure, two replicate SRs were removed from the holder, packed in two layers of aluminium foil, put in a polyethylene zip-lock bag and transported to the laboratory in a cooling box. Passive samplers were replaced by fresh samplers. The monitoring continued for one year. The dates of deployment periods are given in Supplementary information (Table S1). Several samples were not retrieved due to bad accessibility, unsuitable deployment conditions (e.g. forming of a thick ice layer on water surface) and loss of sampler during field exposure. After exposure, samplers were stored in a freezer at −18 °C until analysis. All samples were analysed for hydrophobic organic pollutants PAHs, PCBs, OCPs and HCB.

2.5. Sampling and analysis of water, suspended matter and surficial sediment

Water samples were collected into amber glass bottles (2.5 L) with a screw cap. Samples were collected in the flow line 1 m below the water surface. Suspended matter was separated by filtration of the whole water sample through a glass fibre filter (Whatman, 2.2 μm pore size). Collection of surface sediments was performed as described in Hilscherova et al. (2007). Sample processing and analysis are described in Supplementary information.

2.6. Extraction and analysis of passive samplers

Following exposure, SRs were rinsed with tap water and distilled water and then wiped with a paper tissue. SRs were Soxhlet-extracted for 12 h in methanol. The extracts were reduced in volume to 15 ml using Kuderna Danish concentrator. The final evaporation was provided with gentle stream of high purity nitrogen to about 2 ml. The samples were cleaned up using silica gel column (sulphuric acid modified silica gel was applied for organochlorines), reduced and internal standards were added. Terphenyl and PCB 121 were used as internal standards for PAHs and PCBs, respectively. Samples were analysed by GC/MS as described by Prokes et al. (2010).

2.7. Statistical analysis

A total number of 70 samples of SR were analysed. The average value of analyte determination in two duplicate samples exposed under the same conditions was taken for analysis, thus the statistical analysis was performed on $N = 35$ samples. Standard robust measures were applied for summary statistics of all examined parameters: estimate of median supplied with 10% and 90% quantiles. Non-parametric strategy was also applied for two samples (Median test) and multiple comparisons (Kruskal–Wallis test). Most concentration parameters revealed log-normal sample distribution (Kolmogorov Smirnov normality test) and therefore log transformation was applied prior to ANOVA analysis that requires normal distribution. Parametric strategy applied for two sample comparisons was also applied (Holm Sidak test).

3. Results and discussion

3.1. Calculation of dissolved water concentrations from passive sampler data

The accumulation of chemicals by passive samplers is characterized by an initial linear uptake stage followed by curvilinear and equilibrium partitioning stages (Booij et al., 2007). In the initial uptake phase, chemical uptake is linear and thus integrative:

$$N = R_S C_W t \quad (1)$$

where N is the mass of a target compound in the sampler at time t, R_S is the sampling rate of the system and C_W is the concentration of a target analyte in water. Because of water boundary layer (WBL) control over the mass transfer to SR samplers for hydrophobic compounds, R_S is expected to vary depending on hydrodynamic conditions during exposure (Huckins et al., 1999; Rantalainen et al., 2000; Vrana and Schüürmann, 2002; Booij et al., 2003a). Estimation of the sampling rates in the absence of information on in situ exchange kinetics based on dissipation of performance reference compounds (PRCs) (Booij et al., 1998; Huckins et al., 2002) can result in significant errors. Their extent depends on the difference between the hydrodynamic conditions in the laboratory and the field, and on the application of the alternative method for minimizing the error in in situ R_S estimation. Such alternative approach was described in our previous work (Prokes et al., 2010) and has been applied in this study as follows.

Booij et al. (2003a) expressed R_S for PCBs, PAHs and chlorobenzenes as a function of log K_{ow}:

$$R_S = AB_W K_{ow}^{-0.044} \quad (2)$$

where A is the sampler surface area and B_W is a constant for a given exposure, but may vary among exposures according to differences in hydrodynamic conditions and sampler geometry. Depending on models used for estimation of diffusion coefficients in water, the dependence for a water boundary layer controlled uptake may vary from $R_S \approx K_{ow}^{-0.02} - K_{ow}^{-0.06}$ (Booij et al., 2003a). Rusina et al. (2010) confirmed this in a calibration of silicone strips for PAHs and PCBs.

In situ sampling rates were estimated using Eq. (2). The value of B_W was determined for each field exposure. For this purpose, it was necessary to determine the absolute value of exposure specific R_S for at least one compound under investigation. The conditions for selection of such compound were: a) it can be found both in the passive sampler and in the water phase at quantifiable concentration; b) it is accumulated under WBL control and remains in linear uptake phase during the whole sampler exposure; c) in filtered water samples it is predominantly present in the dissolved phase. These conditions are most likely fulfilled for moderately hydrophobic compounds with log $K_{ow} \approx 4–5$, e.g. phenanthrene or anthracene. For such a compound, in situ R_S can be calculated using the rearranged Eq. (1):

$$R_S = \frac{N}{C_W t} \quad (3)$$

where C_W is the mean value of the compound concentration in spot samples of water taken during sampler exposure (two values; before and after exposure). It was assumed that concentration of anthracene did not widely fluctuate during exposure. A check was performed using Eq. (4) that the sampler does not equilibrate with water for the compound. In the next step, value of log AB_W was calculated by substituting the calculated reference R_S value of anthracene into Eq. (2). Sampling rates of compounds with log $K_{ow} > 4.5$ were then extrapolated using Eq. (2) with adjusted exposure specific log AB_W value and the log K_{ow} values of individual compounds. It has been verified that comparable R_S values are obtained, when the calculation of exposure specific log AB_W is based on other reference compounds with similar physicochemical properties, such as phenanthrene or fluoranthene (Supplementary information, Table S3).

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3.2. Sampler equilibration time

In the linear uptake mode, i.e. far from equilibrium, the aqueous concentration of analyte was calculated from the absorbed amount using rearranged Eq. (1) (Booij et al., 2003b). When the analyte has reached equilibrium, its aqueous concentration was calculated using the SR/water partition coefficient.

An uptake remains essentially linear until 50% of equilibrium concentration is reached. The time interval it takes to reach the equilibrium concentration ($t_{1/2}$) can be estimated (Booij et al., 2007):

$$t_{1/2} = \ln 2\, K_{sw}\, m_S / R_S \quad (4)$$

where K_{sw} is the sampler/water partition coefficient, m_S is the mass of the sampler. K_{sw} values published by Smedes et al. (2009) were used. For HCH isomers, K_{sw} values for bulk silicone material were not available and log K_{sw} = 2.6, obtained using solid phase microextraction fibre coated with polydimethylsiloxane was used (Paschke and Popp, 2003). A correction of K_{sw} for temperature was not performed (Booij et al., 2003a). HCHs, naphthalene, acenaphthylene, acenaphthene and fluorene, compounds with low values of partition coefficient (log $K_{sw} < 3.7$), equilibrate during 28 days in all sampler exposures and the equilibrium partitioning model was applied:

$$C_W = \frac{N}{m_S K_{sw}} \quad (5)$$

For the remaining compounds, linear uptake model (Eq. (1)) was applied. This approach is illustrated in Table 2.

Table 2
Mean concentrations of PAHs, PCBs and OCPs found in SR (ng per sampler; $n = 2$), calculated sampling rates R_S, estimates of concentrations from SR C_{ws}, and concentrations measured in bulk water samples C_b collected at the beginning and the end of a 28 day sampler exposure at the site MA (period 14, Supplementary information, Table S1).

Compound	N [ng]	Sampling mode	R_s [L d^{-1}]	C_{ws} [ng L^{-1}]	C_{b1} [ng L^{-1}]	C_{b2} [ng L^{-1}]
Naphthalene	96	Equilib.[a]	n.e.[b]	6.72[d]	6.9	3.7
Acenaphthylene	31	Equilib.	n.e.	0.59[d]	0.4	0.3
Acenaphthene	695	Equilib.	n.e.	28.83[d]	4.5	3.6
Fluorene	814	Equilib.	n.e.	10.10[d]	3.6	3.1
Phenanthrene	2648	Linear	14.0	6.77	7.9	7.1
Anthracene	293	Linear	13.9	0.75	0.7	0.8
Fluoranthene	3545	Linear	13.1	9.67	9.6	7.5
Pyrene	2078	Linear	13.0	5.69	7.5	6.5
Benz(a)anthracene	188	Linear	12.2	0.55	1.1	0.8
Chrysene	328	Linear	12.2	0.96	2.0	1.5
Benzo(b)fluoranthene	57	Linear	12.2	0.17	0.7	0.5
Benzo(k)fluoranthene	37	Linear	12.2	0.11	0.6	0.4
Benzo(a)pyrene	23	Linear	12.0	0.07	0.7	0.4
Indeno(1,2,3cd)pyrene	5	Linear	11.5	0.01	0.4	0.2
Dibenz(a,h)anthracene	<1	Linear	11.2	<0.01	n.d.[c]	n.d.[c]
Benzo(g,h,i)perylene	6	Linear	11.5	0.02	0.6	0.4
PCB 28	29	Linear	12.5	0.08	0.1	0.1
PCB 52	6	Linear	12.2	0.02	<0.1	0.1
PCB 101	6	Linear	11.6	0.02	<0.1	<0.1
PCB 118	2	Linear	11.2	0.01	<0.1	<0.1
PCB 153	8	Linear	11.1	0.03	0.1	0.1
PCB 138	6	Linear	11.0	0.02	<0.1	<0.1
PCB 180	3	Linear	10.5	0.01	<0.1	<0.1
p,p′-DDE	53	Linear	12.4	0.15	0.2	0.1
p,p′-DDD	22	Linear	12.7	0.06	0.1	0.1
p,p′-DDT	6	Linear	11.8	0.02	0.1	0.1
α-HCH	24	Equilib.	n.e.	5.21[d]	0.2	<0.1
γ-HCH	18	Equilib.	n.e.	6.37[d]	2.0	0.8
HCB	58	Linear	12.7	0.16	0.2	0.2

[a] Eq. – partitioning equilibrium between sampler and water has likely been achieved.
[b] n.e. – not estimated.
[c] n.d. – not detected.
[d] Estimated using equilibrium partitioning model (Eq. (5)).

3.3. Relation between spot sample and passive sampler data

With a few exceptions, a good correlation was obtained between water concentrations obtained from SR (C_{ws}) and the mean water concentration value from filtered samples of water taken before and after sampler exposure sampling (C_b), assuming log-normal data distribution. Such comparison was only possible for compounds that were present at quantifiable concentrations in samples from both matrices. The mean value of the linear regression correlation coefficient from 30 exposures was 0.77. Results of this correlation for individual sampling sites and sampler deployment periods are available in Supplementary information (Table S4). Passive sampling provides concentrations that are lower than those obtained using from filtered spot samples of water. In general, the difference of both values increased with decreasing analyte concentrations; a typical example is shown in Fig. 2. Concentrations of compounds in samples decreased with their increasing hydrophobicity. An increased difference between spot and passive sampling is expected for more hydrophobic compounds (log $K_{ow} > 6$) since passive samplers accumulate only dissolved chemicals, whereas even filtered water samples contain a significant fraction of compounds sorbed to colloids that can pass through the filter. This was confirmed, when the observed difference (expressed as log C_b – log C_{ws}) was plotted against the compound hydrophobicity, as illustrated in Fig. 3. Concentrations found in filtered samples of spot water overestimated the truly dissolved concentrations of very hydrophobic compounds (log $K_{ow} > 6$) by up to 2 orders of magnitude in most cases. This observation illustrates the usefulness of passive samplers for the measurement of truly dissolved concentrations of extremely hydrophobic compounds, which is not possible using conventional techniques, e.g. filtration of water samples followed by liquid–liquid extraction.

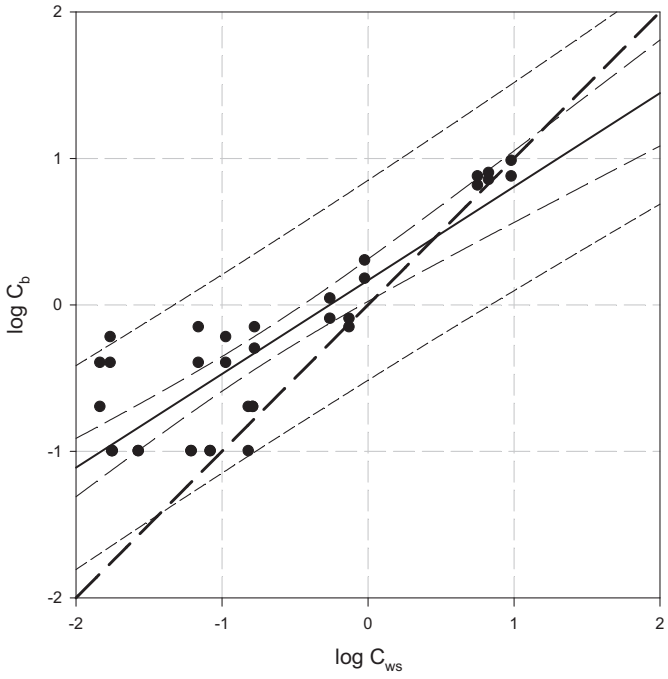

Fig. 2. An example of relation between dissolved concentrations in water determined using SR samplers (log C_{ws}) and those determined as a mean of two samples of water taken before and following passive sampler exposure (log C_b) at the site MA (period 14). Thin dashed lines present 95% confidence and prediction intervals, respectively. The thick dashed line indicates the equality of values.

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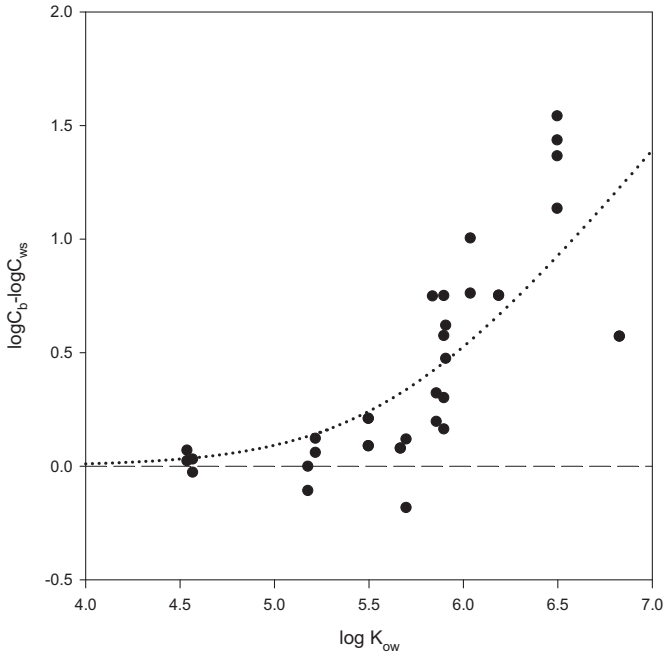

Fig. 3. A typical relation of the observed difference between dissolved concentrations in water determined using SR samplers and those from spot samples of water (log C_b − log C_{ws}) as dependent on compound hydrophobicity (log K_{ow}). The example is from the measurement at the site MA (period 14). The thin dotted line illustrates an empirical model that assumes sorption of compounds to colloids according to their hydrophobicity. The thick dashed line indicates the equality of values.

3.4. Space vs. time-related changes of dissolved contaminants

Tables 3 and 4 show the overall summary of dissolved concentration of contaminants at the five sampling sites during one year monitoring campaign where the sources of variability are assessed. No significant differences could be observed among regions across time for most studied contaminants with a few exceptions. A significantly elevated concentration of anthracene was observed at sites SP and CE in comparison with the site BE. Also, the sum of PAHs was significantly elevated at the site MA in comparison with all remaining sites. Finally, concentration of HCB was significantly lower at the site MA in comparison with the sites located in the main stream of the river Morava (BE, SP, CE).

Low MW PAHs were found to be relatively more dynamic contamination components in the dissolved phase over the year than high MW PAHs. Also, the absolute concentrations in the dissolved phase were dominated by low MW PAHs, which can be explained by their better water solubility and lower adsorption to suspended solids.

Highest median concentrations of all PAHs in water (excepting anthracene) were observed in river Dřevnice (site MA), which is likely due to the presence of local pollution sources as Dřevnice river collects pollution from the industrial agglomeration with chemical, plastic, rubber, shoe and machinery industry. The relatively small river with less than 5% average flow discharge of the river Morava at their confluence is more impacted by local pollution sources than the river Morava, where pollutants can be diluted more effectively. A similar pattern of PAHs was observed at all sampling sites, which indicates that the main pollution sources are similar (Fig. 4). Their spatial variability in water was relatively small, ranging between 7.8 and 25.7%, with the exception of anthracene, characterized by a higher variability of 47.7%. Elevated concentration and large fluctuation of anthracene in the area downstream the industrial zone of Zlín (site SP) is likely caused by specific contamination originating from a local point source, the anthraquinone producer DEZA Otrokovice, located between sites BE and SP on the river Morava. Regional distribution of recent sediment contamination in the Morava river also revealed a distinct anthracene peak just downstream of Otrokovice (Babek et al., 2008). Highest concentrations of PCBs, HCHs and DDT (but not HCB) were observed at the site MA. The contamination pattern by PCBs, OCPs and HCB was similar, which indicates that diffusive pollution sources dominate over local point sources (Fig. 5). The

Table 3
Summarised dissolved concentrations of PAHs in water, derived from SR passive samplers, at the five sampling sites.

Contaminants [ng L^{-1}]	Median values (10%; 90% quantiles); calculated over the whole monitored period						
	BE	MA	SP	CE	CR	p value[c]	Components of variability[d] (Between sites differences)
No. of measurements	$N = 9$	$N = 6$	$N = 11$	$N = 4$	$N = 5$		
Naphthalene	15.87[ab] (4.91; 28.20)	24.99[ab] (6.14; 35.20)	8.87[ab] (2.20; 27.40)	3.95[ab] (2.12; 25.80)	9.02[ab] (5.29; 12.84)	0.329	12.3%
Acenaphthylene	0.69[ab] (0.28; 3.92)	0.96[ab] (0.54; 3.41)	0.40[ab] (0.13; 4.66)	0.26[ab] (0.14; 3.18)	0.54[ab] (0.27; 1.20)	0.519	7.8%
Acenaphthene	14.65[ab] (7.90; 19.84)	20.56[ab] (8.70; 31.25)	10.61[ab] (1.40; 17.53)	8.54[ab] (1.93; 15.78)	9.25[ab] (4.53; 17.04)	0.317	n.a.
Fluorene	8.60[ab] (4.71; 10.05)	8.38[ab] (5.17; 14.66)	7.34[ab] (0.89; 12.05)	5.45[ab] (1.60; 9.43)	6.78[ab] (3.87; 10.70)	0.666	11.3%
Phenanthrene	8.91[ab] (3.19; 16.51)	12.52[ab] (7.75; 43.74)	4.78[ab] (2.56; 12.63)	6.25[ab] (2.40; 12.32)	3.84[ab] (2.08; 7.37)	0.072	21.3%
Anthracene	0.90[ab] (0.29; 1.33)	1.05[ab] (0.80; 4.28)	3.40[ab] (1.65; 8.70)	3.45[ab] (1.56; 5.55)	1.80[ab] (1.26; 3.19)	0.003	47.7%
Fluoranthene	14.27[ab] (2.76; 17.47)	18.36[ab] (10.37; 50.30)	10.97[ab] (5.08; 23.68)	8.74[ab] (6.44; 13.79)	7.74[ab] (4.84; 10.01)	0.226	18.5%
Pyrene	7.58[ab] (1.37; 11.00)	12.22[ab] (7.14; 30.74)	7.89[ab] (3.95; 14.93)	6.65[ab] (4.64; 9.99)	4.80[ab] (2.95; 6.22)	0.182	21.6%
Benzo(a)anthracene	0.38[ab] (0.24; 1.07)	1.24[ab] (0.71; 2.35)	0.88[ab] (0.35; 1.84)	0.66[ab] (0.35; 0.93)	0.53[ab] (0.37; 0.79)	0.187	20.0%
Chrysene	0.83[ab] (0.30; 1.82)	2.11[ab] (1.13; 4.04)	1.43[ab] (0.55; 2.58)	1.07[ab] (0.62; 1.60)	0.97[ab] (0.58; 1.24)	0.215	18.9%
Benzo(b)fluoranthene	0.18[ab] (0.08; 0.39)	0.35[ab] (0.24; 0.65)	0.21[ab] (0.11; 0.68)	0.26[ab] (0.15; 0.33)	0.26[ab] (0.17; 0.37)	0.455	14.4%
Benzo(k)fluoranthene	0.10[ab] (0.03; 0.19)	0.24[ab] (0.15; 0.39)	0.13[ab] (0.05; 0.41)	0.15[ab] (0.09; 0.30)	0.15[ab] (0.10; 0.22)	0.255	16.2%
Benzo(a)pyrene	0.10[ab] (0.02; 0.16)	0.15[ab] (0.10; 0.30)	0.25[ab] (0.05; 0.46)	0.10[ab] (0.05; 0.35)	0.09[ab] (0.06; 0.15)	0.099	25.0%
Indeno(1,2,3-cd)pyrene	0.03[ab] (0.01; 0.06)	0.06[ab] (0.02; 0.10)	0.02[ab] (0.01; 0.10)	0.02[ab] (0.01; 0.02)	0.03[ab] (0.02; 0.04)	0.408	10.2%
Dibenzo(a,h)anthracene	0.01[ab] (<0.01; 0.03)	0.02[ab] (0.01; 0.03)	0.01[ab] (<0.01; 0.02)	<0.01[ab] (<0.01; 0.01)	0.01[ab] (<0.01; 0.01)	0.419	n.a.
Benzo(g,h,i)perylene	0.03[ab] (0.01; 0.06)	0.06[ab] (0.03; 0.10)	0.02[ab] (0.01; 0.09)	0.03[ab] (0.02; 0.03)	0.03[ab] (0.02; 0.04)	0.352	9.5%
∑ PAHs	76.22[ab] (27.82; 104.80)	93.19[ab] (77.90; 202.71)	72.15[ab] (40.81; 88.18)	47.77[ab] (25.18; 94.61)	48.37[ab] (42.84; 53.51)	0.012	25.7%

n.a. – not analysed. [ab]

[ab] Marks of statistical significance of multiple comparison tests between sampling sites. Values within one row marked by the same letter are not mutually significantly different ($p > 0.05$; multiple median test).

[c] Overall p value of Kruskal–Wallis test comparing sampling sites.

[d] Component of overall variability that belongs to the differences between sampling sites. This was calculated as ratios of relevant sum of squares (ANOVA model; based on log-transformed concentration data).

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Table 4
Summarised dissolved concentrations of PCBs, OCPs and HCB in water, derived from SR passive samplers, at the five sampling sites.

Contaminants [ng L^{-1}]	Median values (10%; 90% quantiles); calculated over the whole monitored period						
	BE	MA	SP	CE	CR	p value[c]	Component of variability[d] (Between sites differences)
No. of measurements	$N = 9$	$N = 6$	$N = 11$	$N = 4$	$N = 5$		
PCB 28	0.07 (0.01; 0.11)	0.17 (0.09; 0.51)	0.07 (0.03; 0.32)	0.21 (0.12; 0.27)	0.07 (0.04; 0.23)	0.130	24.6%
PCB 52	0.02 (0.01; 0.05)	0.05 (0.02; 0.11)	0.02 (0.01; 0.08)	0.04 (0.03; 0.06)	0.03 (0.01; 0.05)	0.537	12.3%
PCB 101	0.02 (0.01; 0.04)	0.03 (0.02; 0.09)	0.02 (0.01; 0.05)	0.03 (0.03; 0.04)	0.03 (0.02; 0.06)	0.239	15.2%
PCB 118	0.01 (<0.01; 0.03)	0.01 (0.01; 0.06)	0.01 (<0.01; 0.02)	0.01 (0.01; 0.02)	0.01 (0.01; 0.02)	0.248	13.4%
PCB 153	0.02 (0.01; 0.05)	0.05 (0.03; 0.12)	0.02 (0.01; 0.09)	0.05 (0.04; 0.05)	0.05 (0.03; 0.10)	0.112	20.8%
PCB 138	0.01 (<0.01; 0.04)	0.03 (0.01; 0.10)	0.01 (0.01; 0.05)	0.03 (0.02; 0.04)	0.03 (0.02; 0.05)	0.140	17.5%
PCB 180	0.01 (<0.01; 0.04)	0.02 (0.01; 0.07)	0.01 (<0.01; 0.02)	0.02 (0.02; 0.02)	0.02 (0.01; 0.05)	0.065	21.5%
∑ PCBs	0.17 (0.04; 0.37)	0.44 (0.18; 0.98)	0.14 (0.09; 0.57)	0.38 (0.28; 0.49)	0.24 (0.14; 0.56)	0.203	18.9%
α-HCH	3.57 (1.39; 5.99)	6.31 (1.56; 20.91)	4.09 (2.38; 12.58)	4.78 (2.14; 11.23)	2.51 (1.91; 5.12)	0.661	8.7%
γ-HCH	3.67 (0.18; 15.63)	11.59 (5.31; 74.74)	2.05 (0.18; 7.07)	4.23 (1.29; 12.98)	2.93 (1.64; 5.00)	0.061	24.3%
∑ HCHs	6.98 (3.36; 22.65)	17.16 (11.62; 91.65)	6.14 (3.04; 18.82)	7.15 (5.27; 23.85)	4.67 (3.94; 10.12)	0.087	23.9%
p,p′-DDE	0.08 (0.02; 0.11)	0.14 (0.06; 0.55)	0.06 (0.04; 0.35)	0.15 (0.13; 0.23)	0.08 (0.05; 0.11)	0.132	18.4%
p,p′-DDD	0.07 (0.01; 0.12)	0.10 (0.04; 0.27)	0.03 (0.02; 0.19)	0.09 (0.08; 0.11)	0.06 (0.04; 0.09)	0.467	10.8%
p,p′-DDT	0.01 (0.00; 0.05)	0.02 (0.01; 0.09)	0.01 (<0.01; 0.01)	0.01 (<0.01; 0.02)	<0.01 (<0.01; 0.01)	0.083	14.6%
∑ DDTs	0.15 (0.04; 0.29)	0.26 (0.11; 0.90)	0.10 (0.07; 0.57)	0.25 (0.25; 0.31)	0.15 (0.09; 0.21)	0.247	20.1%
HCB	1.44[a] (0.63; 2.67)	0.21[b] (0.17; 0.75)	1.28[a] (0.39; 4.54)	1.69[a] (1.20; 2.10)	0.42[ab] (0.23; 0.72)	0.007	27.2%

[ab]Marks of statistical significance of multiple comparison tests between sampling sites. Values within one row marked by the same letter or unmarked are not mutually significantly different ($p > 0.05$; multiple median test).
[c] Overall p value of Kruskal–Wallis test comparing sampling sites.
[d] Component of overall variability that belongs to the differences between sampling sites. This was calculated as ratios of relevant sum of squares (ANOVA model; based on log-transformed concentration data).

spatial component of variability in water was small, ranging between 8.7 and 27.2%.

The compounds concentrations of which are susceptible of covarying in the environment were identified in this study on the basis of the correlation coefficient values. This statistical approach is based on the fact that each pollution source produces a characteristic compound pattern; so, the correlation factors between the concentrations of all the individual compounds can give an idea whether they all originate from the same source or not (Soclo et al., 2000). At sites in and downstream the industrial zone of Zlín (MA, SP), concentrations of PAHs with 3–5 aromatic rings in water positively correlate with concentrations of PCBs, DDT congeners and HCB (Supplementary information; Tables S6 and S7). The industrial complex of Zlín presents an over 100-year old environmental burden with multiple contaminant sources and deserves a more detailed investigation in the future. Contaminant pattern observed upstream the industrial zone of Zlín (site BE) is different (Supplementary information; Tables S5), which can be explained by a different type of human activities (agriculture) prevailing in that area.

3.5. Effect of environmental variables

To investigate effects of environmental variables, i.e. temperature, flow and suspended particulate matter (SPM) content on the concentration of pollutants in the water column, data on mean temperature, volume discharge, SPM content and concentration of analytes in water bound on SPM were correlated with concentrations of individual compounds in water, estimated from SR. The correlation was possible only at sites with the minimum of six measurements per year (BE, MA, SP). Correlations are shown in Tables 5–7. Water temperature and volume discharge were negatively correlated at all investigated sampling sites, with correlation coefficients ranging from −0.75 and −0.80, respectively. SPM did not significantly correlate with temperature or volume discharge at any of the three sites.

3.5.1. Effect of temperature

A clear trend in concentration decrease with increasing water temperature was observed at sites BE, MA, SP for the two most volatile PAHs, naphthalene and acenaphthylene, respectively (Fig. 6). A weak trend of concentration decrease of fluorene and phenanthrene with increasing temperature was also observed at

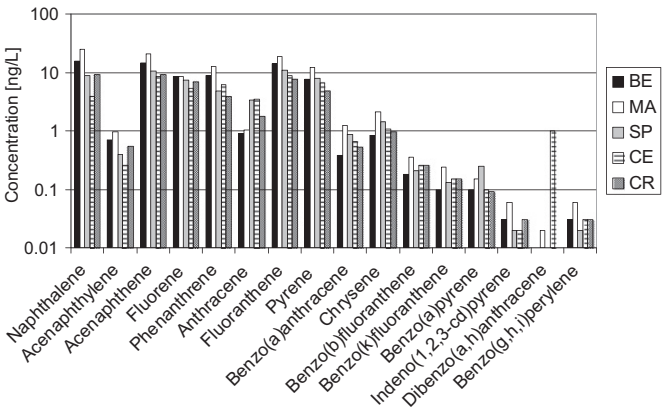

Fig. 4. PAH contamination pattern at the five sampling sites in the Zlín area, expressed by annual median values of water concentrations calculated from SR passive samplers.

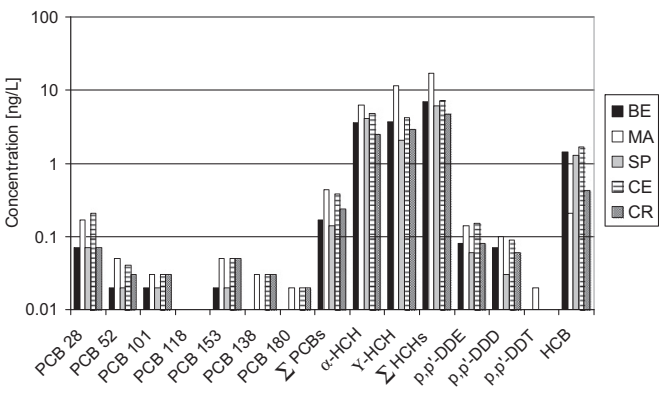

Fig. 5. PCB and OCP contamination pattern at the five sampling sites in the Zlín area, expressed by annual median values of water concentrations calculated from SR passive samplers.

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Table 5
Correlation of dissolved concentrations of PAHs in water with mean water temperature (T) mean discharge (Q), suspended particulate matter content (SPM) and concentration of analytes in water bound on suspended particulate matter [ng L^{-1}] (CP).

Sampling site	BE				MA				SP			
Parameter	T	Q	SPM	CP	T	Q	SPM	CP	T	Q	SPM	CP
Q [m^3/s]	−0.75[a]		−0.22		−0.85[a]		−0.43		−0.80[a]		−0.14	
Naphthalene	−0.90[a]	0.70[a]	−0.65	0.73[a]	−0.79[a]	0.72	−0.21	0.29	−0.84[a]	0.74[a]	−0.43	0.81[a]
Acenaphthylene	−0.76[a]	0.42	−0.51	−0.27	−0.76[a]	0.47	−0.39	−0.49	−0.88[a]	0.68	−0.50	−0.28
Acenaphthene	0.52	−0.48	0.71[a]	0.70[a]	0.78[a]	−0.74[a]	0.77	0.04	−0.09	0.29	−0.26	−0.26
Fluorene	−0.22	0.06	0.28	0.36	0.58	−0.60	0.89[a]	−0.65	−0.68	0.68	−0.48	0.09
Phenanthrene	−0.45	0.56	0.24	0.46	0.32	−0.33	0.97[a]	0.47	−0.66	0.77[a]	0.10	0.35
Anthracene	−0.52	0.71[a]	0.11	0.25	0.37	−0.35	0.99[a]	0.86[a]	0.57	−0.30	0.94[a]	0.93[a]
Fluoranthene	−0.20	0.42	0.44	0.48	0.37	−0.32	0.93[a]	0.93[a]	0.10	0.12	0.78[a]	0.82[a]
Pyrene	−0.40	0.53	0.21	0.25	0.31	−0.28	0.93[a]	0.95[a]	0.25	−0.08	0.66	0.70[a]
Benzo(a)anthracene	−0.54	0.62	−0.02	0.07	0.24	−0.21	0.85[a]	0.92[a]	0.23	−0.18	0.39	0.42
Chrysene	−0.49	0.59	0.08	0.13	0.28	−0.23	0.84[a]	0.80	0.19	−0.05	0.66	0.66
Benzo(b)fluoranthene	−0.46	0.60	0.03	0.15	0.06	0.00	0.55	0.64	0.43	−0.25	0.59	0.49
Benzo(k)fluoranthene	−0.43	0.52	0.07	0.13	0.07	−0.02	0.64	0.70	0.58	−0.42	0.48	0.43
Benzo(a)pyrene	−0.55	0.22	−0.33	−0.23	−0.17	0.20	0.14	0.25	0.47	−0.44	0.11	0.11
Indeno(1,2,3-cd)pyrene	−0.34	0.70[a]	−0.23	−0.18	−0.63	0.34	−0.24	−0.34	−0.30	0.31	0.00	0.00
Dibenzo(a,h)anthracene	−0.17	0.47	−0.22	−0.20	0.02	−0.12	0.62	0.67	−0.44	0.49	−0.01	0.02
Benzo(g,h,i)perylene	−0.41	0.75[a]	−0.28	−0.22	−0.59	0.27	−0.03	−0.15	−0.32	0.33	−0.02	−0.03
∑ PAHs	−0.49	0.49	0.12	0.24	0.29	−0.28	0.98[a]	0.94[a]	−0.61	0.75[a]	0.03	0.14

[a] Significant Pearson product moment correlation coefficients ($p < 0.05$; non-directional t-test) and higher than 0.7.

the site SP. For the remaining compounds no clear trends with temperature were observed at any of the three sites. The increase of volatile compound concentrations in water with decreasing temperature corresponds with enhanced combustion and related increased atmospheric concentration and atmospheric deposition of PAHs in winter months and potential loss of PAHs from the water column due to evaporation in summer months, respectively.

3.5.2. Effect of water flow

At the site BE, the concentrations of most PAHs in water (with exception of acenaphthene) tend to increase with water flow, although this correlation was in most cases weak. At the site SP, a similar trend was observed for light PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene and phenanthrene). Possibly, these correlations are artificial from a negative correlation of PAHs concentrations with temperature and a simultaneous negative correlation of water flow with temperature. Interestingly, trends of phenanthrene and anthracene at SP site with flow (and also temperature) were opposite to each other, although these compounds have very similar physicochemical properties. This confirms that phenanthrene and anthracene at SP site in water column originate from distinct pollution sources. A major local source of anthracene is the former anthraquinone producer DEZA, in Otrokovice, located between sites BE and SP on the river Morava. At the site MA, different weak trends with flow were observed; the volume discharge was not a significant factor affecting the contaminant concentrations in the dissolved phase.

3.5.3. Effect of suspended particulate matter

In river systems, hazardous hydrophobic contaminants are predominantly transported in association with suspended particulate matter (SPM). SPM that contains adsorbed contaminants can release them to the dissolved phase. We investigated whether increased dissolved concentrations of hydrophobic compounds are related to SPM content in the water column and concentration of analytes in water bound on SPM.

At the site BE upstream the industrial zone of Zlín, a positive correlation of concentration in water with SPM content was observed only for pesticides p,p′-DDD, p,p′-DDE and HCB (Tables 6 and 7). Concentrations of these compounds in the dissolved phase also positively correlate with their particle-bound concentrations in collected water samples. This can be explained by erosion of soil particles from large agricultural area upstream of BE, and possibly also by re-suspension of sediment particles from the same region during the high water discharge events. For PAHs and PCBs (with exception of naphthalene and acenaphthene), such trends were not observed. Concentrations of most PAHs and PCBs at this site seem to be affected mainly by diffusive combustion, atmospheric deposition and several environmental factors, none of them being dominant.

At the sampling site MA in river Dřevnice that flows through the industrial agglomeration of Zlín a good correlation of concentration in dissolved phase with SPM content in water was observed for PAHs with 3 and 4 aromatic rings, PCBs, DDT isomers and HCB (Tables 5–7). Concentrations of these compounds in the dissolved

Table 6
Correlation of concentrations of PCBs in water with mean water temperature (T) mean discharge (Q) and suspended particulate matter content (SPM) and concentration of analytes in water bound on suspended particulate matter [ng L^{-1}] (CP) at three sampling sites.

Sampling site	BE				MA				SP			
Parameter	T	Q	SPM	CP	T	Q	SPM	CP	T	Q	SPM	CP
Q [m^3/s]	−0.75[a]		−0.22		−0.85[a]		−0.43		−0.80[a]		−0.14	
PCB 28	0.21	0.31	0.63	−0.77[a]	0.29	−0.21	0.62	0.40	0.45	−0.21	0.90[a]	−0.32
PCB 52	−0.04	0.47	0.04	−0.09	0.32	−0.31	0.83[a]	0.70	0.51	−0.29	0.78[a]	−0.22
PCB 101	−0.05	0.44	−0.05	−0.19	0.40	−0.40	0.96[a]	0.88[a]	0.52	−0.32	0.76[a]	0.94[a]
PCB 118	−0.11	0.43	−0.19	n.d.	0.25	−0.33	0.86[a]	0.56	0.31	−0.09	0.75[a]	0.80[a]
PCB 153	−0.03	0.46	0.02	−0.03	0.37	−0.35	0.87[a]	0.85[a]	0.57	−0.38	0.62	0.80[a]
PCB 138	−0.02	0.42	−0.06	0.12	0.47	−0.45	0.96[a]	0.95[a]	0.52	−0.35	0.60	0.69
PCB 180	−0.08	0.43	−0.14	0.09	0.29	−0.35	0.91[a]	0.87[a]	0.21	−0.02	0.70[a]	0.66
∑ PCBs	−0.01	0.45	0.05	0.04	0.35	−0.32	0.83[a]	0.81[a]	0.49	−0.26	0.84[a]	0.87[a]

[a] Significant Pearson product moment correlation coefficients ($p < 0.05$; non-directional t-test) and higher than 0.7.

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Table 7
Correlation of concentrations of OCPs and HCB in water with mean water temperature (T), mean discharge (Q) and suspended particulate matter content (SPM) and concentration of analytes in water bound on suspended particulate matter [ng L^{-1}] (CP) at three sampling sites.

Sampling site	BE				MA				SP			
Parameter	T	Q	SPM	CP	T	Q	SPM	CP	T	Q	SPM	CP
Q [m^3/s]	−0.75[a]	1.00	−0.22		−0.85[a]	1.00			−0.80[a]	1.00	−0.14	
alfa-HCH	−0.29	−0.03	−0.20	0.00	−0.68	0.33	−0.55	0.14	−0.13	−0.25	−0.18	0.33
gama-HCH	0.14	0.18	0.59	−0.06	−0.56	0.14	−0.24	−0.70	0.24	0.10	0.92[a]	0.45
p,p′-DDE	0.24	0.31	0.65	0.74[a]	0.49	−0.35	0.71	0.72	0.54	−0.35	0.63	0.65
p,p′-DDD	0.25	0.28	0.69	0.84[a]	0.44	−0.34	0.76	0.77	0.53	−0.30	0.83[a]	0.86[a]
p,p′-DDT	−0.27	0.56	−0.21	−0.25	0.50	−0.41	0.92[a]	0.92[a]	0.15	0.18	0.81[a]	0.64
∑ DDT	0.12	0.42	0.48	0.56	0.48	−0.35	0.75	0.76	0.54	−0.32	0.74[a]	0.70[a]
HCB	0.31	0.05	0.80[a]	0.80[a]	0.40	−0.26	0.75	0.64	0.41	−0.33	0.57	0.70[a]

[a] Significant Pearson product moment correlation coefficients ($p < 0.05$; non-directional t-test) and higher than 0.7.

phase also positively correlated with their particle-bound concentrations in analysed water samples. A similar trend was also observed at the sampling site SP downstream the industrial zone (Fig. 7). This observation indicates that the levels of hydrophobic compounds ($\log K_{ow} > 4.5$) measured in the dissolved phase at sites MA and SP reflect the release of contaminants from polluted suspended particles in the water column. The particles likely appear in the water column as a result of emission, dry and wet atmospheric deposition and soil erosion from industrial zones.

3.6. Sediment/water fugacity ratios

To assess the net flux of PAHs between water and sediment at the sampling sites, fugacity ratios (ratio of the fugacity in the sediment f_S to the fugacity in the water f_W) were calculated using the passive sampler – derived dissolved concentration (C_W) and the sediment concentration data (C_S) (Mackay, 1979; Di Toro et al., 1991).

$$\frac{f_S}{f_W} = \frac{C_S}{C_W}\frac{1}{f_{oc}\rho K_{oc}} \quad (6)$$

The derivation of Eq. (6) has been shown previously (Vrana et al., 2001); f_{oc} is the fraction of sediment organic carbon, ρ is the sediment bulk density (relative to water) and K_{oc} is the sediment organic carbon–water partition coefficient. K_{oc} was calculated using Karickoff's approximation (Karickoff, 1981), i.e. $K_{oc} \sim 0.41 \times K_{ow} \cdot f_{oc}$ measured in sediments ranged between 2.1% and 5.3%. The substitution of Karickoff's equation by alternative correlations proposed to estimate K_{oc} from K_{ow} (Sabljic et al., 1995; Baker et al., 2000) yields comparable PAH concentrations in pore water (of the same order of magnitude).

The fugacity ratio can be cautiously interpreted as an indication of sediment–water equilibrium status. A ratio of unity indicates equilibrium, a ratio of less than unity indicates net flux from water to sediment and a ratio of more than unity indicates net flux from sediment to water.

A fair degree of equilibrium (f_S/f_W between 0.2 and 5) exists between the pore water and the overlying water for organochlorine pesticides and PCBs at sites BE, SP and MA. An example for the SP site is shown in Fig. 8. During the monitored period of one year, investigated sediments presented neither a contaminant sink nor a significant pollutant source for these compounds. By contrast, the sediment at all three locations are a significant potential source of

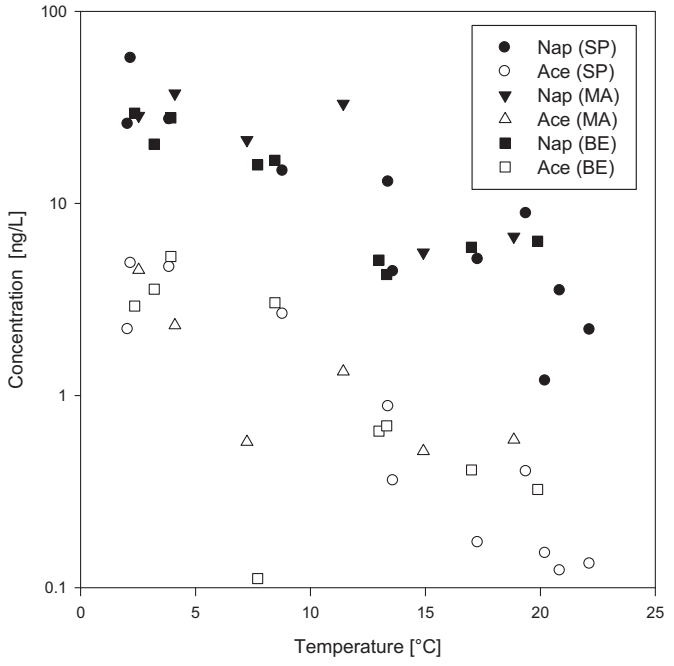

Fig. 6. The dependence of naphthalene (Nap) and acenaphthylene (Ace) concentration on temperature at sampling sites BE, MA and SP, respectively.

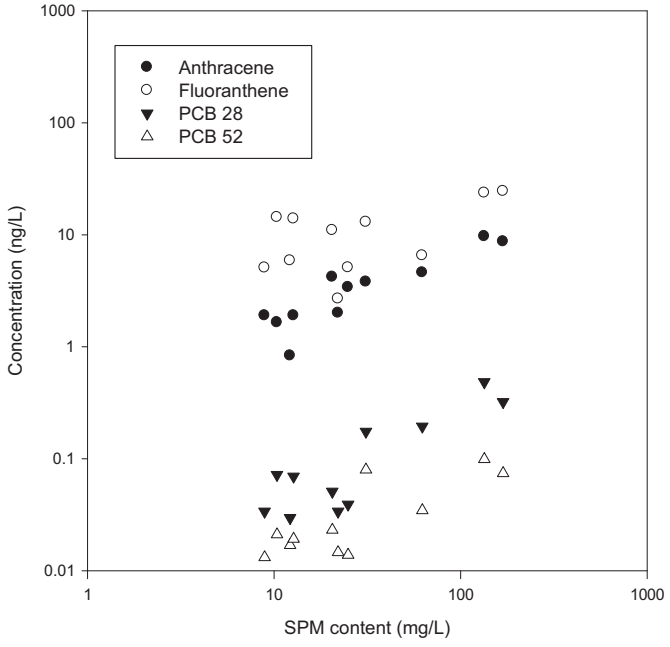

Fig. 7. The dependence of anthracene, fluoranthene, PCB 28 and PCB 52 dissolved concentrations on average SPM content in water samples collected before and after sampler exposure at the site SP.

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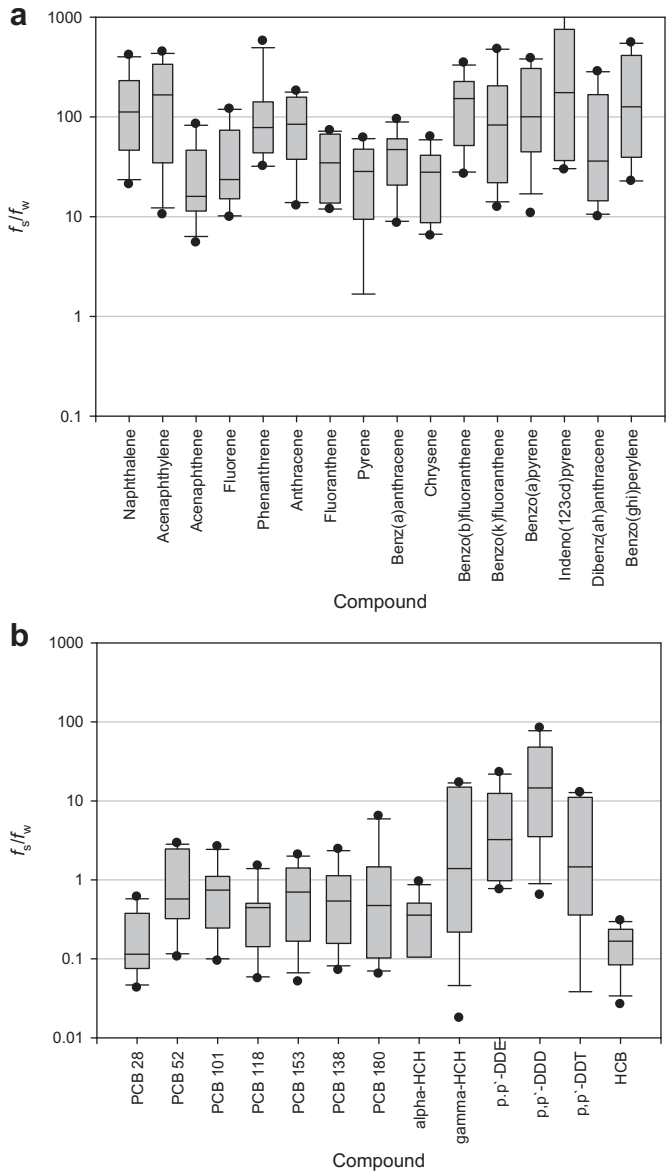

Fig. 8. Sediment/water fugacity ratios of the PAHs (a), PCBs and OCPs (b) at the sampling site SP, calculated as described in the text. The ratio range between 0.2 and 5 is approximately where the sediment is predicted to be close to equilibrium with the aqueous phase. The boundaries of the box indicate the 25th and 75th percentile, a line within the box marks the median. Data points that lie outside the 10th and 90th percentiles (whiskers) are shown as symbols.

PAHs, with the concentrations in the pore water being up to three orders of magnitude higher than in the water column. However, the fugacity in sediment may be overestimated by the presence of PAHs sorbed to soot particles in sediment. These were co-extracted during the analysis of PAHs in sediment, but they are not readily available for desorption to sediment pore water. Thus, the estimate of PAH flux between sediment and water column is not unambiguous without further experiments that will characterize the PAHs fraction that can be mobilized to water in a reasonable timescale.

4. Conclusions

Passive samplers provide a reliable tool for an assessment of long-term pollution status within the water bodies. For compounds accumulated under WBL control, however, fluctuations in water flow velocities result in significant fluctuations of the sampling rates making it more difficult to derive truly dissolved concentrations of organic pollutants from their amounts accumulated in the sampling media. In situ assessment of the sampling rates based on dissipation rates of the performance reference compounds (PRCs) is therefore strongly recommended in the field studies. In this study, we demonstrated application of an alternative method that can reduce bias in estimation of the truly dissolved concentrations in the absence of PRCs. The passive samplers provide complementary information to the sediment samples. Sediment concentration patterns may not be representative for estimation of bioavailable concentrations in the upper levels of the water column as they provide a long-term contamination record which is further a subject to change due to weathering and ageing. On the contrary, the passive samplers integrate water concentrations only during the sampling period and reflect the actual pollution situation in a water body.

The spatial variability of dissolved POPs in the studied region was relatively small, which indicates that diffusive pollution sources dominate over local point sources. The only exception was anthracene. Elevated and fluctuating concentrations, as well as a unique ratio of anthracene to phenanthrene concentration downstream the city of Zlín can be related to a specific industrial point source of this compound.

Concentrations of the most volatile PAHs decreased with increasing water temperature in the whole region indicating that atmospheric emission from domestic heating sources and consequent dry and wet deposition represent an important pathway of PAHs to aquatic ecosystem of the region in the winter period.

Distinct hydrophobic contaminant (log $K_{ow} > 4.5$) distribution patterns between dissolved phase and SPM were observed upstream and downstream the industrial zone of Zlín. Dissolved phase concentrations of these compounds were positively correlated with their particle-bound concentrations downstream the industrial zone (sites MA, SP) indicating release of contaminants from polluted suspended particles deposited to the water bodies via dry and wet atmospheric deposition and soil erosion.

Upstream (site BE), a positive correlation of dissolved water concentration with SPM content was observed only for hydrophobic organochlorine pesticides (DDT including metabolites and HCB) suggesting erosion of soil particles from agricultural areas, and re-suspension of sediment particles during the high water discharge events.

Inspection of the sediment/water fugacity ratios revealed a fair degree of equilibrium between the pore water and the overlying water for organochlorine pesticides and PCBs. In contrast, the calculated concentrations of PAHs in pore water were up to three orders of magnitude higher than those in the water column indicating that sediments can act as a potential pollution source. However, the applied model did not account for the specific sediment carbon composition or quality that affects the availability of PAHs for desorption.

Our study provided insight into the spatial and temporal variability of bioavailable concentrations of POPs in aquatic ecosystem and their potential sources. Similar field studies increase the body of information available for assessment of factors that affect distribution and fate of POPs in the natural environment. Moreover, they support regulators in assessing opportunities for using passive sampling for monitoring water quality within a legislative framework.

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Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.envpol.2012.02.022.

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Príloha 21

Jarošová B., Bláha L., **Vrana B.**, Randák T., Grabic R., Giesy J. P., and Hilscherová K., Changes in concentrations of hydrophilic organic contaminants and of endocrine-disrupting potential downstream of small communities located adjacent to headwaters, ***Environ. Int.*, 2012, 45, 22–31.**

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Changes in concentrations of hydrophilic organic contaminants and of endocrine-disrupting potential downstream of small communities located adjacent to headwaters

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ABSTRACT

Endocrine-disruptive potential and concentrations of polar organic contaminants were measured in seven headwaters flowing through relatively unpolluted areas of the Czech Republic. Towns with Wastewater Treatment Plant (WWTP) discharges were the first known sources of anthropogenic pollution in the areas. River water was sampled several kilometers upstream (US) and several tens of meters downstream (DS) of the WWTP discharges, by use of Pesticide and Pharmaceutical Polar Organic Integrative Samplers (POCIS-Pest, POCIS-Pharm). Extracts of passive samplers were tested by use of a battery of *in vitro* bioassays to determine overall non-specific cytotoxicity, endocrine-disruptive (ED) potential and dioxin-like toxicity. The extracts were also used for quantification of polar organics. There was little toxicity to cells caused by most extracts of POCIS. Estrogenicity was detected in all types of samples even though US locations are considered to be background. At US locations, concentrations of estrogen equivalents (EEq) ranged from less than the detection limits (LOD) to 0.5 ng EEq/POCIS. Downstream concentrations of EEqs ranged from less than LOD to 4.8 ng EEq/POCIS. Concentrations of EEq in POCIS extracts from all DS locations were 1 to 14 times greater than those at US locations. Concentrations of EEq measured in extracts of POCIS-Pest and POCIS-Pharm were in a good agreement. Neither antiestrogenic nor anti/androgenic activities were detected. Concentrations of 2,3,7,8-TCDD equivalents (TEq_{bio}) were detected in both types of POCIS at concentrations ranging from less than the LOD to 0.39 ng TEq_{bio}/POCIS. Nearly all extracts of POCIS-Pharm contained greater concentrations of TEq_{bio} activity than extracts of POCIS-Pest. Concentrations of pesticides and pharmaceuticals in extracts of POCIS were generally small at all sampling sites, but levels of some pharmaceuticals were significantly greater in both types of POCIS from DS locations. Chemical analyses along with the results of bioassays documented impacts of small towns with WWTPs on headwaters.

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1. Introduction

Municipal and industrial waste waters can be sources of compounds that are able to cause acute toxicity as well as sublethal chronic abnormalities including disruption of hormonal balance in aquatic organisms (endocrine disruption, ED). Persistent and bioaccumulative organic chemicals have been conventionally monitored, but less persistent and less hydrophobic organic compounds are currently used as pesticides, prescription and non-prescription drugs and personal care products. Despite their lesser bioconcentration potential, relatively large fluxes of some of these compounds into aquatic systems might be acutely toxic and/or induce sublethal chronic abnormalities (Alvarez

Abbreviations: AEq, androgenic equivalent; AhR, Aryl hydrocarbon receptor; DS, downstream; E1, estrone; E2, 17β-estradiol; E3, Estriol; EC, effective concentration; ED, endocrine disruption; EDCs, endocrine disruptive compounds; EE2, 17α-ethynylestradiol; EEq, estrogenic equivalent; HpOCs, hydrophilic organic compounds; K_{ow}, octanol–water partition coefficient; LOD, limit of detection; LOQ, limit of quantification; NR, Neutral Red; PCBs, polychlorinated biphenyls; PCDDs, polychlorinated dibenzodioxins; PCDFs, polychlorinated dibenzofurans; PNEC, Predicted No Effects Concentration; POCIS, Polar Organic Chemical Integrative Sampler; POCIS-Pest, Polar Organic Chemical Integrative Sampler optimized for polar Pesticides; POCIS-Pharm, Polar Organic Chemical Integrative Sampler optimized for most Pharmaceuticals; R_s, sampling rate (L/day); TEq_{bio}, dioxin-like equivalent obtained in bioassay; TCDD, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin; US, upstream; WWTP, Waste Water Treatment Plant.

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et al., 2007). Furthermore, some of these chemicals (particularly pharmaceuticals) can be highly potent, such that even concentrations at or near analytical detection limits may have biological activity.

Concentrations and/or ecotoxicological effects of hydrophilic organic compounds (HpOCs, contain one or more polar functional groups or a significant molecular dipole moment) have been reported in discharges of Waste Water Treatment Plants (WWTP) and/or downstream receiving waters (Aguayo et al., 2004; Bolong et al., 2009; Caliman and Gavrilescu, 2009). Downstream reaches of rivers have been shown to be polluted by compounds of both industrial and communal origin (Bolong et al., 2009), and therefore it is difficult to evaluate contributions and effects of pollutants released by individual towns. There are fewer sources of HpOC pollution in the headwaters and their potential impacts are not easy to assess, since there is limited information on concentrations of pollutants in the background areas.

Although different groups of HpOCs can contribute to adverse effects, xenoestrogens and xenoandrogens have emerged as environmental issues due to their ability to mimic or otherwise adversely affect functions of natural reproductive hormones, which could result in impaired reproduction of aquatic organisms (Matthiessen and Johnson, 2007). Even though the efficiencies of conventional WWTPs with activated sludge systems to remove estrogenic and androgenic compounds seem to be relatively high (88–>99% for estrogens and 96–>99% for androgens (Korner et al., 2000; Leusch et al., 2010; Murk et al., 2002; Svenson and Allard, 2004), concentrations of these endocrine disruptive compounds (EDCs) in some effluents are sufficient to cause ED (Kirk et al., 2002). Since some EDCs can cause adverse effects at small concentrations (ng/L), it is difficult and expensive to detect them by instrumental analyses (Korner et al., 2000). Moreover, because they occur in mixtures, even if they can be quantified, it is difficult to predict the potential effects of these compounds (Leusch et al., 2005). Therefore, *in vitro* bioassays can serve as cheaper and more environmentally relevant alternative to screen for the combined effects of mixtures on specific biological endpoints (Kinnberg, 2003).

The most frequently reported effect connected with EDs in surface waters is feminization of male fish downstream of WWTPs (Jobling and Tyler, 2003). Among estrogenic EDCs, the steroidal estrogens estrone (E1), estradiol (E2), and synthetic estrogen analogue, ethinyl estradiol (EE2), are some of the most potent endocrine disruptors in sewage effluents, all having more than thousand times greater potency to cause ED, at least in fish, than most other xenobiotics (Young et al., 2004). Under environmental conditions, steroidal hormones have been identified to be primarily responsible for observed adverse estrogenic effects on fish downstream of WWTPs although other weakly estrogenic compounds, such as alkylphenols and bisphenol A, can contribute to the effects (Desbrow et al., 1998; Gross-Sorokin et al., 2006). Important is also the fact that effluents from WWTPs can contain antiandrogenic chemicals as well. Their presence has been suggested by previous studies as a potential complication in establishing the chemical causation of fish sexual disruption (Tyler and Jobling, 2008). Efforts to identify the contributing antiandrogens are now underway, using a targeted fractionation process combined with screening by recombinant yeast assay and high-quality analytical chemistry. It should also be mentioned that certain compounds may act as both estrogens and antiandrogens (*e.g.* Suzuki et al., 2005).

There are two different approaches of sampling water, either active or passive. We chose to use passive integrative sampling, rather than traditional grab or composite sampling, for two reasons: i) passive sampling permits determination of time-weighted average concentrations of HpOCs in water, which is especially important when concentrations of HpOCs fluctuate over time because of changes in weather or variable diurnal patterns of consumption of products which are primary sources of HpOCs and, ii) the most potent EDCs usually occur at small concentrations (ng/L) and passive integrative samplers serve as an effective alternative to collecting and handling large volumes of water (Alvarez et al., 2007).

One useful passive sampler for HpOCs is the Polar Organic Chemical Integrative Sampler (POCIS). Relatively good correlations have been observed between concentrations of estrogenic equivalent (EEq) determined in bioassays for POCIS and grab water samples (Arditsoglou and Voutsa, 2008; Vermeirssen et al., 2005). POCIS has been shown to sample a wide variety of polar as well as moderate hydrophobic organic compounds with log K_{ow} of less than 4. Two types of adsorbents are considered standard for deployment of POCIS in the field. One of the two standard configurations, POCIS-Pest, preferentially concentrates waterborne HpOCs such as polar pesticides, natural and synthetic hormones, and other wastewater-related contaminants. The other, POCIS-Pharm, incorporates a sorbent optimal for sequestering polar pharmaceuticals (Alvarez et al., 2007).

Both types of POCIS exhibited linear uptake of phenolic and steroid compounds during 28-day tests conducted in laboratory during which concentrations of analytes in water were held constant. The correlation coefficients of the linear regression with respect to timescale were greater than 0.995 for POCIS-Pest and 0.985 for POCIS-Pharm, which suggests that uptake was time-integrative and the rate of uptake was not time-dependent during the exposure period. Moreover, rates of sampling (R_s) were not affected by changes in concentrations of tested compounds (Arditsoglou and Voutsa, 2008; Matthiessen and Johnson, 2007).

In the present study, water quality in terms of HpOCs and EDCs was studied in several headwaters in the Czech Republic. A combination of instrumental analyses of individual chemicals and *in vitro* assays with extracts from POCIS-Pest and POCIS-Pharm was conducted to: i) determine background levels of anti/estrogenic, anti/androgenic and dioxin-like activities in headwater streams upstream of known sources of anthropogenic pollution, and ii) evaluate the impacts of small towns and their WWTP discharges on concentrations of mixtures of EDCs in rivers.

2. Methods

2.1. Collection of samples

One POCIS-Pest and one POCIS-Pharm (Exposmeter AB, Sweden) sampler were deployed at each location. Study locations were upstream and downstream of seven municipal WWTPs, which were situated on small rivers and streams in relatively unpolluted areas of the Czech Republic (Fig. 1). Upstream (US) POCIS were placed from 2 to 5 km upstream of WWTPs in highland forest areas with minimal anthropogenic impact, while downstream (DS) sites were within 150 to 250 m of WWTP effluents. The towns studied, Králíky, Jilemnice, Cvikov, Tachov, Volary, Vimperk and Prachatice, are the upstream-

Fig. 1. Location of the sampling sites on small rivers in the Czech Republic: 1 — River Tichá Orlice near town Králíky; 2 — Stream Roudnický potok (upstream) and Jizerka river (downstream) near town Jilemnice; 3 — Stream Boberský potok near town Cvikov; 4 — River Mže near town Tachov; 5 — River Volyňka near town Vimperk; 6 — Stream Volarský potok near town Volary; 7 — Stream Živný potok near town Prachatice.

most sources of anthropogenic pollution on the assessed rivers/streams. These rivers/streams have natural or seminatural habitats flowing mostly through woodlands but there are agricultural fields or pastures in close proximity (0.2–3 km) to most of the towns. All WWTPs applied mechanical–biological treatment with activated sludge and Cvikov WWTP had an additional stabilizing pond (1.4 ha). All locations were sampled in June 2008, except for Prachatice, which was sampled in January 2008. Duration of deployment of samplers was 2 to 3 weeks. Duration of deployment should be within the linear uptake period for most HpOCs. Characteristics of WWTPs and river/stream conditions are summarized (Table 1).

2.2. Extraction of POCIS

After collection of POCIS, all samples (entire POCIS) were stored at −18 °C until analysis. The exposed POCIS was disassembled; the sorbent was transferred to the glass gravity flow chromatographic column with glass wool plug and analytes were eluted by the appropriate solvent mixture. Methanol was used as the eluent for POCIS-Pharm and a mixture of dichlormethane: methanol: toluene (8:1:1) was used for POCIS-Pest. The eluate was then evaporated to a small volume, the solvent was changed to methanol and the sample volume was adjusted to 2 mL for chemical analyses. Hexane, dichloromethane, acetone, toluene (all in Suprasolv purity), water and methanol (Hypergrade for LC/MS) were purchased from Merck (Darmstadt, Germany). The aliquots of extracts were further concentrated four-fold under a gentle stream of nitrogen to decrease the LOD for *in vitro* assays. The process blank samples were prepared following sample preparation procedure of both POCIS types and they were analyzed together with the other samples.

2.3. Bioassays

Four individual bioassays were used to determine overall cytotoxicity, anti/estrogenicity, anti/androgenicity and dioxin-like potencies of extracts of POCIS-Pest and POCIS-Pharm samplers. The reporter gene assays employed mammalian cell lines MVLN and H4IIE-*luc* and two types of recombinant *Saccharomyces cerevisiae*. MVLN are human breast carcinoma cells stably transfected with luciferase gene under the control of estrogen receptor, which were used for the assessment of cytotoxicity and anti/estrogenicity. Cytotoxicity of the samples was also investigated by recombinant strain of *S. cerevisiae* which expresses genes for enzyme luciferase under standard conditions (Leskinen et al., 2005). The potency of POCIS extracts to modulate androgen receptor-mediated responses was examined by use of recombinant *S. cerevisiae* that were modified to express human androgen receptor along with firefly luciferase under transcriptional control of androgen-responsive element (Michelini et al., 2005). H4IIE-*luc* are rat hepato-carcinoma cells stably transfected with the luciferase gene under control of Aryl hydrocarbon receptor (AhR) and they were used for the assessment of dioxin-like activity (Sanderson et al., 1996). At least two independent experiments were conducted in each bioassay for each exposure variant. All dilutions of POCIS extracts or controls were tested at least in triplicate.

Cytotoxicity of the samples can bias the results of the bioassays, therefore viability of cells was assessed several ways: Viability of MVLN cells was determined by use of the Neutral Red (NR) test where the NR dye is incorporated in the lysosomes of living cells and the uptake of NR is proportional to the number of viable cells. For cytotoxicity testing by NR-test, MVLN cells were seeded at a density of 25 000 cells/well in 96-well microplate ViewPlates™ (Packard, Meriden, CT, USA) and incubated for 24 h at 37 °C under atmosphere enriched with 5% CO_2. During this period cells were grown in DMEM-F12 without phenol red (Sigma Aldrich, USA) containing 10% foetal calf serum previously treated with dextran-coated charcoal to reduce concentrations of natural steroids in the serum. After 24 h, cells were exposed to dilutions of extracts from POCIS and solvent control (methanol, 0.5% v/v). Cytotoxicity was determined after 24 h of exposure, when NR (Sigma-Aldrich, Czech Republic) was added to the exposure medium in microplates to make a final concentration of 0.5 mg/mL. Cells were then incubated for 1 h at 37 °C. Afterwards, the cells were washed twice with phosphate buffered saline and lysed in the presence of acetic acid–ethanol solution (25:25:0.5; ethanol:water:acetic acid) for 15 min on a shaker. Finally, NR uptake was determined spectrophotometrically (Power Wave, BioTek, USA) at 570 nm. Absorbance was related to the response of the solvent control and the percentage of cytotoxicity of each sample dilution (viability of the cells exposed to the sample dilution relative to viability of cells exposed to solvent control (considered as 100%)) was determined. For the other way of assessing the viability, the recombinant strain of *S. cerevisiae* which expresses genes for enzyme luciferase under standard conditions (Leskinen et al., 2005) was used. In the presence of cytotoxic substances in the medium, luminescent light, produced normally by interaction between luciferase and added substrate luciferin, is less. When reaching a linear phase of growth, yeast were seeded into 96-well culture ViewPlates™ (Packard, Meriden, CT, USA) and exposed to vehicle, dilutions of POCIS extracts or to medium alone. Yeast cells were incubated for 2.5 h at 30 °C and then the signal was detected after addition of D-luciferin substrate. Detected luminescence was used to express the percentage of cytotoxicity caused by each sample dilution, as determined by the viability of the cells exposed to sample dilution relative to viability of cells exposed to solvent control, which was assigned a value of 100%.

Exposure for the determination of the anti/estrogenic potency of extracts in MVLN cells was conducted the same way as for the NR cytotoxicity evaluation described above with the following difference: cells were exposed to dilutions of POCIS extracts, calibration of the reference estrogen E2 (dilution series 10^{-12}–0.5×10^{-9} M E2, Sigma-Aldrich, Czech Republic) and solvent control (methanol, 0.5% v/v). After 24 h of exposure, the intensity of luminescence was measured

Table 1
Description of sampling sites, river parameters and sampling dates and duration.

Site no.	Name of town	Inhabitants no.	Name of recipient river(stream)	Effluent %[a]	River Q355 [m^3/s]	River flow velocity [m/s]	Sampling duration [day]	Date of sampling[b]
1	Králíky	4800	Tichá Orlice	20%	0.07	0.23	16	26 May–11 June
2	Jilemnice	6000	Roudnický potok (US)/Jizerka (DS)[c]	5%	0.02	0.08 (US) 0.02 (DS)	16	26 May–11 June
3	Cvikov	1900	Boberský potok	10%	0.08	0.13	21	21 May–11 June
4	Tachov	13000	Mže	15%	0.40	0.17	22	21 May–12 June
5	Vimperk	7650	Volyňka	4%	0.11	0.06	21	22 May–12 June
6	Volary	4000	Volarský potok	5%	0.07	0.12	21	22 May–12 June
7	Prachatice	13000	Živný potok	30%	0.15	0.17	23/16[d]	7/14[d]–30 January

[a] Average contribution of WWTP effluent to the recipient.
[b] All samples were taken in 2008.
[c] US = upstream site, DS = downstream site.
[d] US POCIS-Pest and both DS POCISes have been exposed for 23 days while US POCIS-Pharm for 16 days.

using Promega Steady Glo Kit (Promega, Mannheim, Germany). After subtraction of the response of the solvent control, luminescence in the estrogenicity assay was related to the maximal response of standard ligand (E2max for estrogenicity) and converted to percentages of E2max. Maximal induction as well as the shape of the curve differed among samples, thus equal efficacy or parallelism of the dose–response curves could not be assumed (Villeneuve et al., 2000). To avoid any predictions beyond the measured responses with all samples and to estimate the estrogenic equivalents (EEq) in the samples (expressed in ng E2/POCIS) the EEq_{20} estimate based on the 20% E2max response was reported, since most of the active samples did not reach the 50% E2max. EEq_{20} values were based on relating the amount of E2 causing 20% of the E2max response (EC_{20}) to the amount of sample causing the same response determined from regression analysis (equivalent of amount of E2 per amount of sample). The EC values were calculated by nonlinear logarithmic regression of dose–response curve of calibration standard and samples in Graph Pad Prism (GraphPad Software, San Diego, USA). The anti/estrogenicity was assessed by simultaneous exposure of the sample extract and 17β-estradiol (33 pM E2).

Duration of sampling varied from 16 to 23 days at different locations. Based on the evidence from previous research that uptake of phenolic as well as steroidal estrogens is linear in terms of time and concentration up to at least 28 days (Alvarez et al., 2007; Arditsoglou and Voutsa, 2008), we present our results normalized to 20 days of deployment along with the primary data in Table 3. The normalization was performed to simplify the comparability of our results among different locations and also with other studies in discussion. The data are presented both these ways to demonstrate the possible influence of the somewhat different deployment periods of the samplers on the results and their interpretation.

Concentrations of EEq in water were estimated by use of the sampling rate of E2 (0.09 L/day) previously determined by Matthiessen and Johnson (2007). It is important to stress, that these recalculated values represent approximate estimates of EEq concentrations in water and the values should not be considered as definite concentrations. This estimation will be further discussed in detail.

Concentrations of EEq in water were calculated (Eq. (1)).

$$C_w = C_{POCIS}/R_s t \quad (1)$$

where: C_w is the estimated concentration of EEq in water (ng/L), C_{POCIS} are concentrations of EEq in extracts from POCIS (ng/POCIS; primary not normalized values), R_s is sampling rate (L/day) of E2 previously determined by Matthiessen and Johnson (2007) and t is the sampling period (days).

As it was mentioned, anti/androgenity of POCIS extracts was determined by use of recombinant strain of *S. cerevisiae*. Plating and dosing were the same as for determination cytotoxicity of sample extracts in another strain of *S. cerevisiae* described above, but in this case, yeast cells were exposed not only to POCIS extracts and controls of pure medium and vehicle but also to dilutions of standard (testosterone in a range from 10^{-11} to 10^{-6} M, Sigma-Aldrich, Czech Republic).

The H4IIE-*luc* model was used for analysis of dioxin-like activity of the samples (Sanderson et al., 1996). Cells were seeded at a density of 15 000 per well in 96-well microplate ViewPlates™ (Packard, Meriden, CT, USA) and incubated for 24 h under 5% CO_2 at 37 °C, in DMEM-F12 medium with phenol red (Sigma Aldrich, USA) containing 10% foetal calf serum. After 24 h, cells were exposed to the reference compound 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD, with a dilution series of 10^{-12}–0.5×10^{-9} M, Ultra Scientific, USA), or dilutions of POCIS extracts and solvent control (methanol, 0.5% v/v). After 24 h of exposure, the intensity of luminescence was measured using Promega Steady Glo Kit (Promega, Mannheim, Germany). Results from the H4IIE-*luc in vitro* assay were analyzed by the same approach as described for the determination of the EEq above. Presented TEq_{bio} are expressed in ng of TCDD per POCIS. TEq_{bio} values were based on EC_{20} values because most samples did not reach greater EC responses.

For each bioassay the limit of detection was determined as the lowest observable effect concentration of standard chemical divided by the greatest non-cytotoxic extract concentration expressed as POCIS equivalent.

Table 2
List of pesticides and pharmaceuticals analyzed in extracts from both POCIS-Pest and POCIS-Pharm and list of perfluorinated organic compounds analyzed in extracts from POCIS-Pest.

Pharmaceuticals	Pesticides		Perfluorinated organics
Carbamazepine	2,4,5-T	MCPA	Perfluoro-1-hexanesulfonate
Cephalexin	2,4-D	MCPP_MECOPROP	2H-perfluoro-2-octenoic acid
Ciprofloxacin	Acetochlor	Metalaxyl	Perfluoro-1-octanesulfonamide
Diaveridine	Alachlor	Metamitron	N-methylperfluoro-1-octanesulfonamide
Diclofenac	Atrazine	Methabenzthiazuron	Perfluorooctanoic acid
Enrofloxacin	Atrazine desethyl	Methamidophos	Perfluorooctane sulfonic acid
Erythromycin	Azoxystrobin	Methidathion	Perfluorononanoic acid
Metronidazole	Bentazone	Metobromuron	
Norfloxacin	Bromacil	Metolachlor	
Ofloxacin	Carbofuran	Metoxuron	
Sulfachloropyridazine	Cyanazine	Metribuzin	
Sulfamethazine	Desmetryn	Monolinuron	
Sulfamethoxazole	Diazinon	Nicosulfuron	
Sulfamethoxypyridazine	Dichlobenil	Phorate	
Sulfapyridine	Dichlorprop	Phosalone	
Trimethoprim	Dimethoate	Phosphamidon	
	Diuron	Prometryn	
	Fenarimol	Propiconazole	
	Fenhexamid	Propyzamide	
	Fipronil	Pyridate	
	Fluazifop-p-butyl	Rimsulfuron	
	Hexazinone	Simazine	
	Chlorbromuron	Tebuconazole	
	Chlorotoluron	Terbuthylazine	
	Imazethapyr	Terbutryn	
	Isoproturon	Thifensulfuron-methyl	
	Kresoxim-methyl	Thiophanate-methyl	
	Linuron	Tri-allate	

2.4. LC/MS/MS analyses

Chemicals such as natrium sulfate, silicagel, methanol *etc.* were purchased from Merck (Darmstadt, Germany). ^{13}C labeled and native perfluorinated compounds were purchased from Wellington Laboratories. ^{13}C labeled Simazine, Sulfamethoxazol, 2.4D and Ciprofloxacin were purchased from Cambridge Isotope Laboratories. Native compounds were purchased from Dr. Ehrenstorfer, AccuStandards and Absolute Standards. All of the standards were purchased from Labicom ltd. (Olomouc, Czech Republic). A list of analyzed compounds is given in Table 2.

A cocktail of internal standards was spiked into each POCIS extract (100 μL of the standard mixture in water was added to 100 μL of POCIS extract). Chemicals were identified and quantified by use of LC/MS/MS. Analyses were performed using three different LC/MS/MS methods.

Chemicals in POCIS extracts were quantified by use of internal standards. A subsample (20 μL for pesticide and 10 μL for pharmaceuticals) was injected onto an analytical column (Phenomenex C18 Aqua, 2 mm × 50 mm, 5 μm particles). The HTS PAL (CTC) autosampler, Rheos2000 (Flux) quaternary pump and TSQ Quantum AccessTM (ThermoScientific, USA) triple quadrupole tandem mass spectrometer were used for analyses of polar pesticides, pharmaceuticals and perfluorinated compounds. Two MS/MS transitions were monitored (where possible) for native analytes to confirm identity. An agreement of results obtained from both transitions better than 30% was accepted as a confirmed result. Isotope dilution and internal standard methods were used for the quantification of target compounds. Quantification limits (LOQs) of analytes were calculated the same way as concentration but peak area corresponding to instrument LOQ was used instead of peak area found in sample. Thus, LOQs are adjusted to internal standards.

Most detected compounds have been shown to be in the linear uptake phase for at least 23 days (the maximal deployment period in our study) (Alvarez et al., 2007). Thus, we present concentrations of those compounds normalized to 20 days of deployment to enable more precise interpretation of our results across different locations and also better comparability with other studies in discussion.

2.5. Statistical analysis

Due to violations of the assumptions of parametric statistical testing, differences between results of the two applied cytotoxicity detection systems as well as between potencies of POCIS-Pest and POCIS-Pharm extracts to induce nonspecific cytotoxicity and act through specific modes of action were evaluated by nonparametric Wilcoxon Matched Pairs test. The same test was applied to assess differences between concentrations of pollutants detected in POCIS-Pest and Pharm extracts. The nonparametric Spearman rank correlation was used to assess the similarity of the potential of POCIS-Pest and Pharm extracts to act through specific modes of action. All statistical analyses were performed with Statistica for Windows® 9.0 (StatSoft, Tulsa, OK, USA), the tests were considered significant at $p<0.05$.

3. Results

There was no response above detection limits observed for blanks in any of the bioassays. The limits of detection in blanks were 0.06 ng EEq/POCIS for estrogenity, 1.29 ng AEq/POCIS for androgenity and 0.03 ng TEqbio/POCIS for dioxin-like activity.

3.1. Cytotoxicity

Most tested concentrations of POCIS extract equivalents (0.00125%–0.25% POCIS/mL) were not cytotoxic to yeast or to MVLN cells. At the greatest tested POCIS extract equivalent concentration 0.5% POCIS extract/mL samples from some locations caused cytotoxicity of as much as 50% (Fig. 2). For both types of POCIS the cytotoxic effects were comparable or greater at DS locations than at US locations with a single exception where the POCIS-Pharm extract at location 5 exhibited greater cytotoxicity at the US location (Fig. 2B). However, the greater cytotoxicity observed DS of WWTPs compared to US was statistically significant only for extracts of POCIS-Pest measured by yeast test. In all other cases, including all extracts of POCIS-Pharm in both bioassays and POCIS-Pest in MVLN cells, the magnitude of differences in cytotoxicity was not statistically significant between US and DS.

Although the yeast test was significantly more sensitive to cytotoxicity of POCIS-Pharm extracts ($p=0.009$) than the MVLN test, the results of the two tests were comparable among POCIS extracts, with no significant difference between the results of the two tests with extracts of POCIS-Pest ($p=0.79$). The yeast test was also significantly more sensitive to POCIS-Pharm extracts than POCIS-Pest extracts ($p=0.01$), whereas there was no statistically significant difference between cytotoxicity of extracts of the two types of samplers in the MVLN test.

3.2. Anti/estrogenicity

Estrogenicity was detected in extracts of both types of POCIS and differences were observed between US and DS locations. No extract showed significant antiestrogenic activity (data not shown). Although samples from DS locations were more estrogenic than those from US locations at all sites, some EEq was detected also in most US samples (Table 3).

Because uptake of the more potent and also some less potent estrogens has previously been demonstrated to be time integrative for more than 25 days (*e.g.* Arditsoglou and Voutsa, 2008), here estrogenic potentials detected in extracts of POCIS are reported also as normalized to 20 days of POCIS deployment. However, differences between data obtained before and after the normalization to 20 days of POCIS deployment were negligible (Table 3).

Concentrations of EEq greater than the LOD (0.1 to 0.6 ng/POCIS) were observed in four out of seven US locations in both types of POCIS. The variation among LOD is caused by slightly different cytotoxicity of extracts. Detected concentrations of EEq in US samples ranged from 0.3 to 0.5 ng/$POCIS_{20\ days}$ in POCIS-Pest as well as in POCIS-Pharm extracts. Since there were no known anthropogenic impacts near US sites, the detected EEq concentrations can be considered as background.

Estrogenic equivalents in extracts from DS samples were greater than the LOD at all sites with the single exception of the POCIS-Pest extract at site 2. Concentrations ranged from 0.7 to 4.0 ng/$POCIS_{20\ days}$ for POCIS-Pest and from 0.5 to 4.2 ng/$POCIS_{20\ days}$ for POCIS-Pharm extracts. The greatest concentrations of EEq were observed at DS locations at sites 3 and 7 (Table 3). At site 3 DS samples contained more than 10-fold greater concentration of EEq than the US sample in the case of POCIS-Pest and more than 14-fold greater concentration of EEq than the US POCIS-Pharm. At site 7 DS samples contained more than 7-fold greater concentrations of EEQ than the US sample from POCIS-Pest and more than 5-fold greater concentration than the US sample from POCIS-Pharm, respectively.

Estrogenic potential of water was estimated (Eq. (1)). For US localities sampled by both types of POCIS the calculated water EEq concentrations detected above LOD varied from 0.1 to 0.3 ng/L. Estimated estrogenic potential in water in DS locations sampled by POCIS-Pest ranged from less than 0.4 to 2.2 ng EEq/L and for those sampled by POCIS-Pharm from 0.3 to 2.3 ng EEq/L (Table 3).

There were statistically significant correlations between estrogenic potentials of the pesticide and pharmaceutical POCIS extracts (Spearman rank 0.79, $N=7$, LOD values were replaced by value of 1/2 LOD), despite the discrepancy at the DS location at site 6. At DS location at site 6, repeated evaluation of estrogenic potential confirmed the difference of estrogenicity in extract of POCIS-Pharm compared to POCIS-Pest. The likeness of estrogenicity in extracts of POCIS-Pest and Pharm was also confirmed by nonparametric Wilcoxon Matched Pairs test, which indicated no significant difference between POCIS-Pest and Pharm ($p=0.81$).

3.3. Anti/androgenicity

There was no significant androgenic activity in any extract in the test with recombinant yeast assay (data not shown). Detection limit was 1.29 ng AEq/POCIS. None of the extracts has shown antiandrogenic activity (data not shown).

3.4. Dioxin-like activity

Dioxin-like activity was detected in most extracts. At US locations sampled by POCIS-Pest, concentrations exceeded the detection limit of 0.03 ng TEq_{bio}/POCIS in only two cases whereas extracts from the POCIS-Pharm sampler deployed at the same locations had detectable concentrations at six out of seven sites (Fig. 3). Concentrations of TEq_{bio} at US locations ranged from less than the LOD to 0.08 and to 0.22 ng TEq_{bio}/POCIS for extracts of POCIS-Pest and POCIS-Pharm, respectively. DS sites mostly showed greater concentrations of TEq_{bio} in extracts from POCIS-Pharm than from POCIS-Pest. Extracts from DS POCIS-Pest contained concentrations of TEq_{bio} that ranged from less than LOD of 0.08 to 0.26 ng TEq_{bio}/POCIS and from 0.08 to 0.39 ng TEq_{bio}/POCIS in extracts of POCIS-Pharm.

When considering all samples together, significantly greater concentrations of TEq_{bio} were observed in extracts of POCIS-Pharm than extracts of POCIS-Pest (Wilcoxon Matched Pairs test; $P=0.0029$). Nevertheless, similar patterns of greater concentrations of TEq_{bio} at DS locations with similar orders of magnitudes were observed in extracts of both types of POCIS. At most sites, concentrations of TEq_{bio} were greater DS of WWTPs (Fig. 3). Concentrations TEq_{bio} in extracts of DS POCIS-Pest at sites 4 and 7 were greater than those in extracts of POCIS-Pest from US, by 1.4- and 4.9-fold, respectively. Concentrations of TEq_{bio} in extracts of POCIS-Pharm at sites 1, 2 and 5 were approximately equivalent

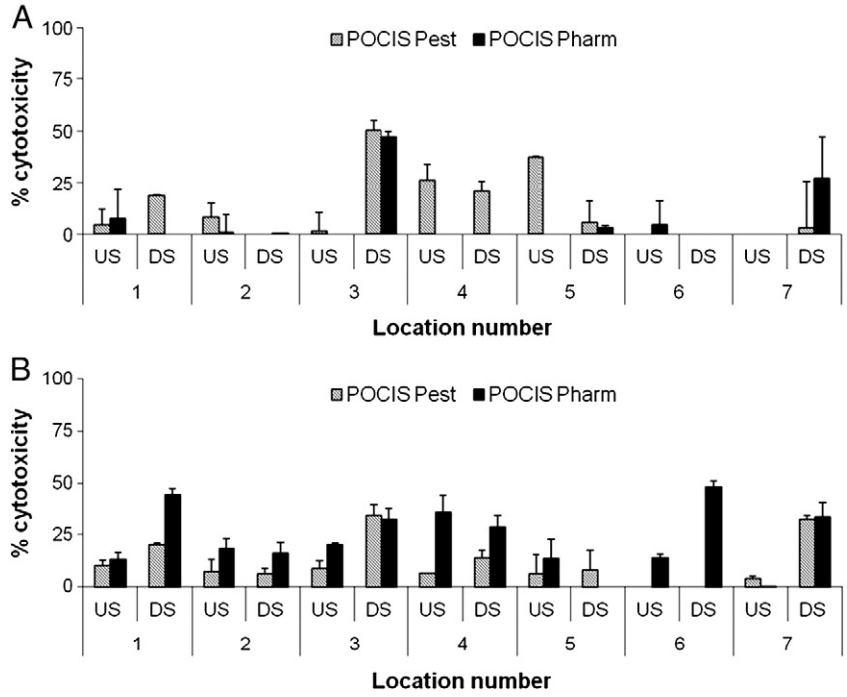

Fig. 2. Cytotoxicity of extracts (concentration of 0.5% POCIS/mL) from upstream (US) and downstream (DS) measured by the yeast screen (A) and by Neutral Red test with MVLN cells (B). Error bars show standard deviations. For samples without any cytotoxic effect, no values are presented.

for US and DS locations, whereas they were about 3-fold greater at the DS location of sites 3 and 4 and at least about 5-fold greater at the DS location at sites 6 and 7.

3.5. Chemical analyses

Although most of the selected chemicals that were monitored were not detected in extracts at concentrations greater than the LOQ (0.1 to 14 ng/POCIS), concentrations of several pharmaceuticals were greater at DS relative to US locations (Table 4). The greatest concentrations of pharmaceuticals were observed at the DS location of site 7. Pharmaceuticals found most frequently and also at the greatest concentrations were carbamazepine and diclofenac. Concentrations of carbamazepine ranged from less than the detection limit (2–8 ng/POCIS) to 9 ng/POCIS$_{20\ days}$ in extracts from US locations and from 13 to 339 ng/POCIS$_{20\ days}$ in extracts from DS locations. The concentrations of diclofenac ranged from less than the LOQ (2–8 ng/POCIS) to 31 ng/POCIS$_{20\ days}$ in extracts from US locations and from 18 to 409 ng/POCIS$_{20\ days}$ in extracts from DS locations. Concentrations in extracts of POCIS-Pest and POCIS-Pharm were comparable with a few exceptions, such as sulfapyridine at sites 3 and 4. Except pharmaceuticals presented in Table 4, a few other compounds — ofloxacin, norfloxacin, ciprofloxacin and erythromycin were detected above the detection limits (LOQ 0.6–14 ng/POCIS), all detected concentrations were lower than 100 ng/POCIS$_{20\ days}$.

Concentrations of most pesticides that were monitored were less than the LOQ (0.1–6.5 ng/POCIS). Most pesticides, which were quantifiable, were triazines, and their concentrations were generally small (<100 ng/POCIS$_{20\ days}$). Concentrations of all detected triazines, including atrazine, atrazine desethyl, hexazinone, simazine and terbuthylazine are summarized in Table 5. Besides triazines, acetochlor at a concentration of 1375 ng/POCIS$_{20\ days}$ was detected in one isolated POCIS-Pest sample from US location of site 2.

Beside the pharmaceuticals and pesticides, perfluorinated organic compounds (listed in Table 2) were also monitored in extracts of POCIS-Pest. However, concentrations greater than the LOQ of 0.21–1.15 ng/POCIS were observed only in a few cases

Table 3
Estrogenic activities in POCIS-Pest and POCIS-Pharm extracts measured by MVLN *in vitro* assay expressed as ng EEq/POCIS, normalized to sampling period of 20 days and recalculated (according to Eq. (1)) to approximate EEq water concentrations.

Site no.	US/DS[a]	POCIS depl.[b] (day)	EEq in POCIS extracts (ng/POCIS)		EEq in POCIS extracts normalized to 20 days of POCIS deployment (ng/POCIS$_{20\ days}$)		Estimated EEq in water derived from E2 R_s[c] and EEq of POCIS extract (ng/L)	
			POCIS Pest	POCIS Pharm	POCIS Pest	POCIS Pharm	POCIS Pest	POCIS Pharm
1	US	16	0.2 ± 0.01	<0.2	0.3	<0.3	0.1	<0.1
	DS		1.0 ± 0.1	0.7 ± 0.2	1.3	0.9	0.7	0.5
2	US	16	<0.3	<0.3	<0.4	<0.4	<0.2	<0.2
	DS		<0.3	0.7 ± 0.6	<0.4	0.8	<0.2	0.5
3	US	21	0.4 ± 0.3	0.3 ± 0.1	0.4	0.3	0.2	0.2
	DS		4.2 ± 1.5	4.3 ± 0.4	4.0	4.1	2.2	2.3
4	US	22	0.5 ± 0.2	0.3 ± 0.1	0.5	0.3	0.3	0.1
	DS		0.9 ± 0.2	0.5 ± 0.02	0.8	0.5	0.5	0.3
5	US	21	0.4 ± 0.1	0.5 ± 0.1	0.4	0.5	0.2	0.3
	DS		0.9 ± 0.6	1.0 ± 0.04	0.9	1.0	0.5	0.5
6	US	21	<0.3	<0.3	<0.3	<0.3	<0.2	<0.2
	DS		0.7 ± 0.7	2.3 ± 0.3	0.7	2.2	0.4	1.2
7	US	23/16[d]	<0.6	<0.6	<0.5	<0.8	<0.3	<0.4
	DS		4.5 ± 1.3	4.8 ± 1.0	3.9	4.2	2.2	2.3

[a] US = upstream site, DS = downstream site.
[b] Duration of POCIS deployment.
[c] R_s = sampling rate.
[d] US POCIS-Pest and both DS POCISes have been exposed for 23 days while US POCIS-Pharm for 16 days.

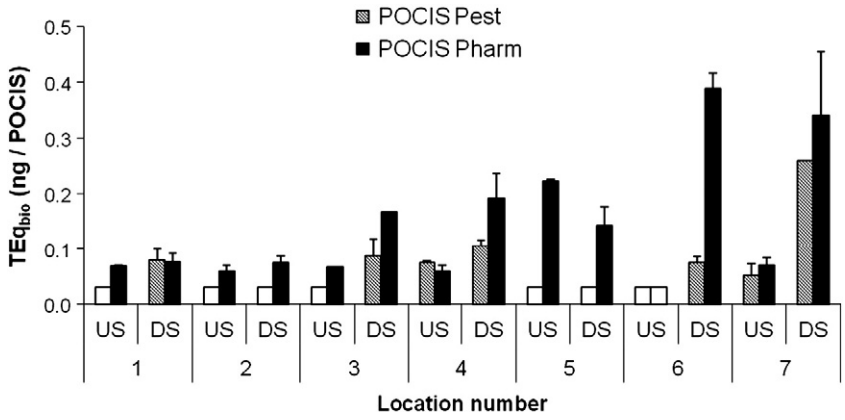

Fig. 3. Dioxin-like activity of upstream (US) and downstream (DS) POCIS-Pest and POCIS-Pharm extracts determined by H4IIE-*luc in vitro* assay. White columns indicate TEq_{bio} concentrations less than our detection limit (0.03 ng/POCIS); error bars show standard deviations.

and were less than 5 ng/POCIS with single exception of perfluorooctane sulfonic acid, which was detected at DS location 2 at concentration 36 ng/POCIS.

4. Discussion

Most previous studies assessing ED contamination of rivers focused on the influence of urbanized areas and larger WWTPs (Kinnberg, 2003), but there is less information on the impact of smaller sources on headwaters where better quality of water would be expected. Our study brings important information on the background levels of ED and HpOCs compounds and the influence of smaller towns without major industrial activities on headwaters pollution. Seven small rivers or streams were sampled by use of POCIS-Pest and POCIS-Pharm passive samplers US and DS of the most upstream sources of anthropogenic pollution, which were small towns with WWTP discharges.

Sampling rates for most compounds, which were investigated by use of POCIS in turbulent conditions, have been reported to range from 0.12 to 0.26 L/day (95%centile of published R_s; Alvarez et al., 2007; Arditsoglou and Voutsa, 2008; Harman et al., 2008; Macleod et al., 2007; Mazzella et al., 2007). This means that in 16 days, which is the minimal time of deployment of POCIS in the study, the results of which are reported here, the amount of the chemicals present in POCIS would be equivalent to 1.92–4.16 L of river water (0.12–0.26 L/day × 16 days). Thus, the least concentration causing cytotoxic effect — 0.5% POCIS/mL, would represent 9.6- to 20.8-fold concentrated river water. Therefore our results suggest little overall cytotoxicity of river water and weak impact of WWTPs onto this unspecific toxicity.

The results of the two systems used to detect cytotoxicity, yeast and mammalian cells, were similar with the exception of greater cytotoxicity of extracts of POCIS-Pharm in the yeast cells. This observation indicates greater sensitivity of the yeast model toward some chemicals that are more concentrated by POCIS-Pharm. Chemical analyses of POCIS-Pest and Pharm extracts did not reveal any significant differences in concentrations of monitored pollutants. However, it has been suggested that some pharmaceuticals have multiple functional groups, which have a tendency to strongly bind to the carbonaceous component of the triphasic adsorbent mixture contained in POCIS-Pest, which results in poor solvent extraction recoveries of some members of this class of compounds during sample processing (Alvarez et al., 2007). Our results demonstrating weak cytotoxicity correspond to another study of Alvarez et al. (2008), who used Microtox® assay to evaluate toxicity of POCIS from surface waters burdened by extensive agriculture. In that study, no extract from passive samplers (POCIS, SPMD) exposed for 29 to 65 days displayed acute toxicity.

Although the study, the results of which are reported here, was conducted in relatively unpolluted areas, some estrogenic activity was detected even at US locations (Table 3). Authors of some other studies had referred to detect concentrations of EEq in reference rivers. Nadzialek et al. (2010), who used active sampling and MCF-7 assay, found EEq concentrations at both tested reference sites in Belgium to be 0.01 and 0.03 ng/L. These concentrations are comparable with those estimated in our study (<0.1–0.3 ng EEq/L) especially if we consider our recalculated results as the worst case scenario. In contrast, Sellin et al. (2009), who used POCIS-Pharm and chemical analyses of their

Table 4
Results of the LC/MS/MS analyses — pharmaceuticals with greatest detected concentrations in extracts from POCIS-Pest and POCIS-Pharm ($ng/POCIS_{20\ days}$). Results are normalized to sampling period of 20 days.

Site no.	US/DS [a]	Sulfapyridine		Sulfamethoxazole		Trimethoprim		Carbamazepine		Diclofenac	
		POCIS Pest	POCIS Pharm	POCIS Pest	POCIS Pharm	POCIS Pest	POCIS Pharm	POCIS Pest	POCIS Pharm	POCIS Pest	POCIS Pharm
1	US	–	–	–	–	–	–	–	–	–	–
	DS	–	–	74	16	13	9	44	28	60	49
2	US	–	–	–	–	–	–	–	–	–	–
	DS	–	14	9	–	–	–	15	15	18	30
3	US	–	–	11	–	–	–	6	–	31	24
	DS	90	25	27	–	10	8	95	36	133	57
4	US	9	3	–	–	–	–	9	3	–	–
	DS	100	13	59	8	28	10	61	13	100	23
5	US	–	–	–	–	–	–	–	–	–	–
	DS	12	16	–	–	8	14	24	40	31	70
6	US	–	–	–	–	–	–	–	–	–	–
	DS	42	26	30	15	35	32	190	238	181	190
7	US	–	–	–	–	–	–	–	–	–	–
	DS	50	36	200	122	209	209	339	304	391	409

"–" less than LOQ (0.6–14 ng/POCIS).
[a] US = upstream site, DS = downstream site.

Table 5
Results of the LC/MS/MS analyses - concentrations of triazines (ng/POCIS$_{20\ days}$), which were the most frequently detected pesticides at tested sites. Results are normalized to sampling period of 20 days.

Site no.	US/DS[a]	Atrazine		Atrazine desethyl		Hexazinone		Simazine		Terbuthylazine	
		POCIS Pest	POCIS Pharm	POCIS Pest	POCIS Pharm	POCIS Pest	POCIS Pharm	POCIS Pest	POCIS Pharm	POCIS Pest	POCIS Pharm
1	US	–	–	–	–	5	7	–	–	15	21
	DS	14	14	8	6	–	–	–	–	2	3
2	US	8	12	18	19	1	–	4	5	1375	1875
	DS	4	7	5	5	4	3	1	1	475	713
3	US	7	7	8	3	32	19	5	4	2	1
	DS	24	11	17	5	49	20	8	4	3	1
4	US	2	3	8	5	6	5	–	–	2	2
	DS	5	2	11	3	8	3	1	–	4	3
5	US	8	7	13	7	18	12	–	–	2	2
	DS	5	11	7	9	12	16	–	1	2	3
6	US	–	–	–	–	1	–	–	–	1	1
	DS	21	31	25	22	20	18	–	1	6	6
7	US	2	2	16	13	9	9	1	2	–	–
	DS	14	11	25	18	10	9	2	1	2	1

"–" less than LOQ (0.1–6.5 ng/POCIS).
[a] US = upstream site, DS = downstream site.

extracts to monitor estrogens in rivers of Nebraska, reported calculated EEq concentrations above detection limit (1 ng/POCIS$_{7\ days}$) in 2 out of 3 reference sites and the concentrations (1.9 and 1.5 ng/POCIS$_{7\ days}$) were at least one order of magnitude greater than those found in our study. Matthiessen and Johnson (2007) evaluated, among others, estrogenic potential of 6 British headwaters with only few sources of estrogenic contamination (isolated houses with septic tanks). They used POCIS, which was previously calibrated in a laboratory study and yeast estrogen screen assay to evaluate estrogenic potential of the POCIS extracts. Their EEq concentrations ranged from less than the LOD (0.08 ng/L) to 1.4 ng/L with a median of 0.3 ng/L (except of 1 site with extremely great EEq value), which are slightly greater but comparable results to ours.

Greater estrogenic potential DS of WWTPs compared to US was detected at all sampled sites (Table 3). Comparable results were obtained by Vermeirssen et al. (2005), who monitored estrogens in POCIS Pest and Pharm extracts deployed US and DS of 5 municipal WWTPs in Switzerland. Four out of the five rivers were, according to earlier DS samples analyses, chosen as moderate to greatly estrogenic whereas one river as less estrogenic. The concentrations of EEq at the least burdened site were very similar to those obtained in our study (0.4 ng EEq/POCIS$_{22\ days}$ in extracts of both types of POCIS placed US and 1.9–2.0 ng EEq/POCIS$_{22\ days}$ in extract of POCIS-Pest and 1.7–1.9 ng EEq/POCIS$_{22\ days}$ of POCIS-Pharm situated DS of the WWTP). In contrast, the river with the greatest estrogenic pollution contained more than 20 ng EEq/POCIS$_{22\ days}$ in both POCIS extracts of US samples and comparable EEq concentrations in DS ones. Similar to our results most DS samples displayed increase of estrogenic activity compared to US ones. Greater concentrations of estrogens in all POCIS samplers deployed DS of municipal WWTPs of smaller towns compared to US sites were also found in Nebraska (Sellin et al., 2009). Those authors determined estrogenic equivalents analytically (based on known potential of steroidal estrogens to cause the effect) and the recalculated EEq concentrations were greater (up to 22.7 ng/POCIS$_{7\ days}$) than those detected by bioassays in our study. However, the greatest EEq concentrations were detected DS of WWTP with trickling filters technology which had been previously proved to be less effective in estrogens removal than activated sludge systems (Svenson et al., 2003) such as those in all WWTPs in our study.

Concentrations of EEq in POCIS extracts were converted to approximate concentrations of EEq in water by use of sampling rate of E2 because: i) in numerous studies steroidal estrogens have been identified to be responsible for most (often more than 90%) of estrogenic activity detected by *in vitro* assays in municipal waste waters effluents (*e.g.* Korner et al., 2001; Routledge et al., 1998) ii) compared to E1, Estriol (E3) and EE2, E2 has the least R_s (Arditsoglou and Voutsa, 2008), which enabled to estimate the worst case scenario (the greatest concentration) and iii) E2 is the standard reference compound used for EEq calculations. For estimating concentrations of EEq in water, R_s for E2 previously established for the same standardized POCIS configuration as used in our study was applied in calculation (0.09 L/day; Matthiessen and Johnson, 2007). From the rates of sampling for E2 given in the literature (Arditsoglou and Voutsa, 2008; Matthiessen and Johnson, 2007), the R_s calibrated at 10 °C was used because the temperature was similar to the conditions in the studied streams and rivers and the application of the lowest R_s value resulted in the worst case scenario estimate. Furthermore, application of the E2 sampling rate calibrated at 23.5 ± 0.5 °C by Arditsoglou and Voutsa (2008) would result in a range <0.1 to 1.8 ng/L EEq, which is similar to the currently presented results (Table 3). Rate of sampling can vary under different environmental conditions (*e.g.* diverse water flow rates, pH or temperature) but all the stations (with exception of location 7) were sampled at the same time eliminating thus at least partially variability. Moreover, the flow rates were always greater than 0.02 m/s and it has been demonstrated that under turbulent conditions sampling rates do not dramatically change as a function of flow velocity (Li et al., 2010). Another line of evidence, which supports the approach of EEq calculation applied in the study, is direct comparison of POCIS with grab samples as reported by Vermeirssen et al. (2005). Those authors measured estrogenic activity in both extracts of POCIS and grab samples and concentrations of EEq in extracts of POCIS were approximately 3-fold greater than the average concentrations of EEq in grab samples. These findings indicated the rate of sampling for estrogenic compounds is approximately 0.14 L/day. This experimentally established R_s is consistent with the results observed in this study where it was assumed that use of R_s for E2 could serve as an approximation to estimate concentrations of EEq in water and that these recalculated results represent a realistic estimate of the worst case scenario.

Even though the most estrogenic extracts came from POCIS exposed DS of Prachatice town (site 7), which has the most inhabitants and the largest proportion of WWTP effluent in relation to the recipient river (Table 1), these two parameters did not correlate with the estrogenic potentials in POCIS extracts from other sites. Other forces, for example different primary sources of estrogens or different WWTP capacity or technology, probably influenced the EEq concentrations in DS samples. Estrogenic activity detected in extracts of POCIS-Pest or POCIS-Pharm was similar, this observation is consistent with previous field as well as calibration studies (Arditsoglou and Voutsa, 2008; Vermeirssen et al., 2005).

Although dioxin-like compounds are usually investigated in less polar matrices such as SPMD or sediments, some recent studies (Dagnino et al., 2010; Reungoat et al., 2010) affirmed this activity also in water phase. In this study, dioxin-like activity was detected in both types of POCIS (0.05–0.39 ng TEq_{bio}/POCIS), even at several US locations. Sampling rates for known AhR active compounds and kinetic of their sampling has not been reported for POCIS yet. Therefore our results cannot be recalculated to water concentrations nor to unified number of days of their deployment. Dioxin-like activity has been traditionally connected with hydrophobic compounds such as polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) or polychlorinated biphenyls (PCBs). Since experimentally-determined values for log K_{ow} range from 6.1 to 8.2 for PCDD and PCDF congeners (Chrostowski and Foster, 1996) and from 4.66 up to 7.44 for PCB congeners, respectively (Zhou et al., 2005), these compounds are not expected to be sampled by POCIS. Our results suggest that less hydrophobic compounds like PAHs, which are also known to bind to AhR, or some unknown compounds might represent non-negligible part of dioxin-like activities in aquatic environment and this issue desires further research.

In this study concentrations of TEq_{bio} in extracts of POCIS-Pharm were approximately 2-fold greater than those in extracts of POCIS-Pest. Up to authors' knowledge, no other comparisons of concentrations of TEq_{bio} in extracts of POCIS-Pest and POCIS-Pharm have been published. However, since the same sorbent mass and membrane were used for both types of POCIS, it seems that different affinity of dioxin-like compounds to the POCIS-Pest *vs.* POCIS-Pharm sorbent might be responsible for the observed difference. Another reason could be the efficiency of extraction methods. However, the most potent and traditionally studied dioxin-like pollutants are hydrophobic substances and POCIS-Pest was extracted by less polar solvent than POCIS-Pharm.

Even though *in vitro* assays revealed some specific potencies of mixtures that might cause effects to the aquatic biota, chemical analyses of a wide range of compounds (Table 2) did not show significant contamination. The greatest effects were observed in estrogenic activity screening assay. However, steroidal estrogens, which have been shown to be responsible for most of the estrogen equivalents in waste waters (Desbrow et al., 1998), were not monitored in this study. Among detected chemicals, some triazines are known to be able to disturb endocrine system of organisms (Danzo, 1997; Vonier et al., 1996). In this study, triazines were detected at concentrations from less than 0.1 to 1875 ng/$POCIS_{20\ days}$ (Table 5) and their previously published sampling rates varied from 0.12 to 0.26 L/day (Alvarez et al., 2007; Mazzella et al., 2007). Estimated concentrations of triazines in water ranged from less than 0.02 ng/L to 781 ng/L, but these compounds are known to be effective at concentrations greater than mg/L (Danzo, 1997; Vonier et al., 1996) and thus their contribution to the responses detected by the *in vitro* systems can be considered negligible.

Concentrations of all monitored chemicals were small compared to the results of other studies (Arditsoglou and Voutsa, 2008; Soderstrom et al., 2009), which was in good agreement with our intention to sample relatively unpolluted areas. Despite the small concentrations of studied contaminants there were obviously increased concentrations of pharmaceuticals in DS samples. This was not so remarkable in case of pesticides. The reason of greater differences of pharmaceuticals concentrations in US and DS extract than pesticides might be the fact that pharmaceuticals are used only in human quarters or farms whereas pesticides are used also in areas distant from towns.

When considering the environmental significance of our results, some of the detected estrogenic equivalents concentrations had been reported to cause adverse effects. Authors of most studies, who observed estrogenic adverse effects on aquatic biota, reported EEq concentrations or corresponding concentrations of estrogens higher than those detected in our study (*e.g.* Sellin et al., 2009; Vermeirssen et al., 2005; Young et al., 2004). However, for example, Vethaak et al. (2005) found elevated levels of yolk protein vitellogenin in male bream (*Abramis brama*) in river with EEq levels determined by *in vitro* ER-CALUX assay as low as 0.17 ng/L. In that study, steroidal hormones were identified as the main contributors to the EEq (Vethaak et al., 2005). To authors' knowledge, the only estrogen, for which LOEC concentrations lower than 0.5 ng/L *in vivo* has been reported, was EE2 (Young et al., 2004). For example, Zha et al. (2008) demonstrated that the reproduction of the F-1 minnows was completely inhibited at EE2 concentration as low as 0.2 ng/L in a multigeneration study with Chinese rare minnows (*Gobiocypris rarus*). In our study, the upstream locations (with estimated EEqs <0.1–0.3 ng/L) were chosen as background sites without any grasslands or human settlements near the catchments and therefore we do not expect steroidal estrogens, particularly the synthetic EE2, to be responsible for the detected EEq. Contrariwise, at downstream locations with estimated EEq <0.2–2.3 ng/L, where municipal waste water effluents were considered as the main sources of estrogens, the presence of highly potent steroidal estrogens would be expected. The relative potency of any estrogens to E2 can differ for *in vitro* and *in vivo* studies (*e.g.* Johnson and Sumpter, 2001). The greatest difference has been reported for EE2. In the *in vitro* assay that we used (MVLN) the estrogenic potency of EE2 relative to E2 is 1.25 whereas in *in vivo* studies concerning production of yolk protein vitellogenin or alteration of ovarian somatic index in fish it has been reported to be approximately 25–30 (Gutendorf and Westendorf, 2001; Young et al., 2004). This indicates that the overall estrogenic equivalents for *in vivo* situation might be even greater that those derived from *in vitro* tests. As far as the authors know, there are no studies available on potential *in vivo* adverse effects in similar locations as examined in our study. Therefore it is not possible to reliably estimate the environmental significance of detected EEq yet.

The levels of vitellogenin in brown trout (*Salmo trutta fario* L.) from US and DS Prachatice (corresponding to our location 7) were investigated in September 2007 by researchers from Faculty of Fisheries and Protection of Waters, University of South Bohemia. There were significantly increased levels of vitellogenin in male brown trout captured downstream compared to the upstream site. The number of examined fish males was 6 at each US and DS location. The median plasma concentration were bellow detection limit of 10 ng/mL in male fish from upstream site and 3035 μg/mL in those from downstream site (Zlabek, personal communication). This corresponds with the results of our study, where the estrogenic activity was bellow detection limit in POCIS exposed upstream of Prachatice, while there were the greatest EEq among all sites in our study detected in POCIS from the Prachatice downstream site (2.3 ng/L). Thus, the increased EEq values from *in vitro* studies might indicate potential *in vivo* effects. Generally, the relevance of *in vitro* determined estrogenic equivalents for *in vivo* situation is a very important issue, which requires further research and which is also in focus of our further studies.

5. Conclusion

The study brought new information about concentrations of polar organic contaminants and endocrine-disruptive potential in relatively unpolluted rivers and about the influence of smaller towns on this type of contamination in affected headwaters. There was an obvious impact on all sites despite the fact that the towns are equipped with municipal WWTPs with advanced activated sludge systems of treatment. Increased exposure potential of estrogenic and dioxin-like compounds (determined by *in vitro* assays) downstream of the towns were demonstrated. Some of the detected estrogenic equivalents concentrations had been reported to cause adverse effects. The study also demonstrated the suitability of passive sampling combined with chemical analyses and *in vitro* bioassays to reveal these impacts.

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Príloha 22

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Use of passive sampling devices for monitoring and compliance checking of POP concentrations in water

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Abstract
Background The state of the art of passive water sampling of (nonpolar) organic contaminants is presented. Its suitability for regulatory monitoring is discussed, with an emphasis on the information yielded by passive sampling devices (PSDs), their relevance and associated uncertainties. Almost all persistent organic pollutants (POPs) targeted by the Stockholm Convention are nonpolar or weakly polar, hydrophobic substances, making them ideal targets for sampling in water using PSDs. Widely used nonpolar PSDs include semipermeable membrane devices, low-density polyethylene and silicone rubber.
Results and discussion The inter-laboratory variation of equilibrium partition constants between PSD and water is mostly 0.2–0.5 log units, depending on the exact matrix used. The sampling rate of PSDs is best determined by using performance reference compounds during field deployment. The major advantage of PSDs over alternative matrices applicable in trend monitoring (e.g. sediments or biota) is that the various sources of variance including analytical variance and natural environmental variance can be much better controlled, which in turn results in a reduction of the number of analysed samples required to obtain results with comparable statistical power.
Conclusion Compliance checking with regulatory limits and analysis of temporal and spatial contaminant trends are two possible fields of application. In contrast to the established use of nonpolar PSDs, polar samplers are insufficiently understood, but research is in progress to develop PSDs for the quantitative assessment of polar waterborne contaminants. In summary, PSD-based monitoring is a mature technique for the measurement of aqueous concentrations of apolar POPs, with a well-defined accuracy and precision.

Keywords Persistent organic pollutants · Passive sampler · Water · Monitoring · Compliance · Quality control · Sampler–water partition coefficient · Sampling rate

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1 Introduction

Measuring aqueous phase concentrations of persistent organic pollutants (POPs) is an important activity for assessing the effectiveness of international treaties on pollution prevention and reduction, such as the Stockholm Convention (SC) on POPs, which was adopted in 2001 and entered into force on 17 May 2004 after being ratified by the fiftieth country (UNEP 2001). It is a global treaty to protect human health and the environment from the adverse effects posed

by POPs. Within the convention, POPs are defined as compounds that are persistent, prone to long-range transport, bioaccumulate and elicit adverse effects. The 12 (groups of) compounds that were included in the SC in 2001 were all hydrophobic: polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans and several organochlorine pesticides (namely aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex and toxaphene). Nine additional compounds were added to the Convention in 2009 (chlordecone, α-, β- and γ-hexachlorocyclohexanes (HCHs)), pentachlorobenzene, hexabromobiphenyl, tetra-, penta-, hexa- and heptabromodiphenylethers, perfluorooctane sulfonic acid and its salts (PFOS) and perfluorooctane sulfonyl fluoride. In 2011, endosulfan was added to Annex A of the Stockholm Convention. With the exception of PFOS, all other POPs are nonpolar or weakly polar, hydrophobic substances, making them ideal targets for sampling in water using nonpolar passive sampling devices (PSDs).

Ten years after the adoption of the SC, an expert meeting was organised on 22–24 May 2011 in Brno, Czech Republic, by the Research Centre for Toxic Compounds in the Environment, which serves as Stockholm Convention Regional Centre for capacity building and transfer of technology in Central and Eastern European countries (Klanova et al. 2011). Among the ten priority areas identified by the participants, there was a need expressed to make better use of 'advanced and cost-effective sensors capable of providing *quasi-real time* concentrations at different latitudes'. This was felt to be particularly important to help with the Global Monitoring Plan (GMP), a key element to the Effectiveness Evaluation of the SC. Currently, the SC monitors human milk and air, with a call for adding water to the matrices being observed regularly (Lohmann and Muir 2010). Overall, there is a dearth of POPs concentrations measured in water, making it difficult to verify multimedia modelling approaches. Another priority area identified at the Brno meeting was to make POPs measurements integral to the Global Earth Observation System of Systems (GEOSS). The GMP of GEOSS aims to interlink existing information systems for environmental and health monitoring.

Regulators recognise the potentially prohibitive cost of incorrect actions based on the use of unrepresentative data in risk assessment. Passive sampling technology is proving to be a reliable and robust tool that could be used in monitoring programmes on a regional and global scale (EU 2009; Lohmann and Muir 2010). Passive sampling enables the determination of concentrations of dissolved contaminants, which is a fundamental part of an ecological risk assessment for chemical stressors (e.g. Leslie et al. 2002; Mayer and Holmstrup 2008).These devices are now being considered as part of a new strategy for monitoring a range of priority and emerging pollutants. The Advisory Committee on the Marine Environment of the International Council for Exploration of the Sea (ICES) recommended that the ICES member countries should continue working on passive sampling techniques as a monitoring tool. They further suggested to the Oslo and Paris Commission for the protection of the marine environment of the North-East Atlantic (OSPAR) that the draft guidelines for integrated monitoring should be formulated in such a way that these techniques can be included (ICES 2005). Although regulatory monitoring of organic contaminants under the European Union's Water Framework Directive (WFD) heavily relies on batch sampling followed by chemical analysis of unfiltered water sampling, the Pan-European drafting group for the chemical monitoring of surface water, sediment and biota under the WFD has listed passive sampling as a complementary method that can help to 'corroborate or contradict spot sampling data', improve water quality assessment and reduce monitoring costs, particularly when concentrations are low and time variable (EU 2009, 2010).

In the following, we present the state of the art of passive water sampling and discuss its suitability for regulatory monitoring, with an emphasis on the information provided by passive sampling results, their relevancy and associated uncertainties.

2 Role of passive sampling in water monitoring

2.1 Partitioning of POPs

Passive sampling methods can measure the concentration of freely dissolved contaminants (C_w), which is directly related to the contaminants' chemical activity (a_w) (Mayer et al. 2003):

$$a_w = \frac{C_w}{S_w} \quad (1)$$

where S_w is the contaminant solubility in water (at the same temperature and salinity). The difference in chemical activity between the two compartments quantifies the potential for spontaneous uptake. This also indicates the bioavailability or pressure (fugacity) of contaminants on organisms (Reichenberg and Mayer 2006) and consequently represents the exposure level for organisms. In an equilibrium situation, Eq. 1 can be extended to all environmental compartments like air, biota, but also sub-compartments such as suspended particulate matter (SPM) and dissolved organic matter (DOM). In non-equilibrium situations, the difference in chemical activity is the driving force for transport of compounds towards an equilibrium situation.

Nonpolar POPs are largely sorbed to particulate material, such that their freely dissolved concentrations are extremely

low. Large volumes of water often need to be sampled with the connected risk of contamination or losses through wall adsorption. Whole water sampling, as presently prescribed in the EU's Water Framework Directive (EU 2000) yields a very poor estimate of a compound's chemical activity, because of the large contribution of contaminant fractions that are bound to SPM and DOM. Similar problems occur with batch water sampling that is followed by filtration and extraction, because the SPM and DOM partly pass through the filter. Furthermore, the freely dissolved fraction may partly adsorb to the filter. Hermans et al. (1992) reported that concentrations of (operationally defined) 'dissolved' PCBs and HCB in coastal water samples were profoundly dependent on the SPM separation method used (filtration versus centrifugation), as well as on the extent of filter clogging. Risk assessment of such hydrophobic substances is therefore often done by estimating aqueous phase concentrations from concentrations in other environmental compartments, e.g. sediment, using equilibrium partition theory (Di Toro et al. 1991) and the appropriate partition coefficients.

$$C_w = \frac{C_{sed}}{K_d} = \frac{C_{SPM}}{K_{SPM}} = \frac{C_b}{BAF} \quad (2)$$

where K_d is the sediment–water partition coefficient, K_{SPM} is the SPM–water partition coefficient, *BAF* is the bioaccumulation factor and C_{sed}, C_{SPM} and C_b are the concentrations in sediment, SPM and biota. A practical problem with the application of Eq. 2 is that K_d, K_{SPM} and *BAF* depend on matrix properties (e.g. amount and quality of the organic carbon and lipids, physiological state of the organism).

Nonpolar passive sampling devices (PSDs) absorb hydrophobic compounds from the aqueous phase and concentrate them to a level that can be easily analysed with standard equipment, thereby avoiding the procedural errors that result from the processing of large water volumes needed in batch water sampling. Uptake is driven by the difference in chemical activity between the PSD and the surrounding environment. The use of nonporous and nonpolar polymeric membranes limits the uptake of particle bound compounds, because the transient cavity sizes that are formed by the random thermal motion of the polymer chains are of the order of 1 nm, which only allows the diffusion of single contaminant molecules (Huckins et al. 1993, 2006). The rate at which PSD–water equilibrium is attained depends on the contaminants, deployment conditions and the PSDs used. For highly hydrophobic compounds and for thick nonpolar PSDs, equilibrium attainment can take months to years. In this case, the samplers yield a time-weighted average C_w over the exposure period. By contrast, equilibrium can be attained within hours to days for compounds with low hydrophobicity and for thin PSDs. More details are given below.

Various PSDs are available for the sampling of POPs in water. The semi-permeable membrane device (SPMD) was the first sampler that was used on an appreciable scale (Huckins et al. 1993, 2006). The typical configuration is a 90-cm low-density polyethylene (LDPE) lay flat tubing of 2.5 cm wide (~460 cm^2 surface) with a wall thickness of ~70–95 μm, filled with 1 mL synthetic triolein. Single-phase polymeric sheets and films also have been used as a PSD: LDPE (Booij et al. 1998; Adams et al. 2007), silicone (Rusina et al. 2010b; Smedes et al. 2009) and polyoxymethylene (Jonker and Koelmans 2001; Cornelissen et al. 2008). A special version of the Chemcatcher was designed for the sampling of nonpolar organic compounds using an octanol-soaked C_{18} Empore disk as an adsorptive phase behind an LDPE membrane (Vrana et al. 2005). The surface area of these samplers can (within limits) be tailored to the needs for a particular sampling programme, but typically ranges between 10 and 1,000 cm^2. Chemical analysis of these samplers includes the conventional extraction and cleanup procedures, followed by injection of an aliquot of the final extract for instrumental analysis. By contrast, a group of other (much smaller) samplers are analysed without extraction and cleanup, by thermal desorption of analytes from the whole sampler, such as solid-phase micro extraction (Arthur and Pawliszyn 1990), stir bar sorptive extraction (Baltussen et al. 1999) and membrane-enclosed sorptive coating (Vrana et al. 2001). Although the principles of operation are similar to those of SPMDs and polymer strip samplers, these samplers appear to be less widely used in environmental monitoring, and our primary focus for this review will not be on this latter group.

2.2 PSDs versus biota

Biomonitoring is a widely used method for assessing environmental POP levels, as exemplified by the 'Mussel Watch Programs' (Goldberg 1975; Monirith et al. 2003; Kimbrough et al. 2009). Some well-known difficulties with biomonitoring are inter-species variability for programmes that cover a wide geographical area, the interaction between environmental conditions and contaminant uptake kinetics of the organisms, mortality and uncertainties that are associated with high initial concentrations in the case of transplanted organisms. Booij et al. (2006) evaluated literature data on co-deployed SPMDs and biota, and concluded that SPMDs yield more reliable estimates of exposure concentrations. SPMDs were deemed more reliable due to a better understanding of their contaminant uptake kinetics and less certainty in knowing in situ BAF values of the organisms. A 4-year monitoring study in Dutch coastal waters with PSDs and co-deployed mussels (eight stations, sampled twice per year) revealed a strong correlation between concentrations in mussels and PSD-derived aqueous concentrations (Smedes 2007). Similarly, a laboratory study in

which polychaetes and LDPE were exposed to contaminated sediments also showed a strong relationship between both sets of results (Friedman et al. 2009).

3 Theory of contaminant uptake by PSDs

3.1 Apolar POPs

The theory of contaminant uptake by nonpolar PSDs is well established (Vrana et al. 2001; Huckins et al. 2006; Booij et al. 2007). At the initial stage of the sampler deployment, the absorbed amounts (N_s) increase linearly with time (t) if the aqueous concentration (C_w) is constant

$$N_s = C_w R_s t \tag{3}$$

During the initial stage, the product $R_s t$ can be seen as the water volume that is extracted during the deployment (amount=concentration×volume), which is why R_s is known as the water sampling rate. At very long exposure times, the sampler equilibrates with the water, and the analyte amounts are given by

$$N_s = C_w K_{sw} m_s \tag{4}$$

where K_{sw} is the sampler–water partition coefficient. The product $K_{sw}\, m_s$ represents the water volume that is extracted by a given PSD at equilibrium. Eqs. 3 and 4 are special cases of the general uptake equation

$$N_s = C_w K_{sw} m_s \left[1 - \exp\left(-\frac{R_s\, t}{K_{sw} m_s}\right)\right] = C_w V_e \tag{5}$$

which is valid during the linear uptake stage (t→0), the equilibrium stage (t→∞), as well as for the transition stage in between. Eq. 5 is always exact, whereas Eqs. 3 and 4 are always approximate, though useful for back-of-the-envelope calculations. Equation 5 allows for estimating the effectively extracted water volume (V_e) at any deployment time, which helps to compare the results from passive sampling with those of batch sampling. Analytes differ widely in the rate at which sampler–water equilibrium is attained. The quotient $R_s/(K_{sw} m_s)$ in Eq. 5 is a first-order equilibration rate constant (k_e), and the characteristic time scale for equilibrium attainment (τ_{eq}) is given by

$$\tau_{eq} = \frac{1}{k_e} = \frac{K_{sw} m_s}{R_s} \tag{6}$$

Thus, compounds with low K_{sw} values quickly attain equilibrium (e.g. naphthalenes, HCHs). PSDs yield a time-integrated C_w for exposure times that are much shorter than τ_{eq}, and closely follow the (possibly variable) environmental C_w for $t >> \tau_{eq}$ (Hawker 2010). τ_{eq} may therefore be used to identify the time window for time-integrative sampling.

Analyte uptake includes advective and diffusive transfer from bulk water, through a water region with reduced turbulence and flow (the water boundary layer, WBL), via a biofilm (if present), into the membrane. In some PSD configurations, an additional sorption phase is present behind the membrane (e.g. triolein in the case of SPMDs, and octanol-soaked C_{18} bonded silica in the case of the nonpolar Chemcatcher). Each of the above transfer steps may be rate limiting, but in most cases, the uptake rates are either controlled by the membrane or by the WBL. Membrane control generally occurs for compounds with low logK_{ow} values and low diffusion coefficients in the membrane, and for PSDs that are exposed at high flows.

Aqueous concentrations can be calculated from the absorbed amounts, using Eq. 5, when K_{sw} and R_s are known. The accuracy of these C_w estimates obviously depends on the accuracy of these parameters, and the choice for one PSD or another should be based on the availability of high-quality calibration parameters for the compounds of interest (see Section 4.6).

In situ calibration of PSDs is necessary, because R_s depends on the exposure conditions, such as temperature, flow and biofouling. This in situ calibration is done by spiking the PSDs with performance reference compounds (PRCs) before exposure (Huckins et al. 2002). Suitable PRCs do not occur in the environment (e.g. isotopically labelled compounds), and have logK_{sw} values in the range 3–7 to ensure that dissipation data cover the full loss range between 0% and 100%. Sampling rates can be determined by fitting the retained PRC fraction (f) as a function of K_{sw} by nonlinear least-squares estimation (Booij and Smedes 2010)

$$f = \frac{N}{N_0} = \exp\left(-\frac{R_s\, t}{K_{sw} m_s}\right) \tag{7}$$

Because R_s not only depends on the exposure conditions, but also is weakly compound-dependent, a suitable sampling rate model should be chosen that relates R_s to compound properties, such as molecular size (see Section 4.6). Using the above method typically allows R_s to be estimated with a precision of about 10%. Uncertainties in the K_{sw} values of the PRCs may result in a bias of about 0.3 log units (Booij and Smedes 2010).

3.2 Polar POPs

With the addition of PFOS, HCH isomers and endosulfan to the SC, consideration has been given to include water as a recommended matrix in the GMP for POPs. Global oceans and large lake waters represent a major sink for PFOS, HCHs and endosulfan and to a lesser extent for other POPs. Nonpolar PSDs such as LDPE, silicone rubber or SPMD are

well applicable for monitoring of HCHs and endosulfane. Due to their low log K_{ow} values these substances attain sampler–water partition equilibrium within several days. Their integrative sampling can be extended by PSDs with a higher mass and/or a smaller surface area (Eq. 6). This also favours lower detection limits, because higher sampler mass implies a larger equivalent water volume that is extracted at equilibrium (Eq. 4). Passive sampling of PFOS presents a specific challenge due to its low affinity to hydrophobic polymer materials used in nonpolar PSDs. Although no quantitative studies aimed at quantification of PFOS and other fluorinated surfactants in water with PSDs have been reported, several studies reported identification of these compounds in adsorbent-based polar organic chemical integrative sampler extracts (Alvarez et al. 2007; Vrana et al. 2010). Performance of various PSDs for sampling PFOS in effluent from a wastewater treatment plant, including comparison with continuous water sampling, is recently being evaluated in an interlaboratory study organised by the NORMAN association (network of reference laboratories for monitoring emerging environmental pollutants, www.norman-network.net). The PSDs that are applied for these polar emerging organic compounds are based on analyte diffusion through microporous membranes and sorption to selective adsorbent materials. Accumulation of polar organic compounds by adsorbents is more complex than absorption of hydrophobic chemicals in nonporous polymers such as LDPE or PDMS. Adsorption distribution coefficients (unlike partition coefficients in sub-cooled liquid polymers) are obtained from sorption isotherms and are concentration-dependent, and competitive adsorption of non-target analytes cannot be ruled out. The PRC approach for in situ R_s estimation is complicated by strong sorption of most compounds to the adsorbents, and desorption kinetics are generally not isokinetic with the uptake. At present, the samplers for polar POPs are not sufficiently well understood to warrant their inclusion in regulatory monitoring, but intense research is being conducted to extend applicability of PSDs for quantitative assessment of polar waterborne contaminants (including PFOS). A position paper that reviews the state of the art has been presented by the NORMAN association (Vrana et al. 2010).

4 Quality assurance and quality control of passive sampling

A number of quality assurance issues that are specific for the use of PSDs should be considered before starting a monitoring project with these samplers, to ensure that the measured aqueous concentrations are fit for purpose. Most importantly, the available K_{sw} values and sampling rate models should be sufficiently accurate. The effect of uncertainties in K_{sw} and R_s on the final C_w estimate can be evaluated by applying the method of error propagation, using Eqs. 3 (kinetic sampling) or 4 (equilibrium sampling). For example, a bias of 0.3 log units in K_{sw} results in a bias of 0.3 log units in the C_w estimate of compounds that attain equilibrium during the exposure. In addition, an initial estimate of the detection limits should be evaluated, based on the analysis of solvent blanks, fabrication control PSDs and field control PSDs (Petty et al. 2000; Huckins et al. 2006; ISO 2011).

4.1 Accuracy of K_{sw}

The accuracy of K_{sw} values is often difficult to assess. For many compound–sampler combinations, only values from a single study are available, often with a very small reported error that is based on replicates in one experiment. Interlaboratory variability (ILV) data yield more realistic error estimates. For LDPE, this ILV amounts to 0.18 log units (RMS value for 18 PCBs and 9 PAHs, based on two to seven laboratories, temperature range 18–24°C), except for the PAHs with five or six aromatic rings, for which the ILV was 0.78 log units (two to four studies) (Muller et al. 2001; Booij et al. 2003b; Adams et al. 2007; Cornelissen et al. 2008; Smedes et al. 2009; Perron et al. 2009; Fernandez et al. 2009b; Hale et al. 2010). For SPMDs, the ILV was estimated from the (salinity-corrected) data compilation by Huckins et al. (2006) as 0.21 log units (RMS value for one PCB and seven PAHs, two to three studies). The ILV for PDMS was estimated from the data compilation by Difilippo and Eganhouse (2010) as 0.45 log units (RMS value based on SPME fibres, PDMS sheets and PDMS traps at 25°C for studies that passed the quality criteria defined by these authors; 11 PAHs, 9 PCBs, 5 chlorobenzenes, 4 BTEX compounds, 6 pesticides, but excluding the pyrethroids; two to nine studies). ILV did not increase with hydrophobicity in this data set. Because not all silicone rubbers are pure PDMS, but may contain fillers and functional groups, users of silicone rubbers should carefully identify the source of the polymer that they intend to use. Differences in K_{sw} values of PCBs and PAHs for silicone rubbers from different sources may differ by up to 0.55 log units (Smedes et al. 2009). For the nonpolar Chemcatcher K_{sw} data are only available from a single study (Vrana et al. 2006). The accuracy of K_{sw} is only critical for compounds that reach (partial) PSD–water equilibrium, and is irrelevant for compounds that remain in the linear uptake stage (c.f., Eq. 3). However, the accuracy of C_w estimates for the latter group strongly depends on the accuracy of R_s, which in turn largely depends on the quality of the K_{sw} values of the PRCs (c.f., Eq. 7).

4.2 Effect of temperature and salinity

The effects of temperature and salinity on K_{sw} are small and well established. The temperature effect on K_{sw} can be estimated using the Van't Hoff equation

$$\log K_{sw,2} = \log K_{sw,1} - \frac{\Delta H_{sw}}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (8)$$

where ΔH_{sw} is the water–sampler transfer enthalpy, T is the absolute temperature and R is the gas constant. Adams et al. (2007) showed for two PAHs and one PCB that ΔH_{sw} for LDPE may be estimated from

$$\begin{aligned} &\text{for } T < T_m : \Delta H_{sw} = \Delta H_{fus} - \Delta H_{sol} \\ &\text{for } T \geq T_m : \Delta H_{sw} = -\Delta H_{sol} \end{aligned} \quad (9)$$

where ΔH_{fus} is enthalpy of fusion, ΔH_{sol} is the enthalpy of solution and T_m is the melting temperature of the target analyte. These authors report ΔH_{sw} values between −12 and −29 kJ mol^{-1}, which indicates a decrease in K_{sw} by a factor of 1.2 to 1.5 for a 10°C temperature increase. Similar ΔH_{sw} values can be estimated from the logK_{sw} values reported by Booij et al. (−9 to −45 kJ mol^{-1}) (Booij et al. 2003b). Muijs and Jonker (2009) report water–PDMS transfer enthalpies of PAHs to decrease with molecular size from −16 kJ mol^{-1} for phenanthrene to −35 kJ mol^{-1} for indeno [1,2,3-*cd*]pyrene, i.e. similar to the ΔH_{sw} for LDPE. Lohmann (2012) suggested using a value of ΔH_{sw} of −25 kJ mol^{-1} for nonpolar compounds. The K_{sw} of chlorobenzenes, PCBs, PAHs and DDE for SPMDs appears to be largely independent of temperature (Booij et al. 2003b; Huckins et al. 2002), possibly with the exception of phenanthrene, for which ΔH_{sw} values of +5 and −23 kJ mol^{-1} have been found.

The effect of dissolved salts on the K_{sw} of nonpolar compounds is small, and can be calculated from the Setschenow equation,

$$\log K_{sw} = \log K_{sw,0} + K_s I \quad (10)$$

where I is the ionic strength (in moles per liter), K_s is the Setschenow constant (in liters per mole) and $K_{sw,0}$ is the sampler–water partition coefficient at an ionic strength of 0. Xie et al. (1997) showed that K_s increases with increasing LeBas molar volume (V_{LeBas}) of the analyte from 0.1 to 0.3 L mol^{-1} when V_{LeBas} increases from 60 to 180 cm^3 mol^{-1} and levels off to a constant value of 0.3 Lmol^{-1} for larger compounds. Jonker and Muijs (2010) reported K_s=0.35±0.02 L mol^{-1} for PAHs with three to six aromatic rings (V_{LeBas} >197 cm^3 mol^{-1}). Adopting an ionic strength of average seawater at 20°C of 0.713 mol L^{-1} (Millero and Sohn 1992; Millero and Huang 2009), and a Setschenow constant of 0.35 Lmol^{-1}, the salt effect on K_{sw} can be seen to be smaller than 0.25 log units in most environments.

The uncertainties in the temperature and ionic strength corrections on K_{sw} are small. With the temperature correction, an error in ΔH_{sw} of 10 kJ mol^{-1} results in a 15% error in K_{sw} over a 10°C temperature range (~ 0.06 log units). Similarly, if the Setschenow constant used is off by 0.1 Lmol^{-1}, then this results in an error in K_{sw} of only 18% for average seawater. This leaves the K_{sw} values determined in ultrapure water as the primary source of error: 0.18 to 0.45 log units, depending on the compound and the sampler. The primary challenge with nonpolar samplers is therefore to reduce the inter-laboratory variability in K_{sw} determinations, rather than to test 'novel' PSDs equipped with yet another sampling matrix.

4.3 Estimating K_{sw}

When experimental values are not available, K_{sw} has to be estimated from empirical correlations with compound properties, and PSD users have to check if the accuracy of these correlations is sufficient, prior to starting a sampling project. Traditionally, correlations with logK_{ow} have been widely used, but this method suffers from the fact that logK_{ow} values often have an uncertainty of about 0.2 log units or more, possibly with the exception of values that have been optimised for thermodynamical consistency (Beyer et al. 2002; Aberg et al. 2008; Ma et al. 2010; Schenker et al. 2005; Shen and Wania 2005; Li et al. 2003; Xiao et al. 2004). Alternatively, K_{sw} values can be estimated using polyparameter linear free energy relationships (Sprunger et al. 2007; Arp et al. 2010; Difilippo and Eganhouse 2010; Endo et al. 2011). Again, the accuracy of K_{sw} is only an issue for PRCs and for target analytes that attain equilibrium with the sampler.

4.4 Accuracy of the R_s model

The next step is to determine if the sampling rate model to be used in Eqs. 3 and 5 is sufficiently reliable. It is well established that sampling rates are limited by diffusion into the sampler for compounds with low K_{ow} values and by transport through the WBL for analytes with high hydrophobicity (Vaes et al. 1996; Leslie et al. 2002;Booij et al. 2003b; 2007; Huckins et al. 2006). The modelling of WBL-controlled uptake is relatively straightforward. Hydrodynamic theory and evidence from the chemical engineering literature states that sampling rates are proportional to the aqueous diffusion coefficient to the power $^2/_3$ (Levich 1962; Boudreau and Guinasso 1982; Booij et al. 2007; Knudsen et al. 1999; Stephens et al. 2005), which only leaves the proportionality constant to be derived from PRC dissipation data. Experimental values of diffusion coefficients of organic contaminants are virtually absent, but the necessary estimates may be obtained from semi-empirical correlations with molar mass (M) or molar volume. Thus, depending on the diffusion coefficient model that is used,

R_s is expected to be proportional to $M^{-0.35}$(Booij et al. 2003b), $M^{-0.47}$ (Rusina et al. 2010b), $V_{LeBas}^{-0.39}$(Huckins et al. 2006). For example, the sampling rate of PCB180 is expected to be smaller than that of phenanthrene by a factor of 1.3, 1.4 and 1.2, respectively. Because molecular size and hydrophobicity are strongly correlated for nonpolar compounds, a weak decrease in R_s with increasing K_{ow} can be expected. Thus, Leslie et al. (2002) found for SPME fibres that R_s/V_s (k_1 in the terminology of these authors) is virtually independent of K_{ow} in the range $3<K_{ow}<6$. Booij et al. (2003b) found for SPMDs that R_s was proportional to $K_{ow}^{-0.044}$, and for silicone rubber strips, Rusina et al. (2010b) reported R_s to be proportional to $K_{sw}^{-0.08}$ and $K_{ow}^{-0.08}$. Empirical R_s models for SPMDs and Chemcatcher predict the R_s of PCB180 to be lower compared with pyrene, by a factor of 2.6 and 14, respectively (Huckins et al. 2006; Vrana et al. 2007). This stronger K_{ow} dependency has been attributed to experimental artefacts caused by sorption to dissolved organic matter in the exposure system, but this hypothesis has not yet been confirmed. Users have to weigh the reliability of these models prior to starting a PSD-based monitoring study for themselves, but our advice is to stick to the models that have a sound theoretical basis and an experimental confirmation.

By contrast, the modelling of membrane controlled uptake is rather complex, because the sampling rates decrease with time, as a result of the fact that the analytes penetrate further into the sampler during the deployment. In addition, diffusion coefficients in the membrane have to be available. A practical but approximate solution is to establish an empirical correlation between membrane-controlled sampling rates and $\log K_{ow}$ at different temperatures, and to assume linear concentration gradients in the membrane, that extend to half the membrane thickness (Booij et al. 2003a, b). More sophisticated solutions for partial and complete membrane controlled uptake are discussed by Fernandez et al. (2009a). Membrane controlled uptake only has to be considered in some exceptional cases, such as very short exposure times (<1 week) and very high mass transfer rates, such as encountered during PSD exposure in sediments, slurries and very high water flow rates (>10 ms^{-1}). In most cases, the compounds that experience membrane-controlled uptake also attain equilibrium during the exposure period. As a rule of thumb, it can be assumed that the uptake is membrane controlled for compounds with $\log K_{ow}<4.5$ for LDPE and SPMDs, and $\log K_{ow}<3.5$ for silicone samplers, except for some rare cases where very high sampling rates are observed. WBL control of the uptake can always be estimated afterwards from

$$R_s \ll \frac{AD_m K_{mw}}{\delta_m} \quad (11)$$

where D_m is the diffusion coefficient in the membrane (Rusina et al. 2007, 2010a; Adams et al. 2007; Hale et al. 2010), R_s is obtained from PRC dissipation data, A is the surface of the sampler, K_{mw} is the membrane–water partition coefficient and δ_m is the membrane thickness for biphasic samplers (SPMD, Chemcatcher) or half the sampler thickness for single-phase samplers of which both sides are exposed. The role of the membrane in the uptake can be neglected if Eq. 11 is satisfied for a PRC that is 50% dissipated.

4.5 Detection limits

After assuring the quality of K_{sw} and the R_s model, the expected detection limits should be assessed from the amounts detected in fabrication controls and field controls. Fabrication controls yield information on the contaminant amounts that are taken up from the laboratory atmosphere during construction. The field controls yield information on analyte uptake during transport and deployment/retrieval operations. Initial approximations of the detection limits can be obtained from Eq. 5 by substituting the average amounts detected in the field control samples or the limit of detection of the analytical method if the compound was not detected. Required estimates of the sampling rate can of course only be obtained after the exposure, but an initial estimate of R_s/A of 2–5 $L dm^{-2}$ day^{-1} usually is a realistic range to work with if the true value of R_s is not yet known.

4.6 Quality control

A number of quality control measures are needed to certify the quality of a running PSD-based monitoring project. These include the analysis of solvent blanks, fabrication controls, field controls and matrix spikes. Comparison of solvent blanks, fabrication controls and field controls can help to identify possible sources of contamination, after which appropriate measures can be taken. Blank subtraction may be done for analytes that were in the linear uptake stage during the exposure, as inferred from PRC dissipation data. Blank subtraction should not be done for compounds that attain (partial) equilibrium, because the amounts detected in exposed PSDs can be lower than those in the field controls, due to dissipation of pre-deployment contamination during the exposure. A conservative sample rejection criterion is to set the minimum amount in exposed samplers to ten times the amounts detected in the field controls, and to review sampler construction and transport operations if this condition is not met. A further quality control parameter is the precision of the PRC-based sampling rates. The quantitation of a highly hydrophobic PRC that is insignificantly dissipated also yields useful information on the precision of the chemical analysis on a per sample basis.

4.7 Standardisation

Progress has been made on the normation of passive sampling methods for their use in monitoring water quality. In March 2011, an ISO standard has been published that specifies procedures for the determination of time-weighted average concentrations and equilibrium concentrations of dissolved organic, organometallic and inorganic substances, including metals, in surface water by passive sampling, followed by analysis (ISO 2011).

Collaborative studies are required to obtain information about the robustness of the whole sampling process including instrumental analysis, sampler calibration and field sampling. Several collaborative exercises were performed recently with the aim to compare performance of various samplers. Allan et al. (2009) evaluated the performance of seven PSDs for the monitoring of PAHs, PCBs, HCB and *p,p'*-DDE through simultaneous field exposures of 7–28 days in the River Meuse. Despite the absence of the analytical comparability test of participating laboratories and different modes of calculation, relatively consistent C_w values were obtained for the different samplers and sources of observed variability were critically discussed. In 2010, the French national water reference laboratory AQUAREF (www.aquaref.fr) organised an inter-laboratory study targeting compounds relevant in chemical monitoring under the WFD, including PAHs, heavy metals and polar pesticides. Another study aimed at monitoring of emerging pollutants was organised by NORMAN. The latter two exercises were designed to cover individual aspects in the passive sampling process, including analytical comparability and, where it was possible, comparison with conventional sampling of water. The results of these studies will be available in 2012.

More proficiency testing schemes are needed for the most frequently used PSD designs to evaluate the contribution of the analytical uncertainty component to total variability of the sampling process. Inter-laboratory studies that compare the performance of various available passive sampler designs at a reference site will allow a realistic evaluation of passive sampling variability for the tested compounds and give information whether a particular passive sampling method provides a satisfactory result within an agreed performance interval. Finally, campaigns where water samples are analysed in parallel with passive samplers are required to evaluate the comparability of these two methods.

5 Application of passive samplers in regulatory monitoring

We are not aware of any cases yet where PSDs have already been accepted for compliance checking. So far, the use of PSDs in monitoring programmes has been limited to occasional studies. PSDs have been used by a number of governmental agencies in the USA (e.g. US Geological Survey, US Environmental Protection Agency, US National Park Service, US Fish and Wildlife Service, Virginia Department of Environmental Quality, Washington State Department of Ecology), the United Kingdom (UK Environment Agency) and the Czech Republic (Institute of Public Health) (ITRC 2006). The Dutch monitoring authorities have used PSDs for trend monitoring since 2001 at eight coastal stations (Smedes et al. 2007), and included several freshwater stations in 2008. Beside this in many other countries (e.g. Australia, Belgium, France, Germany, Ireland, Norway, Slovakia, Sweden and Switzerland), trials and/or repeated sampling using PSDs is occurring, although mainly on project basis. Within ICES/OSPAR, a trial survey was organised in 2006 in order to investigate the possibilities of passive sampling for OSPAR monitoring. In a mutual effort 13 laboratories sampled 30 stations all over Europe demonstrating the potential of PSDs for wide-scale monitoring (Smedes et al. 2007).

For many POPs, regulatory limit values such as EU environmental quality standards (Lepom et al. 2009) refer to concentrations in water that are extremely low (low nanograms per liter) and traditionally established low-volume water sampling techniques very often fail to comply with minimum performance criteria in terms of limit of quantification and measurement uncertainty. Alternative, more sensitive sampling techniques, such as high-volume sampling devices are costly and hardly applicable in monitoring campaigns on a large scale. Moreover, discontinuous water sampling with a low sampling frequency may not provide information with required confidence and precision for compliance checking where concentrations of pollutants fluctuate in time (e.g. with seasonal variation in use of pesticides or sporadic industrial discharges). The unique performance characteristics of passive samplers that include their time integrative nature combined with extremely low limits of quantification for most POPs may represent the only practicable way to monitor these substances in the water column. Since reliable values of K_{sw} and R_s with associated uncertainty can be derived for most of priority pollutant POPs in nonpolar PSDs such as LDPE and silicone rubbers, fulfilment of legally binding minimum method performance criteria and QA/QC provisions for compliance checking can be demonstrated.

6 Summary and recommendations

PSDs can effectively be used as a tool in regulatory monitoring as the obtained freely dissolved concentration is a strong indicator for exposure to aqueous organisms. PSDs are suitable matrices for trend monitoring of hydrophobic

POPs because they integrate concentration fluctuations in time in a specific water body and long-term comparisons can be made with lower sampling frequency at the required sensitivity and statistical power to detect temporal or spatial trends. The major advantage of PSDs over alternative matrices used for trend monitoring, e.g. sediments or biota, is that PSDs constitute a well-defined sample medium with known uptake capacity. In contrast to results based on sediment or biota, PSD data require no corrections for organic carbon, lipid content or species to compare data on a worldwide scale. Passive samplers can safely be sent around and deployment requires no specialists, making it possible to monitor POPs across the world. Furthermore, different sources of variance including analytical and environmental variance can be much better controlled, which in turn results in reduction of the required number of analysed samples to obtain results with comparable statistical power. Compliance checking with regulatory limits and analysis of temporal and spatial contaminant trends are two possible fields of application. The objection against passive sampling has been that PSDs are qualitative (or at best semi-quantitative) tools for assessing water quality. In the present article, we argue that PSDs can now be regarded as fully quantitative tools with well-defined accuracy and precision that allow concentrations of dissolved organic contaminants to be compared against legal standards. This would require an adaptation of legal standards away from total concentrations towards dissolved concentrations that better reflect the compound's chemical activity and related exposure level in the environment.

Meanwhile, the scientific community should take further steps towards improving the accuracy and precision of passive sampling technology, by means of inter-laboratory comparison studies and inter-calibration studies. The focus of these studies should be on PSD handling, chemical analysis and data processing, as well as on the development of strict protocols for the accurate determination of PSD–water partition coefficients. In addition, further research is needed for improving the accuracy of PSDs for polar organic compounds.

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Príloha 23

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Estrogen-, androgen- and aryl hydrocarbon receptor mediated activities in passive and composite samples from municipal waste and surface waters

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ABSTRACT

Passive and composite sampling in combination with *in vitro* bioassays and identification and quantification of individual chemicals were applied to characterize pollution by compounds with several specific modes of action in urban area in the basin of two rivers, with 400,000 inhabitants and a variety of industrial activities. Two types of passive samplers, semipermeable membrane devices (SPMD) for hydrophobic contaminants and polar organic chemical integrative samplers (POCIS) for polar compounds such as pesticides and pharmaceuticals, were used to sample wastewater treatment plant (WWTP) influent and effluent as well as rivers upstream and downstream of the urban complex and the WWTP. Compounds with endocrine disruptive potency were detected in river water and WWTP influent and effluent. Year-round, monthly assessment of waste waters by bioassays documented estrogenic, androgenic and dioxin-like potency as well as cytotoxicity in influent waters of the WWTP and allowed characterization of seasonal variability of these biological potentials in waste waters. The WWTP effectively removed cytotoxic compounds, xenoestrogens and xenoandrogens. There was significant variability in treatment efficiency of dioxin-like potency. The study indicates that the WWTP, despite its up-to-date technology, can contribute endocrine disrupting compounds to the river. Riverine samples exhibited dioxin-like, antiestrogenic and antiandrogenic potencies. The study design enabled characterization of effects of the urban complex and the WWTP on the river. Concentrations of PAHs and contaminants and specific biological potencies sampled by POCIS decreased as a function of distance from the city.

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1. Introduction

There is increasing evidence that environmental contaminants have the potential to disrupt endocrine processes. This might result in adverse effects on reproduction, cause certain cancers, and other toxicities related to (sexual) differentiation, growth, and development (Giesy et al., 2000; Miles-Richardson et al., 1999; Sanderson and van den Berg, 2003; Snyder et al., 2000). A variety of pollutants that are found in surface and waste waters, such as organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polychlorinated dioxins and furans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs), alkylphenols, synthetic steroids, pesticides, pharmaceuticals and personal care products (PPCPs), but also natural products such as phytoestrogens, have been shown to elicit endocrine disruptive effects.

Sources of endocrine disrupting compounds (EDCs) are associated with larger urbanized and industrial areas. However, influences of smaller local sources can also be significant, especially where dilution is minimal (Jarosova et al., 2012). EDCs are also released to aquatic environments from both municipal and various industrial waste waters (Garcia-Reyero et al., 2004). Relative contributions of EDCs to surface waters depend on efficacies of sewage treatment systems, which is dependent on both capacity and technology of the wastewater treatment plant (WWTP). Potential risks of adverse effects of effluents from WWTPs to aquatic environments are influenced by volume of effluent, discharge of the receiving river, weather conditions and probably other factors that affect dissipation through dilution and/or degradation (Sumpter, 1995). Wastewater treatment plants receive mixtures of molecules from domestic, agricultural, and/or industrial wastes and

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thus waste waters can contain mixtures of many of the above listed pollutants and their degradation products (Alvarez et al., 2005). Despite intensive removal of xenobiotics by municipal WWTPs, which can range from 88 to >99% and 96 to >99% for xenoestrogens and xenoandrogens, respectively (Korner et al., 2000; Leusch et al., 2010; Murk et al., 2002; Svenson and Allard, 2004), they often do not remove all chemicals from the effluent. Moreover, during treatment some contaminants can be deconjugated to their more biologically active forms (Desbrow et al., 1998). Thus, most effluents still contain complex mixtures of molecules, including transformation products formed during treatment.

Adverse effects on endocrine function and/or reproductive health associated with exposure to effluents from WWTPs, which can persist several kilometers from the point of effluent entry (Harries et al., 1996), have been demonstrated in wild fish populations (Jobling et al., 1998) or fishes caged downstream from WWTPs (Snyder et al., 2004). Several studies combining the use of chemical analyses and *in vitro* assays have revealed steroid estrogens as the most potent endocrine disruptors in WWTP effluents with thresholds for adverse effects of a few ng/L (Korner et al., 2000; Matsui et al., 2000; Nakada et al., 2004; Routledge et al., 1998; Snyder et al., 2000). However, other EDCs can be effective in various landuse conditions (Sole et al., 2000) and special consideration should be paid to mixtures of pollutants. Also, more information is needed to assess the potential contribution from other sources than just the WWTPs.

Selection of an appropriate sampling approach is crucial to determining the presence of contaminants and assessment of their potential for effects on aquatic environment. Traditional grab samples represent the immediate situation, thus only those contaminants present at the time of sampling are characterized. Episodic events such as spills or stormwater runoff can be missed since contaminants can dissipate prior to the next sampling (Alvarez et al., 2005; Huckins et al., 1990, 1993). A more representative way to sample, that represents an integrated estimate of the time-averaged exposure is composite samples collected over time. But, even this type of extensive sampling represents isolated conditions over relatively short durations. This sort of intensive sampling program is resource-intensive, requiring sampling staff and/or special equipment, which cannot be easily employed at many sites, especially at locations where equipment might be at risk to vandalism.

An alternative protocol is passive sampling, which enables estimation of time-weighted concentrations of contaminants and sequesters residues from episodic events commonly not detected by use of intermitent grab sampling. Passive sampling requires minimal resources of both personnel and equipment. Passive samplers have no moving parts to fail and require no electricity to function. They can be placed out of sight to avoid vandalism. Passive sampling can be used in situations of variable water conditions and because they concentrate residues from water they can enable detection of ultra-trace, yet toxicologically relevant concentrations of contaminant mixtures over extended durations (Alvarez et al., 2004). Other advantages include relatively simple, single deployment as compared to collecting and processing multiple water samples, greater mass of chemical residues sequestered, and the ability to detect chemicals which dissipate quickly (Alvarez et al., 2005; Huckins et al., 1990). Passive sampling also eliminates the need for some tedious and time-consuming clean-up steps associated with other types of sample collection.

Semipermeable membrane devices (SPMDs) have been developed as *in situ*, integrating passive samplers for monitoring of trace-level, waterborne hydrophobic contaminants (Huckins et al., 1993) and have been used for effective sampling of multiple classes of chemicals, including PAHs, PCBs, OCPs, PCDD/Fs, alkylated phenols, moderately polar organophosphate insecticides, pyrethroid insecticides, neutral organometallic compounds, and certain heterocyclic aromatic compounds (Petty et al., 2000a). Since SPMDs can mimic accumulation by aquatic organisms that can bioconcentrate trace amounts of organic contaminants, SPMDs measure not only the presence, but also the bioavailability and bioconcentration potential of organic contaminants (Huckins et al., 1990; Petty et al., 2000b). Polar Organic Chemical Integrative Samplers (POCIS) sequester waterborne hydrophilic contaminants, such as polar pesticides, pharmaceuticals, ingredients from personal care and consumer products, natural and synthetic hormones (Alvarez et al., 2004, 2005; Petty et al., 2004). Depending on the sorbent used, POCIS can be modified for sampling of general hydrophilic contaminants or pharmaceuticals (Alvarez et al., 2005).

The aim of this study was characterization of the influence of the industrialized urban region of Brno, Czech Republic and its associated municipal WWTP on contamination of the Svratka and Svitava rivers by compounds with endocrine disruptive potency by joint use of bioassays, two types of passive samplers and identification and quantification of selected organic chemicals. One goal was to assess the year-round variability in endocrine disruptive potency of WWTP influent and effluent water and thus treatment efficiency for EDCs by collecting composite samples monthly. The second major goal was to determine the relative magnitude of contributions of the urban area and the WWTP on contamination of these two urban rivers by endocrine disruptive compounds that can modulate the arylhydrocarbon (AhR), estrogen (ER) and androgen (AR) receptors. A battery of *in vitro* bioassays was used to assess potencies of agonists of these three receptors. Two types of passive samplers, POCIS and SPMD, were used to collect integrated samples of hydrophobic and hydrophilic compounds and assess their potencies to interfere with the three receptors signalling.

2. Materials and methods

2.1. Sampling design

Samples were collected from the region around Brno, the second largest metropolitan district of the Czech Republic in Central Europe. The metropolitan region of Brno with more than 400,000 inhabitants is spread through the basin formed by the Svratka and Svitava Rivers. The city has a central wastewater treatment plant and a variety of industrial activities. The municipal WWTP treats wastewater conveyed by a system of sanitary sewers from the city of Brno and increasingly also by a system of pumping stations from its surroundings. The WWTP was recently reconstructed and enhanced to a capacity of 513,000 population equivalent with permissible volume of discharged wastewater of 4222 L/s. Waste water is subjected to primary (mechanical) treatment followed by biological stage of activation with pre-denitrification and anaerobic phosphorus removal (system of circulatory activation with change of anaerobic, anoxic and aerated zones). Excess activated sludge is then anaerobically stabilized (Brněnské vodárny a kanalizace, 2010; Ministry of the Environment, 2010).

The influent and effluent of the WWTP were sampled monthly from May 2007 until April 2008. In addition, SPMD and POCIS passive samplers were placed in the influent (*site 5*) and effluent (*site 6*) of the WWTP and at seven sites in the Svratka, Svitava and Bobrava Rivers at locations upstream and downstream of Brno and downstream of the WWTP effluent (Fig. 1). Passive samplers were deployed for 23 days and collected during October 2007. Sampling locations in the Svratka River were: *Knínicky* (*site 1*) upstream of the city of Brno (downstream of the dam of Brno reservoir) and a site downstream of Brno upstream of the confluence with the Svitava River (*Svratka before confluence*, *site 2*). Locations monitored in the Svitava River included *Bílovice* and *Svitavou* (*site 3*), a small town upstream of Brno, and another site downstream of Brno upstream of the confluence with the Svratka River (*Svitava before confluence*, *site 4*). Another sampling site was selected in the *Bobrava River* (*site 9*), which is a tributary affected mostly by agriculture that flows into the Svratka River downstream of the WWTP. Downstream of the WWTP and the confluence of the Bobrava and Svratka rivers samples were collected near a small town *Rajhradice (site 7)* and at *Zidlochovice* (*site 8*, approximately 20 km downstream from Brno).

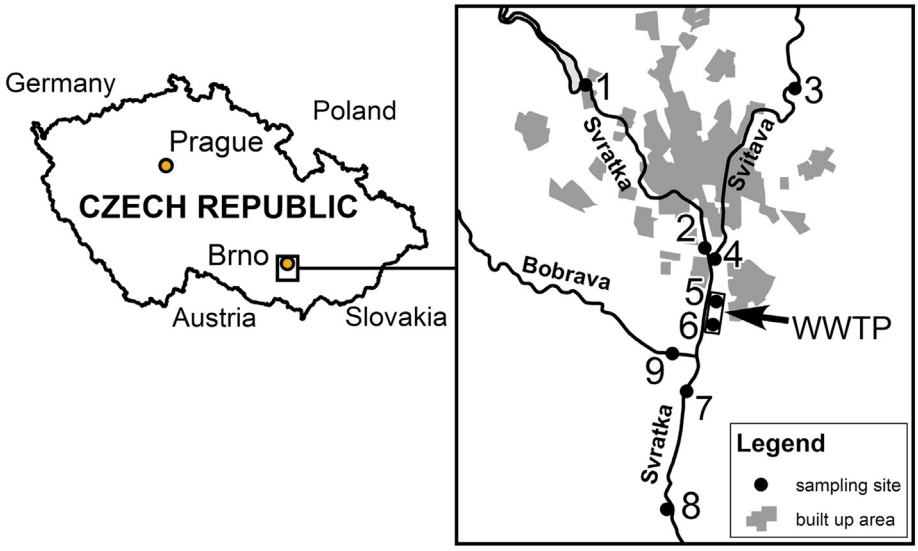

Fig. 1. Map of the Czech Republic showing locations of sampling sites in the vicinity of Brno. Sampling sites: 1—Svratka River, Knínicky, 2—Svratka River before confluence, 3—Svitava River, Bílovice nad Svitavou, 4—Svitava River before confluence, 5—WWTP Modřice, influent, 6—WWTP Modřice, effluent, 7—Svratka River, Rajhradice, 8—Svratka River, Zidlochovice, 9—Bobrava River.

2.2. Passsive water sampling and preparation of extracts

SPMD and POCIS disks were obtained from Exposmeter AB, Tavelsjo, Sweden. Prior to passive sampling, the sampling protocol was prepared with QA/QC. One POCIS was used for both chemical analysis and bioassay testing. Two SPMDs were used in duplicates for chemical analysis, one SPMD was used for toxicity assessment. SPMDs for chemical analysis contained performance reference compounds (PRC) used as onsite SPMDs calibration. Four deuterated PAHs ([$^2H_{10}$]acenaphthene, [$^2H_{10}$]fluorene, [$^2H_{10}$]phenanthrene, and [$^2H_{12}$]chrysene) and four $^{13}C_{12}$-labeled PCBs (PCB 3, 8, 37, and 54) were used as PRCs. Transport, field and laboratory blanks were used. A standard sampling arrangement was used as described in Grabic et al. (2010). It consists of a combination of POCIS and SPMDs mounted on commercially available stainless steel holders in protective deployment canisters made of perforated stainless steel plates. These samplers were suspended at 0.5–1 m depth of the water column in cryptic locations to minimize vandalism. After exposure for 23 days, samplers were recovered, cleaned and sealed in airtight, metal cans and placed on ice in a cooler for transport to the laboratory. Membranes were stored in sealed cans in a freezer at −18 °C until analysis. Before analysis SPMDs were cleaned and dialyzed with hexane in accordance with previously published methods (Ellis et al., 1995). Combined dialysates were adjusted to a volume of 10 mL. Chemical residues sampled by POCIS were recovered from the sorbent by organic solvent elution with a combination of methanol:toluene:dichloromethane (1:1:8, v/v/v). Volumes of all extracts were reduced by rotary evaporation and under a gentle stream of nitrogen, then solvent was exchanged to methanol (Alvarez et al., 2005). The final equivalent concentrations were 1 sampler/mL. A portion of each extract was transferred into DMSO for testing in bioassays.

2.3. Processing of waste water

Samples of influent and effluent were collected from the municipal WWTP on the Svratka River, downstream of Brno, once a month for 12 months. Water was collected every 2 h and composited over a 24-h period. Samples of influent were prefiltered through glass wool and 47 mm diameter glass fiber filter with 2.7 μm pores (Filap, Czech Republic) and both influent and effluent samples were filtered through glass fiber filters (1 μm pores, Whatman, Sigma-Aldrich, Czech Republic) to prevent solid phase extraction (SPE) cartridges from clogging during later extraction. Filters were extracted and tested separately to ensure that no compounds with significant potency in any of the assays were removed by filtration. Organic compounds in filtrates were extracted within 24 h by SPE by use of Oasis HLB cartridges (Waters, Czech Republic). Cartridges were activated by methanol and equilibrated by water according to producer instructions. After samples had passed through cartridges, they were dried by air for 10–15 min and eluted by use of 15 mL methanol. Extracts were rotary evaporated to reduce the volume to approximately 2 mL and then evaporated in a gentle stream of nitrogen to final volumes of 1 mL.

2.4. Instrumental analyses

Organic extracts of SPMD and POCIS samplers were analyzed for wide range of organic compounds. Samples were analyzed in accordance with standard EN ISO/IEC 17025. Detailed analytical procedures were described in Grabic et al. (2010). A set of internal standards was used in the analyses. These included carbon $^{13}C_{12}$-labeled PCBs (3, 15, 31, 52, 118, 153, 180, 194, 206, 209), TCS, PFOC (perfluorooctanesulfonic acid [PFOS], perfluoro-nonanoic acid [PFNA], perfluoro-octanoid acid [PFOA]), and native standards purchased from Wellington Laboratories (Canada). ^{13}C-labeled OCPs (γ-HCH and DDE), PAH ($^{13}C_{2-6}$-labeled PAHs U.S. Environmental Protection Agency [U.S. EPA] 16 PAH cocktail), and polar compounds (simazine, 2,4-D, sulfamethoxazol, ciprofloxacin) were purchased from Cambridge Isotope Laboratories (USA). The native ones were purchased from Dr. Ehrenstorfer, AccuStandards, and Absolute Standards via Labicom (Czech Republic). All solvents, including hexane, dichloromethane, acetone, toluene (SupraSolv purity), water, and methanol (hypergrade for LC/MS) were of the highest quality from Merck (Germany). Organic extracts of SPMDs were characterized by quantifying 16 US EPA polycyclic aromatic hydrocarbons (PAH): acenaphthene, acenaphthylene, anthracene, benzo[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*ghi*]perylene, benzo[*k*]fluoranthene, chrysene, dibenzo[*a*,*h*]anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene), polychlorinated biphenyls (PCBs): tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and deca-congeners, organochlorine pesticides (OCPs): hexachlorbenzene, α-, β-, γ-, δ-stereoisomers of hexachlorohexane (HCH), two congeners of dichlorodiphenyltrichloroethane (DDT) and its degradation products,

dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD), triclosan (TCS) and its environmental transformation product methyl triclosan (MeTCS) and polybrominated diphenyl ethers (PBDEs), expressed as the sum of congeners. POCIS extracts were analyzed for polar pesticides, pharmaceuticals and perfluorinated compounds (PFCs), expressed as the sum of perfluoroorganic compounds (PFHxS, FHUEA, FOSA, N-MeFOSA, PFOA, PFOS, PFNA). A complete list of individual pesticides and pharmaceuticals analyzed in POCIS is attached in footnotes to Table 1. Gas chromatography/mass spectrometry (GC/MS) was used for identification and quantification of PAHs. PAHs with more rings that could not be analyzed by use of GC/MS were analyzed by use of high performance liquid chromatography with fluorescence detector (HPLC/FLD). Quantification of PCBs, OCPs, PBDEs, triclosan and its metabolite were performed by GC/MS-MS. Polar pesticides, pharmaceuticals and PFCs were identified and quantified by use of HPLC/MS-MS.

Limits of detection for identified groups of chemicals were as follows: PAHs 3 ng/SPMD, MeTCS/TCS 3 ng/SPMD, OCPs 0.2 ng/SPMD, PCBs 0.1 ng/SPMD, polar pesticides: 0.5–5 ng/POCIS, antibiotics: 1–2 ng/POCIS, other pharmaceuticals 5 ng/POCIS. Analytical procedure involved evaluation of recoveries of internal standards. Recoveries were within following ranges: PAHs: 80–100 %, MeTCS/TCS: 60–100 %, OCPs, PCBs: 60–100 %, polar pesticides, pharmaceuticals: 55–80 %. Both trip and analytical blanks were analyzed. Laboratory blanks were subtracted. Trip blanks contributed 0–5 % of the total exposure, therefore no subtraction was performed.

2.5. In vitro bioassays

Four transactivation reporter gene bioassays were used to assess receptor-mediated potencies of organic extracts of waters from the WWTP and passive samplers. All assays were conducted in 96 well microplates and included several dilutions of extracts in triplicate to provide a dose-response curve for each sample. All media and chemicals were purchased from Sigma-Aldrich (Czech Republic) unless otherwise specified.

2.5.1. AhR-mediated potency

AhR-mediated (dioxin-like) potency was determined by use of the H4IIE-*luc* bioassay, which is rat hepatoma cell line containing a luciferase reporter gene under control of dioxin-responsive enhancers (DRE) (Hilscherova et al., 2001; Sanderson et al., 1996; Villeneuve et al., 2002). H4IIE-*luc* cells were cultured in Dulbecco's modified Eagle's medium (DMEM) (BioTech, Czech Republic) supplemented with 10% fetal calf serum Mycoplex (PAA, Austria). The H4IIE-*luc* cells were seeded in the culture medium at density of 15,000 cells/well and after 24 h exposed to samples, calibration reference or solvent control. Standard calibration was performed with 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD; Ultra Scientific, USA; dilution series 1–500 pM). After 24 h of exposure, intensity of luciferase luminescence corresponding to the receptor activation was measured by use of Promega Steady Glo Kit (Promega, USA).

2.5.2. ER-mediated potency

Estrogen receptor mediated potency was evaluated by use of the MVLN bioassay, a human breast carcinoma cell line transfected with the luciferase gene under control of estrogen receptor activation (Demirpence et al., 1993; Freyberger and Schmuck, 2005; Hilscherova et al., 2002). MVLN cells were cultured in medium DMEM/F12 supplemented with 10% fetal calf serum Mycoplex (PAA, Austria). MVLN cells were seeded at density of 20,000 cells/well in DMEM/F12 supplemented with 10% dialyzed fetal calf serum (PAA, Austria), which was additionally dextran/charcoal treated to further decrease background concentrations of hormones. Approximately 24 h after plating, cells were exposed to samples, calibration reference or solvent control in DMEM/F12. Standard calibration was performed with 17β-estradiol (E_2; dilution series 1–500 pM). Effects of extracts on MVLN were assessed either singly or in combination with competing

Table 1
The results of chemical analysis of passive samplers extracts. Ranges: the sum of detected compounds—the sum of detected compounds plus limit of detection for the nondetected compounds.

POCIS Sampling site	Pesticides[a]	Sulfonamides[b]	Other antibiotics[c]	Other pharmaceuticals[d]	PFCs
	ng/POCIS				
1	376–464	157–172	12–68	231–239	6–9
2	285–388	104–128	2–52	253–261	3–6
3	382–491	824–838	54–105	904–911	33–36
4	463–603	721–733	32–81	808–814	38–41
5	279–394	924–938	290–317	1242–1249	12–15
6	2726–2836	10,087–10,104	1534–1551	18,550–18,559	272–274
7	474–599	992–1004	120–157	1344–1350	29–32
8	342–441	889–903	98–138	1147–1154	21–24
9	613–723	926–938	51–108	1003–1009	10–12

SPMD Sampling site	PAHs	PCBs	OCPs	Triclosan	MeTriclosan	PBDEs
	ng/L	pg/L	pg/L	pg/L	pg/L	pg/L
1	40.8	408–438	809–825	431	168	16–27
2	52.9	724–734	831–845	190	155	8.8–14
3	38.2	2155–2168	737–747	360	812	21–28.2
4	40.8	1370–1373	718–720	247	642	13.7–16.8
5	2160	825–861	831–839	32,817	84.2	162
6	31.6	1440–1446	1183–1194	8747	24,365	136–140
7	36.2	1252–1259	775–782	1115	3197	27.6–30.2
8	28.6	1548–1567	1040–1044	1680	3344	30.3–37.4
9	51.2	507–526	684–701	554	867	10.3–19.2

[a] Pesticides: clopyralid, bentazone, bromoxynil, 2,4-D, MCPA, dichlorprop, mecoprop (MCPP), 2,4,5-T, imazethapyr, thifensulfuron-methyl, methamidophos, nicosulfuron, rimsulfuron, metamitron, dimethoat, atrazin_desethyl, metoxuron, phosphamidon, cyanazin, metribuzin, simazin, bromacil, carbofuran, hexazinon, thiophanate-methyl, monolinuron, chlorotoluron, isoproturon, metobromuron, atrazin, desmetryn, dichlobenil, methabenzthiazuron, diuron, methidathion, ethofumesat, azoxystrobin, linuron, terbuthylazine, chlorbromuron, propyzamide, prometryn, metolachlor, fenhexamid, fenarimol, acetochlor, terbutryn, fipronil, kresoxim-methyl, tebuconazole, diazinon, propiconazole, phorate, phosalone, fluazifop-p-butyl, tri-allate, pyridate, alachlor, metalaxyl.

[b] Sulfonamides: sulfapyridin, sulfamethazin, sulfamethoxypyridazin, sulfachloropyridazin, sulfamethoxazol.

[c] Other antibiotics: metronidazol, cefalexin, ofloxacin, norfloxacin, ciprofloxacin, enrofloxacin, erythromycin, trimetoprim.

[d] Other pharmaceuticals: diaveridin, carbamazepin, diclofenac.

endogenous ligand (33 pM 17β-estradiol)—given concentration is near its EC_{50} value. Exposure duration and final measurement was the same as in the case of H4IIE-*luc* bioassay described above.

2.5.3. AR-mediated potency

(Anti)androgenicity of passive samplers extracts was assessed in a bioassay with MDA-kb2 cells, a human breast carcinoma cell line stably transfected with luciferase reporter gene under control of functional endogenous androgen receptor (AR) and glucocorticoid receptor (GR) (Wilson et al., 2002). MDA-kb2 cells were cultured in L-15 Leibovitz medium supplemented with 10% fetal calf serum Mycoplex (PAA, Austria). MDA-kb2 were seeded at density of 50,000 cells/well and exposed after 24 h to samples, calibration reference or solvent control in L-15 Leibovitz medium supplemented with 10% dextran/charcoal treated dialyzed fetal calf serum. Standard calibration was performed with dihydrotestosterone (DHT; dilution series 1 pM–10 μM). In addition to androgenic effects, antiandrogenicity was assessed in combination with competing endogenous ligand (1 nM dihydrotestosterone). After 24 h of exposure, intensity of luciferase luminescence was measured with prepared luciferase reagent (Wilson et al., 2002).

Organic extracts of influent and effluent waters were assessed in a bioluminescent yeast assay based on recombinant *Saccharomyces cerevisiae* cells modified to express human androgen receptor along with firefly luciferase under transcriptional control of androgen-responsive element to detect compounds affecting AR-mediated hormonal signalling. The assay with the androgen-responsive yeast model was performed according to Leskinen et al. (2005). Yeast cells were seeded in 96-well microplates and exposed to reference testosterone (T; dilution series 1 pM–10 μM), the sample alone or in combination with testosterone (10 nM) to determine antiandrogenic effect. Yeast cells were incubated for 2.5 h and then the signal was detected after addition of D-luciferin substrate.

2.5.4. Cytotoxicity

Non-cytotoxic sample concentrations to be used in each bioassay with mammalian cell lines were determined by use of the neutral red uptake assay (Freyberger and Schmuck, 2005). Particular bioassays with individual cell lines were processed as previously described. At the end of the exposure period, neutral red solution (0.5 mg/mL of media) was added and cells were incubated for 1 h at 37 °C. Medium was removed and cells washed with PBS and lysed with 1% acetic acid in 50% ethanol. Absorbance was measured in a microplate spectrophotometer at 570 nm.

Yeast strain of recombinant *S. cerevisiae* constitutively expressing luciferase, which has shown greater sensitivity compared to the mammalian cells, was used for detailed cytotoxicity assessment (Leskinen et al., 2005; Michelini et al., 2005). Complete dose–responses relationships of cytotoxic effects for all samples were determined after 2.5 h exposure. The intensity of luciferase luminescence after addition of D-luciferin corresponded to the number of surviving cells (Leskinen et al., 2005).

2.6. Data analysis

Sample responses expressed as relative luminescence units were converted to percentage of maximum response of the standard curves (% TCDDmax/E_2max/DHTmax/Tmax). The response of the solvent control was substracted from both standard and sample responses prior to the conversion. EC values were calculated by nonlinear logarithmic regression of dose–response curves of calibration standards and samples (Graph Pad Prism, GraphPad® Software, San Diego, California, USA). Relative potencies expressed as TCDD equivalents (BIOTEQ)/E_2 equivalents (EEQ)/androgen equivalents (AEQ) were calculated by relating the EC_{50} value of standard calibration with the concentration of the tested sample inducing the same response (Villeneuve et al., 2000). Due to cytotoxicity, it was not possible to obtain complete dose–response curves in testing of waste water samples in the yeast assay. Thus, their AEQ values were calculated as point estimates because maximum detected luminescence induction at noncytotoxic concentrations did not exceed 15%.

Cytotoxicity, antiestrogenicity and antiandrogenicity corresponded to the decrease in detected luminescence/absorbance signal given by solvent control in case of cytotoxicity and specified amount of competing standard ligand for the other effects. IC_{50} values for antiestrogenicity and antiandrogenicity or IC_{20} values in cases that the effects did not cause 50% response, were calculated from dose–response curves expressed in percentage of signal of competitive concentration of added natural ligand (33 pM E_2, 1 nM DHT, 10 nM testosterone). For better clarity of the trends in graphs the values are expressed as an index of antiestrogenicity (AE) or antiandrogenicity (AA), which corresponds to reciprocal value of IC_{20} or IC_{50}. Similarly, the index of cytotoxicity was derived as the reciprocal value of IC_{20} or IC_{50} for the cytotoxic response.

2.7. Calculation of dissolved water concentrations from passive sampler data

Concentrations of target analytes in water were calculated from the mass absorbed by the SPMD, the *in situ* sampling rate of the compounds and their sampler–water partition coefficients using the kinetic uptake model by Huckins et al. (2006). Sampling rates of target compounds were estimated from dissipation of performance reference compounds (PRCs) from SPMDs during exposure using nonlinear least squares method by Booij and Smedes (2010), considering the fraction of individual PRCs that remain in the SPMD after the exposure as a continuous function of their partition coefficients, with sampling rate as an adjustable parameter. The necessary sampler–water partition coefficients values were estimated from the respective octanol/water partition coefficients according to Huckins et al. (2006).

For the purpose of comparison of toxic potencies of extracts from SPMDs from different sampling sites the measured toxic equivalent concentrations (TEQ) in extracts [ng/SPMD] were translated to water concentrations $C_{W\text{-}TEQ}$ [ng/L or pg/L] at the individual sites. Since physicochemical properties of the compounds that exhibit bioassay response in the extracts are not known, linear uptake was assumed (Eq. (1)).

$$C_{w-TEQ} = \frac{TEQ}{R_s t} \quad (1)$$

Where: R_S is the sampling rate and t is the exposure time. The necessary R_S values were obtained using the PRC model described above. Since R_S is only a weak function of hydrophobicity, values of R_S with a medium molecular mass (MW = 300) were applied in all calculations.

For POCIS data, no correction for the potential effect of environmental variables was performed and results were simply compared on the basis of toxic equivalent concentrations (TEQ) in sampler extracts [ng/POCIS]. It has been demostrated that water flow rate has a relatively minor influence on the accumulation of a number of pollutants including EDCs into POCIS (Li et al., 2010). Thus, it appears not necessary to adjust sampling rates for POCIS when they are deployed in areas where the water flows vary only slightly.

3. Results

3.1. Concentrations of individual residues

Greatest concentrations of polar pesticides, pharmaceuticals and perfluoroorganic compounds in POCIS were detected at site 6 (WWTP effluent) (Table 1). Concentrations of contaminants found in

POCIS from WWTP influent (site 5) were less than in POCIS at WWTP effluent and comparable or greater than in those from the other sites. The explanations of greater detected levels of some contaminants and biological potencies in passive samplers from WWTP effluent are elaborated in detail in the Discussion section. Concentrations of some pharmaceuticals in POCIS from the sites upstream of Brno were slightly greater than downstream, but concentrations in the Svratka River were generally approximately 4-fold less than in the Svitava River. Similarly, concentrations of PFCs were approximately 6-fold greater in Svitava than in Svratka, while concentrations of pesticides were comparable in both rivers. Greater concentrations of pesticides were found at site 9 on the tributary of the Svratka River. Concentrations of pharmaceuticals were greater bellow the WWTP effluent. There was a slight decrease of concentrations of contaminants in POCIS as a function of distance from the city and WWTP.

The greatest concentrations of most pollutants sampled by SPMD were observed in samples from the WWTP, with concentrations of PAHs and triclosan greatest in the influent (site 5), while concentrations of methyl triclosan were greatest in the effluent (site 6) (Table 1). Greater concentrations of PCBs and methyl triclosan were detected already upstream of Brno in the Svitava River (sites 3, 4). Concentrations of most pollutants did not increase much directly downstream of Brno on both rivers (sites 2, 4), except for PCBs in the Svratka River. Concentrations of PAHs were slightly lesser downstream of the WWTP (site 7) and further decreased at the longer distance from the city (site 8), while no such trend was observed for concentrations of PCBs and OCPs. Concentrations of PBDEs, triclosan and methyl triclosan were significantly greater downstream of the WWTP.

3.2. Cytotoxicity

Some samples of WWTP influent water caused 20% cytotoxicity even at 25-fold dilution, but effluent water samples caused cytotoxicity only at 100% water equivalents or were not cytotoxic (Fig. 2A). Removal efficiency for cytotoxicity in waste water was 83 to 98% throughout the year, except of one time point when toxicity of the influent was small and thus efficiency of removal was lower (46%). All POCIS extracts elicited cytotoxic effects, with the greatest cytotoxicity observed for samples from the WWTP effluent (site 6, Fig. 2B), which was about 50% greater than the effect of the WWTP influent sample (site 5). Cytotoxicity of POCIS exposed to river water was 4 to 10-fold lower, with greater toxicity in water from the Svitava River. It slightly increased downstream of the WWTP (site 7). A greater than 93% decrease in cytotoxicity after treatment of wastewater was observed in SPMD samples (Fig. 2C), where the WWTP influent sample (site 5) exhibited the greatest cytotoxicity. Cytotoxicity of compounds sampled by SPMD from upstream of Brno was greater in Svratka river, and it increased in river Svitava after flowing through the city and also downstream of WWTP (Fig. 2C).

3.3. AhR-mediated potency

Significant AhR-mediated (dioxin-like) potency expressed as bioassay-derived 2,3,7,8-TCDD equivalents (BIOTEQ) was detected in most samples. Samples of influent water from the WWTP generally elicited greater dioxin-like potency than did effluent water (Fig. 3A). Concentrations of BIOTEQ were between 0.1 and 3.4 ng TCDD/L for influent and 0.1 to 0.7 ng TCDD/L for effluent. Efficiency of treatment of the WWTP for compounds with dioxin-like potency varied during the year from 13 to 90%, except for two cases when the removal efficiency was even negative. In February and April effluent samples contained 8 and 27% greater levels of BIOTEQ than corresponding influent samples, respectively. Significant dioxin-like potency in POCIS samples was detected only for samples from the WWTP (sites 5, 6) and site 7 (sampling site directly downstream of the WWTP) (Fig. 3B, insert). Concentrations of BIOTEQs were between 0.3 and 2 ng TCDD/POCIS. Potency detected in the WWTP effluent (site 6) was 5-fold greater than that in the influent (site 5). All extracts of SPMD contained detectable AhR-mediated potency with the greatest response in the WWTP influent sample (site 5) and also in the Bobrava River which was affected by agriculture (site 9, Fig. 3B). Concentrations of BIOTEQ determined from SPMD ranged from 8.2 to 14.6 pg TCDD/L.

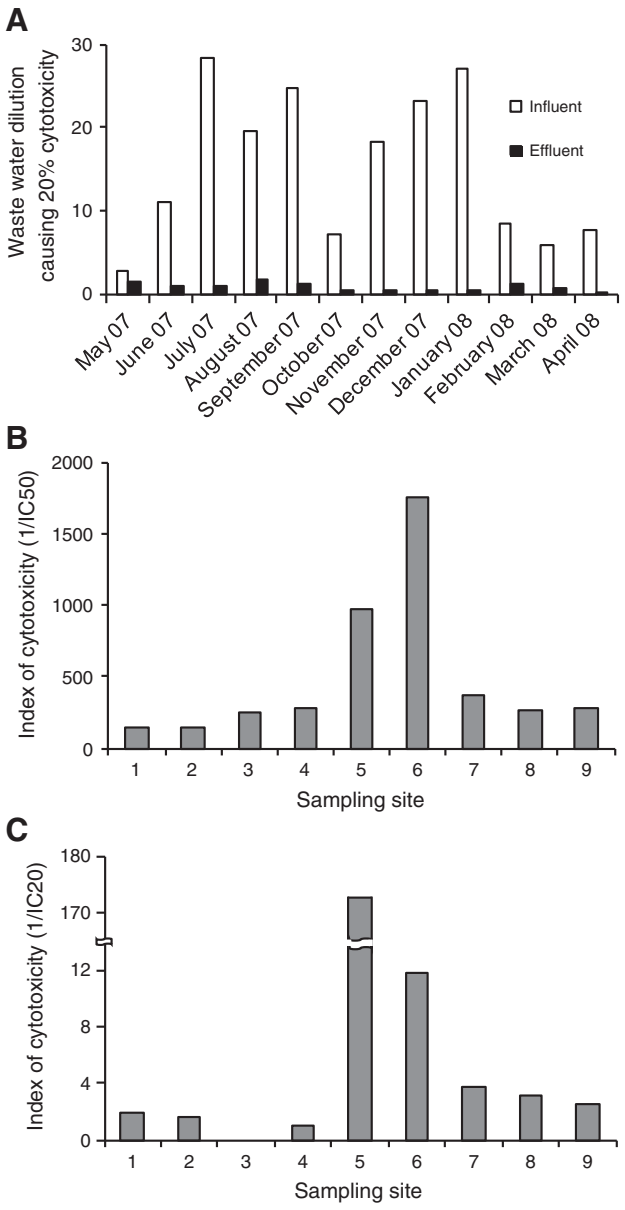

Fig. 2. Cytotoxicity of samples extracts detected in the bioluminescent yeast assay: (A) influent and effluent water samples from the WWTP; (B) POCIS (Index of cytotoxicity expressed as reciprocal value of IC_{50}, $[sampler/mL]^{-1}$); (C) SPMD (Index of cytotoxicity expressed as reciprocal value of IC_{20}, $[L/mL]^{-1}$); no column = no significant activity.

3.4. ER-mediated potency

Potency of ER agonists was detected in water from the WWTP during all samplings throughout the year (Fig. 4). Values of 17β-estradiol (E_2) equivalents (EEQ) varied from 5.4 to 124 ng E_2/L in influent and from 0.1 to 5.1 ng E_2/L in effluent. Efficiency of treatment to remove EEQ ranged from 80 to greater than 99 %. POCIS sample from the WWTP influent (site 5) had a concentration of EEQ of 7.3 ng E_2/

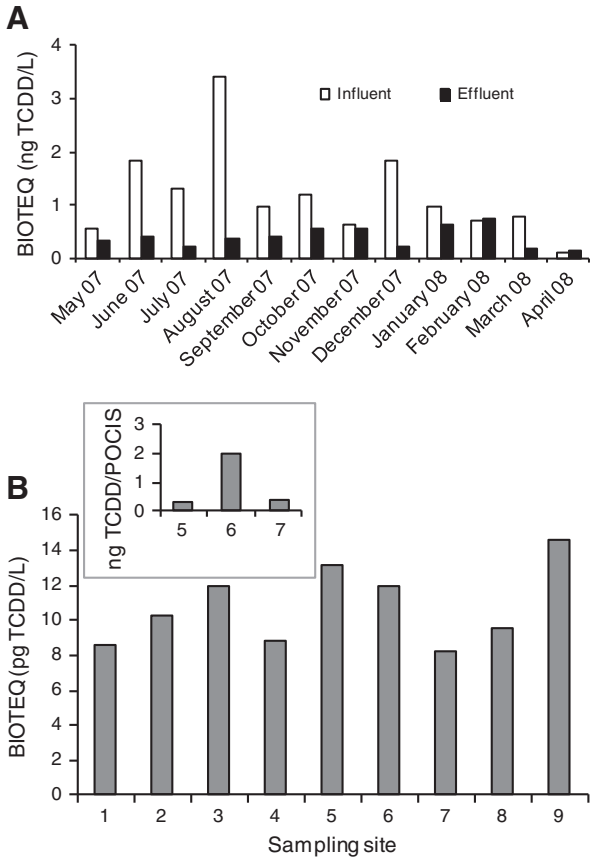

Fig. 3. AhR-Mediated (Dioxin-like) potency of samples extracts detected in H4IIE-*luc* assay expressed as BIOTEQ equivalents: (A) influent and effluent water from the WWTP; (B) SPMD and POCIS.

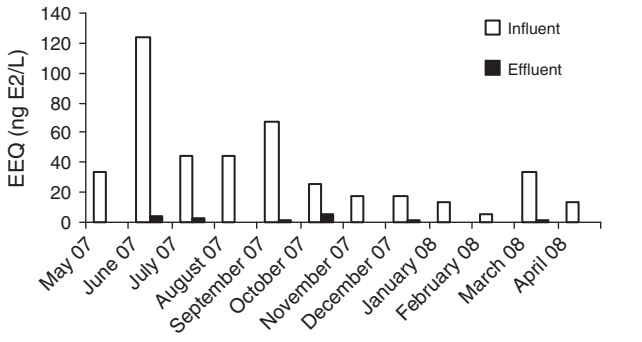

Fig. 4. Estrogenic potency, expressed as estradiol equivalents (EEQ) of extracts of WWTP influent and effluent water, detected in MVLN assay; no column = no significant activity.

sampler. The concentration of EEQ in the extract of POCIS exposed to effluent (site 6) was less than 0.6 ng E_2/sampler, which was the limit of detection. There were no EEQ detectable in POCIS from the rivers or in any SPMD samples.

Influent and effluent water samples from the WWTP showed no significant antiestrogenic potency when tested in the presence of E_2. Alternatively, antiestrogenic potency was detected in extracts of SPMD and POCIS from all sites. Data from SPMDs indicate greater antiestrogenicity in sites from river Svratka compared to Svitava already upstream of Brno. Greatest antiestrogenicity was observed in POCIS exposed to WWTP effluent while all samples from rivers and WWTP influent showed comparable potency (Fig. 5).

3.5. AR-mediated potency

Significant androgenic potencies were found mostly at the greatest non-cytotoxic concentrations of influent water samples and concentrations of androgen equivalents (AEQ) ranged from <23 to 193 ng testosterone/L (Table 2). Concentrations of AEQ determined for non-cytotoxic concentrations of effluent extracts were less than the limit of detection, which was 1–4 ng testosterone/L. Efficiency of treatment to remove androgenic compounds was greater than 96–99%. POCIS from WWTP influent and effluent were the only other samples to exhibit detectable AEQ with concentrations of 32.6 and 6.9 ng DHT/sampler, respectively. No antiandrogenic potency was observed in non-cytotoxic concentrations of samples from influent or effluent water from the WWTP. Antiandrogenic potency in competition with the added endogenous ligand DHT was detected in most extracts of SPMD and POCIS. The greatest antiandrogenic potency in extracts of POCIS was observed at site 4 in the Svitava River, directly downstream of Brno (Fig. 6A). The antiandrogenic potency of the extract of the POCIS exposed to WWTP influent (site 5) was comparable with the potency observed in samples from most sites on the rivers. There was no antiandrogenic potency observed in POCIS exposed to WWTP effluent (site 6). There was generally no antiandrogenic potency in extracts of SPMD exposed upstream of the WWTP, while there was antiandrogenic potency in samples from the WWTP (sites 5, 6) and from sites downstream of the WWTP. The antiandrogenic potency of compounds sampled by SPMD was approximately 60% greater in WWTP influent than that in effluent (Fig. 6B).

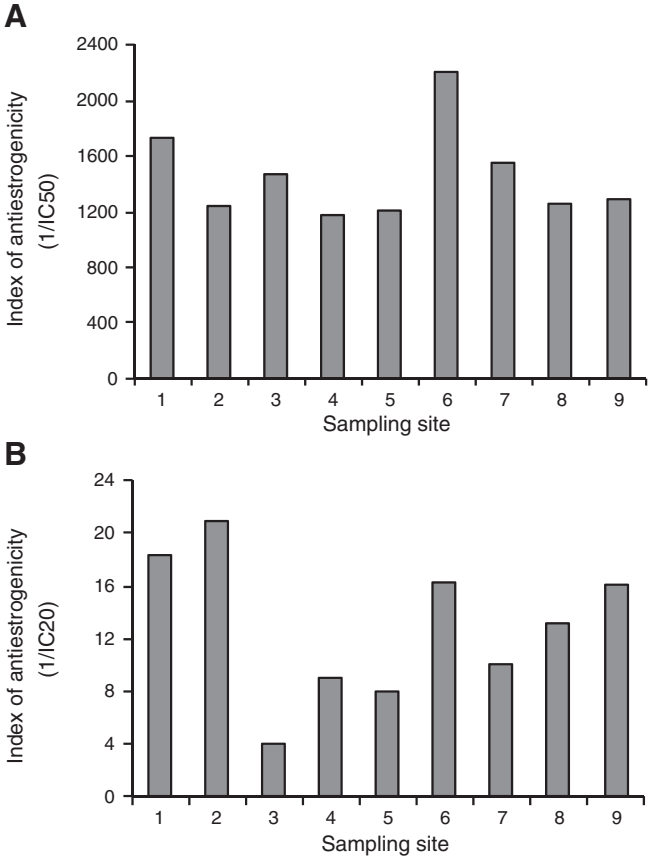

Fig. 5. Antiestrogenic potencies of samples extracts determined by use of the MVLN assay in the presence of 33 pM estradiol expressed as index of antiestrogenicity: (A) POCIS—reciprocal value of IC_{50} [sampler/mL]$^{-1}$), (B) SPMD—reciprocal value of IC_{20} [L/mL]$^{-1}$).

Table 2
Androgenic activity of influent and effluent water extracts from the WWTP detected in the yeast assay. (LOD ranged from 1.3 to 70 ng testosterone/L because of variable cytotoxicity of samples).

Sampling date	AEQ (ng testosterone/L)	
	Influent	Effluent
May 07	155	<3.7
June 07	97	<2.2
July 07	<70	<2.2
August 07	<70	<2.6
September 07	<23	<1.3
October 07	80	<1.3
November 07	193	<1.3
December 07	96	<1.3
January 08	107	<1.3
February 08	140	<1.3
March 08	47	<1.3
April 08	35	<1.3

4. Discussion

Rivers can be contaminated by many chemicals, some of which have the potential to affect normal reproduction, development and behavior of wildlife species and potentially also human health. Some of these compounds can be released to rivers from large city agglomerations via WWTP and other point-discharge or diffuse sources (Cargouet et al., 2004; Jobling et al., 1998; Sabaliunas et al., 2000; Snyder et al., 2000). In recent years, WWTP have been studied as potential sources of endocrine disruptive compounds to the aquatic environment (Harries et al., 1996; Murk et al., 2002; Tan et al., 2007). There are several studies that have investigated WWTPs by use of various approaches including passive sampling combined with instrumental analysis and/or bioassays (Tan et al., 2007; Vermeirssen et al., 2005). However, there has been less information on other possible sources. Moreover, the studies using bioassays were focused mainly on estrogenic potency and there is limited data on other specific biological potencies in mixtures extracted from surface or waste waters. In addition, mostly known endocrine disruptive compounds, such as estrogens, androgens, phthalates or alkylphenols are analyzed, but more data is needed for other pollutants, such as widely used compounds from the group of pharmaceuticals and personal care products.

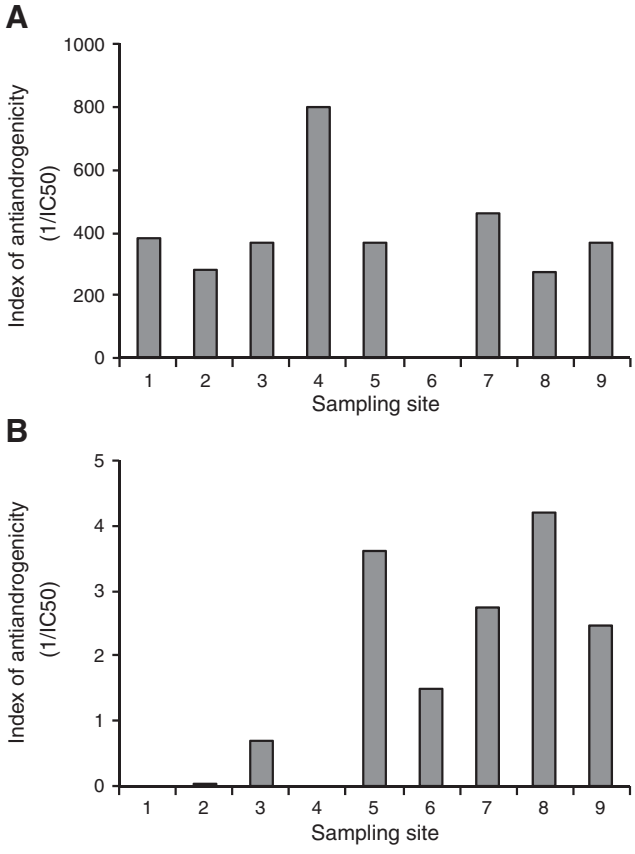

Fig. 6. Antiandrogenic potency of samples extracts determined by use of the MDA-kb2 assay in the presence of 1 nM dihydrotestosteron (DHT), expressed as an index of antiandrogenicity (reciprocal value of IC_{50}): (A) POCIS $[sampler/mL]^{-1}$, (B) SPMD $[L/mL]^{-1}$; no column = no significant activity.

In this study potencies for ligands in mixtures to interact with specific receptors as well as concentrations of several classes of pollutants were measured in waste waters and surface waters of two rivers in an urban metropolitan area in Central Europe with a variety of industries and modern recently renovated WWTP with advanced treatment capacity and efficiency. The sampling design and a complex approach using passive sampling along with chemical analysis and bioassays enabled to characterize the distribution and sources of pollutants in the model part of river basin. Based on measured residues, water of the Svitava River upstream of Brno seems to be more polluted than the Svratka River. Specifically, concentrations of pharmaceuticals, PFCs, PCBs and methyl triclosan were lower in the Svratka River. Furthermore, greater potencies for cytotoxicity of the hydrophilic fraction were observed in the Svitava River upstream of Brno. These data point to some pollution sources on river Svitava upstream of Brno agglomeration. There was no obvious influence of the city itself or WWTP on the concentrations of PAHs and organohalogenated compounds except of somewhat increased PCBs in Svratka downstream of Brno. Thus, neither runoff from the metropolitan region of Brno nor the effluent of the WWTP contributed significantly to the pollution with these compounds. Alternatively, concentrations of pharmaceuticals, antibiotics, triclosan and PBDEs were not affected by the city, but increased downstream of the WWTP, despite its up-to-date treatment technology. The data from passive samples document highly efficient removal of hydrophilic antiandrogenic and about 60% removal of hydrophobic antiandrogenic pollutants during WW treatment. Despite this removal, the concentrations of hydrophobic antiandrogenic pollutants in the river increased downstream of the WWTP similarly to the cytotoxic potency. Concentrations of triclosan and methyl triclosan were increased by the WWTP. For polar pesticides there was no influence of the city itself or WWTP. Concentrations of most of the polar compounds sampled by POCIS and associated biological potencies went down at the last study site about 20 km downstream of the city. There was no such decrease in levels of hydrophobic pollutants sampled by SPMD and their biological potencies, except of PAHs. The decrease of PAHs concentrations downstream of WWTP was not due to particle adsorption and sedimentation after flow out from WWTPs, since there was no increase of PAHs levels in river sediments (data not shown).

For all pollutants sampled by POCIS as well as some pollutants sampled by SPMD, the greatest concentrations were detected in WWTP effluent. Similarly, in the POCIS exposed to effluent there was also the greatest cytotoxicity, dioxin-like and antiestrogenic potency. All these concentrations and potencies were greater than for the WWTP influent. There are at least two explanations of the observed elevated concentrations and toxic potencies of compounds accumulated in passive samplers in the WWTP effluent in comparison to influent. Passive sampling methods measure the concentration of freely dissolved contaminants, which is directly related to the contaminants' chemical activity (Mayer et al., 2003). This also indicates the bioavailability or pressure (fugacity) of contaminants on organisms and consequently represents the exposure level for organisms. In the WWTP influent hydrophobic compounds are largely sorbed to the suspended particulate material so that their freely dissolved concentration is small (Lohmann et al., 2012). In the wastewater

treatment process the content of suspended material is efficiently reduced, which in turn results in a strong decrease of sorption capacity for hydrophobic compounds in WWTP effluent. However, some persistent compounds are not eliminated by the treatment process. As a result of the reduced uptake capacity of the particulate matter, free dissolved concentrations (chemical activity) in the effluent are higher than in the influent, which is in turn reflected in their levels found in passive samplers, especially in SPMDs.

Differences in uptake might be affected by different passive sampler exposure conditions in WWTP influent and effluent, respectively. Among potential factors that affect uptake kinetics into passive samplers, hydrodynamics and fouling are the most important ones. The visual observation of channels in WWTP influent and effluent indicates a similar turbulent water flow character in both cases. Thus, influent/effluent differences in hydrodynamics can hardly explain the observed up to ten-fold increase in accumulated amounts of some compounds in passive samplers (e.g. compounds in POCIS; Table 1). We hypothesize that fouling of samplers is the more important factor that affects the uptake of both hydrophobic as well as hydrophilic compounds into passive samplers. The raw waste water is a very complex mixture which contains debris, mud, various particles and even dispersed emulsions of liquids that are non-miscible with water (such as fats). Fouling and layers of dirt can reduce uptake of compounds into passive samplers (Stuer-Lauridsen, 2005) and lead to lower sampling rates by a) physical blockage of active surface of samplers by debris; b) thickening the diffusion barriers; c) reduction of the driving force for sampler uptake by shifting the partitioning equilibria between sampler and the surrounding environment. Our study indicates that passive sampling (especially for POCIS samples) may not be a reliable method in raw sewage water and could lead to significant underestimation of actual concentrations of dissolved pollutants. This problem is really specific to the raw sewage water and does not concern passive samples from any other site.

Most studies using *in vitro* assays include cytotoxicity tests, which determine the greatest possible sample concentration that is not cytotoxic for the cells to be used as the maximal tested concentration for the specific effects. In this study, dose–response curves and IC_{50} of extracts on yeast cells were determined. The efficient decrease of cytotoxicity in SPMD and waste water after waste water treatment might be due to activated sludge processes as well as flocculation, which have been shown to have the greatest efficiency of removal of cytotoxic compounds (Ma et al., 2005). Cytotoxicity of waste waters did not correlate with estrogenic or androgenic potencies of these waste waters. This observation is consistent with the results reported by Vega-Lopez et al. (2007), who found no correlation between estrogenic disruption and toxicity determined in MCF-7 cells for samples of water from two Mexican lakes, which receive domestic and industrial wastewaters after secondary treatment. These results support the theory that estrogenic potency in waste waters is caused primarily by steroidal estrogens, which are potent at ng/L concentrations and therefore does not correlate with the overall cytotoxicity. Cytotoxicity of extracts of all POCIS in the yeast assay can be related to sesquestered pollutants, especially antibiotics and other pharmaceuticals determined by chemical analysis.

There are few studies that have focused on effects of urban pollution on the overall toxicity of waters in municipal rivers. Toxicity determined by the Microtox assay was directly proportional to urban land cover in streams around six metropolitan areas in the USA (Bryant and Goodbred, 2009). Toxicity of river water sampled by SPMD in Microtox and *Daphnia pulex* test has been observed in the Neris River after flowing through the capital city of Lithuanina (Sabaliunas et al., 2000). This finding is consistent with the observation of greater toxicity of compounds sampled by SPMD from the Svitava River downstream of the metropolitan area compared to upstream of Brno observed in this study.

Detected AhR-mediated potency in both SPMD and POCIS indicated contribution of both hydrophobic and polar compounds to the overall dioxin-like potential of samples. Similarly in river sediments, mass-balance calculations based on fractionation with subsequent quantification have suggested that PAHs can account for a considerable portion of the dioxin-like potency together with unidentified more polar AhR-active compounds (Hilscherova et al., 2001). Dioxin-like potency found in all extracts of SPMDs was probably linked with the presence of known hydrophobic AhR ligands, such as PAHs or PCBs. Although dioxin-like compounds are usually investigated in less polar matrices such as SPMD or sediments, some recent studies (Dagnino et al., 2010; Reungoat et al., 2010) confirmed AhR potency in water phase. Results of another study (Jarosova et al., 2012) reported dioxin-like potency of 0.05 to 0.39 ng BIOTEQ/POCIS in headwaters with small local sources of pollution. In the current study, POCIS samples exhibited dioxin-like potency only at three sites, inside and downstream of the WWTP, which suggests that waste waters contain some hydrophilic dioxin-like compounds that are not completely removed during treatment. This result is in agreement with the dioxin-like potencies detected WWTPs influent and effluent waters. The data for waste water samples show dioxin-like potency specifically for the polar methanolic extracts and thus might not include influence of some hydrophobic pollutants. Efficiency of treatment by the WWTP determined from BIOTEQs of the waste water samples was not as great for chemicals with dioxin-like potency as in the case of elimination of cytotoxicity or hormone-like potencies. Efficiencies of treatment varied substantially throughout the year. Release of some particle-bound compounds during treatment and lesser efficiency of treatment related to greater persistence of some AhR-active compounds might have contributed to this difference. However, the absolute concentrations of BIOTEQ were less than those observed in other studies eventhough only a limited number of papers report dioxin-like potency in the dissolved phase. For example, Dagnino et al. (2010) detected AhR potency (by the same method as we used) in influent and effluent of French municipal WWTPs with an activated sludge system supplemented with biofilter to be as great as 37 to 112 ng TCDD/L, and 2.8 to 11.6 ng TCDD/L, respectively. Efficiency of removal was approximately 90% and the authors concluded that removal of AhR potency in this type of WWTPs depends primarily on removal of suspended solids with which they are associated. Alternatively, Ma et al. (2005) did not find concentrations of BIOTEQ that were greater than 14 pg TCDD/L in either influents or effluents from a pilot plant in a Beijing WWTP, China.

The observation that xenoestrogens and xenoandrogens were detected in waste water and POCIS samples from the WWTP, but not in SPMDs, implies that polar compounds accounted for the estrogenic and androgenic potencies. Since feminization of fish downstream from WWTPs has been observed in rivers worldwide, estrogenic potential of different types of waters has been evaluated in multiple studies. Examples of estrogenic potencies detected by various *in vitro* assays documenting the comparability of our findings to the situation in other parts of the world are compiled in Table 3.

Relatively great efficiency of removal of estrogenic potency in various WWTPs has been documented both by composite water sampling as well as POCIS sampling. The majority of municipal or domestic WWTPs have implemented at least physical and biological treatment techniques. Activated sludge processes, similar to those of WWTP investigated in this study, are the most widely used types of biological treatment processes worldwide. Most studies that have focused on WWTP of similar types to that studied here found the treatment efficiencies for estrogens ranging from >88 to >99% (Leusch et al., 2005; Murk et al., 2002), 90–95% (Korner et al., 2000; Murk et al., 2002) or greater than 95% (Tan et al., 2007), but other studies have reported lesser efficiencies (Cargouet et al., 2004). Efficiency of removal of estrogenic potency, as determined by the MVLN assay, in four mechanical–biological municipal or domestic WWTPs in Paris

Table 3
Examples of estrogenic activities in waste waters and surface waters as detected by various *in vitro* assays.

Matrix	EEQ ng/L	Country	In vitro assay[a]	Reference
Wastewater influent	51–70	Germany	E-Screen	Korner et al. (2000)
	17–23	Queensland, Australia	E-Screen	Leusch et al. (2005)
	1.1–120	The Netherlands	ER-CALUX, YES	Murk et al. (2002)
	35–72	Japan	YES	Onda et al. (2002)
	1–30	Sweden	YES	Svenson et al. (2003)
	108–356	Queensland, Australia	E-Screen	Tan et al. (2007)
	5.4–124	Czech Republic	MVLN	This study
Wastewater effluent	6	Germany	E-Screen	Korner et al. (2000)
	<0.75	Queensland, Australia	E-Screen	Leusch et al. (2005)
	0.03–16	The Netherlands	ER-CALUX, YES	Murk et al. (2002)
	4–25	Japan	YES	Onda et al. (2002)
	<0.1–15	Sweden	YES	Svenson et al. (2003)
	0.6–6.2	Japan	YES	Nakada et al. (2004)
	1.9–15	USA	MVLN	Snyder et al. (2001)
	<1–67.8	Queensland, Australia	E-Screen	Tan et al. (2007)
	0.1–5.1	Czech Republic	MVLN	This study
Surface water	0.07–0.5	The Netherlands	ER-CALUX	Murk et al. (2002)
	0.01–1.4	Belgium	E-Screen	Nadzialek et al. (2010)
	<0.18	Portugal	YES	Sousa et al. (2010)
	0.86–11	USA	MVLN	Snyder et al. (2001)
	<0.006–4.96	Sweden	YES	Svenson et al. (2003)
	0.025–0.68	Korea	E-Screen	Oh et al. (2009)

[a] E-Screen—cell proliferation assay, ER-CALUX—estrogen receptor chemical activated luciferase gene expression assay, YES—yeast estrogen screen, MVLN—luciferase reporter gene-based assay using the MVLN cell line.

ranged from 62 to 97% (Cargouet et al., 2004), which was similar to those reported for five WWTPs in the United Kingdom, which had reported efficiencies of 70 to 100% (Kirk et al., 2002). Efficiency of removal observed in this study was 80 to >99%, but in most tested samples it was greater than 96%.

In previous studies, concentrations of estrogen equivalents (EEQ) of river water upstream and downstream of several WWTPs, quantified by use of the yeast estrogen screen (YES), was significantly correlated with EEQ based on chemical analysis of steroidal estrogens for grab samples and POCIS (Vermeirssen et al., 2005). Also chemical and biological (E-Screen assay) analyses used to determine the concentrations of 15 endocrine disrupting compounds and estrogenicity in grab and passive samples from five municipal WWTPs showed good agreement (Tan et al., 2007). Alternatively, assessment of contamination of headwater streams from livestock farms documented that measured waterborne steroids accounted for some of the detected estrogenicity, but a considerable portion of estrogenicity could not be attributed to concentrations of identified estrogens (Matthiessen et al., 2006).

Androgenic potency of waste water in bioassays was shown to decrease during progression through the WWTP (Michelini et al., 2005). Concentrations of AEQ and efficiencies of removal observed in our study are similar to those reported for three Swedish municipal WWTPs that used activated sludge systems, and had androgenic potencies in yeast androgen screen (YAS) in influents ranging from 30 to 75 AEQ ng/L (and 0.8–3 AEQ ng/L in effluents) with efficiencies of removal of 96–98% (Svenson and Allard, 2004). However, some studies detected androgenic potencies in waste water influents that were greater than those observed in our study (Kirk et al., 2002; Leusch et al., 2006). Androgenic potencies in effluents of some WWTPs were as great as hundreds of ng AEQ/L, but in other WWTPs effluents they were less than the limits of quantification (Blankvoort et al., 2005; Kirk et al., 2002; Leusch et al., 2006; Sousa et al., 2010). Efficiencies of removal of androgens ranged from 82 to more than 99% when activated sludge was included in treatment processes, but significantly less when only primary treatment or for example biological trickling filters were employed (Kirk et al., 2002; Leusch et al., 2006). This observation is consistent with efficiencies of removal determined in this study which were greater than 96% in all cases. Also results obtained with POCIS samples confirmed significant removal of compounds with estrogenic and androgenic potency. Our results document that the efficiency of removal of both estrogenic and androgenic potency of the Brno WWTP can be ranked among the most efficient clarification WWTPs that do not implement advanced treatment. However, the results reported here also show that the efficiency of treatment can vary especially for dioxin-like and cytotoxic compounds, and thus one timepoint sampling might not be sufficient for its determination.

Results of this study provide unique information on the variability of cytotoxicity and specific potencies in waste waters during the whole year. Estrogenic potency seemed to be greater in the dryer summer season when there is less dilution than during winter when more precipitation results in greater runoff, but also greater dilution (Fig. 4). However, there was no clear trend for androgenic potencies. Lower temperatures in winter did not negatively influence removal of estrogenic potency by the WWTP, but it might have affected the breakdown of more persistent compounds causing the dioxin-like potency. The greatest cytotoxicity was observed during summer, which might be correlated with lesser dilution (Fig. 2), but with another peak in winter, when probably some other types of pollutants associated with more typical winter sources (such as combustion) might play more significant role. However, the dioxin-like potency did not vary as much as estrogenicity throughout the year, except for August when it was approximately 3-fold greater than during the rest of the year. This observation is probably due to less dilution in summer and possibly also some immediate pollution situation that can affect the samples collected during a single day. There is limited information on seasonal variability of specific potencies of contaminants in waste waters. A study conducted in the UK (Kirk et al., 2002) found that estrogenic and also androgenic potencies in influents and effluents were less in samples collected in months of rainy weather. The recombinant yeast assay was used to assess variability of estrogenic potencies in influent and effluent of Canadian municipal WWTP implementing an additional cleaning step of UV disinfection (Fernandez et al., 2008). Estrogenic potencies of composite samples of influent taken every week from September to December were not dependent on sampling season, while EEQ levels in final effluents were very high, exceeding 100 ng EEQ/L in September and ranging from about 50 to 80 ng EEQ/L from the end of October till the end of the campaign. Lower EEQ concentrations in effluent in autumn and winter compared to summer were seen also in our study, but the ranges of EEQ values were much lower than those reported by Fernandez et al. (2008).

Similar to the results of this study, small estrogenic potencies and/or concentrations of industrial estrogen mimics and natural estrogens were frequently detected in WWTP discharges, due to their incomplete removal by WWTPs (Table 3). However, even these concentrations have been shown to be effective in causing some biological effects. It has been demonstrated in a 7-year whole-lake experiment that long term exposure to estrogens (5-6 ng/L ethinyl estradiol) can affect sustainability of wild fish populations (Kidd et al., 2007). Moreover, a multigeneration study of Chinese rare minnows (*Gobiocypris rarus*) demonstrated that reproduction of the F_1 minnows was completely inhibited at the ethinyl estradiol concentration as low as 0.2 ng/L (Zha et al., 2008). These results suggest that even when efficiencies of removal of estrogen are as great as those observed in this study, risks to aquatic organisms can still occur due to the concentrations of estrogens that are constantly released from waste water effluents. The risk seems to be greatest in cases when the volume of effluent waters represents a greater proportion in relation to the receiving waters.

Next to the estrogenic and androgenic potencies detected in POCIS and water from WWTP, there were also some antiestrogenic and antiandrogenic pollutants in passive samples from WWTP, which however were not detected in the influent and effluent water samples. This difference indicates that antiestrogenic and antiandrogenic potency is related probably to less polar compounds, which were not in sufficient concentrations included in the methanolic extract of waste water. Moreover, the antiestrogenic/antiandrogenic potencies in waste waters could be masked by relatively great cytotoxicity of the methanolic extracts. Furthermore, passive samples enable higher preconcentration of the compounds compared to the composite water samples and thus the antiestrogenic/antiandrogenic activity detected in passive samples might have been bellow the limit of detection for the water samples. The passive samples from rivers exhibited neither estrogenic nor androgenic potency, but rather antiestrogenic and antiandrogenic potential. The antiestrogenic potency was detected in extracts from passive samplers exposed upstream of the city. In the study by Garcia-Reyero et al. (2001) (anti)estrogenicity was detected by recombinant yeast assay in waste waters and all samples of river water. The lack of estrogenic potency in POCIS and SPMD from river water in the study reported here could be caused by the presence of sufficient concentrations of chemicals that have been shown to have antiestrogenic potency, including pesticides, such as linuron or atrazine (Orton et al., 2009). Antiandrogenic potency was detected at most sampling sites. Hydrophilic antiandrogenic compounds were found in POCIS at sampling sites upstream of the city, whereas antiandrogenic potency in SPMD associated with the more hydrophobic pollutants was detected namely in the WWTP and downstream of the WWTP. Multiple contaminants are known to be associated with antiandrogenic potency (Orton et al., 2009; Sohoni and Sumpter, 1998), including some pesticides, which were detected by chemical analysis (e.g. p,p′-DDE, diuron).

5. Conclusion

This study revealed the presence of compounds with endocrine disruptive potency in both river water and WWTP influent and effluent. The results of year-round waste water assessment confirmed high treatment efficiency of the WWTP for cytotoxic compounds, xenoestrogens and xenoandrogens. There was significant seasonal variability of efficiency of treatment, especially of dioxin-like potencies. Despite its high efficiency WWTP had impact on the pollution with endocrine disruptive compounds. The approach employed enabled determination of contributions of the metropolitan urban area and the WWTP to contamination of the rivers. Concentrations of PAHs and most pollutants sampled by POCIS decreased as a function of distance downstream of the city. Passive sampling, along with *in vitro* bioassays and chemical analysis allowed determination of a broad spectrum of contaminants and specific biological potencies and revealed the pollution situation in this model region. More research should be performed in the future to better characterize passive sampler performance under complex exposure conditions in raw wastewaters.

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Passive sampling: An effective method for monitoring seasonal and spatial variability of dissolved hydrophobic organic contaminants and metals in the Danube river

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ABSTRACT

Application of passive samplers is demonstrated for assessment of temporal and spatial trends of dissolved polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and priority metals in the middle stretch of the Danube river. Free dissolved concentrations of PAHs, measured using SPMD samplers, ranged from 5 to 72 ng L^{-1}. Dissolved PCBs in water were very low and they ranged from 5 to 16 pg L^{-1}. Concentration of mercury, cadmium, lead and nickel, measured using DGT samplers, were relatively constant along the monitored Danube stretch and in the range <0.1, <1–20, 18–74, and 173–544 ng L^{-1}, respectively. Concentrations of PAHs decreased with increasing temperature, which reflects the seasonality in emissions to water. This has an implication for the design of future monitoring programs aimed at assessment of long term trends. For such analysis time series should be constructed of data from samples collected always in the same season of the year.

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1. Introduction

In December 2000 the European Union adopted the Water Framework Directive (WFD) to secure water resources for future generations (EU, 2000). In the implementation process of the WFD, all EU member states are required to perform trend monitoring on several pollutants priority substances in surface water that tend to accumulate in sediment and/or biota in surface water (EU, 2008). Long term measurements in water provide important information that can be used in evaluation of effects of accepted measures on lowering the emissions. Such a trend monitoring can be carried out in water, suspended particles and sediments as well as in biota. The decision, which matrix to survey is difficult especially for compounds present in water at very low concentrations, such as heavy metals and hydrophobic organic pollutants like polycyclic aromatic hydrocarbons (PAH) or polychlorinated biphenyls (PCBs). Among other available monitoring methods passive sampling presents a promising approach because it provides sensitive and time integrative measurement of free dissolved concentrations of contaminants in water (Greenwood et al., 2007). Diffusion of organic pollutants from sampled media to the sampler is driven by the high affinity of analysed compounds to the sorbent material in the sampler. The concentration found in a passive sampler can be used for calculation of time weighted average (TWA) water concentration over extended periods of time. The major advantage of passive samplers over alternative matrices used for trend monitoring, e.g. sediments or biota, is that passive samplers constitute a well-defined sampling medium with a known uptake capacity. In contrast to results based on sediment or biota, passive sampling data require no corrections for organic carbon, lipid content or species to compare data on a temporal or spatial scale. Free dissolved concentration is a measure of organism exposure in water and passive sampling allows measurement even for compounds that cannot be measured in biota because of their excretion or metabolism by organisms. Furthermore, different sources of variance including analytical and environmental variance can be much better controlled, which in turn results in reduction of the required

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number of analysed samples to obtain results with comparable statistical power (Lohmann et al., 2012). Another advantage of use of passive samplers is the determination of free dissolved concentration in water, which is one of the important parameters for the assessment of pollutant bioavailability and fate in the aquatic environment. The freely dissolved concentration of contaminants in the water column is directly proportional to their fugacity in the water phase (Mayer et al., 2003). Pollution monitoring based on direct water measurement of dissolved concentrations of hydrophobic organic compounds by bottle sampling is not reliable, since the individual spot samples of water collected at the sampling sites reflect only the pollution situation at the moment of sampling. Measurement of truly dissolved concentration of these compounds in water cannot be easily achieved by conventional liquid/liquid or solid phase extraction techniques because of potential bias of these methods introduced by co-extraction of analytes bound to colloids present in water samples.

In this study, passive samplers were applied to characterize the temporal and spatial variability of dissolved heavy metals, PAHs and PCBs in the Danube river between the cities of Vienna and Bratislava (Fig. 1). This paper presents particular results of a larger study aimed at comparison of the most promising available monitoring methods (bottom sediments, suspended particulate samplers and passive samplers) for those pollutants (PAHs, selected heavy metals) to give a technical recommendation on how to perform a trend monitoring in the aquatic environment (www.umweltbundesamt.at/umweltsituation/hestia_home). This comparison will provide the basis for a technical recommendation on how to implement the WFD as well as for a future national and regional cooperation in monitoring and consistent evaluation of the quality of the water body.

2. Materials and methods

2.1. Chemicals

Organic solvents: acetone (Mikrochem, Slovakia), n-hexane SupraSolv (Merck, Germany), dichloromethane SupraSolv (Merck, Germany), hydrochloric acid 36%, p.a. (Merck, Germany), Triolein (Sigma Aldrich, Belgium), silicagel 60 (Merck, Germany). Gases for GC–MS/ECD equipment: nitrogen ECD and helium 6.0 (both Messer Tatragas, Slovakia). Etalons of 16 polycyclic aromatic hydrocarbons for calibration of equipment (PAH mix 9, 100 μg mL^{-1} in cyclohexane), 6 polychlorinated biphenyls (10 μg mL^{-1} in cyclohexane), perdeuterated polycyclic aromatic hydrocarbons applied as performance reference compounds (D_{10}-acenaphthene, D_{10}-fluorene, D_{10}-phenanthrene, D_{12}-chrysene, D_{12}-benzo(e)pyrene), surrogates (D_8-naphthalene, D_{10}-anthracene, D_{10}-pyrene, D_{12}-benzo(a)anthracene, D_{12}-benzo(k)fluoranthene, D_{12}-benzo(a)pyrene D_{12}-benzo(g,h,i)perylene), PCB30 and PCB185 were purchased from Dr. Ehrenstorfer, Germany. Terphenyl and PCB 121, the internal standards for instrumental analysis by GC/MS were purchased by Sigma–Aldrich, Germany. Physicochemical properties of analytes are given in Supplementary Information.

2.2. Passive samplers

2.2.1. SPMDs

The SPMDs consisting of an LDPE membrane filled with 1 mL of triolein (95% purity), in nominal dimensions 2.54 × 91.4 cm (exposure surface area 460 cm^2), wall thickness of 75–90 μm were purchased from (Exposmeter, Sweden). Samplers contained 2 μg/sampler of individual performance reference compounds (PRCs; D_{10}-Acenaphthene, D_{10}-Fluorene, D_{10}-Phenanthrene, D_{12}-Chrysene, D_{12}-Benzo(e)pyrene). Before use they were stored in gas tight metal containers at −20 °C. The volume of sampler (triolein + membrane) is 4.95 mL.

2.2.2. DGTs

DGT (diffusive gradients in thin film samplers) samplers were purchased by DGT Research Ltd, Lancaster, UK. Two versions of the sampler were applied: one for sampling mercury ions and another version for sampling heavy metals nickel, cadmium and lead. The sampler is composed of a plastic body, which contains a prefilter with a surface area $A = 3.14$ cm^2, diffusive hydrogel (0.8 mm thick) and adsorptive resin-gel (0.16 mL volume) layers.

2.3. Sampling sites

2.3.1. Altenwörth an der Donau

Altenwörth on the Danube represents the location upstream of the Vienna area. The actual sampling site was located at the bridge on the left bank Danube river side arm in Altenwörth, approximately at the river kilometre (rkm) 1980, cca 55 km upstream Vienna agglomeration. This sampling site was not located directly in the main stream of the Danube, since the installation of the sampling equipment would have been logistically very difficult in the area of the adjacent Danube power plant. The sampled surface water is not affected by the backwater area of the Danube dam that is located downstream. The water level gradient at the bridge provides suitable conditions for operation of suspended sediment traps that were deployed simultaneously with passive samplers. The fast water current at the bridge enabled to achieve elevated sampling rates with SPMDs and thus to accumulate higher amounts of analytes.

2.3.2. Langenzersdorf

The site Langenzersdorf is located at the weir 2 of the Marchfeld channel just upstream the main Vienna city agglomeration. The artificially constructed channel represents an important source of irrigation water for vegetable farmers of the Marchfeld area between the rivers March/Morava and the Danube. The site is located 1 km downstream the intake structure of Marchfeld channel from the left

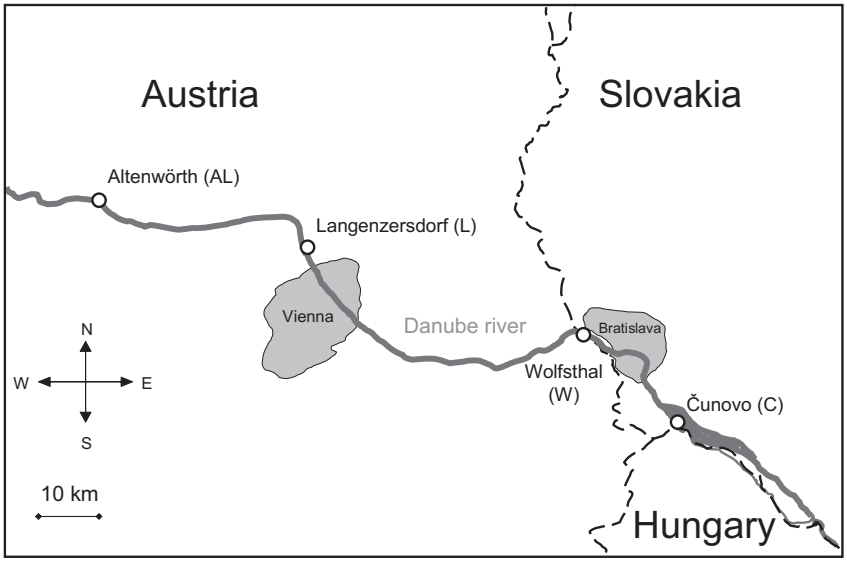

Fig. 1. Map of the sampling sites in the Danube river in Austria and Slovakia. Site symbols are given next to the site location names.

bank of the Danube at the rkm 1938. It is assumed that the flow velocity of Danube is slightly affected by the backwater of the Freudenau dam that is located 17 km downstream, but this should have only a minimum effect on water quality.

2.3.3. Wolfsthal

The sampling was performed at the Wolfsthal on-line monitoring station at Hainburg/Donau on the right Danube bank, approx. 15 km upstream Bratislava at the rkm 1879. The water from the Danube for passive sampler exposure was pumped into the monitoring station using submersible pumps operating at 1000–2000 L h^{-1} that were installed in the main stream of Danube. During the sampling campaign performed in 2010, passive sampling was simultaneous with other alternative sampling methods including continuous collection of water samples and suspended particulate matter. For the purpose of this sampling campaign non-filtered water from the Danube was evenly distributed to particular sampling devices that included automatic water sampler, suspended particulate matter sampler and passive samplers, respectively. Data comparing various sampling techniques will be reported separately. The station facility was adapted to perform passive sampling as described in the sampling campaign description below.

2.3.4. Cunovo

The sampling site is located 15 km downstream the city of Bratislava at the rkm 1836 on the dam at the right bank in Čunovo. The Čunovo dam is a part of the Danube dam system Gabčíkovo and its basic function is to ensure the flow into the old Danube riverbed in the agreement between Slovakia and Hungary. The sampling was performed at the water intake object of the hydroelectric power plant in the Čunovo dam (http://www.gabcikovo.gov.sk/svdgn/stup_Cun.htm). In 2011, after nearly 20 years since the completion of the dam system, sediment dredging activities started in the reservoir Hrušov that is located just upstream the Čunovo dam. There are about 2 million cubic metres of sediment that must be removed in the coming years. These dredging activities can, potentially mobilize also pollutants that are assessed in the present study. During the sampling campaign the dredging project was performed at the right bank, and the flow of sampled water passed the area of dredging activities.

2.4. Sampling campaigns

2.4.1. 2010

In 2010 passive sampling was performed at a single monitoring site at the online monitoring station in Wolfsthal. Continuous sampling in 14-days passive sampler exposure periods started in July and ended in December 2010 with a single interruption from 14th September to 5th October for station maintenance. During each of the ten 14-day exposures three samplers of each type (SPMD, DGT) were deployed in parallel. For deployment samplers were mounted using a stainless steel wire holder inside a 1 m high glass cylinder with 5 cm inner diameter. The flow of Danube river water through the cylinder was kept constant at 140 L h^{-1} for the entire 14-day exposure period. The dates of deployment periods are given in Table 1. In parallel with passive sampling, ten composite samples of whole water, representative for each of the 14-day sampler deployment period, were collected using an automatic water sampler installed in the monitoring station. Details are given in Supplementary Information. Concentrations of PAHs and heavy metals were determined in these composite samples.

2.4.2. 2011

The monitoring included 4 season sampling campaigns, in the months of February, April, July, and October 2011. The dates of deployment periods are given in Table 2. During each campaign 3 samplers in parallel were deployed at each site during 14 days cycles.

For deployment at the online monitoring station Wolfsthal samplers were mounted in a flow-through column as described for the 2010 campaign. At the remaining three sites samplers were placed into protective cage made of perforated stainless steel plate, preventing their mechanical damage and deployed in the river approximately 1 m below the water level with the help of ropes, buoys and anchors. After 14 days of exposure the samplers were collected, inspected for mechanical damage and the biofilm formation, photographed, transported to the laboratory in the protection package in a portable cool box. The prevention of contact of SPMDs with plastic materials and other potential sources of contamination were ensured. An additional field control sampler was exposed to air while samplers were being deployed and collected. The field control was processed as the deployed samplers and was used to measure contamination during transportation and handling. Three sampler fabrication controls were also analysed to determine contamination arising from the manufacturing process, sampler components, laboratory storage, processing and analytical procedures, but also to determine the initial concentration of PRCs in the SPMD samplers before exposure (Huckins et al., 2002; Booij et al., 2007). Several samplers were not retrieved due to loss of samplers during field exposure, namely by vandalism at site Langenzersdorf in April, and by sampler cage tear off at site Altenwörth in July. The SPMD samplers and their extracts were stored at separate place from chemicals, in a freezer under the temperature −20 °C. SPMD samplers were analyzed for hydrophobic organic pollutants PAHs and PCBs. DGT samplers were stored at 4 °C until processing and analysed for priority pollutant heavy metals nickel, cadmium, lead and mercury.

Table 2
Description of sampling sites in the study area.

No.	Sampling site	Symbol	Water body	River kilometre	Longitude	Latitude
1.	Altenwörth	AL	Danube	1980	15°51′54″	48°22′44″
2.	Langenzersdorf	L	Danube	1938	16°21′22″	48°17′35″
3.	Wolfsthal	W	Danube	1879	16°59′15″	48°09′52″
4.	Čunovo	C	Danube	1836	17°13′29″	48°01′49″

2.5. Sample extraction and analysis

2.5.1. SPMDs

SPMD samplers were cleaned from debris and mud and analytes were extracted two times 24 h by dialysis to hexane. Dialysates were further cleansed by gel permeation chromatography and silica gel or sulphuric acid modified silica gel for PAH and PCB analysis, respectively. The analysis of PAHs was performed using 6890N GC (Agilent, USA) equipped with a 30 m × 0.25 mm × 0.25 μm HP5-MS column (Agilent, USA) coupled to 5972 MS operated in electron impact ionization mode. PCB analysis was performed using GC–MS/MS 6890N GC (Agilent, USA) equipped with a 60 m × 0.25 mm × 0.25 μm DB5-MS column (Agilent J&W, USA) coupled to Quattro Micro GC MS MS (Waters, Micromass, UK) operated in EI+ ionization mode. Details of sample processing and instrumental analysis are given in Supplementary Information.

2.5.2. DGTs

Heavy metals accumulated in the DGT sampler adsorption resin were extracted with 1 mL of 1 mol L^{-1} HNO_3 solution for 24 h. The determination of heavy metals nickel and lead in extracts was performed according to ISO 15586:2003, whereas cadmium was analysed according to DIN 38406/19. The analysis proceeded by atomic absorption spectrometry with graphite furnace (ET-AAS). Mercury analysis was performed by a microwave digestion with HNO_3 and H_2O_2 and an amalgam enrichment and reduction with sodium borohydride, followed by analysis of mercury by cold vapour atomic absorption spectrometry.

Table 1
Description of the sampling campaign at the site Wolfsthal in the Danube in 2010.

Exposure nr.	Exposure period		Exposure (days)	Water temperature (°C)	Mean discharge (m^3 s^{-1})[b]	SPMD-sampling rate R_S (Ld^{-1})[a]
	Start	End				
I	06.07.2010	20.07.2010	14	21	2176	16.4
II	20.07.2010	03.08.2010	14	20	2766	11.4
III	03.08.2010	17.08.2010	14	18	3371	6.0
IV	17.08.2010	31.08.2010	14	18	2417	6.6
V	31.08.2010	14.09.2010	14	15	2918	7.2
VI	05.10.2010	19.10.2010	14	12	1428	4.1
VII	19.10.2010	02.11.2010	14	10	1414	3.7
VIII	02.11.2010	16.11.2010	14	10	1364	3.4
IX	16.11.2010	30.11.2010	14	8	1469	3.7
X	30.11.2010	14.12.2010	14	4	1897	2.0

[a] R_S is the equivalent water volume extracted by SPMD per day for a compound with a medium molecular weight (Mw = 178; phenanthrene).
[b] Calculated from volume discharge data available for the monitoring station in Bratislava.

Table 3
Description of the sampling campaign in the Danube in 2011.

Campaign Nr. and sampling site	Exposure period		Exposure (days)	SPMD-sampling rate R_S (L d^{-1})[a]	Water temperature (°C)	Mean discharge (m^3 s^{-1})[b]
	Start	End				
I Al Altenwörth	16.02.	02.03.	14	15.8	4	1496
I L Langenzersdorf	16.02.	02.03.	14	11.5	3	
I W Wolfsthal	03.03.	17.03.	14	4.4	3	
I C Cunovo	03.03.	17.03.	14	12.9	3	
II Al Altenwörth	14.04.	28.04.	14	16.3	12	1346
II L Langenzersdorf	14.04.	28.04.	14	NA[c]	13	
II W Wolfsthal	14.04.	28.04.	14	4.14	13	
II C Cunovo	14.04.	28.04.	14	18.6	13	
III Al Altenwörth	22.06.	7.07.	14	NA[c]	19	2063
III L Langenzersdorf	22.06.	07.07.	14	20.9	19	
III Wolfsthal	22.06.	07.07.	14	12.0	19	
III C Cunovo	22.06.	07.07.	14	14.8	19	
IV Al Altenwörth	13.10.	27.10.	14	26.2	12	2021
IV L Langenzersdorf	13.10.	27.10.	14	17.6	11	
IV W Wolfsthal	13.10.	27.10.	14	3.4	11	
IV C Cunovo	13.10.	27.10.	14	19.7	11	

[a] R_S is the equivalent water volume extracted by SPMD per day for a compound with a medium molecular weight (Mw = 178; phenanthrene).
[b] Calculated from volume discharge data available for the monitoring station in Bratislava.
[c] NA-not available because of SPMD sampler loss.

2.6. Calculation of dissolved water concentrations from passive sampler data

2.6.1. SPMDs

Dissolved water concentrations of target analytes were calculated from amounts accumulated in SPMDs as follows. Amounts of analytes absorbed by the samplers follow a first-order approach to equilibrium. Aqueous concentrations were calculated from the mass (*Ns*) absorbed by the SPMD, the in situ sampling rate of the compounds R_S and their sampler–water partition coefficients K_{SW}:

$$C_w = \frac{N_S}{V_S K_{SW}\left[1 - \exp\left(-\frac{R_S t}{K_{SW} V_S}\right)\right]} \quad (1)$$

where V_S is the volume of the SPMD (4.95 mL) and t is the sampler exposure time.

PRC dissipation also follows first-order kinetics. Sampling rates R_S were estimated from dissipation of PRCs from SPMDs during exposure using nonlinear least squares method by Booij and Smedes (2010), considering the fraction f of individual PRCs (D_{10}-acenaphthene, D_{10}-fluorene, D_{10}-phenanthrene and D_{10}-chrysene) that remain in the SPMD after the 14-day exposure as a continuous function of their K_{SW}, with R_S as an adjustable parameter.

$$f = \exp\left(-\frac{R_S t}{K_{SW} V_S}\right) \quad (2)$$

Here, $f = N_{PRC}/N_{0,PRC}$; $N_{0,PRC}$ = initial amount of the PRC at $t = 0$, N_{PRC} = amount of each PRC remaining after exposure, and t is exposure period (14 days). Assuming water boundary layer controlled uptake, R_S of individual target compounds in the higher hydrophobicity range was estimated by substituting Eq. (3) derived by Rusina et al. (2010) into Eq. (2).

$$R_S = FAM^{-0.47} \quad (3)$$

Here M is the molecular weight of the analyte, A is the surface area of SPMD (460 cm^2). The factor F represents the effects of environmental conditions (temperature, flow, biofouling). It was obtained as an optimized value of adjustable parameter using nonlinear least squares method for estimating sampling rates (Booij and Smedes, 2010) after substitution of R_S in Eq. (2) by Eq. (3). The necessary K_{SW} values were intrapolated from the empirical equation (Huckins et al., 2006)

$$\log K_{SW} = -0.1618(\log K_{OW})^2 + 2.321 \log K_{OW} - 2.61 \quad (4)$$

Booij et al. (2003a) observed that SPMD-water partition coefficients K_{SW} did not significantly change with temperature in the range from 2 °C to 30 °C, thus, for our calculations partition coefficients were not corrected for effect of temperature.

2.6.2. DGTs

Dissolved water concentrations C_{DGT} of metals were calculated from their masses accumulated in DGTs (N) according to Warnken et al. (2007).

$$C_{DGT} = \frac{N\Delta g}{DtA} \quad (5)$$

where Δg is the thickness of the diffusion gel layer, t is exposure time, A is the sampler surface area and D is the temperature dependent diffusion coefficient of a metal ion. Applied values of D were taken from the DGT manufacturer (www.dgtresearch.com). It is assumed that mass transfer of metal species into DGT is controlled by diffusion in the gel layer. Thus, sampling by DGT should not be affected by the flow velocity/turbulence, as is the case for SPMDs.

2.7. Assessment of PAH patterns using principal component analysis

Principal component analysis (PCA) was used to compare the PAH levels and patterns in the dissolved phase, which was monitored at four sampling sites during four seasons in the 2011 sampling campaign. PCA analysis was based on absolute analyte concentrations and data were modelled according to the procedure described by Vrana et al. (2001).

3. Results and discussion

3.1. Aspects of sampling with SPMDs

The repeatability within three parallel determinations of PAH concentrations represented by mean relative standard deviation

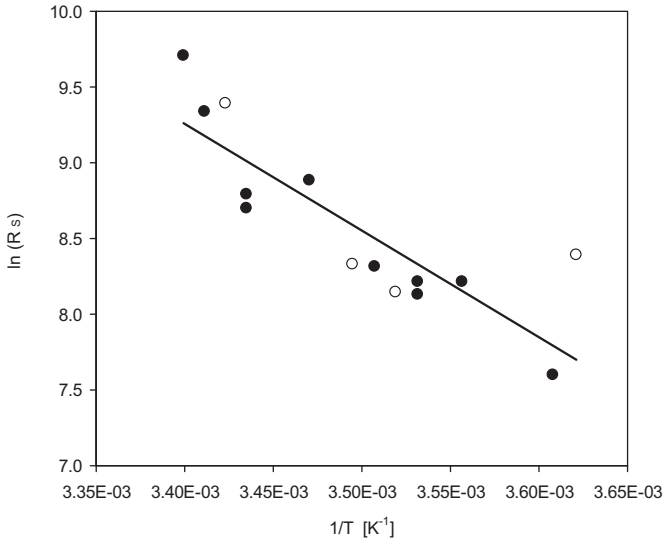

Fig. 2. Effect of water temperature on SPMD sampling rate of phenanthrene obtained during individual 14-day exposures at the site Wolfsthal in 2010 (black circles) and 2011 (white circles), respectively. The line represents linear regression of all SPMD sampling rates (expressed as natural logarithm; ln R_S) vs. reciprocal value of absolute temperature ($1/T$). The activation energy of mass transfer ΔE_a of 58 ± 10 kJ mol^{-1} was calculated from the slope of the line multiplied by gas constant R according to Eq. (6).

was 24%, in that all the processes of analytical determination are included – sampling, extraction and determination by GC–MS. SPMD fabrication and field blanks contained concentrations of PAHs and PCBs that were below the instrumental limit of detection, with exception of naphthalene (up to 40 ng/SPMD). Blank subtraction for naphthalene in field exposed samplers was not done, because any naphthalene present in blanks dissipates from SPMDs during exposure to level which is at equilibrium with water (Lohmann et al., 2012). Solvent blanks processed concurrently with samplers did not contain quantifiable amounts of target analytes. In some exposed samples compounds as benzo[b]fluorantene, benzo[k]fluorantene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene were present at concentrations below limit of quantification. Those compounds are

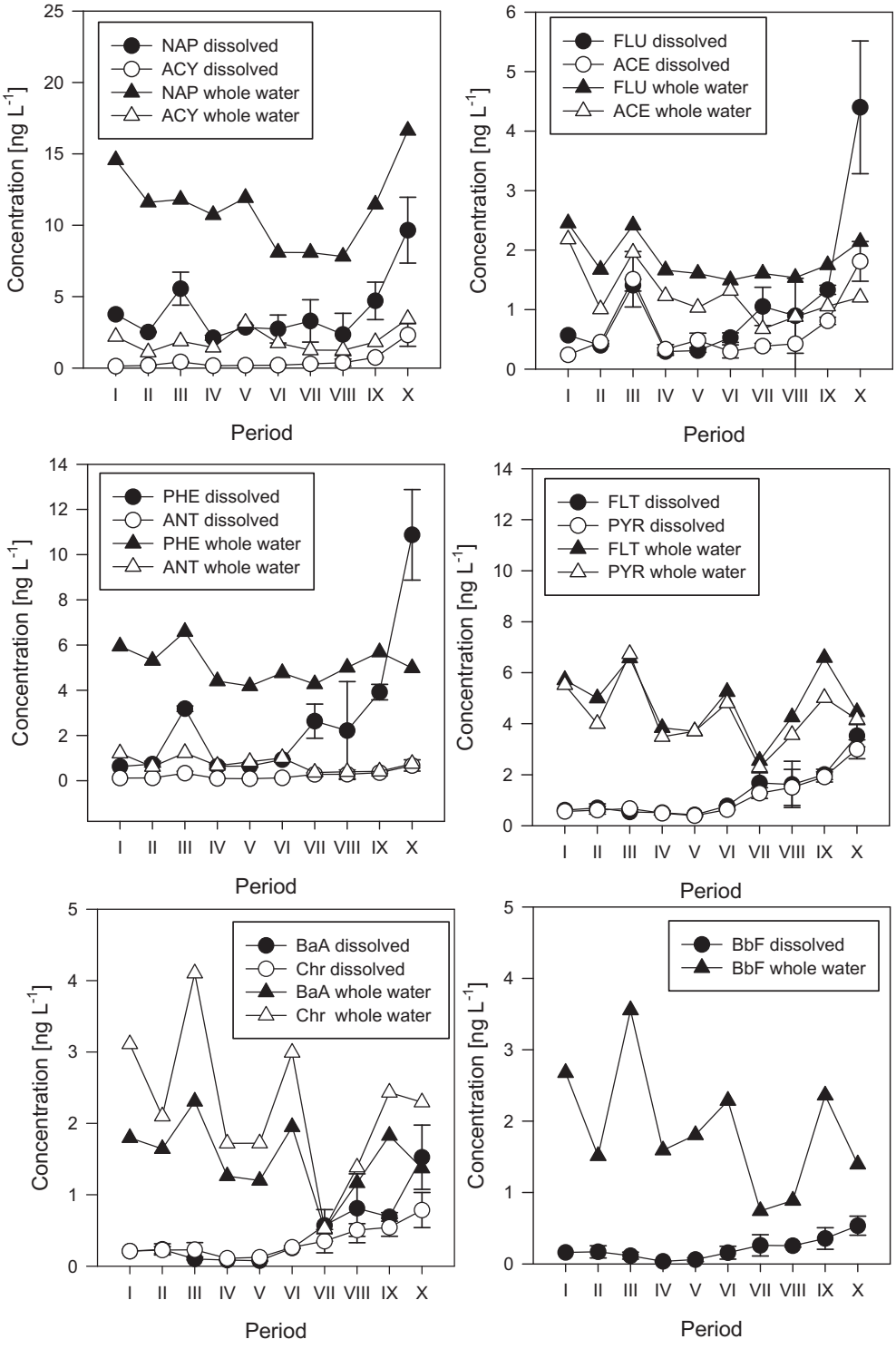

Fig. 3. Temporal variability of free dissolved (using SPMD) water and whole water (using continuous water sampler) PAH concentrations, at the online monitoring station in Wolfsthal in July–December 2010. Samplers were continuously exposed in 14-day deployment periods. Deployment and retrieval dates are reported in Table 1.

hydrophobic and predominantly partitioned to suspended particles and colloids in water and only a small fraction is present in the dissolved phase. For the calculation of the mean concentration of those compounds in water according to Eq. (1). the mass in sampler N_S was substituted by instrumental limit of quantification (LOQ). In such case the calculated water concentration of those compounds represents the highest possible concentration. Water concentrations estimated from LOQ for the above compounds were in range 0.01–0.29 ng L^{-1}. The highest LOQ values were calculated for the sampling site in Wolfsthal, because of low R_S values obtained at this site due to slow water motion inside the exposure tube. Where method LOQ was applied in mean value estimates, data in Figs. (4–5) are labelled with an asterisk. Detection limits in water can be significantly improved by a longer sampler exposure time or by exposure conditions, e.g. higher water turbulence. One option to increase sampling rates would be the use of samplers with a larger surface area, since the sampling rate is a product of mass transfer coefficient and sampler surface area. The 14-day exposure of samplers in this study was a result of a compromise to enable a direct comparison with other tested sampling methods (suspended particle traps and composite water samples).

The PRC-derived sampling rates R_S for phenanthrene from all field exposures are shown in Tables 1 and 3. R_S values for other compounds were derived using Eq. (3), which estimates a slight decrease in R_S with increasing molecular mass. Phenanthrene R_S values ranged from 2.0 L d^{-1} at Wolfsthal in December 2010 to a maximum of 26.2 L d^{-1} at Altenwörth in October 2011. In agreement with assumption of water boundary layer uptake different R_S values were obtained at different sites and during different seasons, which is related to differences in flow rates of water in the river and the position of sampler in the stream. Further relevant factors that affect mass transfer include the temperature and possibly the presence of biofouling and particle deposition on the surface of sampler. At the monitoring station Wolfsthal the sampler was placed in a glass tube, where the river water was pumped with lower flow velocity/turbulence than is in the river. This explains the generally lower sampling rates at this site. With exception of the sampling site Čunovo SPMD sampling rates increase with increasing temperature. The effect of temperature on passive sampling with SPMDs could be quantified at the site Wolfsthal (Fig. 2). Since the effect of flow velocity/turbulence on mass transfer into passive sampler at this site could be kept relatively constant, temperature was the only variable factor in exposures, when neglecting potential variable effects of biofouling and suspended particulate matter concentrations on mass transfer. At other sites, such evaluation was not possible because flow conditions could not be controlled for caged samplers. The effect of temperature on R_S can be quantified in terms of activation energies (ΔE_a) for mass transfer, as modelled by the Arrhenius equation

$$R_S = R_{S\infty} \exp\left(-\frac{\Delta E_a}{RT}\right) \quad (6)$$

where $R_{S\infty}$ is the sampling rate at the hypothetical upper limit where temperature is infinite, R is the gas constant and T is the absolute temperature. Values of ΔE_a can be determined by plotting the natural logarithm of R_S ($\ln R_S$) vs. the reciprocal absolute temperature ($1/T$). The activation energy can then be calculated by multiplying the slope of the linear regression line with the gas constant. The calculated activation energy for phenanthrene in this study ΔE_a of 58 ± 10 kJ mol^{-1} is in line with the average ΔE_a of 37 ± 21 kJ mol^{-1} summarised for a broad range of studies by Huckins et al. (2006). This means that a temperature increase from 10 to 20 °C causes an increase in sampling rate by a factor about 2.3.

3.2. Temporal and spatial variability of PAHs in the Danube river

In 2010 temporal variability of PAH concentrations was investigated at a single sampling site in the Danube at Wolfsthal. Sum of concentrations of free dissolved PAHs determined from SPMDs deployed during the 2010 campaign were 5–39 ng L^{-1}. The SPMD data (Fig. 3) show that the freely dissolved concentrations of individual PAHs in the water column increase during the winter months. This may reflect the higher PAH emissions from pollution sources, mainly from burning of fossil fuels, in winter. The atmospheric deposition is one of the important transport processes, by which PAHs enter the water phase. The higher activity of emission sources in winter in combination with climatic conditions such as temperature inversion that limits the vertical dispersion and less intensive atmospheric reactions create favourable conditions for PAH deposition to water phase. Moreover, Henry's law constant increases with increasing temperature and thus, higher equilibrium concentrations in water are expected at lower temperatures even when atmospheric concentration remains constant (Staudinger and Roberts, 2001).

In addition to the general trend of concentration increase with decreasing water temperature, an increase of concentrations of

Table 4
Correlation of free dissolved (C_{free}) and whole water (C_{total}) concentrations of PAHs at the site Wolfsthal during the sampling campaign in 2010 with mean water temperature (T), suspended particulate matter content (SPM), and total organic carbon content (TOC).

Compound		Log K_{ow}	C_{total}				C_{free}		
			C_{free}	T	SPM	TOC	T	SPM	TOC
Naphthalene	NAP	3.37	[a]0.70	0.03	0.28	0.34	−0.41	0.19	0.30
Acenaphthylene	ACE	4.00	[a]0.79	−0.31	0.28	0.15	−0.61	0.02	0.06
Acenaphthene	ACY	3.92	0.23	0.54	0.31	0.57	−0.33	0.38	0.57
Fluorene	FLU	4.18	0.37	0.27	0.28	0.57	−0.60	0.03	0.12
Phenanthrene	PHE	4.57	−0.01	0.29	0.17	0.55	[a]-0.62	0.06	0.11
Anthracene	ANT	4.54	0.00	0.52	0.48	[a]0.65	−0.61	0.14	0.16
Pyrene	PYR	5.18	−0.11	0.31	0.31	[a]0.64	[a]-0.68	0.01	−0.12
Fluoranthene	FLT	5.22	−0.15	0.19	0.10	0.42	[a]-0.72	−0.09	−0.20
Chrysene	CHR	5.86	−0.14	0.34	0.33	[a]0.67	[a]-0.69	−0.02	−0.14
Benzo[b]fluoranthene	BbF	5.90	−0.29	0.43	0.42	[a]0.67	[a]-0.62	−0.01	−0.15
Benz[a]anthracene	BAA	5.91	−0.19	0.33	0.27	0.58	[a]-0.75	−0.17	−0.24
Benzo[a]pyrene	BAP	6.04	−0.32	0.56	0.49	[a]0.75	[a]-0.81	−0.20	−0.23
Benzo[ghi]perylene	BP	6.50	−0.53	[a]0.63	0.52	0.59	[a]-0.77	−0.13	−0.20
Indeno[1,2,3-cd]pyrene	IP	6.50	0.36	0.08	0.37	0.47	[a]-0.77	−0.13	−0.20
Dibenz[a,h]anthracene	DahA	6.75	−0.53	0.41	0.31	0.48	[a]-0.77	−0.13	−0.20

[a] Significant Pearson product moment correlation coefficients ($n = 10$, $p < 0.05$; non-directional t-test) and higher than 0.62.

Table 5
Dissolved concentrations (ng L^{-1}) of sum of PAHs, Cd, Ni and Pb measured in urban impacted European rivers.

River	PAHs	Cd	Ni	Pb	Reference
Danube	13–72	2–14	205–544	18–74	This study
Morava	25–203				Prokeš et al., 2012
Marne		7–19			Thévenot et al., 1998
Seine		9–70			Thévenot et al., 1998
		11–67			Chiffoleau et al., 1999
	15–50	8–111	338–3760		Tusseau-Vuillemin et al., 2007
	3.5–106				Bourgeault and Gourlay-Francé, 2013
Thames			800		Neal et al., 2000
Rhône	55	11	423	76	Miege et al., 2012
Bosna	20–480				Harman et al., 2013
		1–24	218–2981	8–1000	Vrana et al., authors unpublished data

some lighter PAHs (naphthalene, acenaphthene, fluorene and phenanthrene) was observed during the third sampler exposure period (03.08. to 17.08. 2010). In August 2010, a local flood occurred at the Danube sampling profile in Wolfsthal and the elevated concentrations of dissolved compounds may be related to mobilization of these compounds during the event.

At the Wolfsthal site free dissolved concentrations of PAHs obtained with passive sampling (C_{free}) can be compared with whole water concentrations (C_{total}) determined in composite water samples representative of each of the 14-day sampler deployment periods (Fig. 3). The comparison reveals that C_{free} in water decreases with increasing compound hydrophobicity (Supplementary information Fig. S5), which reflects the adsorption of hydrophobic compounds on particles or colloids. A significant positive correlation (Table 4) between C_{free} and C_{total} was observed only for the two most hydrophilic compounds (naphthalene and acenaphthylene), which are predominantly present in water in the dissolved phase. While C_{free} was negatively correlated with temperature for most compounds, such trend was not observed for C_{total}. With exception of the most hydrophilic compounds (naphthalene and acenaphthylene), C_{total} of PAHs was positively correlated with total organic carbon (TOC) content in water, which confirms that hydrophobic compounds are associated with organic matter present on particles and in colloids in water. One hypothesis for the absence of correlation between C_{free} and C_{total} is that a fraction of compounds adsorbed on suspended particulate matter is bound irreversibly and cannot partition into dissolved phase, however, such investigation was beyond the scope of this study and more research is needed to prove it. Since whole water concentration measurements were performed with a single composite sample during each sampling period, no data on precision of whole water sampling in one laboratory is available in this study. Collection and analysis of replicate samples would likely reveal whether absence of correlation with free dissolved concentration can be attributed to low precision of sampling and analysis. However, considering the very high sampling and processing effort needed to obtain a representative water sample for a 14 day period, such experiment is practically not feasible.

In addition to samples collected during our study, information is available on concentrations of PAHs in spot samples of whole water (1 L) that were collected monthly in 2010 at the Wolfsthal monitoring station by Water Research Institute Bratislava for the purpose of chemical status assessment in the river Danube (Water

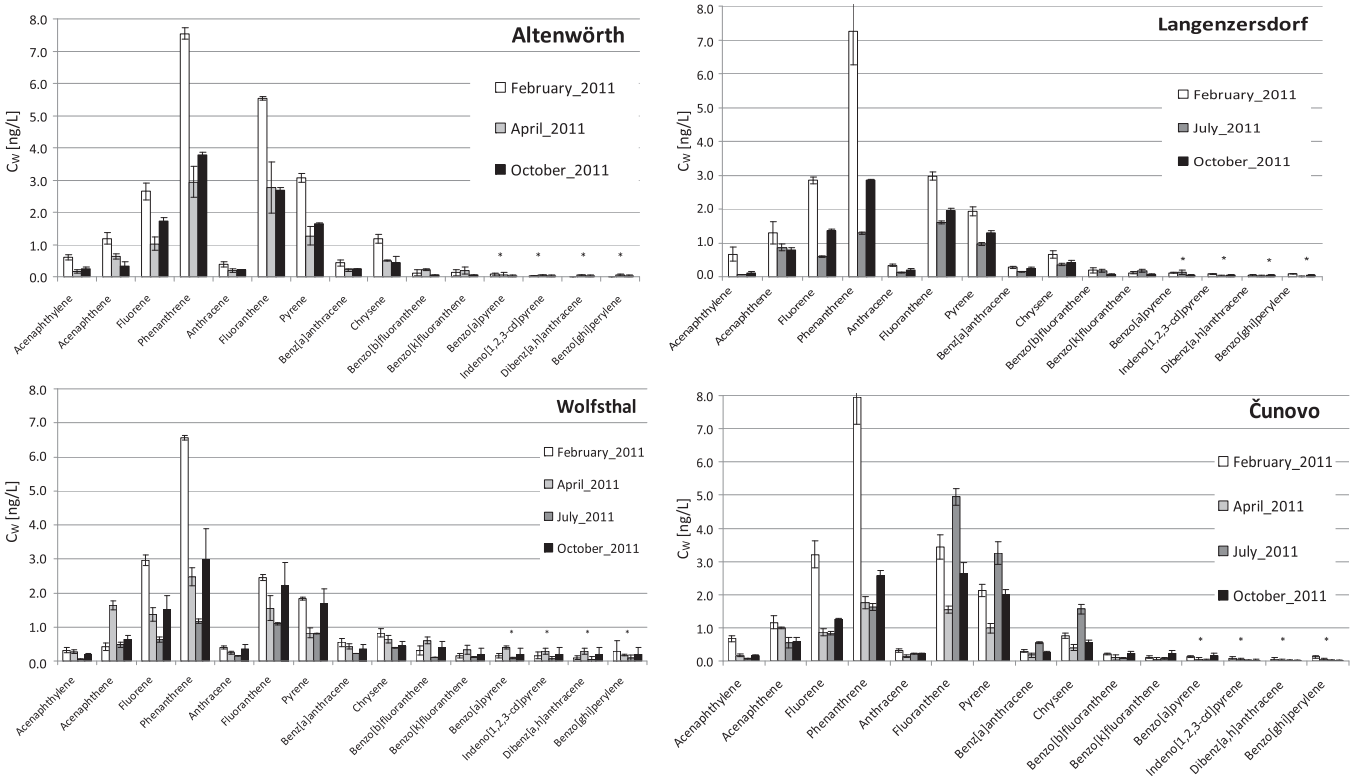

Fig. 4. Temporal variability of free dissolved PAH concentrations, monitored using SPMD passive samplers at four sampling sites along the Danube river in 2011. Data points labelled with asterisks include individual measurements below limit of quantification.

Research Institute, Bratislava, 2013). During the whole duration of sampling campaign, concentrations of all monitored priority pollutant PAHs were below their respective LOQs. The LOQs of individual compounds were relatively high (2–30 ng L^{-1}; Supplementary data, Table S1). The data do not contradict our observations, however, no statements on temporal variability of pollution can be made on their basis. Although data from regulatory monitoring, obtained using low volume spot sampling, can be applied for checking compliance with environmental quality standards, they are not suitable for assessment of temporal and spatial variability of PAHs.

The availability of water discharge data at the Wolfsthal monitoring station enabled to estimate fluxes (as a product of discharge and concentration) of free dissolved as well as total PAHs in the rived Danube. The estimated flux of dissolved PAHs (sum of 16 compounds) ranged from 0.9 kg d^{-1} in October to 6.6 kg d^{-1} in December 2010, respectively. Estimated total PAH flux in Danube ranged from 3.3 kg d^{-1} in October to 16.7 kg d^{-1} in August (period III), respectively. The maximum total flux coincides with the above mentioned elevated water flow event. The average contribution of free dissolved compounds to total flux was 31%. We stress that the ultimate aim of passive sampling is to obtain a measure of the level of pollution that gives a representative measure of the exposure of organisms and compare the contaminant levels in time and space, but not to assess mass balance of compounds in water bodies.

In 2011 the samplers were deployed during four seasons at four sampling sites to characterize the temporal and spatial variability of priority metals, PAHs and PCBs in the water column of the Danube river between the cities of Vienna and Bratislava. Total concentration of PAHs determined from SPMDs in the campaign conducted at four sampling sites in 2011 were 13–72 ng L^{-1}. A comparison with free dissolved concentrations measured with passive sampling in other urban impacted European rivers shows that the pollution of Danube by PAHs is 1.5–7 times lower than in the rivers for which data is compiled in Table 5. Temporal variability of PAH concentrations at the four sites is shown in Fig. 4. In agreement with observations from 2010 the highest PAH concentrations at all four sampling sites were observed in winter (February) and the lowest ones in summer (July), respectively. A single exception to this general trend were elevated concentrations of fluoranthene, pyrene and chrysene that were observed at Čunovo in July 2011. This event may have been related to on site sediment dredging activities or from accidental release of PAHs from ships, but would require a more detailed investigation. Spatial variability of PAHs during different seasons along the monitored Danube stretch is shown in Fig. 5. To visualize spatial trends of free dissolved concentrations, data from sites downstream the Altenwörth site (AL) were presented as percentual concentration increase or decrease against the levels measured at AL site. Visualisation was performed only for compounds where concentrations exceeded their respective LOQs. No systematic spatial trends in PAH concentrations could be observed along the monitoring stretch since different and often opposite trends were observed during different seasons. The spatial variability of PAH concentration was not dramatic and for most compounds the concentrations varied less than two-fold in both directions in comparison with those measured at the AL site. In

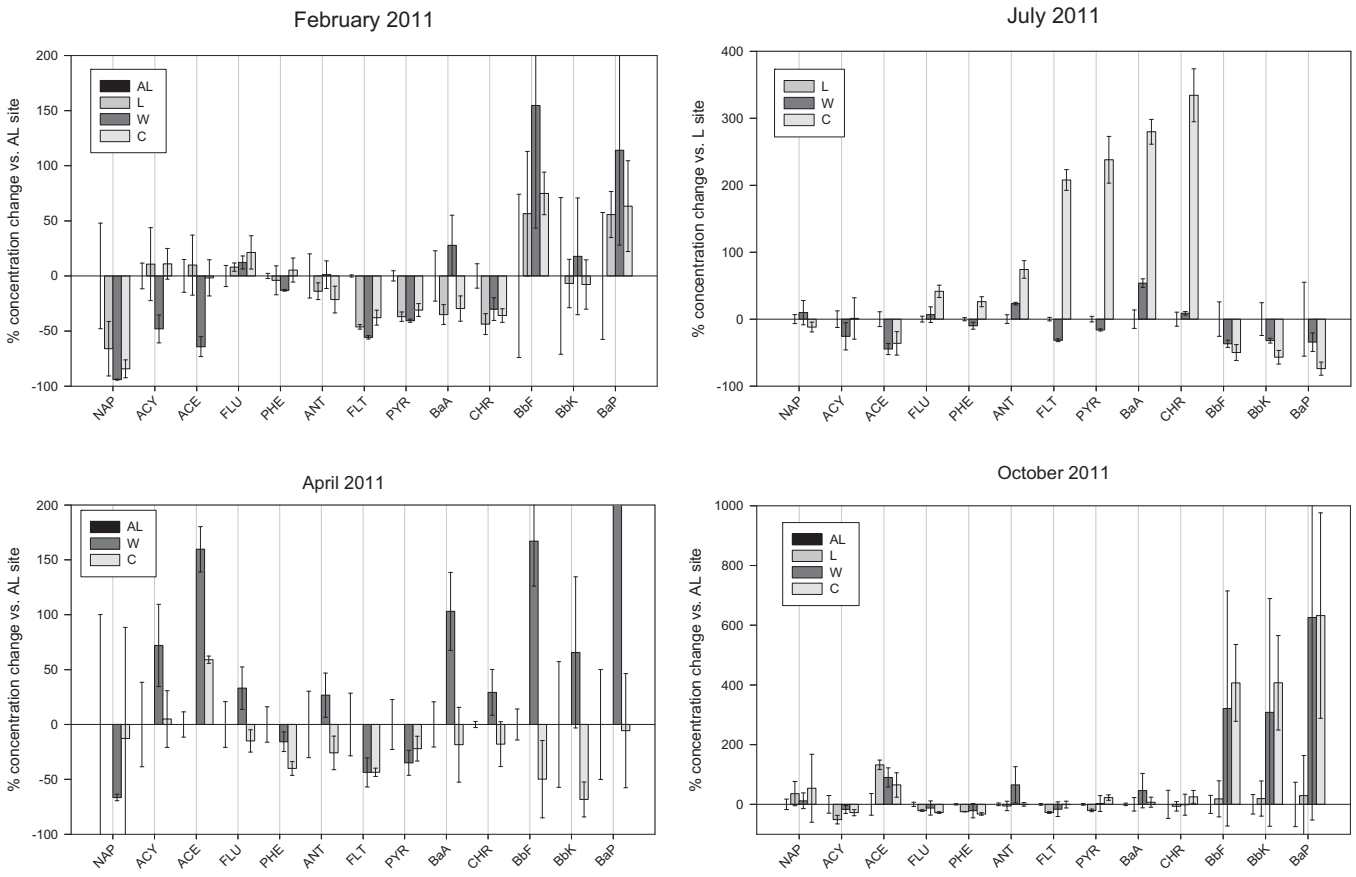

Fig. 5. Spatial variability of free dissolved PAH concentrations along the Danube river, monitored using SPMD passive samplers during four seasons in 2011. Data from sites downstream the Altenwörth site (AL) are presented as percentual concentration increase or decrease against the levels measured at the AL site. For data collected in July 2011, Langenzersdorf (L) was taken as the reference site.

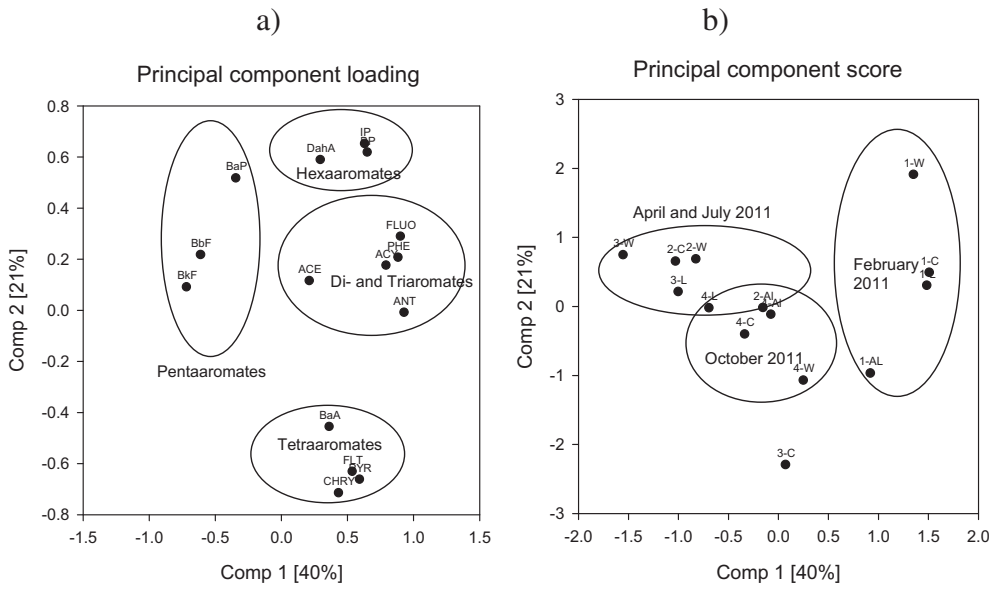

Fig. 6. Principal component plot (Component 1 vs. Component 2) for comparison of the PAH profiles in the dissolved phase at four sampling sites monitored during four seasons in 2011. Graph a) shows loadings for the individual PAHs. Graph b) shows scores of samples. Sampling sites and events are described in Table 3.

many cases these differences were lower than the precision of the passive sampling method and thus not significant. An exception were the above mentioned significantly elevated concentrations of fluoranthene, pyrene, benzo(a)anthracene and chrysene in Čunovo in summer.

From an inspection of the PCA pattern analysis for the samples from the 2011 campaign, the score plot [Component 1 vs. Component 2, Fig. 6(a)] shows the separation of the samples along the principal components. As can be seen in the loading plot [Fig. 6(b)], the compounds (PAHs) are separated on the principal component plane (PC1 vs. PC2) according to their molecular weight or hydrophobicity. Water concentration patterns calculated from SPMD data cluster together on the PCA plot for most samples collected at the four sites along the Danube in April, July and October 2011. Thus, both concentration levels and patterns remain relatively constant during most of the year along the monitored Danube stretch. A distinct contamination pattern of PAHs can be observed in samples collected in February 2011. In winter season, contaminant patterns also differ more between sites. This corresponds with higher concentration levels observed in winter; the differences in PAH fingerprint may correspond with a higher diversity of contaminant sources in winter. A specific case is the PAH pattern observed in Čunovo in July 2011, which was discussed above.

The two city agglomerations of Bratislava and Vienna do not seem to have a significant effect on downstream PAH concentrations in water. Our observations support the hypothesis that concentrations in the water phase are related to diffusive rather than point pollution sources and the observed periodic annual variability is related to seasonal changes of atmospheric PAH concentrations. Point sources of PAHs in the both cities are likely to be transient rather than continuous and likely related to rain fall, stormwater overflow and direct runoff. It is likely that these point discharges are effectively diluted by the river that has a usual water discharge of more than 2000 $m^3\ s^{-1}$ in the area of interest. In addition, the concentrations in the dissolved phase are probably well buffered by contaminant partitioning between water column and bed sediments along the river.

3.3. Temporal and spatial variability of PCBs in the Danube river

SPMD samples from the 2011 campaign were analysed for PCBs. The calculated dissolved PCB concentrations were very in sub ng L^{-1} range (Table 6) and close to method limit of quantification. Sum of 6 indicator PCB congeners ranged from 5 to 16 pg L^{-1}. No temporal or spatial trends of pollution could be observed along the monitored Danube stretch. Better method sensitivity would be required for a better characterization of levels and contaminant patterns of PCBs. The simplest way to achieve this is to significantly extend SPMD exposure up to several months.

Table 6
Dissolved concentrations of PCBs, in water, derived from SPMD passive samplers, at the four sampling sites in Danube during four seasons in 2011.

Campaign	I (February–March 2011)				II (April 2011)				III (July 2011)				IV (October 2011)			
Concentration (pg L^{-1})	AL	L	W	C	AL	L[a]	W	C	AL[a]	L	W[b]	C[b]	AL	L	W[b]	C[b]
PCB 28	5.8	5.8	5.9	3.3	6.1		14.0	3.4		1.8			2.6	4.8		
PCB 52	2.7	1.6	<2.1	0.4	2.4		<2.2	0.9		0.5			0.9	1.4		
PCB 101	2.9	1.7	1.4	0.8	4.5		3.1	0.5		2.0			3.0	1.8		
PCB 153	2.2	1.8	<2.3	0.8	3.6		<2.4	0.3		1.4			4.0	1.2		
PCB 138	0.7	<0.9	<2.3	<0.8	1.3		<2.4	<0.6		<0.4			0.3	<0.6		
PCB 180	1.8	1.5	1.6	<0.8	1.8		<2.5	<0.6		0.7			1.9	<0.6		
Σ PCBs	16.1	12.4	8.9	5.2	19.5		17.1	5.0		6.5			12.7	9.1		

[a] Not reported because of loss of samplers.
[b] Not reported because of bad repeatability of analysis.

3.4. Temporal and spatial variability of heavy metals in the Danube river

DGT fabrication and field blanks contained concentrations of that were below the instrumental detection limit of 0.5, 5 and 5 ng/DGT for Cd, Ni and Pb, respectively. The calculated dissolved Cd, Pb and Ni concentrations measured from metal amount accumulated in DGT samplers were very low and always in the sub μg L^{-1} range. Concentration of mercury was always below the detection limit of the applied method (0.10 ng/DGT sampler). When this limit is applied in Eq. (5) together with the diffusion coefficient of mercury in water 9×10^{-6} cm^2 s^{-1} (Dočekalová and Diviš, 2005), the estimated concentration of mercury in water is less than 0.1 ng L^{-1}. In 2010 concentration of Cd, Pb and Ni were in the range <1–20, 18–49, and 173–544 ng L^{-1}, respectively (Fig. 7). The repeatability within three parallel determinations of concentrations represented by mean relative standard deviation was 23%. Similarly as was observed for less hydrophobic PAHs, an increase of Cd concentration was measured during the third sampler exposure period (03.08. to 17.08.2010). In August 2010, a local flood occurred at the Danube sampling profile in Wolfsthal and the elevated concentrations may be related to mobilization of these compounds during the event. DGT-derived water concentrations were also compared with composite samples of whole water analysed during the sampling campaign in 2010 as well as with data from spot samples of filtered (through 0.45 μm pore size filter) water that were collected monthly at the Wolfsthal monitoring station for the purpose of chemical status assessment (Water Research Institute, Bratislava, 2013). DGT-derived concentrations reflect the dissolved contaminant fraction and were always lower than whole water concentrations. They should be comparable with concentrations found in filtered water samples, but it must be taken into account that spot samples reflect just the concentration in water at one moment, whereas DGT sample provides a time weighted average measure of concentration over 14 days.

For Cd, concentrations in spot samples as well as in composite whole water were below limit of quantification during the whole campaign. For Pb, quantifiable concentration (4 μg L^{-1}) was found only in a single spot sample collected during sampling period II. Although elevated whole water concentration was detected during the same period in composite whole water sample, it was lower than in the filtered spot sample. A possible explanation is that spot sampling detected accidentally a peak of Pb contamination that was short enough to be not detected in time averaged DGT and composite water samples. Similarly, elevated concentrations of Ni were measured in spot samples during sampling period II and III, Composite water analysis was available only for period II, with concentration slightly above method LOQ, however, lower than that found in spot sample. Since only five pairs of data were available for comparison, no conclusions can be made on presence or absence of correlation between free dissolved and total metal concentration in water. Estimated total metal flux in Danube ranged from <12–24, 22–220, and <118–406 kg d^{-1} for Cd, Pb and Ni, respectively. The mean contribution of free dissolved metals to total flux was 3, 10, and 28% for Cd, Pb and Ni, respectively.

In 2011 concentration of Cd, Pb and Ni were in the range <2–6, 18–74, and 205–457 ng L^{-1}, respectively. The repeatability within three parallel determination of concentrations represented by mean relative standard deviation was 21%. A comparison with dissolved concentrations measured in other urban impacted European rivers shows that the pollution of Danube by heavy metals is comparable or up to one order of magnitude lower than in the rivers for which data is compiled in Table 5. Monitoring with DGTs confirmed at all sites relatively constant concentrations of the three priority pollutant metals and neither a systematic temporal nor a spatial trend of pollution could be observed along the monitored Danube stretch (Fig. 8). The variability of measured metal concentrations was mostly lower than method precision and thus not significant. The data suggest that pollution sources along the monitored stretch do not significantly affect heavy metal concentrations in the dissolved phase.

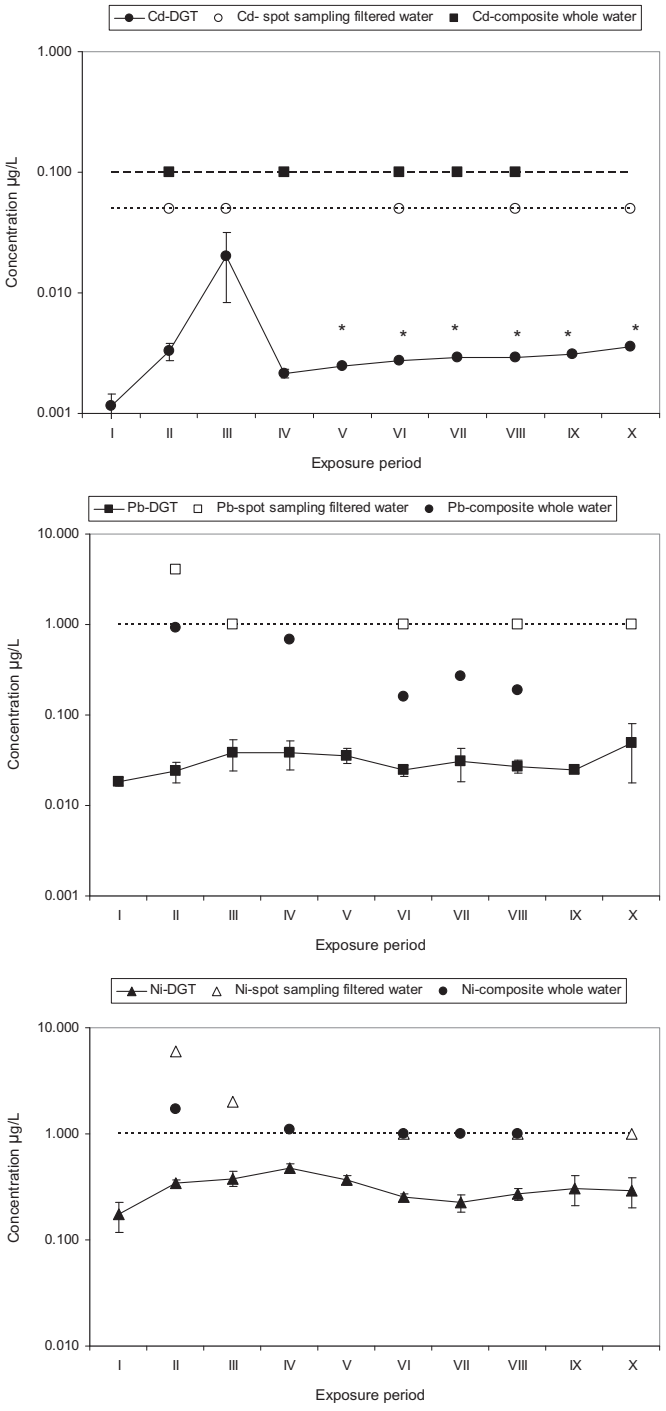

Fig. 7. Temporal variability of dissolved (using DGT), whole water (using continuous water sampler) and filtered water (using monthly spot sampling) metal concentrations, at the online monitoring station in Wolfsthal in July–December 2010. Samplers were continuously exposed in 14-day deployment periods. DGT concentrations labelled with asterisks were lower than limit of quantification. Dotted and dashed lines show the limits of quantification in spot and composite water samples, respectively.

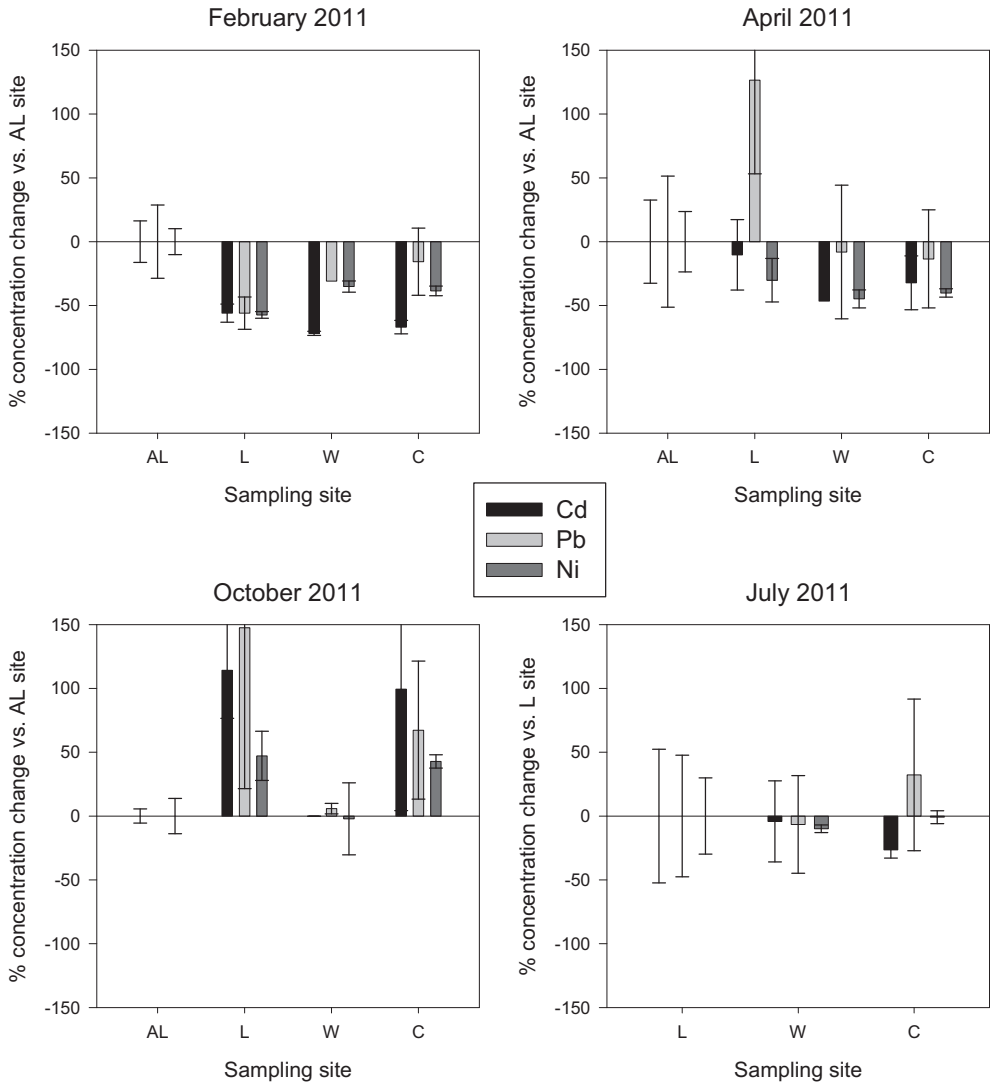

Fig. 8. Spatial variability of free dissolved heavy metal concentrations along the Danube river, monitored using DGT samplers during four seasons in 2011. Data from sites downstream the Altenwörth site (AL) are presented as percentual concentration increase or decrease against the levels measured at the AL site. For data collected in July 2011, Langenzersdorf (L) was taken as the reference site.

4. Conclusions

Passive samplers provide a useful tool for an assessment of pollution status and related temporal and spatial trends within water bodies. They enable to collect information on trace concentrations of priority pollutants with a good precision and, unlike in case of chemical monitoring in biota, the effect of variable exposure conditions can be kept under control. It is possible to directly compare monitoring data obtained at different sites and seasons, which makes passive samplers a promising tool in assessment of spatial and temporal pollutant trends. Passive samplers provide complementary information to chemical monitoring in sediment or suspended particulate matter. Sediment concentration patterns may not be representative for estimation of immediate concentrations in the water column, but they provide a long-term contamination record. On the contrary, the passive samplers integrate water concentrations only during the sampling period and reflect the actual pollution situation in a water body. When total extraction techniques are applied in sediment or suspended particulate matter analysis they cannot distinguish between contaminants that are irreversibly adsorbed to sediment and those that can be easily partitioned to pore water and then released to the water column.

Spot sampling with a frequency once per month produces often data that are below detection limits and sometimes accidentally detects elevated concentrations that originate from short term concentration variation that is representative only for the moment when sample was collected. This makes spot sampling less suitable for assessment of temporal concentration trends in comparison with techniques that provide an average concentration over extended period, such as continuous water sampling or integrative passive sampling. From the later techniques, passive sampling is much less laborious. Moreover, both DGT and SPMD techniques allow measurements of bioavailable concentrations of pollutants in water with a better sensitivity than can be achieved with conventional water sampling techniques. When accepting that free dissolved concentration is a suitable measure of contaminant levels to which organisms are exposed, absence of a correlation between C_{free} and C_{total} observed for PAHs in this study invokes a question whether whole water concentration is a suitable parameter for assessment of risks associated with pollutants in water.

The spatial variability of dissolved PAHs and heavy metals in the studied region was small, which indicates that diffusive pollution sources dominate over local point sources. Concentrations of PAHs decreased with increasing water temperature in the whole region indicating that atmospheric emission from domestic heating sources and consequent deposition represent an important pathway of PAHs to aquatic ecosystem of the region in the winter period. For PAHs we observed a similar trend in the Danube left bank tributary, the river Morava (Prokeš et al., 2012), which indicates that cyclic seasonal oscillation of PAH concentration occurs in most water bodies in the geographic area. This has an implication for the design of future monitoring programs aimed at assessment of long term trends. For such analysis, based on passive sampling measurements of PAH concentrations, time series should be constructed of data from samples collected always in the same year period. For heavy metals seasonal variability does not seem to be significant.

Our study provided insight into the temporal and spatial variability of bioavailable concentrations of selected priority pollutants in a selected stretch of the Danube river, one of the biggest streams on the European continent. Similar field studies increase the body of information available for assessment of factors that affect distribution and fate of pollutants in the natural environment. Moreover, they support regulators in assessing opportunities for using passive sampling for monitoring water quality within a legislative framework.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.08.018.

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Príloha 25

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Measurement of environmental pollutants using passive sampling devices – an updated commentary on the current state of the art

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The following provides a short overview of the important topics arising from the 6th International Passive Sampling Workshop and Symposium (IPSW 2013) held in Bordeaux, France between 26 and 29th June, 2013. Most of the discussions focussed on monitoring non-polar and polar organic pollutants in water with less coverage on air (probably already seen as a mature technology for this medium) and sediments. The use of passive sampling devices within regulatory water monitoring programmes was also a major theme of the Workshop.

Environmental impact

Passive samplers can be used to monitor environmental pollutants in air, sediments, soils and water. A wide range of different technologies is available. They can used to give either equilibrium or time weighted average concentrations of a chemical. Information from these devices can be used for assessment of long-term pollution trends, assist in checking compliance with environmental quality criteria, improving risk assessments and to better inform decisions on undertaking potentially expensive remedial actions. This commentary provides an overview of the current state-of-the-art, where research gaps currently exist and where new opportunities for the use of passive samplers may arise in the future.

Introduction

A number of passive samplers have been available for over forty years to measure chemicals in different environmental media (*e.g.* air, soils, sediments and water).[1] The technique can be used to measure either equilibrium or time-weighted average concentrations (TWA) of the analyte of concern. Historically, such devices have been used to monitor localised ambient work place chemicals or atmospheric pollutants on a global scale (*e.g.* within the United Nations Stockholm Convention on the *trans*-boundary movement of persistent organic pollutants using large networks of samplers). The use of passive samplers for monitoring pollutants in sediments, soils and water is a more recent development, but one that is gathering momentum internationally. It is now recognised that these devices can have important roles in monitoring water quality across the European Community within the remit of various legislative (*e.g.* Water Framework Directive (WFD) and Marine Strategy Framework Directive (MSFD)) regulations.[2–4] Typically, data obtained from samplers can be used alongside information obtained from conventional spot sampling of water to assist in checking compliance with environmental quality criteria or for assessment of long-term pollution trends. Use of this combined approach helps to improve risk assessments and to better inform decisions on undertaking potentially expensive remedial actions. Devices can also be used for sampling of more complex environmental matrices such as sediments and to mimic the uptake of chemicals by biota. For example, the measurement of the freely dissolved concentration of a chemical in pore waters of sediments and soils as well as its accessible (releasable) concentration from these media, are important parameters in environmental risk assessments.

At the 6th International Passive Sampling Workshop and Symposium (IPSW 2013) held in Bordeaux, France between 26 and 29th June, 2013 (the previous European events took place in the Czech Republic in 2004 and 2009, Slovakia in 2006 and Poland in 2011) a number of important developments and the future challenges in the use of passive sampling technology were discussed. The event was attended by over 70 delegates from 17 countries and provided a timely opportunity for international experts to discuss key research and regulatory issues. The following article provides an update of the important topics arising from the symposium since the last commentary

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published in 2011;[5] most being centred on monitoring organic pollutants in water with less coverage on air (probably already seen as a mature technology for this sector) and sediments.

Measuring concentrations of non-polar pollutants in water

The use of passive samplers to monitor non-polar chemicals (*e.g.* PAHs, PCBs, chlorinated pesticides and industrial chemicals) in water was the first application of such devices for this medium. In the 1990s, nearly all trials used the semi-permeable membrane device (SPMD): an enclosed low-density polyethylene (LDPE) membrane filled with a small amount of the lipid triolein as receiving phase.[6] With this sampler and with these classes of pollutants, performance reference compounds (PRCs) can be used for *in situ* calibration. PRCs reduce the uncertainty of the TWA concentration data produced during field deployments where changes in the water temperature and turbulence can affect the sampler uptake rates (usually measured in L per day). Over the last ten years there has been a move away from SPMDs to using low-cost single-phase polymers such as low-density polyethylene (LDPE) and silicone rubber.[7] Such materials are flexible as they can be fashioned to any size or thickness for varying field applications. Robust cleaning procedures are available to remove contaminant chemicals or residual monomers from these materials. In addition, their extraction and clean-up procedures are relatively simple in comparison to those needed for SPMDs. Robust calibration procedures (to measure the sampler uptake rate and the sample/water partition coefficient (K_{sw}) for different chemicals) are in place for single-phase samplers and hence these can be used with confidence in regulatory monitoring programmes. Other polymers may be used for niche applications (*e.g.* polyimide, polyoxymethylene, polypropylene) and to cover a wider range of pollutant classes. The use of specific physicochemical properties (*e.g.* Hansen solubility parameter) of an analyte and matching these to the chemistry of a specific polymer was highlighted as a way to aid in material selection and for modelling purposes. This work is being undertaken by the Safety and Environmental Assurance Centre within Unilever, UK. Application of single-phase samplers to monitor specific classes of emerging pollutants such as methyl siloxanes and organo-tins were presented at the meeting. As their dissolved concentrations are very low (ng L^{-1} or sub ng L^{-1}) this is often below the detection limit of analytical instrumentation used to measure these compounds; the use of passive samplers offers a significant advantage over spot sampling approaches.

Another application is to use such polymers (typically silicone rubber) deployed on research ships and ferries. Rubber samplers were used by Cefas (Lowestoft Laboratory, UK) housed within their research vessel RV Endeavour. Sea water was pumped across the devices (contained in a special box) in a controlled way to minimise flow effects on sampler uptake rate for the target pollutants. Information on the spatial distribution of pollutants could be obtained and at a lower cost compared with conventional means of collecting such data. This approach was also used on Joint Danube Survey (JDS3: http://danubesurvey.org/) where an "active" passive sampler system was installed on board the expedition ship. Water sampling took place over a series of 5-day intervals as the vessel moved downstream along defined stretches of the river. High sampler uptake rates were achieved with subsequent enhanced analytical detection limits for chemicals. This temporally- and spatially-integrative sampling approach provides representative information on water quality over defined stretches of the Danube. Samplers can also be deployed easily on gliders and other remotely controlled apparatus used in oceanographic surveys and can potentially give data on concentrations of pollutants with water depth as well as spatially.

Measuring concentrations of polar pollutants in water

Over the last five years there has been increased interest in measuring the concentration of a range of polar chemicals in water.[8] Many of these substances are classified as 'emerging pollutants'. Two designs of sampler are generally used, the polar organic compound integrative sampler (POCIS) and the polar version of the Chemcatcher®. Most published work used the POCIS. Both devices use receiving phases that sequester polar pollutants by an adsorption or ion-exchange mechanism rather than by partition and both use a thin protective polyethersulphone (PES) diffusion membrane. Typically, sampler uptake rates are 10–250 mL per day for polar compounds. Uptake for most analytes remains in the linear phase over about a 14-day period with most chemicals exhibiting only a short lag time. The mechanism of uptake for polar compounds is not well understood, particularly the transfer kinetics of chemicals across the PES membrane and this is an area for further research. Changing the type of diffusion membrane (*e.g.* Nylon) to decrease lag-phase phenomenon and to improve uptake kinetics has been proposed.

A further drawback is that there is a lack of theoretical models able to predict the uptake of a chemical into a POCIS or Chemcatcher® based on the compounds physicochemical properties (*e.g.* log K_{ow}). Hence, this necessitates extensive laboratory-based calibration experiments to measure compound specific uptake rates (and in some case the effects of temperature, turbulence and salinity) before the samplers can be used in the field to measure TWA concentrations.[9] The use of PRCs with adsorption or ion-exchange based systems is still not fully demonstrated, although some groups have shown that preloading the receiving phase with deuterated (d_5) deisopropylatrazine can possibly be used for this purpose.[10] These factors thus limit the utility of these samplers beyond screening or semi-quantitative assessment of pollutants. The development of an organic version (o-DGT) of the diffusion in thin films (DGT) device used for metals is however showing some promise.[11] Here a thick diffusion gel layer is added, which helps control the uptake of analytes into the receiving phase and limits the effects of water flow. This may address the problem of the lack of a PRC approach for the polar Chemcatcher® and POCIS samplers.

Several groups questioned the effect of uneven distribution of the loose sorbent within POCIS, which can sag towards the base of the device during extended deployments, potentially reducing the active sampling surface area. This issue may be

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resolved easily by directly replacing the powder by a commercially available 47 mm extraction disk (*e.g.* 3M Empore™ or Horizon Technology Inc. Atlantic® disks) that is available for a range of chemistries. Using such a simple design modification should help minimise variability of field data. Natural Resources Wales are starting to deploy this new design of sampler in effluents at waste water treatment plants; initial results for the screening of pharmaceuticals using such devices and liquid chromatography with time-of-flight mass spectrometry detection techniques are encouraging.

Applications of polar samplers to measure pharmaceuticals, personal care products and other chemicals (*e.g.* polar pesticides, acid herbicides, alkylphenols) in various aquatic matrices (*e.g.* drinking, surface and waste water and hospital effluents) were discussed. As there is a paucity of reliable uptake rates available in the literature for polar compounds, when quantitative results are required an extensive laboratory calibration step is required. No standard calibration (*e.g.* using static, semi-static, or through-flow tanks) procedure is being used among practitioners and this naturally increases the variability of results. In addition, the aqueous matrix used for calibration can have a significant impact on the value of the sampling rate obtained. For example sampling rates are known to be different when measured in laboratory-grade distilled water compared with those obtained using a waste water effluent.[12] A novel approach is to use *in situ* field calibrations in order to obtain sampler uptake rates and this is particularly suited for hydrophilic chemicals. If the field concentration of a substance is known to be relatively constant (the concentration usually first established by the intensive collection of water samples over an extended period of time) then *in situ* calibration is a possibility. It is useful for substances such as human metabolites of pharmaceuticals that are difficult and expensive to obtain in sufficient quantities needed for laboratory tests. Typically samplers can be deployed in the influent or effluent of a well controlled waste water treatment plant to obtain such calibration data. *In situ* calibration may also be attractive in other complex matrices such as estuarine, halo-saline and marine environments where salinity may influence uptake kinetics.

In future better guidance on the range of approaches for the calibration of samplers is needed, particularly if devices are to be incorporated into large scale monitoring programmes. Such a document would be a useful adjunct to the ISO standard: Water quality—Sampling Part 23: Guidance on passive sampling in surface waters (ISO 5667-23:2011). This was designed to help standardise the application of different passive samplers by end users and thus to facilitate the use of this technology within a regulatory monitoring framework.

Measuring concentrations of metals and other inorganic compounds in water

Passive samplers have been used to monitor metals and other inorganic compounds in water for many years. Most work uses the DGT device and sometimes the metals version of the Chemcatcher®.[13] Often devices are used alongside other types of samplers to monitor a wide suite of pollutants in the water column. In addition, the DGT can be used to measure pollutants in sediments and soils. The design of the DGT is flexible and work to replace the generic Chelex-100 receiving phase with a number of bespoke resins suited for specific analytes was described. For example, a titanium dioxide layer has been shown to have a good affinity for the sequestration of low levels of uranium in a range of environmental waters. Workers in Japan replaced the chelating resin disk with a special Empore™ Rad caesium disk in the Chemcatcher and used the device for monitoring radio-caesium (^{137}Cs) in contaminated field sites around the Fukushima nuclear reactor plant. Preliminary results with the new sampler were encouraging and gave comparable values of ^{137}Cs to those found in concentrated extracts obtained from large volume spot water samples. However, the overall sample preparation time was significantly reduced as counting measurements were undertaken directly off the disk. There was also less risk of exposing laboratory staff to low level radiation during sample processing.

Although the use of passive samplers for measuring concentrations of metals and some nutrients is unequivocal, often workers have given little attention to the effects that water chemistry and method of field deployment may have on results. Information on using these types of sampler in large long-term monitoring campaigns is still quite sparse in comparison to devices used for non-polar substances. How the ambient water quality affects the availability of a given metal for uptake into a sampler is complex and needs to be taken into account if the technology is to be used with confidence in a routine regulatory setting. For example: across the seasons, water flow-rate, temperature, pH and amount of suspended and dissolved particulate matter and nutrients (and hence the propensity for bio-fouling of the diffusional surface) will vary significantly. Each factor affects the distribution of a metal in the water column and hence availability of uptake. The design of the apparatus used to deploy any sampler also has an impact on uptake kinetics. Although in most cases the field location dictates the type of equipment that can be employed, often little consideration is given to this aspect by end users where a range of different kit is utilised in a given monitoring campaign.

Use of passive sampling devices in regulatory monitoring programmes

It is evident that there is worldwide interest in the use of passive samplers for environmental monitoring. This was not the case 10 years ago when most end users had to be convinced of applicability and reliability of the technology. The recent resurgence of interest in Europe has, in part, been driven by the revised water quality legislation (*i.e.* WFD in 2001 and the MSFD in 2008 introduced across the Community). A number of large research and demonstration projects funded by the Commission have shown the potential of passive samplers, used in conjunction with other techniques, for monitoring water quality within a regulatory framework. A recent change to the WFD illustrates this point. The updated Directive 2013/39/EU on priority substances with respect to Community water policy introduced very low environmental quality standards (EQSs) for

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several compounds in surface waters[14] (*e.g.* 8–80 pg L^{-1} for cypermethrin, 60–600 pg L^{-1} for dichlorvos, 32–1300 pg L^{-1} for heptachlor/heptachlorepoxide and 130–650 pg L^{-1} for PFOS). This means using low-volume spot samples of water combined with conventional laboratory analysis will result in method quantification limits higher than the respective EQS. Such methods will not be accepted by the Commission for compliance monitoring within the Directive. An option is the use of passive samplers for *in situ* extraction of such pollutants from water. Many samplers have high uptake rates (from hundreds of mL to several L per day), so this may be an option to measure very low concentrations in the field. Moreover, measurement of the free dissolved concentration in water using passive samplers provides a better assessment of exposure of aquatic organisms to priority pollutants than whole water sampling. For example, more than 90% of the compounds identified using a combination of different passive samplers in a trial undertaken by the Environment Agency of England and Wales in 2011 were not identified using routine spot sampling techniques. Many of the substances identified by passive sampling were priority hazardous substances listed in Annex X of the WFD. A similar approach may be needed for fulfilling the future requirements of MSFD. In coastal and marine waters the concentration of most pollutants is generally much lower than those found in surface water due to significant dilution effects. The measurement of such low concentrations by conventional water techniques in these environments will prove challenging.

Nevertheless, passive sampling is not yet applied in regulatory compliance monitoring as the EQSs are not defined for the compartments sampled by this method, *e.g.* the freely dissolved concentration of a pollutant in the water column. In July 2013, the Network of reference laboratories for monitoring emerging environmental pollutants (NORMAN Association – http://www.norman-network.net) organised an expert group meeting to bring together eco-toxicologists and experts on monitoring to investigate how the EQS defined for various pollutants could be related to their respective concentrations measured using passive sampling devices – or should the Commission reconsider how EQS are derived? The conclusions are to be disseminated in a position document clarifying where passive sampling fits into the schemes that are currently applied for assessment of the chemical and ecological status of water bodies under the WFD.

Another revision within Directive 2013/39/EU was the opportunity for Member States to use matrices (*e.g.* biota or sediment) other than water for monitoring very bio-accumulative compounds; provided they could supply evidence that an equal level of protection of aquatic life was being achieved. For these chemicals, biota is the preference for chemical monitoring and the Directive sets out EQS for this matrix. Concentrations of pollutants in biota are related to their concentrations in the aqueous phase. Use of organisms for chemical monitoring, however, introduces natural variability (caused by variable size, age, sex and physiological conditions of sampled organisms) into reported data, which complicates or in some cases precludes their spatial and temporal comparability. Moreover, the specific biota species required for chemical monitoring may not be available at some sampling sites. A potential solution is to apply abiotic passive sampling methods that provide "biomimetic" pollutant measurements, *i.e.* simulate the bio-concentration of pollutants from water into aquatic organisms, with a low inherent variability. Partition-based samplers equilibrated with water or sediment can be used to estimate lipid normalised concentrations of pollutants in aquatic organisms in the monitored system, providing the relevant lipid/polymer partition coefficients are available. Another application is based on direct equilibration of polymer-based passive samplers with biota tissue. The equilibrium concentrations obtained in tissue enable a direct comparison of contaminant levels between organisms, species or trophic levels when studying bio-magnification.

Within this topic area an update of the inter-laboratory study on the use of passive samplers for monitoring of emerging pollutants organised in 2011 by the NORMAN Association together with the European DG Joint Research Centre was given.[5] Study participants were free to apply passive samplers that they use routinely in their laboratories. In addition, organisers provided silicone rubber (for non-polar compounds) and POCIS (for polar compounds) samplers to be analysed in all participant laboratories. The exercise showed that the within laboratory precision obtained from use of the samplers was mostly satisfactory, but the laboratory analysis was in most cases the main source of between laboratory variability. The commonly used liquid chromatography/mass spectrometry technique is very susceptible to matrix effects, especially when using electrospray ionisation.[15] These effects include enhancement of ionisation as well as suppression. Extensive clean-up of extracts from samplers may be required to produce data that is fit for purpose. It is clear, however, for future successful application of these devices in monitoring campaigns the variability that originates from laboratory analysis must be minimised. This will require training of laboratories in routine preparation and analysis of extracts from samplers as well as organisation of proficiency testing schemes. The final report from the study is in preparation. In parallel, there must also be knowledge of how to interpret information obtained from passive samplers, particularly in the area of uncertainty of data.

The presentations at IPSW 2013 showed some of the key developments taking place in the area of passive sampling, with a key focus on monitoring of water quality. Some areas where polymeric devices can be used to assist regulators meet the new EQS for a wide range of priority substances within the latest revision of the WFD showed the future potential of this monitoring approach. Several challenges still remain, particularly for measuring polar pollutants and further research is needed here. The work of the NORMAN Association is doing much to disseminate the potential of the technology that is now being taken up by an ever increasing number of end users.

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Amdany R., Chimuka L., Cukrowska E., Kukučka P., Kohoutek J., and **Vrana B.**, Investigating the temporal trends in PAH, PCB and OCP concentrations in Hartbeespoort Dam, South Africa, using semipermeable membrane devices (SPMDs), ***Water SA*, 2014, 40, 425–436.**

Investigating the temporal trends in PAH, PCB and OCP concentrations in Hartbeespoort Dam, South Africa, using semipermeable membrane devices (SPMDs)

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ABSTRACT

The seasonal variability of persistent organic pollutants in Hartbeespoort Dam, South Africa, was investigated using semipermeable membrane devices (SPMDs) as passive samplers. Freely dissolved waterborne polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) were sampled to investigate seasonal changes in their concentrations. Exposure of the passive samplers was done for 14 days at the same sampling site in each of the four seasons of the year, in 2011. The SPMD-derived analyte amounts enabled the calculation of time-weighted averages of free dissolved waterborne levels of the contaminants. Concentrations ranged from 30.0 ng·ℓ^{-1} to 51.5 ng·ℓ^{-1} for PAHs, 38 pg ℓ^{-1} to 150 pg·ℓ^{-1} for PCBs, 9.2 to 10.4 ng·ℓ^{-1} for HCHs and 0.3 to 0.8 ng·ℓ^{-1} for DDTs, respectively. It was also noted that the winter season generally exhibited higher contaminant concentrations for most compounds studied, which likely reflects the seasonality of their atmospheric deposition. An attempt was also made to identify possible sources of PAH contaminants in the dam by examining PAH ratios. These diagnostic ratios were inclined towards pyrogenic sources of pollution, except for the winter season where both pyrogenic and petrogenic sources likely contribute to the contamination pattern.

Keywords: Hartbeespoort dam, persistent organic pollutants, semipermeable membrane devices, water-dissolved concentrations, temporal trends.

INTRODUCTION

Globally, huge quantities of organic pollutants, including persistent organic pollutants (POPs), are released into the environment. Due to their ubiquitous nature, hydrophobic organic compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) have been identified as environmental contaminants in almost every compartment of the global system (ATSDR, 2009). As byproducts of incomplete combustion of organic compounds, pyrosynthesis or pyrolysis of hydrocarbons, PAHs are released to the environment by both natural and anthropogenic sources (Levinson et al., 2008). PAHs may also reach water systems through oil spills and direct industrial effluent discharges. PCBs and OCPs, on the other hand, are POPs of anthropogenic origin. Chemically stable, strongly lipophilic and considerably toxic, OCPs have slow degradation rates and tend to bioaccumulate in lipid-rich tissues (Tiemann, 2008) of living organisms. PAHs, PCBs and OCPs are of particular interest because of their potential toxicity, carcinogenicity, possible mutagenicity as well as tendency to bioaccumulate. They are present in the aquatic environment both as truly dissolved and particle-bound. The easily bioavailable fraction, which corresponds to the free dissolved fraction, is of primary interest for risk assessment (Sabaliunas and Sodergren, 1997). It is generally assumed that particle- and colloid-bound compounds cannot cross biological membranes, bioconcentrate and cause biological effects (Landrum et al., 1985). The concentration of freely-dissolved POPs in the water column is directly proportional to their chemical activity and fugacity in the water phase and is an important parameter in modelling their fate in the environment (Mayer et al., 2003).

Due to their characteristically high hydrophobicity and very low solubility in water, these compounds are adsorbed onto finely-dispersed colloids and particulates. Thus, their free dissolved concentrations in water are often several orders of magnitude lower than the total concentrations. Indeed, the water-dissolved concentrations are generally low (ng·ℓ^{-1} to pg·ℓ^{-1} range) and insufficient for reliable quantitative chemical analysis by conventional methods. Consequently, proper analysis of free dissolved PAHs and PCBs in natural water is not easy and many sampling problems are encountered.

A viable alternative to a grab sampling approach is to use passive samplers. These devices usually combine sampling, selective analyte isolation, pre-concentration and, in some cases, speciation preservation, in one step (Vrana et al., 2005). The long accumulation period by the samplers allows for detection of very low concentrations of target analytes (Sabaliunas and Sodergren, 1997), which would otherwise be impractical to achieve. By providing time-weighted average (TWA) values that take into account episodic fluctuations in pollutant concentrations, these devices are better suited for long-term monitoring of contaminants in an environmental compartment (Kot et al., 2000). Among passive sampler devices (PSDs), semipermeable membrane devices (SPMDs) have been widely applied to estimate the concentrations of hydrophobic contaminants in the water phase (Huckins et al. 2006; Verweij et al., 2004; Huckins

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et al., 1993). These passive samplers are composed of a triolein-receiving phase for contaminant accumulation enclosed in a low-density polyethene membrane (LDPE). Contaminant residues sequestered by the SPMDs represent an estimation of the dissolved or readily bioavailable concentration of hydrophobic contaminants in water, which is not provided by most analytical approaches (Vrana et al., 2001). Sampling rates (R_s) for highly hydrophobic compounds are influenced by the environment's hydrodynamic conditions (Booij et al., 2007), such as water turbulence, biofouling and temperature at the sampling site. Through incorporation of performance reference compounds (PRCs) during SPMD fabrication, differences in environmental exposure conditions between deployment sites, times and different monitoring programmes can be adjusted for by studying the dissipation of these compounds (Huckins et al., 2002; Booij et al., 1998). PRCs are non-native, non-interfering compounds characterised by moderate to high fugacities, usually added to the lipid of the SPMD during sampler construction, prior to field exposure. Information on the rate of PRC dissipation during field exposure of samplers can then be applied to estimate the in-situ sampling rates of the compounds of interest (Booij et al., 2010).

Although South Africa is a signatory of the Stockholm Convention and also has a relatively strong industrial presence, information on pollution by POPs remains scanty. Unlike the Northern Hemisphere countries which experience moderate climatic conditions and where most of the studies on POPs have been conducted, South Africa's climate is characterised by high temperatures, little precipitation and long summers (Quinn et al., 2009). Thus, findings from Northern Hemisphere studies cannot be reliably applied to the South African situation. Nevertheless, studies on POPs in South African, such as Nieuwoudt et al. (2011), Das et al. (2008), Bouwman (2003) and Bouwman et al. (1990), among others, have been documented in the literature, but are not adequate to fully describe the South African situation. Apart from a recent study by Degger et al. (2011) on the use of SPMDs to determine POPs in some South African marine environments, very little other information on application of passive sampling in South Africa is available in the literature.

This study was aimed at determining the water-dissolved concentrations of the 16 US EPA priority PAHs, PCBs and OCPs in Hartbeespoort Dam, South Africa, using SPMDs. Specifically, temporal trends in POP concentrations in the dam were investigated.

MATERIALS AND METHODS

Chemicals and reagents

The PAH standard mixture containing the 16 US EPA priority PAHs (all > 97% pure) was purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. Performance reference compounds – D_{10}-acenaphthene, D_{10}-fluorene, D_{10}-phenanthrene and D_{10}-pyrene – were sourced from Dr Ehrenstorfer GmbH, Augsburg, Germany. D_8-Naphthalene, D_{10}-anthracene, D_{12}-fluoranthene, D_{12}-benzo(a)anthracene, D_{12}-benzo(k)fluoranthene, D_{12}-benzo(g,h,i)pyrene, PCB 30, PCB 185 and d_6-gamma HCH (Dr Ehrenstorfer GmbH, Augsburg, Germany) were used as recovery standards. PCB 121 and terphenyl (Dr Ehrenstorfer GmbH, Augsburg, Germany) were used as internal standards for PCB and PAH instrumental analysis, respectively. Pesticide residue analysis grade n-hexane, dichloromethane, trichloromethane and all other solvents

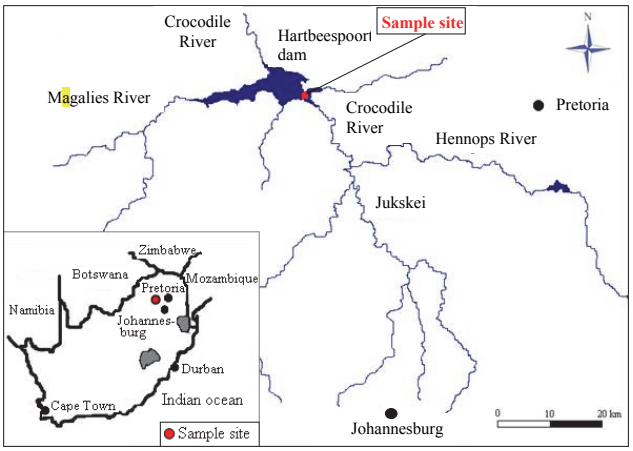

Figure 1
Map showing the sampling site in the Hartbeespoort Dam, South Africa

(all > 97% pure) used were purchased from Sigma-Aldrich (Prague, Czech Republic). Milli-Q water (18MΩ·cm) was obtained from the Millipore Simplicity 185 system (Millipore, Bedford, MA, USA).

Sampling site

The sampling site was located in the Hartbeespoort Dam, 25°45′09.97″S, 27°53′04.39″E, about 37 km west of Pretoria and on the Crocodile River in North West Province, South Africa (Fig. 1). The dam is a 20.7 km^2 water reservoir sandwiched between the Magalies mountain range in the Highveld region of northern South Africa (Nyoni et al., 2011). The dam reservoir receives water from a catchment area of about 4 100 km^2, via the Jukskei and Hennops rivers that flow into the Crocodile River (Harding et al., 2004). The five catchment basins of the dam are, from west to east: the Magalies/Skeerpoort, the Crocodile, the Juskei, the Hennops and the Swartspruit basin (Van Rei, 1987). The Crocodile River accounts for about 90% of the dam's water supply with rainwater being the major source in summer. This scenario dramatically changes during the dry season (winter) as 50% of the water received by the dam then comprises treated wastewater from urbanised areas upstream (Harding et al., 2004), which creates environmental challenges for the water body. Although the origins of the Crocodile River system can be traced to the north of the city of Johannesburg, extensive rural crop farming is still carried out within the dam's drainage area, using its water. Considerable urban development is also present along the shorelines of the basin, and a portion of the impounded water from the dam is utilised for domestic supply, both within the riparian community and in downstream urban centres (DWA, 2012).

Monitoring of the water body for PAHs, PCBs and OCPs using SPMDs was done in each of the four seasons of the year: winter, spring, summer and autumn, as described in Table 1.

Sampling procedure

At the deployment site, the samplers, including the field controls, were unpacked from the metal cans and placed on clean aluminium foil. The samplers were then mounted onto the deployment devices (protected by a steel casing). Once ready, they were quickly immersed in the water at between 1 and 1.5 m depth below the water surface. The steel cages housing

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TABLE 1 Deployment periods and some water quality parameters				
	Sampling period	Water temperature (°C)	pH	Dissolved oxygen (mg·ℓ$^{-1}$)
Winter	19-04-2011 to 04-05-2011	11.6	8.0	5.01
Spring	19-08-2011 to 02-09-2011	14.2	8.2	5.23
Summer	18-11-2011 to 02-12-2011	25.5	9.0	6.04
Autumn	24-02-2012 to 09-03-2012	19.7	8.6	5.75

the samplers were tied using ropes and anchored firmly to buoys. Finally, the field blanks were placed in airtight tin cans and transported in portable ice chests ('cool boxes') to the laboratory, where they were stored at –20°C.

SPMD sampler preparation and deployment

SPMDs (dimensions: 2.5 × 91.4 cm, 460 cm^2 external surface area, and a wall thickness of 70 µm) were prepared from LDPE layflat tubing (Brentwood Plastics, MO, USA) and filled with 1 mℓ of high purity triolein (1,2,3-tri(cis-9-octadecenoyl)glycerol) (99% pure) which had previously been spiked with performance reference compounds, namely, fluorene-d_{10}, acenaphthene-d_{10}, anthracene-d_{10}, phenanthrene-d_{10} and pyrene-d_{10}, to yield a nominal concentration of 2 µg·g^{-1} triolein. Prepared samplers were stored in airtight sealed metal cans under freezing temperatures (–20°C) awaiting deployment. SPMDs were deployed in the water body in triplicates for a 14-day period. On retrieval, samplers were placed in airtight metal containers and quickly transported to the laboratory where they were stored at –20°C until processing.

SPMD processing

After removing particulates and biofouling from the surface of affected SPMDs using a soft brush and tap water, they were briefly immersed in diluted (10%) hydrochloric acid to rid them of adsorbed carbonates acquired during field deployment. The samplers were again flushed with sufficient amounts of tap water, and dried using acetone and a soft paper tissue. Each sampler was transferred into a pre-cleaned, empty 250 mℓ glass bottle with a ground joint stopper and 100 mℓ of HPLC grade n-hexane added. Each sampler was then spiked with surrogate standard solutions, namely, naphthalene-d_8, fluoranthene-d_{12}, benzo(a)anthracene-d_{12}, benzo(k)fluoranthene-d_{12}, benzo(g,h,i) pyrene-d_{12}, PCB 30 and 85, and d_6-gamma HCH, and extraction done twice for 24 h in the dark at room temperature. The extracts were combined and reduced to about 10 mℓ using a rotary evaporator (Heidolph Laborata4000, Germany) at 40°C before concentrating further to about 0.5 mℓ. Finally, the extracts were reconstituted in 1 mℓ of pesticide residue analysis-grade trichloromethane.

Removal of lipids that diffused into the extract during dialysis was achieved using a gel permeation chromatography (GPC) system equipped with a high pressure pump (HPP5001) and a fraction collector (ECOM, Prague, Czech Republic). A gel 5 µm 50 Å, 7.5 x 300 mm, high performance size exclusion chromatography column (Agilent PL) was used to fractionate the extracts with chloroform as the mobile phase at a flow rate of 0.6 mℓ·min^{-1}. Analytes were collected from 18 min 20 s to 41 min 40 s and reduced to the last drop using a gentle stream of nitrogen gas. Subsequently, the extract was reconstituted to 1 mℓ n-hexane. The GPC eluate was subjected to further clean-up by activated silica gel.

One portion (20%) of the GPC extract targeting PAHs was cleaned using activated silica gel packed in a glass column and eluted with 10 mℓ of n-hexane followed by 20 mℓ of dichloromethane. The remaining portion (80%) targeting PCBs and OCPs was cleaned with sulphuric acid–modified activated silica gel, prepared by mixing 33 mℓ of concentrated sulphuric acid (> 98%) with 50 g of freshly prepared activated silica gel. Thorough homogenisation of the mixture was ensured before column packing. Target analytes were eluted with 30 mℓ dichloromethane. After reduction to 1 mℓ using a gentle stream of nitrogen gas, terphenyl or PCB 121 internal standards were added to the sample, and ultimately analysed by GC-MS/MS for PAHs and PCBs/OCPs, respectively.

Instrumentation

The PAHs of interest were analysed using a 6890 GC system coupled with a 5971 mass selective detector (Agilent Technologies). Chromatographic separation of the components was done using a capillary column (30 m x 0.25 mm internal diameter, 0.25 µm film thickness) HP-5MS and helium as the carrier gas flowing at 1.5 mℓ·min^{-1}. Conditions of gas chromatography separation were as follows: injector temperature was set at 250°C, initial column temperature was set at 70°C and held for 0.5 min. This ramped at 25°C·min^{-1} to 150°C. It was then ramped at 30°C·min^{-1} to 200°C. This was further ramped at 8°C·min^{-1} to 280°C and held for 20 min. Detection of the separated PAHs was achieved using a MS/MS system operated in selected ion monitoring mode with the electron impact ionisation set at 70eV. The temperatures of the ion source, transfer line and the quadrupole were held at 230°C, 280°C and 150°C, respectively. Quantitation of the residues was accomplished using a 7-point standard calibration curve in the concentration range of 0 to 1 000 ng·ℓ$^{-1}$. GC-MS/MS was used for indicator PCBs and OCPs analysis. 6890N GC (Agilent, USA) equipped with a 60 m x 0.25 mm x 0.25 µm DB5-MS column (Agilent J&W, USA) coupled to Quattro MicroGC MS (Waters, Micromass, UK) operated in EI+ was used; at least 2 MRM transitions were recorded for each compound analysed. Injection was done in splitless mode at 280°C and 1 µℓ sample loaded. Helium was used as carrier gas at the flow of 1.5 mℓ·min^{-1}. The GC temperature programme was 80°C (1-min hold), then 15°C·min^{-1} to 180°C, and finally 5°C·min^{-1} to 300°C (5-min hold). Raw data were processed using TargetLynx software (Waters, Micromass, UK).

Quality control

Fabrication controls and field blanks were used to account for contamination of the SPMDs during device construction, and sampler deployment and retrieval from the site. Vapour-phase contamination during deployment of the SPMDs was factored in by the field blanks. These blanks were subjected to identical processing treatment as the deployed devices.

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TABLE 2
Mean concentrations of PAHs, OCPs and DDTs in SPMDs (ng SPMD^{-1}, n = 3)

Compound	Season			
	Winter	Spring	Summer	Autumn
PAHs				
Naphthalene	307 ± 11	149 ± 11	171 ± 4	286 ± 20
Acenaphthylene	158 ± 5	76 ± 6	132 ± 2	180 ± 7
Acenaphthene	37 ± 3	20 ± 2	25 ± 1	38 ± 3
Fluorene	76 ± 11	61 ± 7	49 ± 4	106 ± 7
Phenanthrene	164 ± 36	71 ± 9	75 ± 5	217 ± 13
Anthracene	875 ± 40	279 ± 5	56 ± 12	164 ± 3
Fluoranthene	147 ± 4	65 ± 3	119 ± 11	97 ± 7
Pyrene	105 ± 2	49 ± 3	88 ± 5	83 ± 8
Benz[a]anthracene	31 ± 1	16 ± 1	32 ± 2	33 ± 1
Chrysene	41 ± 1	22 ± 5	45 ± 6	44 ± 1
Benzo[b]fluoranthene	35 ± 4	26 ± 8	36 ± 1	38 ± 2
Benzo[k]fluoranthene	36 ± 2	ND	36 ± 2	38 ± 2
Benzo[a]pyrene	34 ± 6	32 ± 0	39 ± 7	43 ± 5
Indeno[1,2,3-cd]pyrene	37 ± 0	19 ± 1	38 ± 1	39 ± 1
Dibenz[a,h]anthracene	ND	ND	ND	ND
Benzo[ghi]perylene	35 ± 1	20 ± 2	41 ± 3	45 ± 2
ΣPAHs	**2 117 ± 57**	**905 ± 21**	**984 ±21**	**1 450 ± 29**
HCHs				
HCB 28	1.1 ± 0.2	0.9 ± 0.1	0.7 ± 0.0	0.6 ± 0.1
α-HCH	55.9 ±3.5	52.5 ± 5.1	32.3 ± 3.6	64.8 ± 5.5
β-HCH	154.3 ±7.8	153.4 ±0.4	70.9 ± 4.0	45.5 ± 2.9
Lindane	8.8 ± 0.9	8.1 ± 0.1	5.9 ± 0.8	9.8 ± 0.9
δ-HCH	3.2 ± 0.2	3.1 ± 0.2	1.4 ± 0.2	2.5 ± 0.4
e-HCH	9.9 ± 0.6	9.8 ± 0.6	4.5 ± 0.1	5.6 ± 0.7
ΣHCHs	**233.2 ± 8.6**	**227.7 ± 5.2**	**106.5 ± 5.4**	**128.7 ± 6.3**
DDTs				
o,p'-DDE	0.6 ± 0.1	0.8 ± 0.1	0.4 ± 0.0	0.3 ± 0.0
p,p'-DDE	5.3 ± 0.2	5.5 ± 0.4	3.6 ± 0.3	3.1 ± 0.2
o,p'-DDD	10.8 ± 1.1	13.6 ± 0.2	5.0 ± 0.4	4.2 ± 0.4
p,p'-DDD	31.1 ± 0.6	43.5 ± 0.8	15.7 ± 3.1	19.9 ± 2.7
o,p'-DDT	ND	ND	ND	ND
p,p'DDT	0.6 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	0.7 ± 0.1
ΣDDTs	**48.5±1.3**	**64.1±0.9**	**25.3±3.1**	**28.2±2.7**
PCBs				
PCB 28	3.5 ± 0.50	3.1 ± 0.30	1.5 ± 0.10	2.1 ± 0.17
PCB 52	1.1 ± 0.06	1.0 ± 0.09	0.6 ± 0.00	0.5 ± 0.04
PCB 101	0.4 ± 0.06	0.4 ± 0.03	0.3 ± 0.07	0.4 ± 0.01
PCB 118	0.2 ± 0.02	0.2 ± 0.00	0.2 ± 0.01	0.2 ± 0.00
PCB 153	0.5 ± 0.03	0.5 ± 0.07	0.4 ± 0.02	0.7 ± 0.05
PCB 138	0.6 ± 0.05	0.3 ± 0.00	0.5 ± 0.05	0.5 ± 0.05
PCB 180	0.3 ± 0.02	0.3 ± 0.00	0.5 ± 0.02	0.4 ± 0.02
ΣPCBs	**6.5 ± 0.51**	**5.8 ± 0.32**	**3.9 ± 0.14**	**4.8 ± 0.19**

ND: not detected

RESULTS AND DISCUSSION

Occurrence of PAHs, PCBs and OCPs in the SPMDs

The absolute contaminant concentrations sequestered by SPMDs deployed at Hartbeespoort Dam during the 14-day deployment period in each of the four seasons of the year are presented in Table 2. Characteristic ions (m/z values) used in the analysis of polycyclic aromatic hydrocarbons in single ion monitoring (SIM) mode by GC/MS and characteristic MRM transitions (m/z values of parent and daughter ions) used in the analysis of PCBs and OCPs are given in the Appendix (Tables A1 and A2). Analyte concentrations were adjusted with respect to their recoveries obtained from recovery standards introduced prior to the dialytic process. The SPMD field blanks showed no quantifiable concentrations of the target

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contaminants. Determination of recoveries for all samples was carried out by spiking them with surrogate standards prior to extraction. Good recoveries were recorded that ranged from 55% to 123% for PAHs, 73% to 94% for PCBs and 72% to 104% for OCPs. The relative standard deviations between co-deployed triplicate samplers did not exceed 22% for PAHs, 24% for PCBs and 17% for OCPs. Limits of detection (LOD) and quantification (LOQs) for the method were 0.1 and 0.4 ng·ℓ$^{-1}$, respectively for PAHs. LODs for PCBs and OCPs were all less than 0.1 ng·ℓ$^{-1}$ whereas LOQs were 0.1 ng·ℓ$^{-1}$.

Estimation of dissolved water concentrations of analytes

Dissolved water concentrations of target analytes were calculated from amounts accumulated in SPMDs as follows: Amounts of analytes absorbed by the samplers follow a first-order approach to equilibrium. Aqueous concentrations were calculated from the amounts (N_s) absorbed by the SPMD, the in-situ sampling rate of the compounds R_s and their sampler-water partition coefficients K_{sw}:

$$C_w = \frac{N_s}{K_{sw}V_s[1 - \exp(-R_s t/(K_{sw}V_s))]} \quad (1)$$

where:

V_S is the volume of the SPMD and t is the sampler exposure time.

PRC dissipation also follows first-order kinetics. Sampling rates R_s were estimated using the non-linear least -squares method of Booij and Smedes (2010), considering the fraction f of individual PRCs (D_{10}-acenaphthene, D_{10}-fluorene, D_{10}-phenanthrene and D_{10}-pyrene) that remained in the SPMD after the 14-day exposure as a continuous function of their K_{sw}, with R_S as an adjustable parameter.

$$f = \exp\left(-\frac{R_S t}{K_{SW}V_S}\right) \quad (2)$$

where:

$f = N_{PRC}/N_{0,PRC}$; $N_{0,PRC}$ is the initial amount of the PRC at $t = 0$

N_{PRC} is amount of each PRC remaining after exposure

t is exposure period (14 days).

Assuming water boundary layer controlled uptake, R_s of individual target compounds in the higher hydrophobicity range was estimated by substituting Eq. (3), derived by Rusina et al. (2010), into Eq. (2).

$$R_S = FAM^{-0.47} \quad (3)$$

where: M is the molecular weight of the analyte, A is the surface area of SPMD (460 cm^2) and F is the regression coefficient that was optimised using the non-linear least squares method for estimating sampling rates. The necessary K_{sw} values were interpolated from the empirical equation (Huckins et al., 2006).

$$\log K_{sw} = -01618(\log K_{ow})^2 + 2.321 \log K_{ow} - 2.61 \quad (4)$$

The calculated free dissolved water concentrations of the PAHs, PCBs and OCPs are presented in Table 3.

Temporal trends of water-dissolved contaminants

Equation (3), which estimates a slight decrease in R_s with increasing molecular mass, was used to calculate compound-specific R_s values for all of the compounds studied. Depending on the water flow velocities, different R_s values were obtained in the various seasons, in agreement with the assumption of water boundary layer uptake. Mass transfer of analytes may also be affected by other factors such as temperature, biofouling and deposition of particulates on the surface of the SPMDs.

Estimated water soluble concentrations generally followed the trend: PAHs > OCPs > PCBs. PAHs are ubiquitous organic pollutants characterised by many natural and anthropogenic sources, unlike OCPs and PCBs (industrial products). Since the dam receives over 90% of its water from the Crocodile River, which originates in Johannesburg city, it is possible that a good portion of the pollutants sampled could be of industrial origin. PCB concentrations are on average 2 to 3 orders of magnitude lower than those of PAHs and OCPs because most of these manufactured products have long been banned and their use stopped, in line with the Stockholm Convention, and whatever was captured by the samplers is attributable to their environmental persistence due to slow degradation. The sum total of water-borne concentrations of the compounds ranged from 30.2 to 60.8 ng·ℓ$^{-1}$ (PAHs), 10.0 to 10.7 ng·ℓ$^{-1}$ (OCPs) and 38 to 150 pg·ℓ$^{-1}$ (PCBs). Generally, the seasonal trends for all of the compounds mirrored the amounts accumulated in the SPMDs. An observed predominance of smaller molecular weight PAHs was evident in all four seasons. This may be attributed to their higher solubility in water due to lower hydrophobicity and, hence, transportation from the point sources was probably more efficient.

PAHs

A remarkable seasonal variability in the amounts of sequestered PAHs was shown by the deployed SPMDs. Estimated total analyte concentrations ranged from 30.0 ng·ℓ$^{-1}$ (in summer) to a high of 60.8 ng·ℓ$^{-1}$ (in winter). These concentrations are comparable to those reported by Wang et al. (2009) (13.8–97.2 ng·ℓ$^{-1}$) at the Three Gorges River, China, and Vrana et al. (2014) (5–72 ng·ℓ$^{-1}$) in the Danube River, Slovakia/Austria. The trend of total concentrations of PAHs dissolved in water was as follows: winter > spring > autumn > summer. Individual PAH concentrations obtained in the various seasons also generally followed the same trend as the totals (Fig. 2). Smaller molecular weight PAHs constituted the highest percentage of the sequestered compounds.

The reported water-soluble concentrations of the heavy molecular weight PAHs in the current study were on average up to 2 orders of magnitude lower than the maximum contaminant limits (MCL) set by international regulatory bodies such as the United States Environmental Protection Agency (USEPA) (0.01 to 0.04 µg·ℓ$^{-1}$).

The elevated concentrations recorded during winter may be attributed to a number of factors. During the winter months, very little precipitation is recorded (average of about 4–9 mm for the study area) and, since the dam depends on river water for replenishment, its volume drastically drops. This in turn increases the percentage of the dam's water originating from treated wastewater, which can exceed 50% of the total volume (Harding et al., 2004). These wastewater treatment plants are located in the industrialised areas north of Johannesburg. In addition, average temperatures substantially drop during winter (to an average air temperature of 4–7°C as measured in the study area) which in turn discourages analyte losses via volatilisation. Atmospheric deposition of PAHs represents an

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TABLE 3
Estimated dissolved water concentrations, C_w, (ng·ℓ$^{-1}$) of PAHs, PCBs and OCPs from SPMDs deployed at Hartbeespoort Dam in different seasons of the year

Compound	Season			
	Winter	Spring	Summer	Autumn
PAHs				
Naphthalene	43.153	43.206	23.980	38.499
Acenaphthylene	3.862	3.897	3.214	4.354
Acenaphthene	1.115	1.173	0.759	1.099
Fluorene	1.176	1.858	0.716	1.646
Phenanthrene	1.283	1.316	0.386	1.808
Anthracene	7.321	2.200	0.310	1.519
Fluoranthene	0.709	1.340	0.223	0.639
Pyrene	0.698	0.994	0.170	0.561
Benz[a]anthracene	0.169	0.287	0.051	0.231
Chrysene	0.226	0.422	0.072	0.302
Benzo[b]fluoranthene	0.221	0.511	0.060	0.279
Benzo[k]fluoranthene	0.222	ND	0.060	0.282
Benzo[a]pyrene	0.199	0.294	0.065	0.233
Indeno[1,2,3-cd]pyrene	0.221	0.362	0.063	0.297
Dibenz[a,h]anthracene	ND	ND	ND	ND
Benzo[ghi]perylene	0.211	0.365	0.070	0.343
ΣPAHs	**60.768**	**58.225**	**30.199**	**52.082**
HCHs				
α-HCH	2.320	2.212	0.666	2.921
β-HCH	6.780	6.661	8.102	6.151
Lindane	0.445	0.389	0.189	0.542
δ-HCH	0.054	0.062	0.024	0.087
ε-HCH	0.442	0.386	0.187	0.260
ΣHCHs	**10.350**	**10.201**	**9.168**	**9.961**
DDTs				
o,p'-DDE	0.004	0.006	0.010	0.007
p,p-DDE	0.033	0.052	0.088	0.062
o,p'-DDD	0.065	0.104	0.176	0.124
p,p'-DDD	0.203	0.323	0.547	0.384
p,p'-DDT	ND	ND	ND	ND
p,p'-DDT	0.004	0.006	0.011	0.008
ΣDDTs	**0.309**	**0.491**	**0.832**	**0.585**
PCBs				
PCB 28	0.019	0.029	0.067	0.020
PCB 52	0.006	0.012	0.025	0.010
PCB101	0.003	0.005	0.014	0.007
PCB 118	0.001	0.001	0.003	ND
PCB 138	0.003	0.006	0.013	0.005
PCB 153	0.004	0.005	0.018	0.004
PCB 180	0.002	0.004	0.012	0.003
ΣPCBs	**0.038**	**0.062**	**0.150**	**0.049**

ND: not detected

important pathway for PAHs into the aquatic ecosystem. The increased concentrations in water in winter may correspond with elevated atmospheric concentrations during the same period due to enhanced combustion of coal for heating. The summer months experience high rainfall coupled with high temperatures. Resuspension of sediment-immobilised PAHs was expected to increase PAH concentrations in the water phase. Inputs from runoff and rivers originating from polluted areas upstream were also thought to be potential PAH sources. Although these factors may have been at play, it seems dilution effects (larger water volumes) as well as losses through volatilisation may have tempered the expected increase in contaminant concentrations. The autumn season is characterised by less precipitation and dropping temperatures. These conditions may have led to lower contaminant losses via volatilisation coupled with increased concentration due to decreased bulk water volumes.

The PCB concentrations obtained from the deployed

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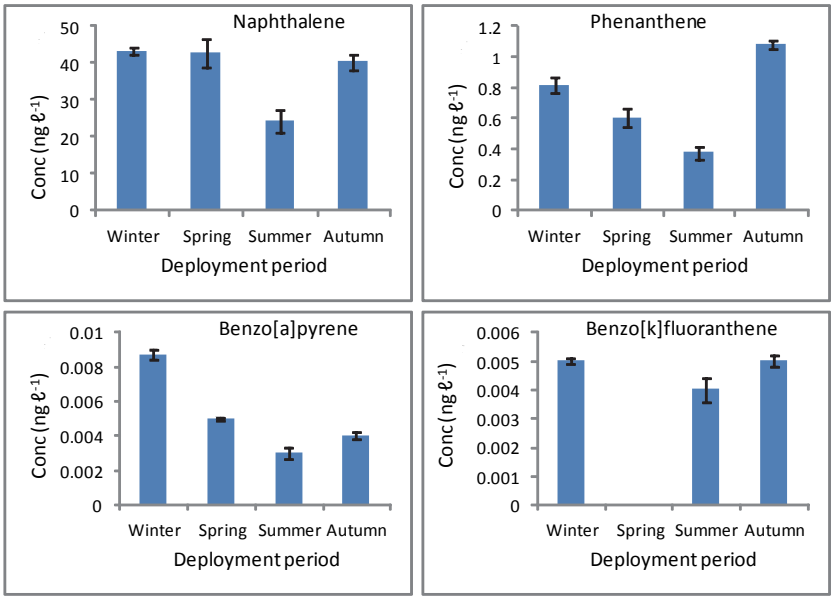

Figure 2
Temporal changes in water-dissolved concentrations of some individual PAHs at the site

SPMDs were generally lower, by about 2 to 3 orders of magnitude, than PAH and OCP concentrations. PCBs are organic contaminants of purely anthropogenic origin, in contrast to PAHs that have both natural and anthropogenic sources. In addition, most PCBs were banned some years back and the remnants captured by the samplers are as a result of the strong persistence of PCBs in the environment. Due to their strong hydrophobicity (shown by higher log K_{ow} values of up to several orders of magnitude), PCBs tend to partition away from the water phase and preferentially adsorb strongly onto particulate matter, colloids and sediments in water. Moreover, their emissions are likely to be much lower than those of PAHs because, unlike the western industrialised countries, South Africa may not have utilised PCBs heavily during its economic growth in the 1980s or later when usage of PCBs was banned (Ogata et al., 2009).

Estimated water concentrations of the sum total of PCBs are shown in Table 3. When ranked in increasing order, the water-dissolved analyte concentrations followed the trend: summer > spring > autumn > winter. Concentrations of the compounds ranged from a low of 0.038 ng·ℓ$^{-1}$ in winter to a high of 0.150 ng·ℓ$^{-1}$ in summer. These concentrations were comparable to those obtained by Vrana et al. (2014) in the Danube River (5 to 16 pg·ℓ$^{-1}$) and Allan and Ranneklev (2011) in the Alna River, Norway (0.7 to 85 pg·ℓ$^{-1}$). Clearly, PCB levels in summer were significantly higher than those recorded in all of the other seasons. This observation may be explained as follows: In the summer rainfall region of South Africa, within which the study area lies, the summer period usually experiences heavy rainfall (90–125 mm).

Most PCB congeners are highly hydrophobic compounds which preferentially adsorb strongly onto soil particles and sediments. Therefore, heavy rain events may disrupt these strong interactions thereby remobilising them into the water phase. This is partly supported by the fact that usage of these compounds has been banned for several years and therefore a majority of inputs could be coming from sediment samples. Surface runoff from urban centres (where these compounds are found in higher quantities) may also add to the pollutant load. A good portion of the water that eventually finds its way to the sample site can be traced to the industrial areas of Johannesburg (Fig. 1).

The estimated freely dissolved water concentrations of OCPs are given in Table 3. Seasonal ranking from lowest to highest followed the trend: summer, autumn, spring, winter. The sequestered amounts of OCPs that comprised hexachlorocyclohexanes (HCHs), and DDX (DDTs, DDDs and DDEs) were up to 2 orders of magnitude higher than PCBs but slightly less than those of PAHs. Among the analysed OCPs, HCHs contributed over 78% of the quantified amount and their free dissolved concentrations ranged from about 9.2 ng·ℓ$^{-1}$ in summer to 10.4 ng·ℓ$^{-1}$ in winter. Figure 3 presents the water dissolved concentrations of selected HCH isomers.

Particularly high levels of β-HCH were detected at the sampling site in all four seasons. This HCH isomer is characterised by a much lower vapour pressure, better solubility in water, and lower Henry's law constant than all of the other HCH isomers, which favour partitioning from air to water. Compared to the gamma- and alpha-HCHs, it is the most recalcitrant isomer (Stockholm Convention, 2007).

In a global monitoring study of persistent organic pollutants (POPs) in coastal waters, Ogata et al. (2009) reported high concentrations of HCHs in samples from South Africa. This was in contrast to levels obtained in other parts of the world (such as USA, Asia and Europe) which were lower. They attributed this observation to the application of lindane in South Africa, which contains γ-HCH as its main component. It is possible that technical-grade HCHs that also contain considerable amounts of β-HCH (5–12%) were applied. Because of its relative volatility, this globally-banned pesticide can easily find its way into water systems via atmospheric deposition.

In the soil-air interface, ratios of HCH isomers have been used to identify the historical pollution sources (Willett et al., 1998). β-/(α+γ)-HCH > 0.5 is an indicator of historical pollution while a ratio less than 0.5 indicates new introduction of HCHs. In the case of the current study, these ratios ranged from 1.8 in autumn to a high of 9.5 in summer. It is therefore proposed that in all four seasons, HCH input to the sampling site is predominantly historical in nature with minimal inputs from current application.

Since the overall seasonal trends of HCHs generally mirrored those of PAHs (with the exception of values obtained in spring), we conclude that the same factors may have affected

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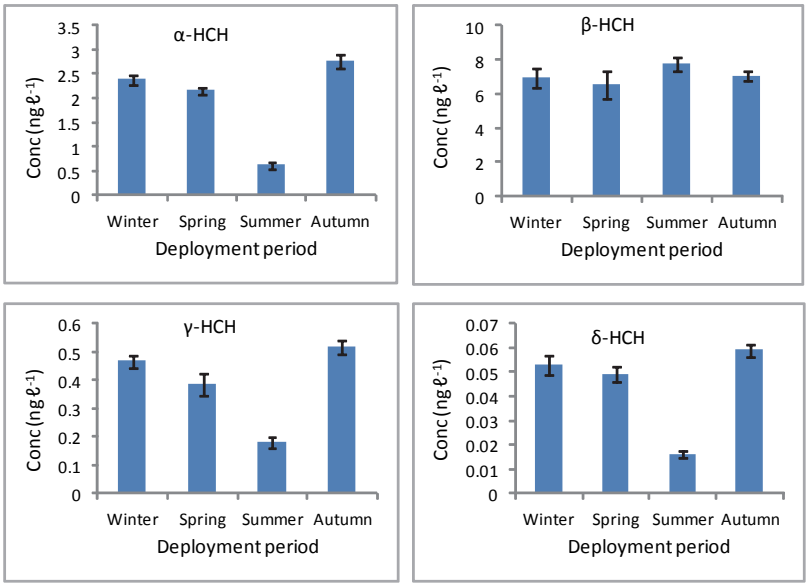

Figure 3
Water dissolved concentrations of individual HCHs as affected by seasonal change

them. However, the decrease in OCP concentrations from winter to spring was insignificant. This observation may be attributed to their comparatively lower volatility. Thus, losses through volatilisation resulting from increased temperatures during spring may not have been a major factor.

Interestingly, DDT and its metabolite residues showed seasonal patterns similar to those of PCBs, even though their water dissolved concentrations were generally higher. Estimated water concentrations of the DDT sum ranged from 0.31 ng·ℓ$^{-1}$ in winter to 0.83 ng·ℓ$^{-1}$ in summer, respectively. Volatilisation is a major route through which DDT and its metabolites are released into the atmosphere and, once there, these chemicals are cycled back to surface water through dry and wet deposition (Stockholm Convention, 2007). Findings from this study suggest that wet deposition of DDT and its metabolites may be playing an important role in re-introducing them to the sample site, as higher water concentrations coincide with high precipitation (summer). Moreover, considering the relatively high log K_{ow} values associated with DDX (5.8–6.79), remobilisation of the particle/sediment-bound fraction as a consequence of heavy rainfall may have been a possibility. Contributions from runoff originating from fields also cannot be ignored. Taken together, these factors may explain the seasonal trends of DDX.

Source identification of PAHs in the Hartbeespoort Dam

The principal sources of PAHs in the environment can be classified as either pyrogenic or petrogenic, with the pyrogenic inputs predominating in aquatic environments (Ekpo et al., 2012). Based on the SPMD-obtained PAH concentrations, identification of the probable sources was attempted. Reports by many authors on the apportionment of PAH sources in the environment using molecular ratios of certain PAHs are available in the literature (Baumard et al., 1998; Vrana et al., 2001; Zhang et al., 2004; Brandli et al., 2008). With respect to passive sampling, ratios of PAHs must be for compounds with near identical sampling rates to minimise bias arising from the mode of calculation of the rates for compounds with widely differing log K_{ow} (Allan and Ranekley, 2011). Furthermore, the same authors observed that unless PAHs are directly emitted to surface water, dissolved phase concentrations may not necessarily be representative of sources of contamination. From among the several available approaches, ratios of fluoranthene/(fluoranthene + pyrene) [Flt/(Flt + Pyr)] and anthracene/(anthracene + phenanthrene) [Ant/(Ant + Phe)] calculated from waterborne concentrations were applied in the identification of the possible sources of PAHs in the site.

Figure 4 shows the diagnostic ratios of PAH concentrations measured with SPMDs in Hartbeespoort Dam. An Flt/(Flt + Pyr) ratio > 0.5 indicates a pyrogenic source, as does an Ant/(Ant + Phe) ratio > 0.5. Ratios of indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene + benzo[g,h,i]perylene) greater than 0.5 point to fossil fuel combustion or pyrogenic sources (Brandli et al., 2008) for the PAHs in the Hartbeespoort Dam. Thus, with the exception of concentrations obtained from SPMDs deployed in winter, all PAHs pointed to a pyrogenic origin. The winter-derived data showed a mixture of both pyrogenic and petroleum combustion sources. The spike in the petrogenic PAH fraction during winter may be attributed to the increased proportion of treated wastewater originating from Johannesburg. As Harding et al. (2004) reported, during winter, precipitation is almost nil and, consequently, more than 50% of the reservoir's inlet water is composed of treated wastewater. A steep increase in the Flt/(Flt + Pyr) ratio was observed from winter to spring before decreasing during summer. A further drop in the ratio, albeit gently, occurred between summer and autumn.

CONCLUSIONS

SPMDs are potentially effective tools for monitoring hydrophobic contaminants in aqueous systems such as those present in the Hartbeespoort Dam, South Africa. In addition to detecting concentrations of PAHs, PCBs and OCPs in the toxicologically most relevant dissolved phase, SPMDs also captured their seasonal variation in the water body. Generally, total contaminant concentrations in the dam increased in the order: summer, spring, autumn, winter. Concentrations of the PAH and HCH isomers decreased with increasing water temperature, which likely reflects seasonality of atmospheric deposition. The dissolved concentrations of PCB and DDT isomers are most likely related to desorption from suspended particles. Diagnostic ratios of PAHs measured in SPMDs were used to identify the possible sources of PAHs in the water. These ratios indicated

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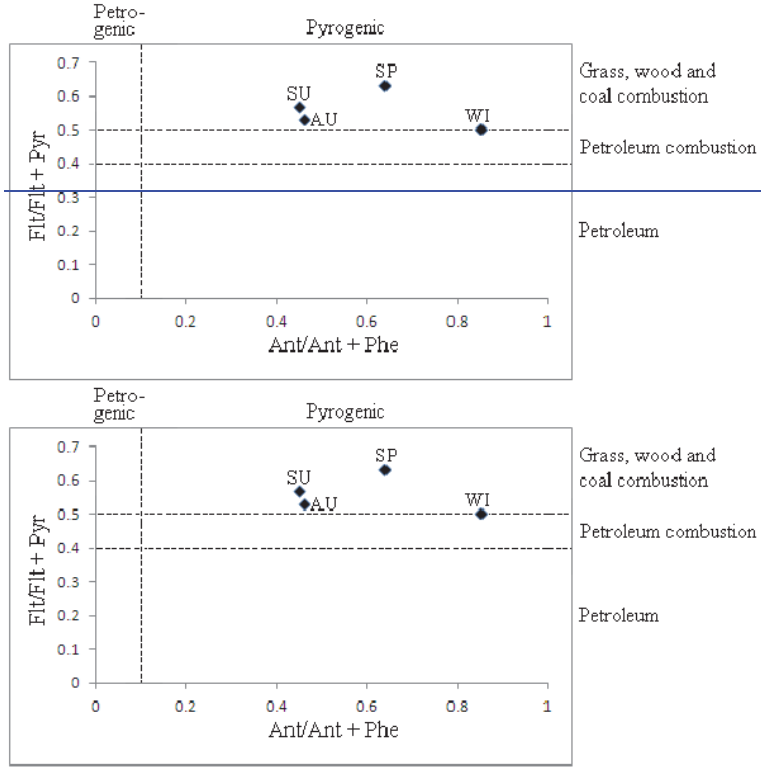

Figure 4
Diagnostic ratios of PAH concentrations measured with SPMDs in the Hartbeespoort Dam. WI: winter; SP: spring, SU: summer, AU: autumn, Flt: fluoranthene, Pyr: pyrene, Ant: anthracene, Phe: phenanthrene.

that the PAH concentrations in the dam during spring, summer and autumn were mainly of pyrogenic origin while the winter levels comprised both pyrogenic and petrogenic sources.

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APPENDIX

TABLE A1
Details of characteristic ions (m/z values) used in the analysis of polycyclic aromatic hydrocarbons in single ion monitoring (SIM) mode by GC/MS

Compound	Retention time (min)	[1]m/z 1	m/z 2	m/z 3
[2]Terphenyl	23.04	230	215	202
Naphthalene	8.37	128	129	126
Biphenyl	10.48	154	153	155
Acenaphthylene	11.49	152	153	150
Acenaphthene	11.91	154	153	155
Fluorene	13.3	166	167	164
Phenanthrene	16.42	178	179	176
Anthracene	16.61	178	179	176
Fluoranthene	21.13	202	203	200
Pyrene	22.09	202	203	200
Retene	23.46	219	234	205
Benzo[b]fluorene	23.9	216	215	217
Benzonaphthothiophene	26.39	234	235	232
Benzo[ghi]fluoranthene	26.58	226	227	224
Cyclopenta[cd]pyrene	27.45	226	227	224
Benzo[a]anthracene	27.49	228	229	226
Triphenylene	27.6	228	229	226
Chrysene	27.66	228	229	226
Benzo[b]fluoranthene	32.17	252	253	250
Benzo[j]fluoranthene	32.18	252	253	250
Benzo[k]fluoranthene	32.29	252	253	250
Benzo[e]pyrene	33.27	252	253	250
Bezno[a]pyrene	33.48	252	253	250
Perylene	33.8	252	253	250
Indeno[123cd]pyrene	38.39	276	277	274
Dibenzo[ah]anthracene	38.51	278	279	276
Dibenzo[ac]anthracene	38.52	278	279	276
Benzo[ghi]perylene	39.7	276	277	274
Anthanthrene	40.41	276	277	274
Coronene	50.13	300	301	298
[3]D_8-Naphthalene	8.37	136	137	134
[3]D_{10}-Phenanthrene	16.33	188	189	184
[3]D_{12}-Perylene	33.69	264	265	260

[1]The ion in the first column was used for quantification, the other two were used as qualifier ions to confirm compound identity
[2]Instrumental internal standard
[3]Recovery internal standard

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TABLE A2
Details of characteristic MRM transitions (m/z values of parent and daughter ion are given) used in the analysis of PCBs and OCPs by GC/MS/MS

Name	Retention time (min)	[1]MRM transition (Quantifcation)	MRM transition (Qualifier)
[2]PCB 121	20.24	325.9 > 255.9	327.9 > 255.9
[3]PCB 30	17.2	256 > 186	258 > 186
[3]PCB 185	27.28	393.8 > 323.9	395.8 > 325.9
PCB 28	17.13	256 > 186	258 > 186
PCB 52	18.15	289.9 > 220	291.9 > 220
PCB 101	21.05	325.9 > 255.9	327.9 > 255.9
PCB 118	23.27	325.9 > 255.9	327.9 > 255.9
PCB 153	23.95	359.8 > 289.9	361.8 > 289.9
PCB 138	24.91	359.8 > 289.9	361.8 > 289.9
PCB 180	27.22	393.8 > 323.9	395.8 > 325.9
PeCB	11.85	250 > 215	252 > 215
HCB	14.52	283.8 > 248.9	285.8 > 213.8
α-HCH	14.31	219 > 183	181 > 145
β-HCH	15.1	219 > 183	181 > 145
γ-HCH (Lindane)	15.29	219 > 183	181 > 145
δ-HCH	16.19	219 > 183	181 > 145
o,p'-DDE	20.89	246 > 176	318 > 248
p,p'-DDE	22.01	246 > 176	318 > 248
o,p'-DDD	22.27	235 > 165	237 > 165
p,p'-DDD	23.52	235 > 165	237 > 165
o,p'-DDT	23.59	235 > 165	237 > 165
p,p'DDT	24.84	235 > 165	237 > 165
ε-HCH	16.45	181 > 145	219 > 183

[1]The MRM transition in the first column was used for quantification, the other was used to confirm compound identity
[2]Instrumental internal standard
[3]Recovery internal standard

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Príloha 27

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Assessment of bioavailable fraction of POPS in surface water bodies in Johannesburg City, South Africa, using passive samplers: an initial assessment

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Abstract In this study, the semipermeable membrane device (SPMD) passive samplers were used to determine freely dissolved concentrations of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in selected water bodies situated in and around Johannesburg City, South Africa. The devices were deployed for 14 days at each sampling site in spring and summer of 2011. Time weighted average (TWA) concentrations of the waterborne contaminants were calculated from the amounts of analytes accumulated in the passive samplers. In the area of interest, concentrations of analytes in water ranged from 33.5 to 126.8 ng l^{-1} for PAHs, from 20.9 to 120.9 pg l^{-1} for PCBs and from 0.2 to 36.9 ng l^{-1} for OCPs. Chlorinated pesticides were mainly composed of hexachlorocyclohexanes (HCHs) (0.15–36.9 ng l^{-1}) and dichlorodiphenyltrichloromethane (DDT) with its metabolites (0.03–0.55 ng l^{-1}). By applying diagnostic ratios of certain PAHs, identification of possible sources of the contaminants in the various sampling sites was performed. These ratios were generally inclined towards pyrogenic sources of pollution by PAHs in all study sites except in the Centurion River (CR), Centurion Lake (CL) and Airport River (AUP) that indicated petrogenic origins. This study highlights further need to map up the temporal and spatial variations of these POPs using passive samplers.

Keywords Free dissolved concentration · Passive sampling devices · Hydrophobic organic compounds · Monitoring · Passive sampling · SPMDs

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Introduction

Water systems that have roots in urbanised areas are normally prone to severe contamination by an array of pollutants that include hydrophobic organic contaminants (HOCs). Pollution may be caused by current and/or previous industrial activities or both. Such water resources need to be secured for the benefit of current and future generations. Assessment of the pollution levels and distribution of the contaminants in water systems can be achieved by employing sound monitoring practices using a variety of available tools and techniques. Grab sampling has traditionally been applied in the determination of HOCs in water. However, successful monitoring is hampered by their existence at very low concentrations in water phase, in addition to frequent temporal changes. Increased sampling frequency, use of large sample volumes, installing automatic samplers and applying more sensitive analytical

techniques are possible solutions, but they come with cost implications. Passive sampling devices (PSDs) have shown promise as better alternatives since they permit unattended large volume- and time-integrated sampling, which compensate for fluctuating concentrations and also give lower detection limits (Harman et al. 2008; Vrana et al. 2014). Use of passive samplers is also advantageous because only the freely dissolved concentration of the analyte in water is sampled. This fraction of the contaminant is critical for the assessment of its bioavailability and fate in the aquatic environment and the risk associated with exposure of aquatic organisms to these contaminants. Among PSDs, the semipermeable membrane devices (SPMDs) have been successfully used as quantitative tools to assess concentrations of HOCs in the waters of various aquatic ecosystems (Huckins et al. 1993; Lu et al. 2002; Vrana et al. 2005, 2014). SPMDs passively accumulate lipophilic organic contaminants by mimicking biological membranes in its ability to allow selective diffusion of the compounds. Typically, organics with partition coefficients (log K_{ow}) higher than 3 are suitable for extraction by this technique (Huckins et al. 1993; Vrana et al. 2005).

In the current study, SPMDs were employed for the initial assessment of the bioavailable fractions of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in the water columns of streams and rivers originating from Johannesburg City, South Africa. Further investigation of the pollution levels in water bodies that receive water from the urban streams and rivers was also undertaken. So far, very little studies have been reported that have investigated the presence of these POPs in water bodies in greater Johannesburg area, South Africa (Sibali et al. 2008; Sibiya et al. 2012, 2013a;). The reported studies have looked at the total concentrations and only for a few PAHs (Sibiya et al. 2012, 2013a) and organochlorine pesticides (Sibali et al. 2008).

Materials and methods

Chemicals and reagents

The 16 US EPA PAH standards with purities>97 % pure were purchased from Sigma-Aldrich Chemie GmbH, (Steinheim, Germany). Performance reference compounds (PRCs): d_{10}-acenaphthene, d_{10}-fluorene, d_{10}-phenanthrene and d_{10}-pyrene, as well as recovery standards d_8-naphthalene, d_{10}-anthracene, d_{12}-fluoranthene, d_{12}-benzo(a)anthracene, d_{12}-benzo(k)fluoranthene, d_{12}-benzo(g,h,i)pyrene, PCB 30, PCB 185 and d_6-gamma hexachlorocyclohexane (HCH) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Internal standards (PCB 121 and terphenyl) for instrumental analysis were also purchased from Dr. Ehrenstorfer GmbH. Sulphuric acid (98 %) and hydrochloric acid (36 %) were purchased from Merck (Darmstadt, Germany). Triolein (97 %,) was purchased from Sigma Aldrich, (Ghent, Belgium), while silica gel 60 was from Merck (Darmstadt, Germany). High-purity (>99 %) *n*-hexane, dichloromethane and trichloromethane were bought from Sigma-Aldrich (Prague, Czech Republic). Reagent water was drawn from a Milli-Q water system (Millipore, Bedford, MA, USA).

SPMD sampler preparation and deployment

Standard size SPMDs in the dimensions 2.54×91.4 cm, 460 cm^2 external surface area were prepared from LDPE membranes (Brentwood plastics, MO, USA) and filled with 1 ml of high-purity triolein (97 % pure) to give a final total sampler volume of 4.95 ml. Initially, 100-cm long portions of the tubes were cut off from the roll before inserting them into pre-cleaned, dry glass bottles using a pair of blunt tweezers. Cleaning was done twice by soaking them overnight in hexane with the aim of removing organic contaminants. After air-drying, the membranes were heat-sealed at one end to form a loop. Each SPMD was spiked (a solution in *n*-hexane was spiked to SPMD using a GC syringe) with individual PRCs at a concentration of 2 μg $sampler^{-1}$ (Vrana et al. 2014). The LDPE membrane was closed using a thermal seal (Impulse sealer ME-300 HI, Mercier Corporation). The devices were stored in air-tight sealed metal cans at −20 °C awaiting deployment. Thereafter, the stainless steel housings containing the SPMDs were lowered about 40 cm below the surface of a river or dam bank. Its end was then tied to nearby branch of tree using a nylon string. At Hartbeespoort Dam (HD), the passive samplers were tied to the bottom of the floating bridges used for recreation purposes in the same way using a string. Samplers were deployed for 14 days; the more commonly used deployment time (Vrana et al. 2014). Sites for sampler deployment were based on our previous study in the same area (Sibiya et al. 2013b) and are described in Table 1. The sampling points are also shown in Fig. 1.

Table 1 Description of sampling sites

Sampling site	Symbol	Water body	Longitude	Latitude
Ifafi (Hartbeespoort Dam)	IFA	Dam	25° 45′ 09.97″ S	27° 53′ 04.39″ E
Juskei River 1	JR 1	River	26° 01′ 07.49″ S	28° 05′ 34.69″ E
Juskei River 2	JR 2	River	26° 00′ 25.30″ S	28° 04′ 45.74″ E
Eagles (Hartbeespoort Dam)	EGL	Dam	25° 44′ 56.29″ S	27° 50′ 06.18″ E
Homestead Lake	HSL	Dam	26° 10′ 25.64″ S	28° 17′ 04.71″ E
Airport River	AUP	River	26° 08′ 29.74″ S	28° 17′ 04.71″ E
Centurion Lake	CL	Dam	25° 51′ 55.41″ S	28° 12′ 23.36″ E
Centurion River	CR	River	25° 51′ 40.01″ S	28° 11′ 22.93″ E

Sampling sites

Jukskei Rivers

The Jukskei River (JR) is one of the river catchments in the Johannesburg metropolis that covers over 800 km^2 (Campbell 1996). The source of the river can be traced to the Bruma Lake situated at the foot of the Witwatersrand area. The river eventually empties its water into the Hartbeespoort Dam after merging with the Crocodile River downstream. The Jukskei River (JR) meanders northwards through a number of residential areas such as the densely populated Alexandra Township. Two sampling sites were chosen along the Jukskei River (JR 1 and JR 2) for the deployment of SPMDs.

Centurion Lake and Centurion River

The Centurion Lake (CL) and Centurion River (CR) form part of the Hennops, a relatively small perennial river, that originate from a marshy area situated a few kilometres east of Kempton Park, Johannesburg (Torien and Walmsley 1979). Further downstream, the river receives treated effluent from a number of wastewater

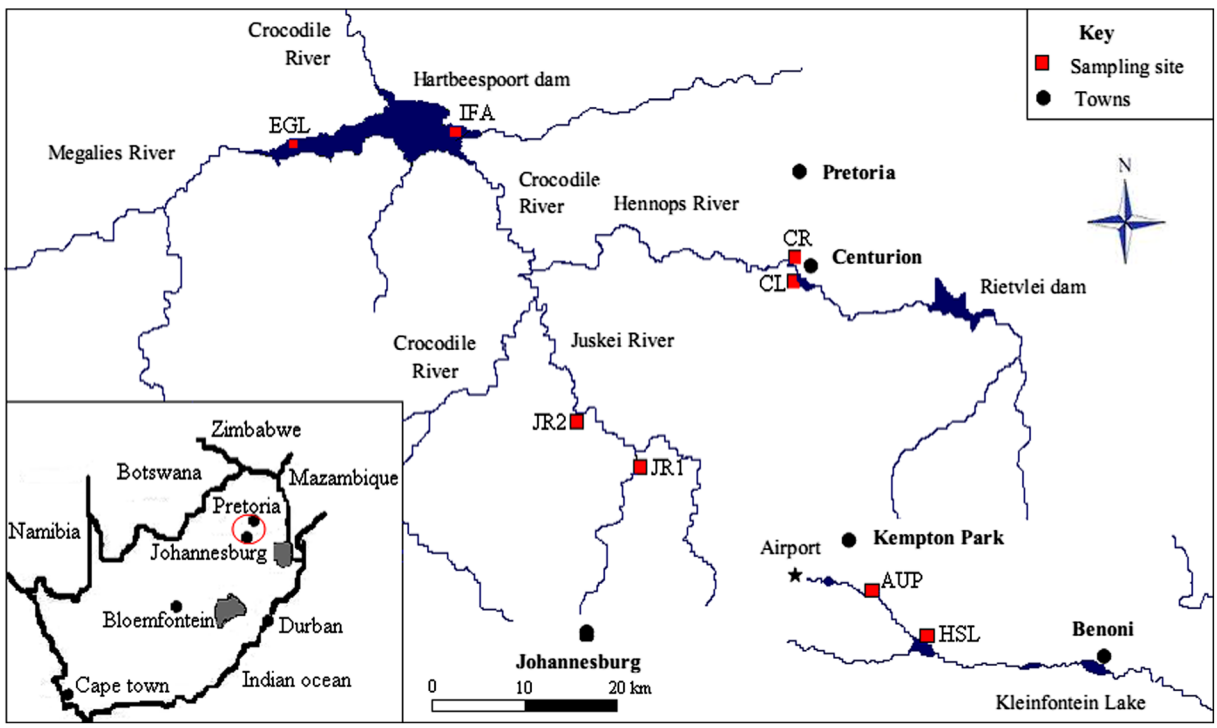

Fig. 1 Map of the sampling sites

treatment plants. Kempton Park area is home to several industries that release their effluent into the river via the treatment plants. The Centurion Lake is surrounded by vibrant business installations such as shopping malls, hotels, recreational facilities and garages.

Hartbeespoort Dam

Two sites were located in the Hartbeespoort Dam: Ifafi (IFA) and Eagles (EGL). The dam is located about 37 km west of Pretoria and along the Crocodile River in North West Province of South Africa. The water body is a 20 km^2 water reservoir sandwiched between the Megaliesberg mountain range in the Highveld region of northern South Africa (Hely-Hutchinson and Schumann 1997; Nyoni et al. 2011). The reservoir receives water from an approximately 4,100 km^2 area all the way from Johannesburg City via the Jukskei and Hennops Rivers that flow into the Crocodile River. This accounts for about 90 % of the dam's water inlet supply with rain water being the major source (Harding et al. 2004). The five catchment basins of the dam are from west to east, the Megalies/Skeerpoort, the Crocodile, the Jukskei, the Hennops and the Swartspruit basin (Van Rei 1987).

Homestead Lake and Airport River

Both Homestead Lake (HSL) and Airport River (AUP) are located about 28 and 35 km, respectively, east of Johannesburg City central business district and a few kilometres from the O.R. Tambo international airport. The origin of the AUP is a swampy area situated at the periphery of the airport. It flows downstream in an easterly direction, passing through a few residential areas before discharging its water into a man-made reservoir called HSL. This dam is surrounded by many residential developments. The HSL also receives water from a small stream originating from the southern part of the airport and about 5 km west of the dam. After exiting the dam, the river flows towards the east rand area of Johannesburg.

Extraction of SPMDs

Debris, particulates and biofouling were removed from the surfaces of retrieved SPMDs using a stream of tap water before briefly immersing in diluted (10 %) hydrochloric acid to rid them of adsorbed carbonates. Further washing of the samplers with deionised water and air-drying at room temperature followed before placement of each device in a 250-ml glass container with a ground joint glass stopper. One hundred milliliters of *n*-hexane was added into each container to fully immerse the SPMD and spiking with surrogate standards in hexane (0.5 μg $sampler^{-1}$ of each compound) done. Dialytic extraction of analytes was carried out over a 24-h period at room temperature and in the dark. After this period, dialysates were transferred into clean, labelled glass containers and fresh batches of 100 ml of *n*-hexane added to the samplers and the process repeated. The extracts were combined and reduced to about 10 ml at 40 °C using a rotary evaporator (Heidolph Laborata 4000, Germany) and further concentrated to the last drop with a gentle stream of nitrogen gas and, thereafter, reconstituted in 1 ml of trichloromethane. Further processing by gel permeation chromatography (GPC) was done to remove triolein and sulphur contaminants prior to instrumental analysis. One thousand microliters of the extract was introduced into a GPC system equipped with a high-pressure pump (HPP5001) and a fraction collector (ECOM, Prague, Czech Republic) and fractionation achieved using a Gel 5 μm 50 Å, 7.5× 300 mm, column (Agilent PL). Dichloromethane acted as the mobile phase flowing at 0.6 ml min^{-1}. Target analytes were collected in the fractions that eluted as from 18.3 to 41.7 min. Prior to eluent volume reduction to near dryness using nitrogen gas, a solvent keeper (0.1 ml of *n*-nonane) was added. The sample was finally reconstituted in 1 ml of *n*-hexane and subjected to activated silica gel cleanup.

For PAHs, each column was packed with 5 g of activated silica gel (prepared by drying at 120 °C for 8 h). Conditioning of the column was done by flushing it with 10 ml of *n*-hexane and the analytes of interest eluted using 20 ml of dichloromethane after sample introduction. The eluate was evaporated to 10 ml at 40 °C and reduced further to 1 ml with nitrogen gas. Sulphuric acid-modified activated silica gel (mixture of 50 g freshly prepared activated silica gel and 33 ml of concentrated sulphuric acid, 98 %) was used to clean PCBs and OCPs. Subsequent elution of the analytes was done with 30 ml dichloromethane. After evaporation and further concentration to 1 ml, terphenyl or PCB 121 internal standards were added to the samples. GC-MS analysis of the compounds followed.

Instrumentation

Prior to analysis of all samples, calibration using standards with concentrations ranging from 0.01 to 0.200 μg ml^{-1} was done. For PAHs, separation was achieved using a HP-5MS capillary column with the dimensions 30 m×0.25 mm internal diameter, 0.25 μm film thickness and helium as the carrier gas flowing at 1.9 ml min^{-1}. Working conditions: splitless injection of 1 μl sample at 250 °C. Column temperature programme 70 °C (0.5 min hold) then ramped at 25 °C min^{-1} to 150 °C followed by 3 °C min^{-1} to 200 °C and finally increased at 8 °C min^{-1} to 280 °C and held for 20 min. Detection of separated analytes was done using a 5971 MS system (Agilent Technologies, USA) set at 320 °C and 70 eV electron impact ionisation. Selected ion monitoring mode was used in the measurements and two to three characteristic ions were chosen for detection and quantification of each compound. The ion source, the transfer line and the quadrupole temperatures were maintained at 230, 280 and 150 °C, respectively. Using external calibration methods, analyte concentrations in the samples were calculated based on the peak areas of the highest characteristic ion in the mass spectrum of the compounds. Recoveries of surrogate standards introduced into the sampler containers prior to dialytic extraction were used to correct such concentrations.

Analysis of PCBs and OCPs in the samples was done on a 6,890 N GC (Agilent technologies, Santa Clara, USA) linked to a Quattro MicroGC MS (Waters, Micromass, UK) operated in EI+ mode was used. Chromatographic separation of target analytes was achieved using a 60 m×0.25 mm× 0.25 um DB5-MS column (Agilent J&W, USA) with the column flow rate of carrier gas (helium) maintained at 1.5 ml min^{-1}. The inlet was operated in the splitless mode at 280 °C and 1 μl sample loaded. For each compound analysed, a minimum of two MRM transitions were recorded. The column temperature was initially 80 °C and held for 1 min, then ramped at 15 °C min^{-1} to 180 °C and finally 5 °C min^{-1} to 300 °C (5 min). TargetLynx software (Waters, Micromass, UK) was applied in processing the raw data. Contaminations that may have occurred during sampler fabrication, deployment and/or retrieval were corrected using fabrication and field blanks.

Water-dissolved concentrations of compounds

Since amounts of analytes absorbed by the samplers follow a first-order approach to equilibrium, water-dissolved concentrations were determined from the quantities sequestered (*N*s) by SPMDs, compound-specific in situ sampling rates (R_S) and their sampler-water partition coefficients (K_{sw}):

$$C_w = \frac{N_s}{K_{sw}V_s[1-\exp(-R_s t/(K_{sw}V_s))]} \quad (1)$$

where V_S=SPMD volume and t=exposure time.

The dissipation of PRCs also obeys first-order kinetics. The nonlinear least squares method (Booij and Smedes 2010) was adopted in the estimation of R_s based on the fraction (f) of individual PRCs that remained in the SPMD after exposure as a continuous function of their K_{sw}, with R_S as an adjustable parameter.

$$f = \exp\left(\frac{R_s t}{K_{SW}V_S}\right) \quad (2)$$

where, $f=N_{PRC}/N_{0,PRC}$ and $N_{0,PRC}$=PRCs at t=0, N_{PRC}=PRCs at t=14 days.

With the assumption that uptake is controlled by the aqueous boundary layer, Eq. (3) (Rusina et al. 2010) was substituted in Eq. (2) enabling the estimation of sampling rates of individual compounds in the higher hydrophobicity range.

$$R_S = FAM^{-0.47} \quad (3)$$

where M=molar mass of compound, A=SPMD surface area (460 cm^2) and F=regression coefficient that was optimised using nonlinear least squares method for estimating sampling rates. K_{sw} values were intrapolated from the empirical Eq. (4) (Huckins et al. 2006). Log K_{ow} values were obtained from various literatures (Vrana et al. 2014).

$$\mathrm{Log}K_{sw} = -01618(\log K_{ow})^2 + 2.321\log K_{ow} - 2.61 \quad (4)$$

Results and discussion

Occurrence of PAHs, PCBs and OCPs in the SPMDs

Amounts of PAHs accumulated in SPMDs after the 14-day exposure period in the various sampling sites are shown in Table 2, while for PCBs and OCPs are presented in Table 3. Field blank SPMDs were devoid of

Table 2 Mean concentrations of PAHs in SPMDs (ng sampler^{-1}) sequestered from different sample sites (n=3)

Compound	Sampling site							
	IFA	JR 1	JR 2	EGL	HSL	AUP	CL	CR
Naphthalene	268±41	247±56	262±16	283±61	389±88	307±26	338±71	148±22
Acenaphthylene	156±30	156±18	158±29	150±12	164±26	197±28	132±11	55±4
Acenaphthene	34±5	38±7	124±6	32±7	38±9	334±6	47±4	74±8
Fluorene	84±15	77±4	355±8	65±11	82±20	71±11	36±8	213±22
Phenanthrene	144±12	246±5	1,192±97	132±15	138±18	174±18	1,220±98	425±13
Anthracene	308±14	287±83	198±11	102±14	49±10	179±22	121±9	31±5
Fluoranthene	127±10	424±47	999±35	156±37	61±15	83±21	118±3	260±19
Pyrene	96±13	367±38	825±91	115±12	42±5	97±19	279±35	260±22
Benz[a]anthracene	32±8	62±7	119±6	32±2	29±0	31±2	189±14	18±4
Chrysene	44±9	133±18	203±28	46±8	34±4	42±5	11±2	31±4
Benzo[b]fluoranthene	38±3	57±4	86±4	34±1	39±6	36±2	17±4	9±0
Benzo[k]fluoranthene	25±5	62±3	86±17	38±4	37±2	71±5	5±1	5±1
Benzo[a]pyrene	30±4	37±13	55±4	79±12	48±6	ND	11±1	4±1
Indeno[1,2,3-cd]pyrene	38±3	41±2	48±10	38±5	37±3	38±0	4±1	8±0
Dibenz[a,h]anthracene	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[ghi]perylene	40±4	45±3	56±5	36±2	36±5	37±2	18±3	ND
ΣPAHs	1,464±60	2,279±121	4,766±147	1,335±79	1,223±98	1,394±57	2,543±128	1,541±46

ND not detected

quantifiable amounts of PAHs, PCBs and OCPs. Prior to dialytic extraction of analytes in the samplers, recovery standards were introduced. Information obtained from their recoveries was then used to adjust the concentrations of the target compounds. Compounds of interest showed good recoveries that ranged from 55 to 115 % for PAHs, 76 to 103 % for PCBs and 69 to 111 % for OCPs. Comparable quantities of the analytes were obtained from triplicate SPMDs deployed in the same site. Relative percent differences between such replicates in all sites were not greater than 25 % for PAHs, except for anthracene at sampling site JR 1 (29 %) and benzo[k]fluoranthene at sample site AUP (34 %). For PCBs, these differences did not exceed 25 %. Save for α-HCH recorded in sampling site JR 2 (34 %), all OCPs exhibited a relative percent difference of less than 21 % between replicates.

In this study, summed-up amounts of SPMD-sequestered analytes ranged from 1,223 to 4,766 ng sampler^{-1} for PAHs, 6.5 to 76.1 ng sampler^{-1} for PCBs and 4.5 to 921.6 ng sampler^{-1} for OCPs. The chlorinated pesticides were primarily composed of HCHs (3.0 to 870.0 ng sampler^{-1}) and dichlorodiphenyltrichloromethane (DDT) and its metabolites (1.5 to 86.5 ng sampler^{-1}).

The use of PRCs (D-PAHs) for other compounds other than PAHs is justifiable. Since hydrophobic compounds with log K_{ow}>4 are accumulated in SPMD under water boundary layer control (WBL), sampling rate is determined by diffusion in water. Diffusion coefficients in water of PAHs, PCBs and OCPs are a weak function of molecular weight (Eq. 3) (Rusina et al. 2010). Since diffusion in water is assumed not to be affected by parameters other than molecular volume/weight, sampling rates of all compounds can be estimated using Eq. 3.

Water-dissolved concentrations of the analytes

R_s values for individual compounds were determined using Eq. 3. Table 4 presents the PRC-derived R_s values for fluorene resulting from SPMD field deployment at the various sampling sites. These values ranged from a low of 1.0 l d^{-1} at HSL in October 2011 to a high of 26.1 l d^{-1} at JR 2 in December 2011. Differences in R_s values at different sites may be attributed to variations in water flow velocities, in agreement with assumption of water boundary layer uptake. Although no flow velocities were measured, dams generally had much lower

Table 3 Mean concentrations of PCBs and OCPs in SPMDs (ng sampler^{-1}) recorded in the different sample sites (n=3)

	Sampling site					
Compound	IFA	JR 1	JR 2	EGL	HSL	AUP
PCBs						
PCB 28	34.3±5.5	44.1±7.8	68.1±12	32.0±6.3	5.9±1	3.2±0.2
PCB 52	1.2±0.2	2.3±0.5	2.4±0.4	0.8±0.1	0.3±0.0	2.4±0.1
PCB101	0.6±0.1	1.1±0.3	1.1±0.1	0.3±0.0	0.1±0.0	2.0±0.0
PCB 118	0.2±0.0	0.5±0.1	0.8±0.3	0.2±0.0	ND	ND
PCB 138	0.6±0.0	0.9±0.2	1.3±0.2	0.5±0.1	0.2	3.1±0.1
PCB 153	0.6±0.1	1.2±0.1	1.4±0.2	0.4±0.1	ND	5.1±0.1
PCB 180	0.7±0.1	0.5±0.1	1.0±0.1	0.4±0.0	ND	4.3±0.0
ΣPCBs	38.2±0.5	50.6±0.9	76.1±0.6	34.6±0.6	6.5±0.1	20.1±0.2
OCPs						
HCHs						
α-HCH	44.4±8	120.4±41	131.5±26	43.2±7	0.8±0.2	1.2±0.3
β-HCH	127.9±16	626.8±98	630.2±82	114.1±20	0.8±0.1	0.7±0.1
γ-HCH	7.0±1.1	16.5±3.7	13.6±2.2	5.9±1.2	1.4±0.2	1.2±0.2
δ-HCH	2.6±0.4	46.5±4.0	65.9±13.4	2.3±0.0	ND	ND
ε-HCH	6.7±1.3	11.4±1.9	28.8±5.6	7.5±1.3	ND	ND
ΣHCHs	*188.5±10*	*821.6±107*	*870.0±87*	*173.0±21*	*3.0±0.3*	*3.1±0.4*
DDX						
o,p′-DDE	0.7±0.1	0.8±0.2	1.5±0.2	0.6±0.1	0.1±0.0	0.1±0.0
p,p′-DDE	7.6±1.3	8.0±1.6	14.4±2.7	5.5±1.0	0.5±0.1	2.1±0.4
o,p′-DDD	20.3±4.8	3.2±0.5	5.2±0.5	28.6±5.5	0.1±0.0	0.6±0.1
p,p′-DDD	55.8±3.4	17.7±3.0	26.6±1.4	47.2±8.1	0.5±0.0	1.5±0.2
o,p′-DDT	1.5±0.0	3.0±0.7	1.8±0.4	1.8±0.3	0.3±0.0	0.5±0.1
p,p′-DDT	0.6±0.1	11.1±2.6	2.1±0.2	0.6±0.0	ND	0.6±0.1
ΣDDX	*86.5±6.0*	*43.8±4.4*	*51.6±3.1*	*84.3±9.8*	*1.5±0.1*	*5.4±0.5*
ΣOCPs	275±12	865.4±107	921.6±88	257.3±23	4.5±0.3	8.5±0.6

ND not detected

All summed numbers are in italic

velocities compared to those samplers deployed on river banks. Other contributors to differences in sampling rates include temperature, biofilm infestation and deposition of particulates on the surface of sampler (Baxter 1990; Cailleaud et al. 2007; Brandli et al. 2008; Booij and Smedes 2010). South Africa has got four seasons with summer starting from mid-October to mid-February and is very hot characterised by afternoon thunderstorms. Autumn is from mid-February to mid-April with little rain and not very hot. Winter starts from May to July, while spring is from August to mid-October. Most of the sampling was done in spring (Table 4) where there is little or no rainfall and is beginning to get hot.

PAHs

Estimation of free dissolved concentrations of the PAHs in water based on the amounts accumulated in deployed SPMDs are presented in Table 5. Since the sampling was not done at the same time and season, it is not easy to compare the results for spatial trends. Total analyte concentrations by site varied from 22.1 ng l^{-1} at RC to 126.7 ng l^{-1} at HSL. The high concentration of PAHs at this site could be linked to previous reported oil spill in the upstream of the Airport River. Airport River (AUP) flows into the Homestead Lake, and this suggests that it is acting as a recipient of PAHs. In the same way, the concentrations of PAHs in the Centurion Lake were

Table 4 Description of the sampling campaign at the sites

Sampling site	Season	Exposure period		Exposure (days)	Water temperature (°C)	SPMD-Sampling rate R_S (l d^{-1})
		Start	End			
IFA	Spring	2 September 2011	16 September 2011	14	19	19.2
JR 1	Summer	3 December 2011	17 December 2011	14	21	19.4
JR 2	Summer	3 December 2011	17 December 2011	14	21	26.1
EGL	Spring	2 September 2011	16 September 2011	14	19	18.3
HSL	Spring	6 October 2011	20 October 2011	14	20	1.0
AUP	Spring	06 October 2011	20 October 2011	14	20	20.0
CL	Spring	12 August 2011	26 August 2011	14	18	10.7
CR	Spring	12 August 2011	26 August 2011	14	18	18.8

much higher than those in the Centurion River. This again may suggest that the dam is acting as a recipient and perhaps a sink of PAHs. A study of PAHs in sediments in the same area found high concentration levels (Sibiya et al. 2013b). The concentration of PAHs in sediments at the Centurion Lake ranged from 61 to 1,690 μg kg^{-1} and 84 to 1,545 μg kg^{-1} at the Homestead Lake (Sibiya et al. 2013b). The reported concentrations in Table 5 for PAHs are comparable to those reported by Karacık et al. (2013) (8.36–76.68 ng l^{-1}) and Wang and coworkers (2009) (19.14–97.17 ng l^{-1}). They were also comparable to those obtained by Vrana et al. (2014) in the Danube River (13–72 ng L^{-1}). However, they were significantly higher than what Allan and Ranneklev (2011) (0.033–9.3 ng l^{-1}) obtained in the Alna River, Norway.

Evidently, water phase PAH concentrations of individual compounds (Fig. 2) generally reflected the trend exhibited by the cumulative concentrations at any given sampling site. The smaller molecular weight compounds (≤ four rings) accounted for the highest percentage (77.6 % at HSL to 96.5 % at AUP) of total PAHs in the water phase. Their relatively higher water solubilities as indicated by lower log K_{ow} values enhance their availability and, hence, uptake by the samplers. On the other hand, strong hydrophobicity of larger molecular weight PAHs encourages increased sorption to larger particulates and colloids in the water column resulting in diminished availability.

PCBs

Freely dissolved PCB levels in the waters of the various sampling sites are presented in Table 5. Estimated water phase concentrations were in the low picograms per liter range. Sum of seven indicator PCB congeners varied between 21 pg l^{-1} at AUP and 121 pg l^{-1} at HSL. These values were about three orders of magnitude lower than for PAHs and up to two orders lower than OCPs. Of the many PCB congeners known, seven of them (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180) were quantifiable in most of the sites, with the less-chlorinated PCBs predominating (up to 89 %). Figure 3 presents concentrations of some of the PCB congeners.

Residue levels obtained were lower than those reported by Allan and Ranneklev (2011), Liu et al. (2013) and Cailleaud et al. (2007) but generally comparable to those obtained by Wang et al. (2009) (66–519 pg l^{-1}). PCBs enter the environment mainly through volatilisation from in-use and disposed equipment or as re-emissions from soils (Wang et al. 2007). Although these compounds were never produced in South Africa, PCB oils as well as equipment containing such oils were imported for use mainly for electricity generation and in manufacturing industries. However, as in many other countries, PCBs are currently outlawed in the country, and their presence in the environment is attributed to previous applications, since these compounds are persistent organic pollutants. Old electricity transformers contained PCBs, but these are now being phased out by Eskom, a South African electricity generation and supply company.

Although sampling sites IFA and EGL are located in an area devoid of major industrial activities, it still recorded significant quantities (33.6 and 27.1 pg l^{-1}, respectively) of the contaminants. Apparently, most of

Table 5 Estimated dissolved water concentrations (ng l^{-1}) of PAHs, PCBs and OCPs at the various sampling sites

Compound	Sampling site							
	IFA	JR 1	JR 2	EGL	HSL	AUP	CL	CR
PAHs								
Naphthalene	37.205	34.705	36.813	38.92	61.185	43.135	47.491	20.795
Acenaphthylene	3.832	3.795	3.828	4.084	13.307	4.777	3.279	1.338
Acenaphthene	1.037	1.154	3.764	0.941	3.194	1.017	1.439	2.247
Fluorene	1.349	1.157	5.280	0.905	6.422	1.063	0.595	3.200
Phenanthrene	1.198	1.699	7.487	0.900	10.465	1.171	11.773	2.942
Anthracene	2.838	1.656	1.306	0.581	3.743	0.918	1.200	0.224
Fluoranthene	0.755	1.938	3.757	0.483	4.753	0.363	0.909	1.194
Pyrene	0.579	1.694	3.152	0.429	3.265	0.427	2.164	1.207
Benz[a]anthracene	0.185	0.276	0.423	0.130	2.409	0.131	1.470	0.081
Chrysene	0.256	0.592	0.726	0.179	2.822	0.178	0.086	0.139
Benzo[b]fluoranthene	0.268	0.263	0.317	0.151	3.370	0.157	0.139	0.042
Benzo[k]fluoranthene	0.141	0.284	0.313	0.198	3.182	0.319	0.041	0.023
Benzo[a]pyrene	0.195	0.171	0.200	0.189	2.023	ND	0.089	0.019
Indeno[1,2,3-cd]pyrene	0.236	0.196	0.182	0.172	3.361	0.174	0.034	0.039
Dibenz[a,h]anthracene	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[ghi]perylene	0.247	0.214	0.212	0.165	3.27	0.167	0.152	ND
ΣPAHs	*50.32*	*49.79*	*67.76*	*48.43*	*126.78*	*53.99*	*70.86*	*33.49*
OCPs								
HCHs								
α-HCH	1.884	5.106	5.576	1.832	0.092	0.051		
β-HCH	5.737	28.103	28.254	5.116	0.094	0.031		
γ-HCH	0.371	0.874	0.721	0.313	0.170	0.064		
δ-HCH	0.046	0.790	1.095	0.039	ND	ND		
ε-HCH	0.301	0.511	1.291	0.336	ND	ND		
ΣHCHs	8.339	35.385	36.937	7.635	0.356	0.146		
DDX								
o,p′-DDE	0.004	0.004	0.006	0.003	0.010	ND		
p,p′-DDE	0.048	0.040	0.055	0.026	0.048	0.010		
o,p′-DDD	0.129	0.016	0.020	0.133	0.010	0.003		
p,p′-DDD	0.354	0.090	0.102	0.227	0.048	0.007		
o,p′-DDT	0.010	0.016	0.007	0.009	0.030	0.003		
p,p′-DDT	0.004	0.059	0.008	0.003	ND	0.003		
ΣDDTs	0.549	0.225	0.198	0.401	0.146	0.026		
ΣOCPs	*8.888*	*35.610*	*37.135*	*8.036*	*0.502*	*0.172*		
PCBs								
ΣPCBs	*0.034*	*0.058*	*0.074*	*0.027*	*0.121*	*0.021*		

ND not detected

All summed numbers are in italic

the water at the sites is supplied through the Crocodile River (Harding et al. 2004) whose major tributaries include the Jukskei and Hennops Rivers. The origins of the two rivers can be traced to the outskirts of Johannesburg City—a probable source. This is especially reinforced by the closeness in the estimated

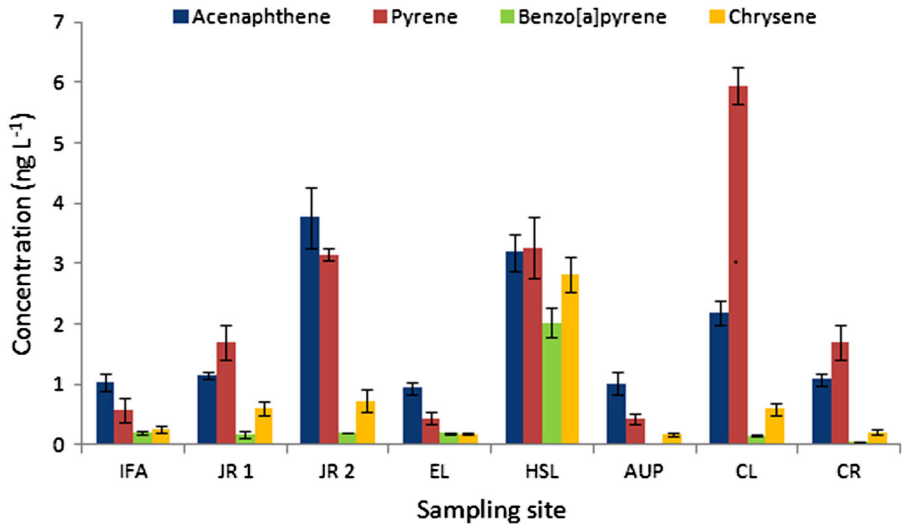

Fig. 2 Estimated water-dissolved PAH concentrations of some individual PAHs in the sampling sites

contaminant concentrations at IFA (34 pg l^{-1}) and EGL (27 pg l^{-1}) sampling sites (both in the same water body).

The lighter-molecular-weight PCB congeners are usually more prone to atmospheric transport (Ockenden et al. 2003) and volatilisation (Wang et al. 2007). However, presence of larger-molecular-weight PCBs such as the dioxin-like PCB 118 (Quinn et al. 2009) in the water body is likely a result of previous application in the immediate surrounding area. Typically, heavier PCB molecules are known to deposit close to the main source, resulting in relatively increased levels in the areas, even decades after initial use, whereas their lighter counterparts can travel for long distances from their sources. Although the heavier congeners

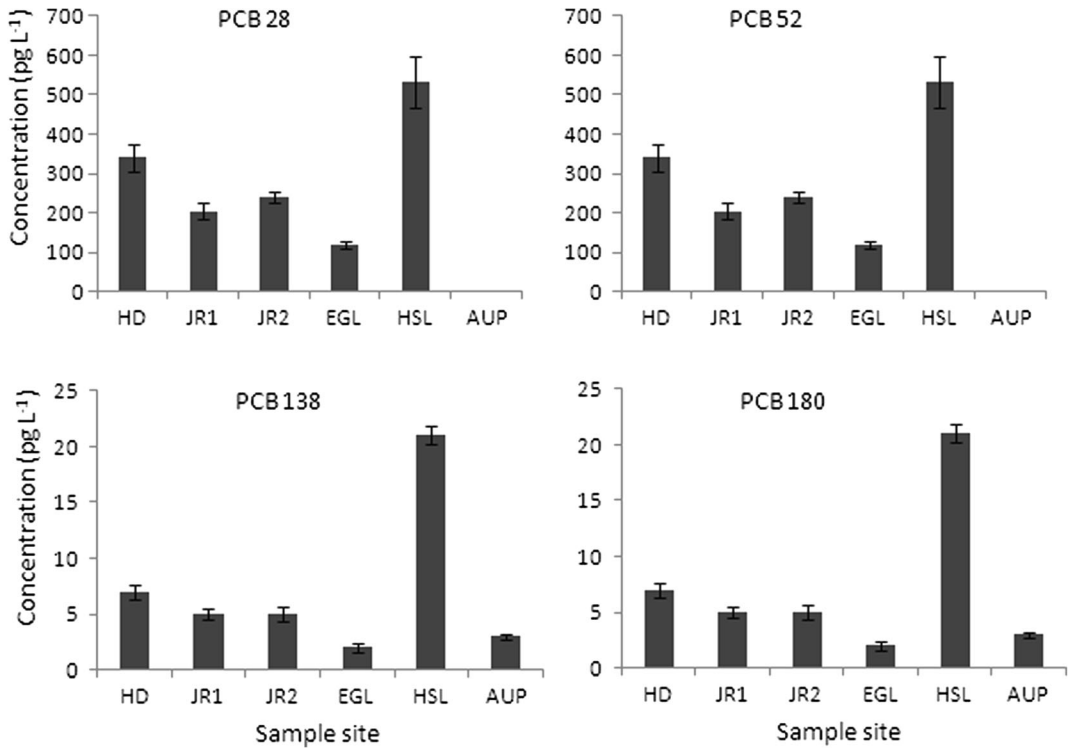

Fig. 3 Water-dissolved concentrations of some individual PCB congeners as estimated from SPMDs deployed in several sample sites

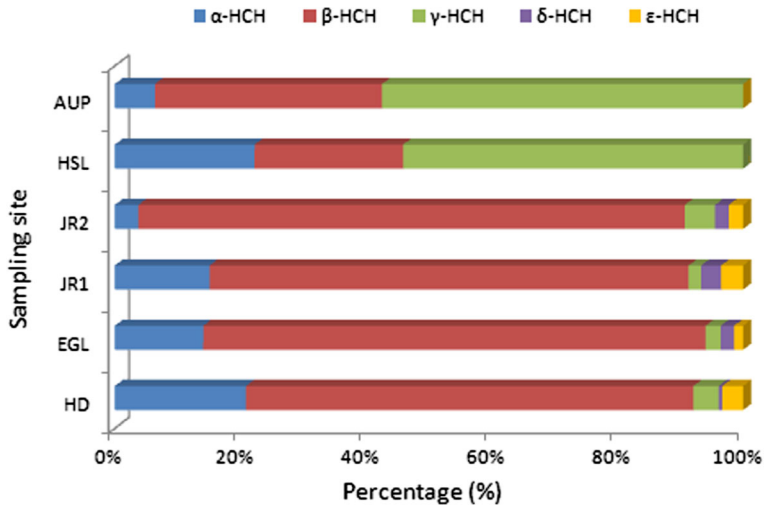

Fig. 4 Percent composition of HCH in water of the several sample sites

were found at very low concentrations in the water phase, their high lipophilicity and biomagnification effects through the food web may be a cause of concern (Degger et al. 2011).

OCPs

Estimated ambient water concentrations of OCPs in the various sampling sites are shown in Table 5. Sum total OCP concentrations ranged from 0.172 ng l^{-1} at AUP to 37.135 ng l^{-1} at JR 2. The principal compositions of these compounds in all the sites were HCH and DDX (DDT, DDD and DDE). HCHs levels were higher than those of DDX with ΣHCHs ranging from 0.146 to 36.937 ng l^{-1} and ΣDDX varied between 0.026 and 0.549 ng l^{-1}. Concentrations of individual isomers generally followed a similar trend as the totals. HCH concentrations from this study were in agreement with those reported by Luo et al. (2004) (5.7–23.3 ng l^{-1}) but higher than those obtained by Wang et al. (2009) (0.10–0.63 ng l^{-1}).

Considering all the study sites, mean water-borne concentrations of individual HCH isomers increased in the order: δ-HCH (2.134 ng l^{-1}), ε-HCH (2.250 ng l^{-1}), γ-HCH (2.446 ng l^{-1}), α-HCH (12.990 ng l^{-1}) and β-HCH (68.998 ng l^{-1}), (Fig. 4), with α- and β-HCHs accounting for over 90 % of the totals. In all cases, the β-HCH predominated. This isomer is characterised by higher water solubility, lower volatility and stronger environmental stability to physical, chemical and biological degradation (Willet et al. 1998; Wang et al. 2009). Concentrations of α-HCH were also higher than for γ-, δ- and ε-isomers. Technical-grade HCH was widely used as an insecticide, and together with its accompanying isomers, it is still readily found in the environment (Wu et al. 1997). Since this type of HCH contains between 60 and 70 % α-HCH (Li and Macdonald 2005), it is expected that for every quantity of the pesticide used (and eventually ending up in the environment), a big percentage constitutes α-HCH. Moreover, its relative volatility aids in long-range transportation to regions afar. However, the lower concentrations (than α- or β-isomers) of γ-HCH observed in all the sampling sites suggest no recent applications of the insecticide in the catchment areas of the water systems. As a signatory of the Stockholm convention, South Africa has phased out the production and use of these compounds.

Sampling sites JR 1 and JR 2, both of which are found in the Jukskei River, recorded the highest water-dissolved HCH concentrations. However, a slight variation in contaminant levels between them was witnessed going downstream (from JR 1 to JR 2). Since the origin of the Jukskei River is very close to Johannesburg City, the high levels of the contaminants recorded may thus be related to previous agricultural activities. Most of the developed parts of Johannesburg long the Jukskei River were previous farms which were later sold and developed for industrial and residential properties. Further downstream (JR 2), the marginal increase in HCH levels is likely resulting from additional input from also previous agricultural activities. Site IFA recorded slightly higher water-dissolved ΣHCH concentrations than EGL, despite the two sites being in the same water body

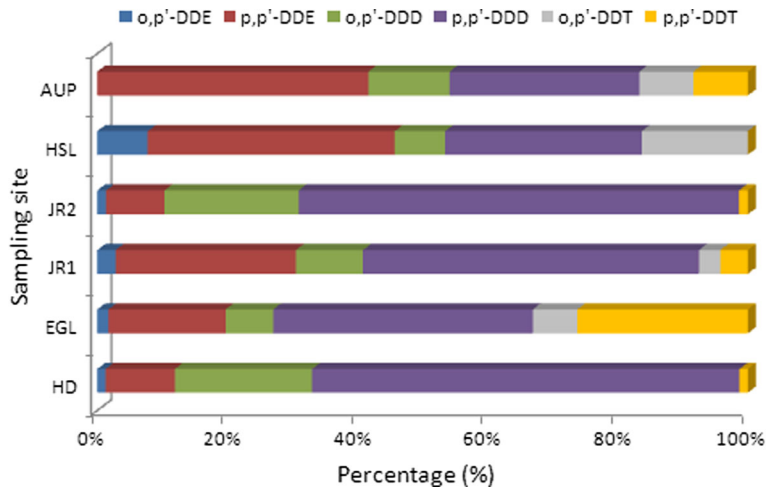

Fig. 5 Percent composition of DDX in water of the various sample sites

(Hartbeespoort dam). The closer proximity of the Crocodile River's entry point into the dam to IFA than to EGL (Fig. 1) may explain this discrepancy.

The summed-up concentrations of estimated free dissolved DDX in each sampling site are presented in Table 5. ΣDDX ranged from 0.026 ng l^{-1} in AUP to 0.549 ng l^{-1} in IFA. Total DDX concentrations were at most two orders of magnitude lower than HCH values. IFA and EGL recorded significantly higher contaminant concentrations (at least twofold) compared to all the other sites. DDX levels obtained in this study were comparable to those reported by Quémerals et al. (1994) and Wang et al. (2009) but lower by several orders of magnitude than those reported by Karacık et al. (2013) and Rajendran et al. (2005).

Ultraviolet radiation as well as microbial activity can degrade DDT to its metabolites, DDD and DDE. These degradation products are representative of historic use of DDT (Wang et al. 2009). The percent contributions of DDT and its metabolites in each of the sampling sites are shown in Fig. 5. Evidently, most of the DDX existed as DDD and DDE, with the former constituting the highest percentage in the majority of sites (IFA=86.8 %; JR 1= 47.4 %; JR2=62.0 %; EGL=88.3 %; HSL=38.6 %; AUP=41.7 %). This was more pronounced at IFA and EGL sampling sites. Two inferences can be made from these observations. Firstly, contamination of the sites is mainly due to past use of DDT and the contribution of current application appears limited. Secondly, reductive dechlorination mechanisms (Baxter 1990; Wedemeyer 1966) of DDT are more prevalent in the studied aquatic systems and, especially, at IFA and EGL. Sibali et al. (2008) is also reported to have looked at the level of organochlorine pesticides along the Juskei River in Johannesburg and including the Hartbeespoort Dam (HD). Soxhlet extraction was used for solid samples,

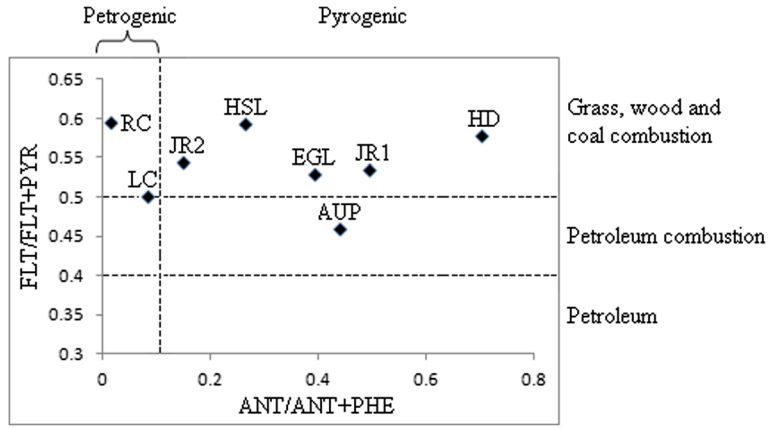

Fig. 6 PAH cross plots for the ratios Ant/(Ant + Phe) vs Flt/(Flt + Pyr)

while water samples were extracted with liquid-liquid extraction; both techniques determines the total concentration. The concentrations of these pesticides were much higher in sediments, mostly in three-digit micrograms per kilogram levels while in water were mostly single- and double-digit micrograms per kilogram levels. High concentration in the sediment indicate accumulation from previous use. Re-desorption processes could be contributing to what is observed in water bodies.

Possible sources of PAHs

PAHs enter the environment through two major pathways: pyrogenic or petrogenic sources. Water-dissolved concentrations of the analytes have been used to predict their probable sources by utilising molecular ratios of certain PAHs (Yunker et al. 2002; Zhang et al. 2004; Brandli et al. 2008; Allan and Ranneklev 2011). Specifically, variations in the ratios of the thermodynamically less-stable PAHs are used as indices in apportioning such sources. For passive samplers, Allan and Ranneklev (2011) suggest that ratios of PAHs must be for compounds with near to identical sampling rates so as to minimise bias arising from the mode of calculation of the sampling rates for compounds with widely differing log K_{ow} values. In the current study, source apportionment of PAHs in each sampling site was attempted using ratios of Anthracene/(Anthracene + Phenanthrene) [(Ant/(Ant + Phe))] against Fluoranthene/(Fluoranthene + Pyrene) [(Flt/(Flt + Pyr))]. As shown in Fig. 6, the majority of the sites sampled gave Flt/(Flt + Pyr) ratios that were greater than 0.5, indicating pyrogenic origins. This may have occurred through combustion of biomass and coal. PAHs at sampling sites AUP and CL were clearly inclined towards petroleum combustion sources. A small ratio (<0.1) of Ant/(Ant + Phe) indicates dominance of petrogenic sources. It is proposed that since AUP is in very close proximity to a busy international airport, aircraft, vehicular and other machinery exhausts may be finding their way into the waters of the sampling site. PAHs detected at sites CL and CR also seem to point to petrogenic origins probably due to the myriad of human activities taking place in the immediate surroundings of this busy urban setup. In general, the use of Ant/Ant + Phe ratio in differentiating petrogenic from pyrogenic sources is at times limited by photolytic degradation of anthracene which can result in lowered ratios (Kamens et al. 1988; Liu et al. 2009).

Conclusions

Passive sampling devices and SPMDs in particular are potentially viable tools in determining water-dissolved concentrations of HOCs such as PAHs, PCBs and OCPs in water systems. The free dissolved fraction of organic micropollutants is critical in terms of their bioavailability and ecotoxicological impacts on aquatic organisms. In this study, though still an initial assessment, three classes of HOCs, PAHs, PCBs and OCPs, were quantifiable in all the study sites. PAH levels were at least one and two orders of magnitude higher than OCPs and PCBs, respectively. Using molecular ratios of certain PAHs, the identification of probable sources of the contaminants in the water phase was attempted. The findings indicated an inclination towards pyrogenic origins in all sample sites except at AUP and CL and CR, which indicated petroleum combustion sources. In general, our study has significant importance in providing basic preliminary data of POP pollution in water systems situated in and around Johannesburg City, South Africa.

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Position paper on passive sampling techniques for the monitoring of contaminants in the aquatic environment – Achievements to date and perspectives

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ABSTRACT

This paper, based on the outcome of discussions at a NORMAN Network-supported workshop in Lyon (France) in November 2014 aims to provide a common position of passive sampling community experts regarding concrete actions required to foster the use of passive sampling techniques in support of contaminant risk assessment and management and for routine monitoring of contaminants in aquatic systems. The brief roadmap presented here focusses on the identification of robust passive sampling methodology, technology that requires further development or that has yet to be developed, our current knowledge of the evaluation of uncertainties when calculating a freely dissolved concentration, the relationship between data from PS and that obtained through biomonitoring. A tiered approach to identifying areas of potential environmental quality standard (EQS) exceedances is also shown. Finally, we propose a list of recommended actions to improve the acceptance of passive sampling by policy-makers. These include the drafting of guidelines, quality assurance and control procedures, developing demonstration projects where biomonitoring and passive sampling are undertaken alongside, organising proficiency testing schemes and interlaboratory comparison and, finally, establishing passive sampler-based assessment criteria in relation to existing EQS.

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1. Introduction

For two decades, several passive sampling devices have been developed for the monitoring of organic and inorganic contaminants in aquatic environments. These passive samplers (PS) enable the improvement of limits of quantification (LOQ) by accumulation and concentration of contaminants over long-term exposure. Moreover, when they are used in the integrative phase of uptake (i.e. integrative samplers), time-weighted average (TWA) concentrations over the exposure period can be derived, leading to a better representativeness of measurements.

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Such passive sampling techniques have been recommended in the European Commission Guidance Document on surface water chemical monitoring [1], then in the Water Framework Directive (WFD) daughter Directive 2013/39/EU [2] as complementary methods to improve the level of confidence in water monitoring data in comparison with conventional spot sampling. PS are assumed to have a positive influence on the future design and output of monitoring programmes in the context of the WFD and the Marine Strategy Framework Directive (MSFD). However, some barriers still remain that prevent regulatory acceptance and actual implementation of these tools for routine monitoring of contaminants in aquatic systems.

In order to endorse PS use in monitoring programmes, several actions have been conducted, including interlaboratory studies (ILS) to evaluate the performances of passive sampling methods with a focus on (i) hydrophobic substances in situ [3], (ii) hydrophobic substances in laboratory (ECLIPSE project, [4]), (iii) priority substances in situ (AQUAREF, www.aquaref.fr, [5]), and (iv) emerging substances in situ (NORMAN network, http://www.norman-network.net/?qHome, with the Joint Research Centre's Institute for Environment and Sustainability, JRC-IES, [6]). Moreover, a NORMAN Expert Group meeting on "Linking Environmental Quality Standards and Passive Sampling" was organised in July 2013 in Brno (CZ) to discuss the possible routes for the implementation of passive sampling in regulatory monitoring for checking of compliance with Environmental Quality Standards (EQS) for WFD priority and river basin-specific substances. And, in collaboration with the International Commission for the Protection of the Danube River (ICPDR) and within the framework of the Joint Danube Survey (JDS3) in 2013, the NORMAN network launched a study to develop and test a methodology for continuous screening of large rivers using passive sampling. The aim was to assess the applicability of a temporally and spatially integrative sampling approach as a water quality monitoring tool for various substances. The results of this study have been published recently [7].

In November 2014, a "Workshop on Passive Sampling techniques for monitoring of contaminants in the aquatic environment", was organised jointly by the NORMAN network and AQUAREF, at Irstea, Lyon, France. This workshop brought together experts involved in passive sampling activities carried out by the NORMAN network and beyond. They discussed the state of the art and defined the strategy and a roadmap of further actions to be fostered by NORMAN, for 2015 and beyond, to improve implementation of passive sampling techniques in environmental monitoring.

The present paper is addressed to scientists and to water managers and decision-makers at river basin, national and European level. The aim of this paper is to provide a common position, as discussed at the workshop in Lyon, of the passive sampling community experts regarding concrete actions required to improve the use of passive sampling techniques in support of risk assessment and risk management and to point to ways of overcoming the remaining barriers to regulatory acceptance and actual implementation of these tools for routine monitoring. Particular attention is given to organic contaminants, for which various types of PS can be used according to their hydrophobicity (Sections 3.1 and 3.2). The discussion on PS for monitoring programmes in water and biota (Sections 3.3 and 3.4) also includes the case of metals, as sampled with the generally accepted PS: Diffusive Gradient in Thin Films (DGT) [8].

2. Method

The first day of the meeting focused on discussions between scientific experts on technical issues surrounding the features and performance of passive sampling techniques. Participation on the second day was also open up to stakeholders and embraced the applicability of PS in regulatory monitoring programmes in the aquatic environment (WFD – MSFD, OSPAR Convention, etc.).

The workshop was organised in four sections which reflect the recurrent questions and challenges identified by decision-makers as regards the use of passive sampling techniques for environmental monitoring:

1. Which PS are suitable for monitoring hydrophobic organic compounds in water? Can we expect to obtain accurate time-weighted average (TWA) concentrations with these PS?
2. Which PS are suitable for monitoring hydrophilic organic compounds in water? Can we expect to obtain accurate time-weighted average (TWA) concentrations with these PS?
3. What is the role of passive and grab sampling approaches in monitoring programmes? Are data obtained by passive sampling comparable with those from grab sampling?
4. What role can passive sampling play in support to chemical monitoring in biota?

The conclusions presented in this paper are organised following these 5 successive items. Parts 1 and 2 focus on organic contaminants, whereas parts 3 and 4 cover all contaminants, including metals.

3. Results and discussion

3.1. Which passive samplers are suitable for monitoring hydrophobic compounds in water?

Various types of PS are available for hydrophobic compounds: the Semi-Permeable Membrane Device (SPMD, biphasic system), silicone rubber and Low Density PolyEthylene (LDPE) strips (monophasic systems) are the most commonly used [8].

It is not possible to recommend a single specific PS. Rather, PS calibration data should satisfy certain performance or quality standard criteria, and uptake and release processes should be in agreement with theory. Recommending a specific PS would also lead to a loss of information and prevent an improvement of existing techniques or new developments.

SPMD is a biphasic PS (a polyethylene membrane filled with lipid), and can therefore generally be considered more complex than monophasic polymers concerning sample processing in the laboratory and modelling of contaminant uptake mechanisms. Given these constraints, it is expected that the use of monophasic samplers will be favoured over the use of SPMD. Nevertheless, the use of SPMD for more than 20 years has generated numerous laboratory and field data. Moreover, it is at present the only standardised and commercially available PS for hydrophobic compounds.

Even so, for practical reasons, monophasic polymers (e.g. silicone rubber, LDPE) appear to be the most suitable PS for sampling of hydrophobic compounds.

Monophasic polymers can be of different qualities and made of different materials; but at the moment, there are no standard commercial products available. It was therefore unanimously agreed that there is a need for commercial supplies of standard monophasic PS.

Suitable polymers should meet the following criteria:

- the uptake of the polymers must be based on absorption (not adsorption) and sampler/water partition coefficients for the compounds of interest should be sufficiently high in order to allow good performance in terms of substance accumulation;
- the diffusion coefficients of target substances inside the polymer should be sufficiently high so water boundary control dominates

the uptake process, even under severe turbulence conditions. This allows the uptake process to be calibrated from the release of Performance Reference Compounds (PRC, i.e. a sort of internal standards) that are dosed prior to deployment [9,10].

For each new monophasic polymer, sufficient diffusion should be confirmed and partition coefficients should be determined either independently or through cross-calibration against a polymer with already known partition coefficients. Such a polymer (e.g. silicone) could serve as a reference material for sampler cross-calibration.

For accurate analysis of PS, there is also a need for certified reference materials (CRMs) of polymers used in passive sampling containing the most widely monitored and regulated compounds. Preparation of such CRMs could be the role of the European JRC for Reference Materials and Measurements (IRMM) and/or of the National Metrology Institutes (NMIs).

The application of PS in waters requires knowledge of polymer-water partition coefficients (K_{pw}) and knowledge that diffusion coefficients (D_p) in the polymer are sufficiently high, both for substances of interest and for those used as PRC. When commercial PS products and CRMs become available, their routine use for monitoring compounds whose diffusion and partition coefficients (and their uncertainty) have been published will not require additional calibration experiments by end-users. The use of accurate K_{pw} constants, PRC for measurement of in situ exchange kinetics, and the application of validated uptake models are sufficient for accurate measurements of contaminant concentrations in waters using PS.

Thus, in order to support the use of PS, it is important to:

- Develop harmonised guidelines, in particular for:
  - the measurement of polymer-water partition coefficients (K_{pw});
  - the measurement of substance diffusion coefficients (D_p) in PS polymers;
  - the definition of criteria for an appropriate application of PRC;
  - the definition of suitable and validated models for calculation of water concentration from PS.
- Perform interlaboratory studies to improve validation of PS for routine use.

As to the latter, it is recommended that interlaboratory studies aimed at validation of PS for routine use should be designed as two-step exercises, in which Step 1 is the Proficiency Test (PT) for the analysis of the contaminants in the extracts of PS, and Step 2 is an interlaboratory study for intercomparison of PS field-deployment and analysis of contaminants in PS, including estimation of water concentration.

Only skilled laboratories (i.e., those that succeeded in Step 1) should be allowed to participate in Step 2. For the choice of contaminants, the focus should be on hydrophobic WFD Priority Substances and other substances (including the new Priority Substances) for which robust analytical methods already exist (for analysis in PS exposed in the aquatic environment).

With respect to the influence of temperature and salinity, K_{pw} values used for calculation of freely dissolved concentrations are usually determined for $T = 20\,^{\circ}C$ and salinity = 0‰. Workshop participants concluded that there is no need to correct K_{pw} for temperature nor salinity, since EQS values are not corrected for the effects of these parameters, when used for compliance monitoring (to be noted that there are specific EQS in marine waters). Moreover, the approach using K_{pw} without correction provides more conservative water concentration estimates (higher concentrations are estimated in scenarios with low temperature and high salinity); such estimates are therefore more protective when referring to compliance with EQS (worst case scenario).

3.2. Which passive samplers are suitable for monitoring of hydrophilic compounds in water? Can we expect to obtain accurate time weighted average (TWA) concentrations with passive sampling?

Various types and configurations of PS exist today for hydrophilic compounds: the Polar Organic Chemical Integrative Sampler (POCIS) (e.g. with different membranes and sorbent phases), the Chemcatcher and the Empore disks are the most commonly used [8]. At present, it is not possible to recommend a preferred specific PS for sampling of hydrophilic compounds.

It was acknowledged that at present the mechanisms of uptake and release of hydrophilic substances from water into these adsorption-based PS are not fully understood. The exchange of compounds between the PS and the aqueous phase can often be considered an anisotropic process. Consequently, it is generally not possible to use the release of PRC to calibrate the uptake rate and allow calculation of time weighted average (TWA) water concentrations for a wide range of compounds. Nonetheless, PRC should be used as surrogates to check that exposure conditions (e.g. temperature, salinity, water flow) are within the limits for which the laboratory derived the calibration data (quality controls).

Currently, adsorption-based PS for hydrophilic compounds allow only semi-quantitative information to be obtained. This is because of the uncertainty in applying laboratory-based sampling rates to in situ field conditions. However, when confidence intervals of estimated TWA concentration are available, these PS data could be used for EQS compliance checking. One of the possible approaches to apply PS data for assessing compliance with a regulatory limit involves the calculation of the upper 90% confidence limit of the PS-derived TWA concentration. Accurate analyses and the use of an equivalent volume of water sampled by the PS smaller than the actual sampled volume to calculate water concentrations would ensure that estimated TWA concentrations are an overestimate of actual concentrations and a robust use of PS. The good status cannot be considered as achieved if the calculated upper TWA concentration limit exceeds the EQS. This is possible for substances for which linear uptake is confirmed for the period of exposure.

Poulier et al. [11] recently proposed a method to determine confidence intervals for each TWA concentration estimate by POCIS, over a period of one year (Fig. 1). The means of maximum and minimum limits of these confidence intervals are defined as MAX and MIN, respectively. Thereafter, the MAX and MIN values are compared to the AA-EQS (annual average EQS) and good chemical status is considered to be achieved if MAX is lower than the AA-EQS (Fig. 1).

Understanding the uptake mechanism of polar compounds into adsorption-based PS is the first and most important issue that needs to be resolved in order to reduce the currently observed uncertainty in passive sampling data. New solutions have to be found to simplify PS construction to an effective minimum. In this process, it is possible that some of the traditionally applied passive sampling designs will have to be abandoned (e.g. application of membranes in PS, which often cause undesired complications of the uptake mechanism).

Even if PS tools for hydrophilic substances still need developments and adaptations, guidelines describing how to conduct PS calibrations are required. In particular, such guidance should define a common set of metadata and calibration conditions (temperature, water flow, type of the exposure system, type of water) to be reported together with the obtained sampler calibration parameters. All this information is required for the

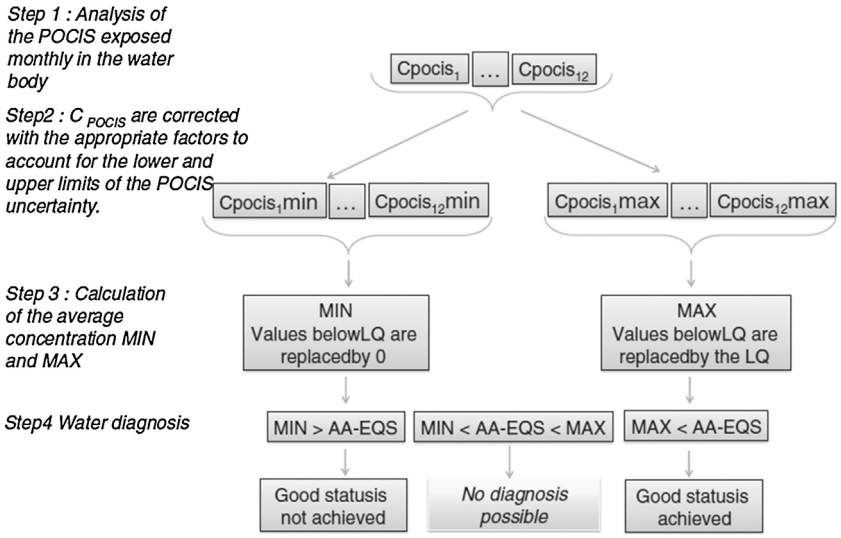


Fig. 1. Proposed procedure to use POCIS data for surveillance monitoring. From Poulier et al. [11]

assessment of the possible relationship between the observed variability in available calibration data and the exposure conditions used in calibrations [12].

In situations where the effect of environmental conditions on the PS performance (especially the sampling rate) in the field cannot be either determined or controlled, application of laboratory-derived calibration parameters will always introduce a systematic error into derived water TWA concentrations. When water concentrations are calculated from passive sampling data, expected variability of applied calibration parameters should be included in the calculation of the reported concentration. The value and uncertainty of applied sampling rates and the approach for calculation of uncertainty should also be reported. More generally, the reporting of passive sampling data requires improved practice, focusing particularly on the data and models used to estimate water concentrations from contaminant masses sorbed into the PS.

In contrast with spot sampling, PS provides time-integrated concentrations of pollutants. If the uncertainty of water concentrations obtained from PS is lower than the variability of environmental concentrations, data obtained by PS represent the contamination situation in the water body as well as or better than the low frequency spot sampling (e.g. based on 4–12 sampling times per year) that is currently used in compliance monitoring for the WFD.

Previous interlaboratory studies (including the AQUAREF ILS [5] in 2010 and NORMAN ILS [6] in 2011) showed that accurate analysis of certain hydrophilic substances (pesticides, pharmaceuticals, steroid hormones, perfluorinated compounds) remains a challenge for a number of laboratories. Inaccurate analyses contributed significantly to the observed high variability of water concentrations derived from PS data which cannot be attributed to inadequacies of the PS process. It was therefore recommended to organise further intercomparison studies. As for hydrophobic compounds, in order to ensure validation of the different parts of the PS process, future intercomparison studies should be designed as two-step exercises, where Step 1 is the PT for analysis of contaminants in extracts of PS, and Step 2 is Interlaboratory comparisons for PS field-deployment and analysis of contaminants in PS. Only skilled laboratories (i.e., those that succeeded in Step 1) should be allowed to participate in Step 2. For the choice of contaminants, the focus should be on WFD Priority Substances and other hydrophilic substances (including new Priority Substances) for which robust analytical methods exist (in PS exposed in real water).

Finally, workshop participants identified the need to develop PS for ionic and highly hydrophilic compounds (e.g. glyphosate).

3.3. Passive versus grab sampling approaches in monitoring programmes

Passive sampling measures the dissolved phase concentration of a contaminant (and not the whole water concentration, as required by Directive 2013/39/EU [2]). As a result, passive sampling cannot be used today to assess compliance with EQS for all organic contaminants under the WFD, but only for moderately polar to polar organic compounds (with log $K_{ow} < 5$) where the concentration in the water column is not dominated by the fraction adsorbed to colloids and particles in water. On the other hand, passive sampling is recommended in the European Commission Guidance Document on surface water chemical monitoring [1] and in the Directive 2013/39/EU [2] as a complementary method to improve the quality of the assessment and as a resource saving measure. In this regard, passive sampling could be used in conjunction with investigative monitoring as a risk-based screening tool to evaluate the presence or absence of chemical contaminants, to identify sources of pollution when the concentration levels (and therefore the required limits of detection) are extremely low or when the source of pollution is intermittent.

Passive sampling can also be employed in trend monitoring both as a qualitative and a quantitative tool. PS offer added value compared to grab sampling when applied as an "early-warning tool" to detect increasing (or decreasing) trends. Exceedance of defined threshold values could be used to trigger further monitoring using conventional sampling techniques, e.g. grab sampling and/or biota monitoring.

Some practical advantages of passive sampling can be highlighted:

- low limits of detection and quantification can be achieved, especially with samplers for hydrophobic compounds;
- in situ sample preconcentration is possible and the handling of large water volumes can be avoided (thereby allowing lower costs for transport and storage in comparison with conventional spot sampling, and easier sampling in remote locations);
- thanks to higher stability of the sampled compounds, it is possible to allow prolonged sample storage;
- analysis of samples can be delayed and, if needed, combined to composite samples;

- unlike water samples, sorbents or extracts of PS are more suitable for long term storage in specimen banks.

As to the quality of the information obtained from PS measurement results:

- information obtained with PS is representative of an extended time period; this integrated information is more relevant to describe the status of a water body than the information which can be obtained with spot sampling;
- only freely dissolved compounds are sampled: for hydrophobic compounds, PS provide a measure directly proportional to the chemical activity of the contaminant of interest in the medium being sampled;
- PS allow a reduction in the effect of blank contamination, since the integrative character of sampling allows concentrations in exposed PS to be found that are significantly higher than levels found in blanks.

There is still a need for pilot field studies to gain experience and demonstrate the usefulness and relevance of passive sampling strategies compared to grab sampling. Such demonstration studies should be designed to show the difference between conventional monitoring (i.e. 4–12 spot water samples/year, or integrative biota monitoring for hydrophobic compounds and metals) and a new, more relevant and practical concept using PS. The study should aim to demonstrate that a TWA concentration via PS is more representative and relevant – compared to conventional monitoring – for the characterisation of the chemical status of water bodies. In France, such a demonstration exercise is planned by AQUAREF for the next WFD monitoring cycle, in close connection with policy-makers, stakeholders and end-users (water agencies). This action could be extended to the European level through NORMAN network activity. In the Netherlands, local water authorities have been using PS for monitoring POPs in surface and coastal waters in parallel with monitoring in mussels [13] for more than a decade. In addition, demonstration studies applying passive sampling in parallel with biota monitoring and led by the Environment Agency in the UK are under way.

Indeed, regulatory implementation of PS requires decision-makers to be convinced of the need to globally change the current monitoring and compliance checking concept under the WFD. The relevance of the signal obtained by passive sampling (integrative sampling, relation of TWA concentrations with the environmental risk to aquatic organisms) should be stressed. Such a change in the monitoring concept recently took place in the anti-doping sector in sports where controls are now performed on hair (integrative information) rather than in urine (punctual information).

It is acknowledged that there is much more experience of large scale PS application for marine water monitoring than for freshwater monitoring. It is therefore necessary to better share this experience between the two expert communities. For example, the three-level approach in place within OSPAR, which consists of drafting of guidance documents, organisation of proficiency tests (via QUASIMEME, http://www.quasimeme.org) and definition of water quality assessment criteria, could also be applied to continental waters [14].

In order to allow improved compilation and comparison of measurement data from PS, experts agreed that it is necessary to define a common and harmonised set of metadata that should accompany the measurement results to be reported in the literature and/or in databases. It is recommended that such a harmonised set of metadata should be included in the next update of the ISO 5667/23 standard [15].

A central European repository (database) would be useful to better share PS monitoring data. This database should gather information on the PS used, the conditions of deployment, the analytical method, the method to treat the results, the concentration in the PS and the estimated water TWA concentration. There is already a NORMAN template for collecting PS data (used for passive sampling data collection from the Joint Danube Survey 3 [7]). This template could be used by the PS community as the basis of a possible upgrade before final validation and adoption as a common data collection template.

Finally, to facilitate communication and dissemination, there is a need to adopt harmonised terminology within the PS research area.

Some knowledge gaps remain as regards the battery of passive sampling devices suitable for very hydrophilic and/or ionisable substances, for some priority substances (e.g. PFOS and mercury) for which biota EQS exist, and for substances with extremely low EQS in water (e.g. dichlorvos, dicofol and heptachlor) [2].

3.4. Applicability of passive sampling in support of chemical monitoring in biota

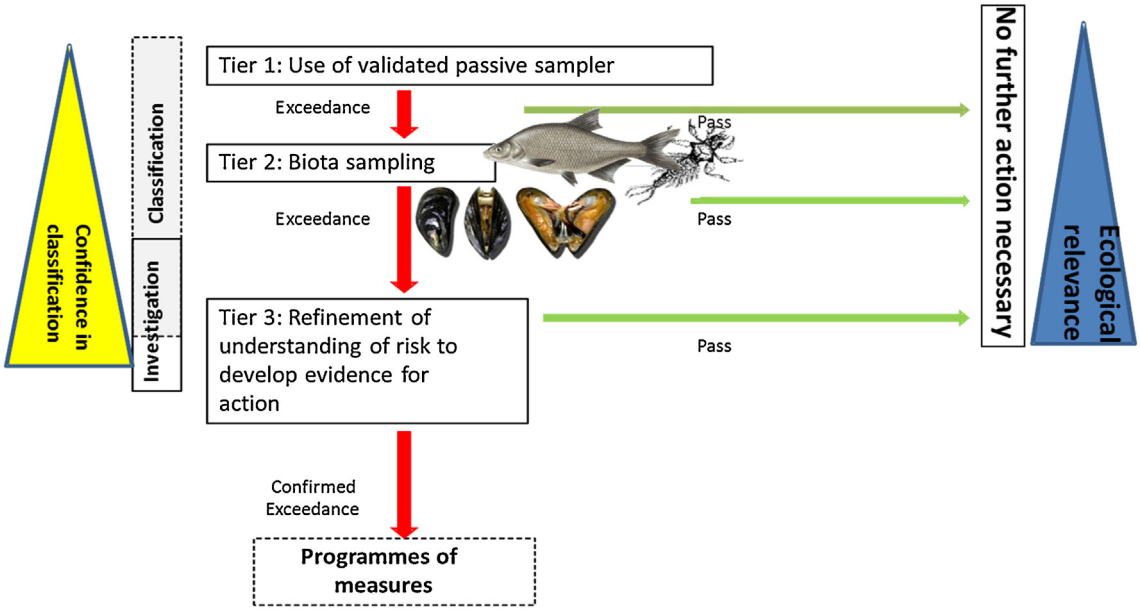
With the recent update of the EQS Directive 2013/39/EU [2], there is a demand for cost efficient monitoring tools that could support data obtained from chemical monitoring in biota. The newly introduced EQS_{biota} for hydrophobic compounds call for the use of analytical methods that meet the requirements of the QA/QC Directive (2009/90/EU) [16]. With these EQS_{biota}, protection of human health via consumption of fishery products, and protection of predators against secondary poisoning were also introduced as new protection goals. Hence, these EQS_{biota} bring new challenges in the design of monitoring programmes and data interpretation for compliance checking and assessment of trends (e.g., the need to normalise biota data based on lipid content, trophic magnification factor).

According to the European Commission technical guidance for the implementation of EQS_{biota} [17], PS can be applied in a tiered approach to identify or rank areas of potential EQS exceedance (Fig. 2, [18]). In such a tiered approach, trigger values (i.e. threshold concentrations, exceedance of which triggers the second tier, monitoring of biota) are needed.

Experts discussed further possibilities of the application of PS, beyond the current recommendation of the European Commission, to support or replace chemical monitoring of hydrophobic compounds and mercury in biota.

Despite the recommended normalisation of biota monitoring data prior to chemical status assessment, the establishment of temporal and spatial trends of bioaccumulating compounds is still expected to be complicated by the inherent variability of the sampled aquatic organisms. Even if "active biomonitoring" for biota (caged organisms) offers some practical solution for marine waters and more recently for continental waters [17,19], experts believe that the inherent variability of passive sampling data can be much better controlled, which presents the main advantage of the abiotic sampling approach.

Experts agreed that passive sampling cannot predict actual concentrations of priority compounds in biota. Passive sampling data can predict the concentrations that would be determined in biota (lipid) if the organism were at thermodynamic equilibrium or steady state with the environment. However, deviations from equilibrium cannot be easily forecasted because of the complexity of uptake processes, trophic magnification, growth dilution, seasonal influences and the "home-range" of the species, which result in a large variability of accumulation of chemical contaminants in biota. As a result, bioconcentration factor (BCF) and bioaccumulation factor (BAF) data reported in the literature are extremely variable. The application of these BCF and BAF literature values to predict concentrations of contaminants in biota



Tier 1: Validated PS "screen" where EQS_{biota} available →Presence/absence. Calibration to validate "non-detection" = no risk to biota. Positive detection → Biota screening
Tier 2: Risk to predators/humans via food chain. Collect larger numbers of small organisms. Human health based EQS → sample Fish/biota. < EQS_{biota} = STOP
Tier 3: Refinement of risk and increasing confidence in assessment (increased sampling programme, geographical aspects etc.)

Fig. 2. Proposed tiered approach to identify potential EQS exceedance using PS. From Whitehouse [18]

from passive sampling derived aqueous concentrations thus lead to a large variability.

In spite of those limitations, experts are of the opinion that PS reflect very well the contaminant levels to which biota are exposed in their natural environment. The same contaminant trends (in time and space) could be observed both in biota data and in passive sampling data (as demonstrated for example by the long-term observation of PS vs mussels performed in the Netherlands for marine waters [13]). Experts concluded that passive sampling is a suitable tool to determine spatial and temporal trends, with lower inherent data variability compared to chemical monitoring in biota. The expert view is that (except for secondary poisoning purposes) measuring contaminant levels in waters can be more appropriate for assessing aquatic biota exposure than measuring their concentration in the organisms. For example, some compounds that are actively metabolised would not be found in organisms (or only at low concentrations), although organisms were exposed to them (e.g. polycyclic aromatic hydrocarbons in fish). Nonetheless, it must be noted that recent studies showed that active biomonitoring in gammarids could provide useful data for metals exposure in freshwater systems [20].

If EQS_{biota} were set only to protect human health from exposure via consumption of fish, there would be no role for passive sampling in water monitoring. In this case it would be sufficient to assess that levels of contaminants in fish used for human consumption do not exceed the defined thresholds. However, since the definition of EQS_{biota} also embraces other protection goals, including protection of aquatic life, PS can still play a significant role in WFD monitoring.

According to the WFD, it is possible to convert EQS_{biota} to equally protective EQS in water (EQS_{water}) and use such standards in regulatory monitoring. The uncertainty of PS concentrations of the most hydrophobic priority substances in water is sufficiently low to allow in principle for a comparison with EQS_{water} [3,21]. This is possible especially because limits of quantification that are achievable by passive sampling for those hydrophobic compounds are lower than the respective EQSs.

From the uptake of hydrophobic pollutants by PS, the freely dissolved concentration is estimated, which represents the driving force for bioconcentration in organisms. PS thus enable the in situ determination of hydrophobic bioaccumulative organic compounds that organisms at the lowest trophic level are exposed to.

The results from passive sampling can also be converted into lipid-based concentrations for an organism considered at equilibrium with the environment to which the sampler was exposed (using lipid–polymer partition coefficients). The advantage of expressing results on a lipid basis is, besides being more closely related to concentrations in biota, that it is an easier unit to communicate to regulators and the public, since it is difficult for a layman to understand that concentrations in the range of fg/L to pg/L in water can pose a hazard. Lipid–polymer partition coefficients will be needed for all substances of interest (i.e. those with existing EQS_{biota}); and for those for which values already exist, further validation may be required.

A major recommendation resulting from this workshop is that, on the sites across Europe where biota monitoring is undertaken for WFD or OSPAR purposes, biota monitoring should be as far as possible complemented by PS exposures. This will help develop the much needed datasets to improve our understanding of bioaccumulation factors. Parallel exposures of PS with biota monitoring (ideally, including multiple trophic levels) at a number of sites in Europe (with different exposure levels) will enable assessment of the variability of BAFs used in the conversion of EQS_{biota} to EQS_{water} ($BAF = C_{biota}/C_{water}$, C_{water} is the freely dissolved concentration from PS, BAF could be established at different river basins). When such variability is known and

acceptable, biota monitoring could be subsequently replaced by monitoring with PS for compliance checking.

4. Conclusions

This paper summarises the outcome of discussions that were held during a NORMAN Network-workshop in Lyon (France) in November 2014. We aimed to provide commonly agreed recommendations to enable the future use of passive sampling for regulatory monitoring of contaminants in aquatic environments. We hope these steps will contribute to increase acceptance of passive sampling by policy-makers. A number of concrete actions required to advance the use of passive sampling techniques in support of contaminant risk assessment and management have been identified:

- Monophasic polymers (e.g. silicone rubber or low density polyethylene) are recommended as the PS of choice for hydrophobic, non-ionised organic substances and the community unanimously agrees that there is a need for commercial supplies of monophasic passive samplers.
- Currently, for hydrophilic organic substances, adsorption-based samplers (e.g. POCIS) provide semi-quantitative data only and further research is needed to either (a) reduce uncertainty of measurement of existing devices, or (b) develop a new sampler design with a simpler (and better controlled) contaminant uptake mechanism. Another viable route for application of these devices in regulatory monitoring, for EQS compliance checking of WFD Priority Substances, is to establish intervals of estimated TWA concentrations and to compare the maximum and minimum limits of these confidence intervals to the AA-EQS values.
- For the future, the development of new PS for ionic and highly hydrophilic compounds is required.
- Uncertainty associated with passive sampling-derived aqueous concentrations can be evaluated and taken into account when PS are used for trend and compliance monitoring. This is confirmed by experience from previous interlaboratory studies, which clearly showed that for certain groups of emerging compounds, inaccurate analysis, rather than the passive sampling technique, is still the main cause of the observed high variability of the results reported by the laboratories. Future intercomparison studies should be organised so that they include different steps in order to ensure validation of each critical part of the sampling and analytical process (i.e. analysis of the contaminants in the extract, PS-field deployment and analysis of the contaminants in the PS, including calculation of water concentration).
- One major feature of passive sampling compared to grab sampling is that PS provide TWA concentration results. These integrated TWA measurement data provide more representative and relevant information for characterisation of the chemical status of water bodies than conventional monitoring (mean values of 4–12 spot samples) data. However, such a shift demands a radical change in the regulatory procedure with which water agencies and decision-makers are familiar. The launch of field studies where the two approaches, the conventional one and the PS approach, would be applied in parallel on a number of selected sites, is highly recommended in order to convince decision-makers that it is advantageous to make this shift.
- PS reflect the contaminant levels to which biota have been exposed in their natural environment.
- As regards chemical monitoring of hydrophobic priority substances in biota, PS can be applied in a tiered approach to identify or rank areas of potential risk of exceedance of EQSs before chemical monitoring in biota. Replacement of chemical monitoring in biota by PS can also be envisaged. The main advantage of such an alternative route is that PS can ensure a lower inherent variability of the concentration data compared to biota monitoring data. PS cannot predict actual concentrations of priority compounds in biota, but passive samplers reflect well the contaminant levels to which biota have been exposed in their natural environment. Since the definition of EQS_{biota} is not limited to protection of human health but also to the protection of aquatic life, and in consideration of the fact that the WFD allows EQS_{biota} to be converted in equally protective EQS_{water}, concentration data obtained with PS can be considered compatible with the protection objectives set by EQS_{biota}.
- In consideration of all the above, steps to be undertaken to convince policy-makers to accept passive sampling in regulatory monitoring are:
  - Drafting of guidelines and clear Quality Assurance/Quality Control rules;
  - Running of demonstration projects/case studies with passive sampling undertaken alongside spot sampling and biota monitoring, in order to demonstrate their applicability for compliance monitoring purposes;
  - Organisation of proficiency testing (PT) schemes and inter-laboratory exercises for passive sampling in water;
  - Development of assessment criteria in relation to EQSs.

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Chapter 7

Theory, modelling and calibration of passive samplers used in water monitoring

Kees Booij, Branislav Vrana and James N. Huckins

7.1 INTRODUCTION

Contaminant uptake by passive sampling devices (PSDs) can be seen as a multi-stage transport process. To illustrate the basic steps involved, we will first discuss contaminant uptake by a PSD that consists of a central sorption phase, surrounded by a membrane. For this exercise, we assume that the sampler is biofouled, and is contained within a protective cage (Fig. 7.1). Coming from the surrounding waters, analytes first have to enter the protective cage, where the motion of water may be reduced relative to the water outside the cage. Close to the biofouling layer, convective transport of analyte molecules is reduced more and more, until all transport takes place by molecular diffusion within the water boundary layer (WBL). When ventilating organisms are present, diffusion may be amended with convective currents that are set up by the organisms. After diffusion through the membrane, analytes are finally sorbed by the central sorption phase. This general picture may differ from case to case. For example, protective cages and biofouling layers may be absent, the membrane may act as the final sorption phase (e.g. various types of solid-phase microextraction devices (SPMEs), and low-density polyethylene (LDPE) and polydimethylsiloxane (PDMS) strip samplers), or the sampler may be equipped with additional phases between the membrane and the central phase (e.g. membrane-enclosed sorptive coating (MESCO) and Chemcatcher samplers).

A variety of models has been used over the past 15 years to better understand the kinetics of contaminant transfer to passive samplers. These models are essential for understanding how the amounts of absorbed contaminants relate to ambient concentrations, as well as for

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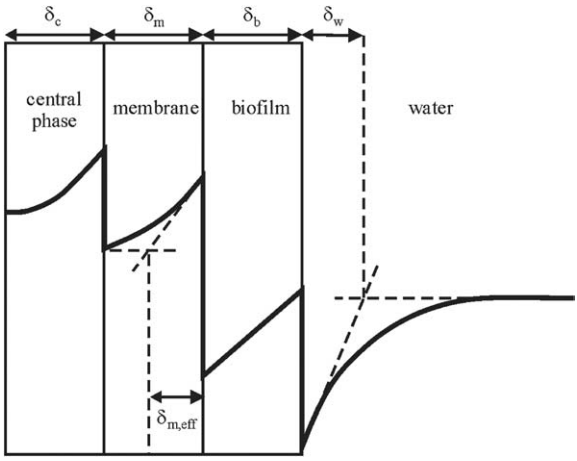

Fig. 7.1. Schematic representation of concentration profiles in a dual-phase PSD with exterior biofilm (i.e. the right half of a symmetrical sampler, or the whole cross section of a sampler with an impermeable boundary located to the left of the central phase). Dashed lines indicate how the effective thickness of the respective phases may be estimated (see Sections 7.5 and 7.6).

the design and evaluation of calibration experiments. Models differ in the number of phases and simplifying assumptions that are taken into consideration, such as the existence of (pseudo-) steady-state conditions, the presence or absence of linear concentration gradients within the membrane phase, the way in which transport within the WBL is modelled and whether or not the aqueous concentration is constant during the sampler exposure.

In the next sections, we will introduce the basic concepts and models used in the literature on passive samplers for the special case of triolein-containing semipermeable membrane devices (SPMDs). These can easily be extended to samplers with more or with less sorption phases. Then we will discuss the transport of chemicals through the various phases constituting PSDs. Finally, we will discuss the implications of these models for designing and evaluating calibration studies.

7.2 BASIC CONCEPTS AND MODELS FOR SPMDS

Mass-transfer coefficients (k_i) are frequently used to link the flux (j_i) through a phase (i) to the concentration difference ΔC_i between the end points of that phase

$$j_i = k_i \Delta C_i \tag{7.1}$$

Equation (7.1) is an expression of the notion that mass fluxes (j) are linearly proportional to a driving force (ΔC_i). The mass-transfer coefficient can be interpreted as a conductivity term, with the dimension of a velocity (e.g. cm day^{-1}). This approach has been followed to model contaminant uptake by a number of PSDs [1–7]. Huckins *et al*. [3] have applied this scheme for the case of contaminant uptake by triolein-filled SPMDs in the presence of biofouling, assuming that the fluxes at both sides of each interface are equal, and that local sorption equilibrium exists at the interfaces. In addition, these authors assumed that the ratios of space-averaged concentrations in the triolein and in the membrane phases are close to the triolein–membrane partition coefficient at all times. The latter assumption was confirmed for the case of SPMDs, by numerical integration of Fick's second law [8]. The differential equation that governs the uptake process can then be expressed as

$$\frac{dC_s}{dt} = \frac{Ak_o}{V_s}\left(C_w - \frac{C_s}{K_{sw}}\right) \tag{7.2}$$

where C_s and C_w are the volume-based contaminant concentrations in SPMD and in water respectively, V_s is the SPMD volume, A is the SPMD surface area, and K_{sw} is the SPMD–water partition coefficient. The K_{sw} equals the volume-averaged partition coefficient for the triolein phase (K_{Lw}) and the membrane (K_{mw}), as shown by Huckins *et al*. [9]

$$K_{sw} = \frac{V_m K_{mw} + V_L K_{Lw}}{V_m + V_L} \tag{7.3}$$

The overall mass-transfer coefficient k_o is given by

$$\frac{1}{k_o} = \frac{1}{k_w} + \frac{1}{K_b K_{bw}} + \frac{1}{k_m K_{mw}} \tag{7.4}$$

where k_w, k_b, k_m are the mass-transfer coefficients for the WBL, the biofilm and the LDPE membrane, and K_{bw}, K_{mw} are the biofilm–water and the membrane–water partition coefficients, respectively. Equation (7.4) is an expression of the fact that the total mass-transfer resistance ($1/k_o$) equals the sum of the resistances posed by the respective phases. Acknowledging that a mass-transfer coefficient equals the ratio of a diffusion coefficient and an effective phase thickness (δ), Eq. (7.4) can also be written as

$$\frac{1}{k_o} = \frac{\delta_w}{D_w} + \frac{\delta_m}{D_m K_{mw}} + \frac{\delta_b}{D_b K_{bw}} \tag{7.5}$$

Bartkow *et al*. [10] have accounted for the transport resistance posed by a protective cage that may surround SPMDs, by adding a term A/Q_v to the right-hand side of Eq. (7.4), where Q_v is the volume rate of water flow to the protective cage and A the surface area of the SPMD. These authors concluded, however, that this resistance can be neglected, except for some rather extreme cage designs.

For short exposure times, the concentration in the SPMD is much smaller than its equilibrium value (i.e. $C_s \ll K_{sw}C_w$), and Eq. (7.2) reduces to

$$dC_s \approx \frac{Ak_o}{V_s} C_w dt \tag{7.6}$$

which yields after integrating over time [3]

$$\int \mathrm{d}C_s \approx \frac{Ak_o}{V_s} \int C_w \mathrm{d}t = \frac{Ak_o}{V_s} C_{w,TWA} t \tag{7.7}$$

where $C_{w,TWA}$ is the time-weighted average (TWA) concentration in the water phase. Three names may be used to refer to the initial stage of the sampling process. When C_w is constant with time, the concentration of accumulated contaminants increases linearly with time. This stage of the uptake is therefore called the linear uptake stage. For scenarios where aqueous concentrations vary with time, the concentration in the SPMD is linearly proportional to the TWA concentration, and sampling is called time-integrative. Finally, because the rate of change of concentrations in the sampler is linearly proportional to the aqueous concentration, this initial sampling stage may be called kinetic sampling. An interesting aspect of Eq. (7.7) is that the product Ak_ot is equivalent to the apparent water volume extracted during the exposure time t. Hence, the product Ak_o can be viewed as an apparent water sampling rate (R_s)

$$R_s = k_o A \tag{7.8}$$

Because R_s represents the volume of water extracted per unit time, it forms a conceptual link between traditional batch water extraction methods and PSD-based methods. Equation (7.8) shows that water sampling rates are linearly proportional to the surface area of the sampler. For this reason, a comparison of sampling rates among different sampler designs only yields meaningful results when differences in surface area are taken into account.

For very long exposure times and a constant C_w, the concentration in the SPMD does not change with time, and Eq. (7.2) reduces to

$$C_w - \frac{C_s}{K_{sw}} = 0 \tag{7.9}$$

which merely is an expression that the concentration in the SPMD attains its equilibrium value ($C_s = K_{sw}C_w$). The corresponding sampling scenario is called equilibrium sampling.

A general solution to Eq. (7.2) for constant C_w is given by [4]

$$C_s = K_{sw}C_w[1 - \exp(-k_e t)] + C_0 \exp(-k_e t) \tag{7.10}$$

where C_0 is the concentration at $t = 0$, and the elimination rate constant (k_e) is given by

$$k_e = \frac{k_o A}{K_{sw}V_s} = \frac{R_s}{K_{sw}V_s} \tag{7.11}$$

Equation (7.10) shows that the uptake from the environment and the elimination of the initial amounts (found in the PSD fabrication controls) are additive. Subtraction of these levels can be problematic when the initial concentration is higher than, or about equal to, the equilibrium concentration. In that case, the concentrations in exposed samplers can be smaller than the concentrations observed in fabrication controls, and control subtraction would yield negative concentrations. Equation (7.10) also shows that the uptake and elimination process of a particular compound are characterised by the same k_e value. This observation is the basis of estimating *in situ* sampling rates from the dissipation rates of performance reference compounds (PRCs) (Section 7.9.4) [11].

When the initial concentration equals zero, Eq. (7.10) takes the form of the more familiar release equation [2]

$$C_s = K_{sw}C_w\left[1 - \exp\left(-\frac{R_s t}{K_{sw}V_s}\right)\right] \tag{7.12}$$

which in the short time limit reduces to the linear uptake equation

$$C_s = \frac{C_w R_s t}{V_s} \tag{7.13}$$

For the dissipation of PRCs that do not occur in the environment ($C_w = 0$) and that are spiked into the sampler prior to exposure, Eq. (7.10) reduces to the more familiar release equation [2]

$$C_s = C_0 \exp(-k_e t) \tag{7.14}$$

Aqueous concentrations can be calculated from the amounts (N_s) absorbed by the PSD, the *in situ* sampling rate of the compounds and their sampler–water partition coefficients, using the rearranged Eq. (7.12)

$$C_w = \frac{N_s}{K_{sw}V_s[1 - \exp(-R_s t/K_{sw}V_s)]} \tag{7.15}$$

For equilibrium samplers, the term in square brackets equals 1 to good approximation, and aqueous concentrations are calculated from

$$C_w \approx \frac{N_s}{K_{sw}V_s} \tag{7.16}$$

For kinetic samplers, operating in the linear uptake mode, the term in square brackets is approximately equal to $(R_s t)/(K_{sw}V_s)$, and aqueous concentrations can be calculated from

$$C_w \approx \frac{N_s}{R_s t} \tag{7.17}$$

The denominators in Eqs. (7.15)–(7.17) can be interpreted as the apparent water volume that is cleared of analyte during the exposure (Fig. 7.2). In the case of equilibrium sampling, this volume is limited by the sorption capacity of the sampler ($K_{sw}V_s$). For kinetic sampling, the apparently extracted water volume is limited by the sampling rate and the exposure time ($R_s t$).

7.3 MODEL APPLICATION TO OTHER PASSIVE SAMPLERS

The discussion in the previous section can easily be extended to other passive samplers that contain any number of sub-phases, provided that sorption equilibrium exists at the interfaces and that (pseudo-) steady-state conditions apply within the barriers between the water and the collection phase (i.e. the difference between the inward and outward fluxes for each intermediate phase should be relatively small). Equation (7.5) may then be generalised as [4]

$$\frac{1}{k_o} = \sum \frac{\delta_i}{D_i K_{iw}} \tag{7.18}$$

where the summation runs over all phases i. The evolution of the analyte amounts accumulated in the receiving phase (i.e. that part of the sampler that is actually extracted and analysed) is given by

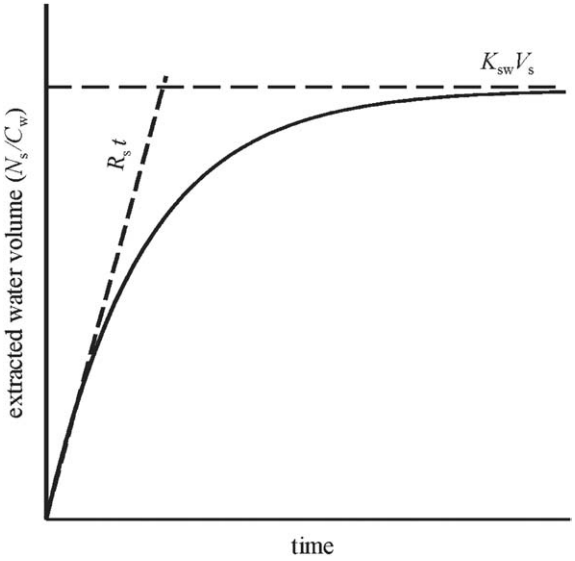

Fig. 7.2. Effectively extracted water volume as a function of time. For long exposure times the extracted volume is constrained by the sorption capacity of the PSD ($K_{sw}V_s$), and at short exposure times by the product of sampling rate and time ($R_s t$).

Eq. (7.12), where K_{sw} takes the general form

$$K_{sw} = \frac{\sum V_i K_{iw}}{\sum V_i} \tag{7.19}$$

and the sampler volume V_s equals the sum of the volumes of all the subphases that are analysed.

In the SPME literature, a slightly different (empirical) model is used to describe the sampler–water exchange kinetics [7,12]

$$\frac{dC_s}{dt} = k_1 C_w - k_2 C_s \tag{7.20}$$

This model is mathematically equivalent to Eq. (7.2), with $k_2 = (Ak_o)/(K_{sw}V_s)$ and $k_1 = K_{sw}k_2$.

7.4 VALIDITY OF THE MODEL ASSUMPTIONS

For the models above, it was assumed that linear concentration gradients exist in the membrane and in the central phase; that equilibrium exists at the interfaces; that molecular diffusion is the predominant

transport mechanism in the membrane with a diffusion coefficient that is independent of time and of concentration.

In the initial stages of the exposure, analytes have to penetrate the membrane to get to the central phase. The resulting time lag has been experimentally confirmed to be about 10 h for the uptake of PCB 52 by SPMDs [2]. A theoretical model for the mass flux through a plane sheet with constant concentration on both sides of the sheet predicts a lag time of [13]

$$t = \frac{\delta_{\mathrm{m}}^2}{6D_{\mathrm{m}}} \tag{7.21}$$

Diffusion coefficients differ widely among polymers. Values for benzene include $3 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$ in PDMS, $2 \times 10^{-12}\,\mathrm{m^2\,s^{-1}}$ in LDPE, $2 \times 10^{-16}\,\mathrm{m^2\,s^{-1}}$ in poly(methylacrylate) and $1 \times 10^{-19}\,\mathrm{m^2\,s^{-1}}$ in poly (vinylalcohol) [14,15]. For 100 μm thick membranes of these polymers Eq. (7.21) predicts lag times of 6 s, 14 min, 4 months, and 4 centuries, respectively, and these values are expected to increase with molecular size. Evidently, for WBL-controlled uptake, the analyte distribution within the membrane does not affect the uptake rates. Adopting an aqueous diffusion coefficient of $5 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$ and an effective boundary layer thickness of 30–300 μm (Section 7.5), lag times of 0.3–30 s may be expected for WBL-controlled uptake. However, when the membrane is discarded, and only the central phase is analysed, the lag time for membrane passage has to be accounted for, even in the case of WBL-controlled uptake.

Linear gradients in the membrane cannot exist when the membrane accumulates analytes, because in this case the flux into the membrane must be larger than the flux out of the membrane. By the same argument, linear gradients cannot exist in the central receiving phase either. The concentration gradient in the middle of the receiving phase (e.g. SPMD, MESCO equipped with a PDMS rod), or next to an impermeable wall (e.g. Chemcatcher, SPME) should be zero. (Otherwise, a discontinuity in the flux would occur.) Yet, the concentration gradient at the outer side of the central phase should differ from zero. (Otherwise, the central phase would not accumulate anything.) Again, for WBL-controlled uptake, the existence of non-linear gradients in the membrane or in the central phase does not invalidate the model, but for membrane-controlled uptake, this phenomenon may have to be accounted for. The non-linearity of concentration gradients can be assessed in terms of an effective phase thickness ($\delta_{\mathrm{i,eff}}$) as shown in Fig. 7.1 for the membrane phase. Using an analytical radial diffusion model for uptake by SPME

fibres, Louch *et al*. [16] showed that the effective membrane thickness deviates less than 20% from the actual membrane thickness for times that are larger than the lag time (Eq. (7.21)). Using numerical methods, Hofmans [8] obtained similar results for SPMDs.

The assumption that instantaneous equilibrium exists at the interfaces is likely to be met for the small mass-transfer rates encountered in passive sampling methods, particularly for rubbery polymers, which are characterised by short relaxation times [14].

Although diffusion coefficients in polymers have been shown to depend on diffusant concentration, this dependence is reported to be weak [14], and can probably be neglected in passive sampling because of the relatively low analyte concentrations encountered.

7.5 WATER BOUNDARY LAYER RESISTANCE

Exact models for mass transfer through the WBL exist only for some simple flow arrangements, such as the flow through ducts and pipes, and parallel flow along an absorbing flat plate [17–20]. Starting at the leading edge of the plate, the momentum of the water that is immediately adjacent to the plate is reduced due to surface friction. As the water moves along the plate, this retarded water layer in turn attenuates the momentum of the water layers at larger distance from the surface, which results in the development of a viscous sublayer, with a thickness that increases with distance downstream of the leading edge. Similarly, analytes are removed from a layer with a thickness that increases downstream, leading to the development of a concentration boundary layer. With increasing thickness of this layer, transport by eddy diffusion becomes increasingly important, since turbulent diffusion coefficients increase with increasing distance from the surface [19,21]. At large distances from the leading edge, a steady-state concentration profile is established that no longer depends on the distance along the plate. Equations for the short-plate limit (growing concentration boundary layers) and the long-plate limit (distance-independent concentration boundary layers) have been given by Opdyke *et al*. [22] for hydrodynamically smooth flows (i.e. flows along surfaces where the roughness elements are embedded in the viscous sublayer). The (surface averaged) mass-transfer coefficients for the short-plate limit are given by [22,23]

$$k_{\mathrm{w}} = 0.81 u_* \left(\frac{D_{\mathrm{w}}}{\nu}\right)^{2/3} \left(\frac{\nu}{u_* L}\right)^{1/3} \tag{7.22}$$

where ν is the kinematic viscosity of the water, L is the length of the plate, and u_* is the friction velocity, which is frequently used in the literature on hydrodynamics to parameterise the shear stress (τ)

$$u_* = \sqrt{\frac{\tau}{\rho}} \tag{7.23}$$

where ρ is the density of water. In turbulent flows, u_* can be interpreted as the characteristic eddy velocity relative to the main stream [24,25]. The friction velocity for an essentially laminar flow along a flat surface is related to the free-stream velocity (U) by [18]

$$u_*^2 = 1.328U^2\sqrt{\frac{\nu}{UL}} \tag{7.24}$$

Equation (7.24) is arranged so as to stress that it is dimensionally consistent (i.e. u_* has the same dimension as the main stream velocity U, and $\nu/(UL)$ is dimensionless). The transition from laminar to turbulent flow takes place at values of $UL/\nu > 4 \times 10^6$ when special precautions are taken to reduce the turbulence intensity of the main flow [17]. When no such precautions are taken, the transition to turbulent flow takes place at lower values, i.e. $UL/\nu > 350{,}000$ to 500,000, depending on the turbulence intensity of the main flow [17].

In the long-plate limit, the mass-transfer coefficients are given by [19,22]

$$k_{\mathrm{w}} = 0.08u_*\left(\frac{D_{\mathrm{w}}}{\nu}\right)^{2/3} \tag{7.25}$$

and u_* (for fully developed turbulent flow) may be estimated from the free-stream velocity by [18]

$$u_*^2 = 0.074U^2\left(\frac{\nu}{UL}\right)^{1/5} \tag{7.26}$$

For more complex scenarios, such as mass transfer for cylinders and packed bed reactors, empirical correlations have been established of the form [18,26]

$$\frac{\mathrm{Sh}}{\mathrm{ReSc}^{1/3}} = B\mathrm{Re}^{\mathrm{m}} \tag{7.27}$$

where the (dimensionless) Sherwood (Sh), Reynolds (Re) and Schmidt (Sc) numbers are defined by

$$\mathrm{Sh} = \frac{k_{\mathrm{w}}d}{D_{\mathrm{w}}} \tag{7.28}$$

$$\mathrm{Re} = \frac{ud}{v} \tag{7.29}$$

$$\mathrm{Sc} = \frac{v}{D_w} \tag{7.30}$$

where d is a conveniently chosen characteristic length scale and u a characteristic velocity. The constant B in Eq. (7.27) is of the order 1 and $m \approx -0.5$ (range -0.3 to -0.7). For the case of mass transfer to a cylinder with its main axis perpendicular to the flow, d equals the diameter of the cylinder, $B = 0.6$ and $m = -0.487$, which is valid for the range $100 < \mathrm{Re} < 3500$ and $1000 < \mathrm{Sc} < 3000$. It follows from Eq. (7.27) that mass-transfer coefficients are proportional to $D^{2/3}$ and to the flow velocity $U^{0.5}$.

Equations (7.22) and (7.25) could be used for passive samplers with a planar configuration. It should be realised, however, that in many situations, the flow near the sampler surface may vary in both time and space. The sampler may be mounted in a protective cage in a zigzag or twisted configuration, and the main flow may generate vortices when passing through ventilation holes or over sharp edges. Furthermore, the sampler surface may bend, twist or vibrate depending on flow velocity, angle of incidence, sampler material. In addition, the flow velocity may vary along the sampler surface, where even dead spots may exist as a result of the mounting pattern. Similarly complex hydrodynamics may exist around samplers with a cylindrical configuration. Despite the complexity of the hydrodynamics near passive samplers, some general conclusions remain, however. First, the number of variables in experiments on mass transfer through the boundary layer may be reduced by correlating the appropriate dimensionless numbers Sh, Re and Sc for a given sampler geometry. Second, a wide number of such empirical correlations from the engineering literature suggests that Sh typically is proportional to $\mathrm{Sc}^{1/3}$, indicating that k_w be proportional to $D^{2/3}$ [18,27]. This in turn indicates that the effective boundary layer thickness increases with increasing diffusion coefficient according to $\delta_w \sim D^{1/3}$. Third, the effective WBL thickness, though useful for visualising the extent to which the concentration gradient penetrates into the main flow, should not be misinterpreted as the thickness of physically unrealistic entities like a stagnant film or an unstirred boundary layer. Fourth, for a given geometry and flow, the k_w values for small samplers can be expected to be larger than for large samplers. Fifth, k_w increases with flow velocity, for a given PSD geometry, but its absolute value is difficult to predict.

TABLE 7.1

Sampling rates of 460 cm^2 SPMDs estimated for the case of laminar flow (Eq. (7.24)) in the short-plate limit (Eq. (7.22)) at parameter values $L = 10$ cm, $\nu = 10^{-6}\,m^2\,s^{-1}$, $D = 5 \times 10^{-10}\,m^2\,s^{-1}$

U (cm s^{-1})	Re	u_* (cm s^{-1})	u_*L/ν	k_w (μm s^{-1})	R_s (L day^{-1})
1	1000	0.2	200	2	7
10	10000	1.2	1200	6	22
100	100000	6.5	6500	18	70

As a check on how far the equations above help to understand sampling rates for boundary layer controlled uptake, we evaluated the case of 460 cm^2 SPMDs that are exposed to water flows of 1, 10 and 100 cm s^{-1} at 20°C, adopting an average stream length over the SPMD of 10 cm (i.e. somewhere between 2.5 and 91 cm), a kinematic viscosity of $10^{-6}\,m^2\,s^{-1}$ and a diffusion coefficient of $5 \times 10^{-10}\,m^2\,s^{-1}$. For these flow velocities, the group UL/ν equals 10^3, 10^4 and 10^5 respectively, which is below the transition to turbulence (see above). Estimating the friction velocity from Eq. (7.24) and k_w for the short-plate limit (Eq. (7.22)) yields sampling rates between 7 and 70 L day^{-1} (Table 7.1). These estimates are in fair agreement with observed sampling rates of 4–10 L day^{-1} at flow velocities $\leqslant$ 1 cm s^{-1} [9,28,29] and 100 L day^{-1} at 90 cm s^{-1} [30], but are higher than the values of about 5 L day^{-1} at 50 cm s^{-1} [29]. However, comparison of estimated and experimental sampling rates is hindered by the fact that reported flow velocities are usually calculated rather than measured.

7.6 MEMBRANE RESISTANCE

Two types of polymeric membranes have been used for passive samplers. Non-porous membranes include LDPE [3,5,6,31,32], polypropylene and polyvinylchloride [3,33], PDMS [3,33–35], polyimide [36], polyacrylate (PA) [37,38] and other non-polar polymers [38]. Microporous membranes include regenerated cellulose [4,39,40], polyethersulfone (PES) [41], polysulfone (PS) [32] and polyacrylamide hydrogel [42]. Some other membranes used are discussed by Stuer-Lauridsen [43] in an extensive review of passive sampling techniques. In some applications, the membrane is also the primary accumulation site of the analytes (Twister™ bars, LDPE strip samplers, SPME, silicone strip samplers). In other applications, the membrane is meant to separate a

sorption phase from the water (diffusive gradients in thin films (DGT), Chemcatcher, MESCO, SPMD) and to reduce the flux to the sorption phase.

The conductivity to mass transport through the membrane is given by

$$k_{\mathrm{m}}K_{\mathrm{mw}} = \frac{D_{\mathrm{m}}K_{\mathrm{mw}}}{\delta_{\mathrm{m}}} \tag{7.31}$$

where δ_{m} is the thickness of the membrane (Eq. (7.5)). Both D_{m} and K_{mw} are compound-dependent. The role of K_{mw} in Eq. (7.31) may be appreciated by considering that compounds with high membrane–water partition coefficients will have similarly high concentrations at the membrane side of the membrane–water interface. As a result, the concentration gradient over the membrane is elevated compared with that found for compounds with low K_{mw} values, and the steeper concentration gradient results in a larger flux through the membrane. Conversely, the selection of a membrane for which the target analytes have a low affinity (e.g. hydrophilic membranes for sampling hydrophobic compounds) results in an enhanced transport resistance posed by the membrane and to reduced sampling rates. Several examples of this effect have been reported. A comparison between solvent-filled cellulose and polyethylene membranes showed that the uptake rates of organochlorine pesticides by the samplers with cellulose membranes were lower by two orders of magnitude [40]. Similarly, the uptake kinetics of hydrophobic contaminants by the MESCO and Chemcatcher were greatly enhanced by replacing the hydrophilic membrane by polyethylene [5,6], and the uptake rates of the polar compounds diazinon, ethynylestradiol and atrazine by the polar organic chemical integrative sampler (POCIS) were much larger with PES membranes than with polyethylene or Nylon-66 membranes. The choice of membrane material has an effect not only on the sampling rates, but also on the flow sensitivity of the sampler. When the membrane resistance becomes smaller, rate control switches more to side of the WBL, which is by nature dependent on the hydrodynamic conditions at the membrane–water interface. Therefore, attempts to reduce the flow sensitivity of passive samplers by installing membranes that have lower partition coefficients for the analytes, automatically reduce the sampling rates. Conversely, membranes with high K_{mw} values enhance sampling rates but also increase the sensitivity of these samplers to changing flow conditions [5]. Whether or not reduced sampling rates are problematic, depends of course on the aqueous concentration levels,

the exposure time and the sensitivity of the analytical equipment. No general rule can be given, but in the light of the above, it seems unlikely that a flow-insensitive passive sampler can be developed that has sufficiently high sampling rates in all environments.

Estimating sampling rates of compounds for membrane-controlled uptake is hindered by the scarcity of data on diffusion coefficients, particularly for compounds of environmental interest. Diffusion coefficients (D_m) in LDPE have been collected from the engineering literature by Hofmans [8]. She proposed to model D_m as a function of molecular weight (M) according to

$$\begin{aligned} &\log D_m = -7.47 - 2.33 \log M \\ &n = 42, s = 0.44, 70 < M < 655 \end{aligned} \tag{7.32}$$

where D_m is in units of $m^2 s^{-1}$. Diffusion coefficients of PAHs in PDMS appear to be higher than in LDPE by about two to three orders of magnitude and D_m values of PAHs in polyoxymethylene are about one order of magnitude lower than in LDPE (Tatsiana Rusina, Research Center for Environmental Chemistry and Ecotoxicology, Masaryk University, Czech Republic, personal communication). These observations are consistent with the theory that diffusion coefficients increase with increasing segmental mobility and free volume fraction of the polymer [14,44,45], and decrease with increasing glass-transition temperature of the polymer [14].

A large volume of data on PDMS–water and PA–water partition coefficients of organic contaminants can be found in the SPME literature [12,38,46–49,50]. A smaller data set is available for the case of LDPE [30,45,51]. Available log K_{mw} values are shown in Fig. 7.3 as a function of log K_{ow}. Although the scatter is rather high, some general trends can be identified. Log K_{mw} values for LDPE are higher than for PDMS by 0.7 log units, on average. In the range $1 < \log K_{ow} < 4.5$, the log K_{mw} values for PA are 0.3 log units higher than those for LDPE, but this trend does not seem to persist in the higher log K_{ow} range. The log K_{mw} data could be modelled by

$$\begin{aligned} &\text{LDPE}: \quad \log K_{mw} = 1.057 \log K_{ow} - 0.72 \\ &(R^2 = 0.96, s = 0.28, n = 41) \end{aligned} \tag{7.33}$$

$$\begin{aligned} &\text{PDMS}: \quad \log K_{mw} = 1.060 \log K_{ow} - 1.39 \\ &(R^2 = 0.92, s = 0.36, n = 74) \end{aligned} \tag{7.34}$$

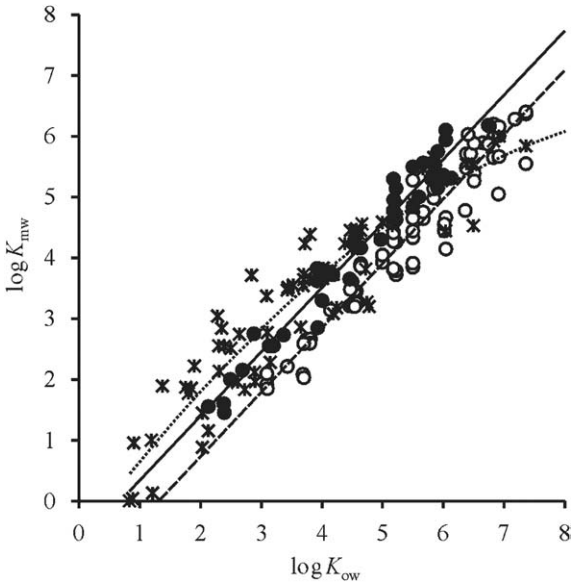

Fig. 7.3. Membrane–water partition coefficients and regression models for LDPE (filled circles, drawn line = linear fit), PDMS (open circles, dashed line = linear fit) and PA (asterisks, dotted line = quadratic fit).

$$\text{PA}: \quad \log K_{\text{mw}} = -0.0629 \log K_{\text{ow}}^2 + 1.341 \log K_{\text{ow}} - 0.62$$
$$(R^2 = 0.88, s = 0.50, n = 74) \tag{7.35}$$

The higher residual errors in the case of PA may be due at least partly to the relatively large number of K_{mw} values of polar compounds, for which K_{ow} is not a very good descriptor. The inclusion of polar interactions and hydrogen bonding appears to be appropriate in this case [12]. For membrane-controlled uptake, it can be expected that samplers that are equipped with a PDMS membrane have 20 times (1.3 log units) higher sampling rates than samplers with an LDPE membrane, i.e. the 0.7 log units lower partition coefficient for PDMS is more than offset by diffusion coefficients that are 2 log units higher. However, for WBL-controlled uptake no difference among membrane types can be expected. Applying Eqs. (7.31)–(7.33) to the case of membrane controlled uptake by 460 cm^2 SPMDs with a 85 μm LDPE membrane, yields sampling rates of 6 L day^{-1} for hexachlorocyclohexanes and 14 L day^{-1} for naphthalene. These estimates are larger than the experimental values of 2 L day^{-1} [28] and 0.9 L day^{-1} [9], respectively, which may be related to the uncertainities in the estimates of D_{m} and K_{mw}.

For membrane-controlled uptake, the slope of a log R_s versus log K_{mw} plot is expected to attain a value of about one, because $R_s \sim k_o \sim D_m K_{mw}$. In practice, somewhat smaller slopes are found, since D_m decreases with molecular size [12,30,50], Alternatively, since $k_e \sim K_{sw}^{-1}$ (Eq. (7.11)), membrane-controlled uptake can be identified when the slopes of log k_e versus log K_{mw} are about 0, or slightly smaller. These conditions are typically observed for compounds with log K_{mw} values <3.5 for SPME with PA fibres [12,50] and for compounds with log K_{ow} values <4.5 in sampling with SPMDs [3,33]. It should be noted, however, that the transition to WBL-controlled uptake depends not only on the properties of the analytes, but also on the hydrodynamic conditions at the membrane–water interface (Eq. (7.5)). Thus, in quiescent or highly turbulent conditions, the critical K_{mw} values for transition to WBL control may be lower or higher respectively [49,52].

7.7 BIOFOULING LAYER

The growth of bacterial mats, periphyton and even macrofauna can intuitively be expected to have a major impact on uptake rates [53]. Richardson *et al*. [54] observed that the amounts of organochlorine pesticides and PAHs, absorbed by SPMDs for which the membrane had been pre-fouled for 1–4 weeks were about 30–40% lower than the amounts absorbed by unfouled SPMDs. These reductions were higher for OCPs than for PAHs, but did not appear to be related to log K_{ow}. Similar reductions of phenanthrene uptake by pre-fouled SPMDs (26–39%) were reported by Ellis *et al*. [55]. Huckins *et al*. [3,11,56] reported that sampling rates of PAHs by pre-fouled SPMDs were smaller than for unfouled SPMDs by 30–70%. These authors reported a weak dependency of the sampling rate reduction with hydrophobicity, with the larger reductions occurring at the higher log K_{ow} end. Assuming that the biofouling layer can be modelled as a water layer with dispersed organic matter (i.e. similar to a layer of sediment), its conductivity for mass transport is given as [3]

$$k_b K_{bw} = \frac{\phi^2 D_w}{\theta \delta_b} \tag{7.36}$$

where ϕ is the porosity and θ the tortuosity of the diffusion pathways within the biofilm (i.e. the ratio of the actual diffusion path length and the thickness of the biofilm). Since both ϕ and θ are of order 1, Eq. (7.36) states that the biofilm behaves essentially like an immobilized water

layer, with a conductivity that is independent of the biofilm–water partition coefficient. As an example, we will apply this model to estimate the thickness of a biofouling layer that causes a reduction in the sampling rate of 460 cm^2 SPMDs from 5 to 2.5 L day^{-1}. Adopting a porosity of 0.9, a tortuosity of 2 and a D_w value of $5 \times 10^{-10}\,m^2\,s^{-1}$, a biofilm thickness of 160 μm can be calculated, which seems to be a reasonable value. It has been suggested by several authors that the use of PRCs allows to quantify the effects of biofouling on the *in situ* uptake rates [11,54], but to date the experimental evidence has not yet been presented in the peer-reviewed literature.

It appears that LDPE is more sensitive to biofouling than PES [41]. Attempts to inhibit biofouling by applying antifouling agents during SPMD deployments [31] have been unsuccessful [55]. Other examples of undesirable impacts of organisms in passive sampling are biodegradation of the regenerated cellulose membranes [6] and physical damage of SPMDs [54]. Although instances of severe biofouling have been reported [54,57], the associated sampling rate reduction seems to be limited to a factor of about 2.

7.8 OTHER INTERMEDIATE PHASES

Next to a central phase enclosed by a membrane phase, other phases have been incorporated as well. Wennrich *et al*. [6] studied the effect of water and air, enclosed between a central PDMS phase and an LDPE membrane, on the sampling rates of organochlorines and PAHs. They found that the air-filled samplers had up to 20 times higher sampling rates than the water-filled samplers, with the exception of β-HCH, γ-HCH and δ-HCH. Higher sampling rates may be expected if the mass-transfer conductivity of a layer of air is larger than that of a water layer of the same thickness, i.e. if

$$\frac{D_a K_{aw}}{D_w} > 1 \tag{7.37}$$

where D_a is the diffusion coefficient in air and K_{aw} the dimensionless Henry's law constant. Calculated ratios ($D_a K_{aw}/D_w$) ranged from 520 for HCB to 0.1 for β-HCH and δ-HCH. For compounds with K_{aw} values $>10^{-4}$, the effect of an unfavourable air–water partition coefficient is offset by a more favourable diffusion coefficient in air ($\sim 5 \times 10^{-6}\,m^2\,s^{-1}$) compared with that in water ($\sim 5 \times 10^{-10}\,m^2\,s^{-1}$). Similar observations have been made for a Chemcatcher sampler, equipped with a central compartment of C_{18}-coated silica and an LDPE membrane [5].

Replacing water by air as intermediate phase resulted in an increase in sampling rates up to a factor of 6. Decreasing sampling rates were observed for the 5-ring PAHs, which showed a decrease in sampling rate by a factor of 2–3 as a result of their very low K_{aw} values ($<3 \times 10^{-5}$). The use of 1-octanol as intermediate phase resulted in an approximately 20-fold increase in sampling rates compared with water as intermediate phase [5]. It should be noted again, however, that reducing the transfer resistances of the internal phases, enhances the relative importance of the mass-transfer resistance of the WBL (Eq. (7.5)), and hence the sensitivity of the sampler to changes in flow conditions.

7.9 CALIBRATION

7.9.1 Static exposure design

In the experimentally convenient static exposure scenario, passive samplers are exposed in a single volume of contaminated water. This method has been used in the past for determining bioaccumulation factors and uptake rates of contaminants by fish and mussels. The evolution of aqueous concentrations in the exposure water is given by [58–60]

$$C_w = \frac{C_{w0}\left\{1 + \frac{K_{sw}V_s}{V_w}\exp\left[-\left(1 + \frac{K_{sw}V_s}{V_w}\right)\frac{R_s t}{K_{sw}V_s}\right]\right\}}{1 + \frac{K_{sw}V_s}{V_w}} \tag{7.38}$$

where C_{w0} is the aqueous concentration at $t = 0$. The concentration in the sampler can be evaluated from the mass balance ($V_s C_s = V_w[C_{w0} - C_w]$)

$$C_s = \frac{C_{w0}K_{sw}\left\{1 - \exp\left[-\left(1 + \frac{K_{sw}V_s}{V_w}\right)\frac{R_s t}{K_{sw}V_s}\right]\right\}}{1 + \frac{K_{sw}V_s}{V_w}} \tag{7.39}$$

which reduces to Eq. (7.12) in the limit $V_w \to \infty$. With Eqs. (7.38) and (7.39) it is assumed that there are no competing sorption phases (equipment and particulate/dissolved organic matter) in the exposure system. In the short time limit, Eq. (7.38) may be approximated by

$$C_w = C_{w0}\left(1 - \frac{R_s t}{V_w} + \cdots\right) \tag{7.40}$$

and the concentration in the sampler may be approximated by

$$C_s = \frac{C_{w0} R_s t}{V_s} \left(1 - \frac{1}{2}\frac{R_s t}{V_w} - \frac{1}{2}\frac{R_s t}{K_{sw} V_s} + \cdots\right) \tag{7.41}$$

When the concentration in the sampler is much lower than its equilibrium value (i.e. $R_s t \ll K_{sw} V_s$), the third term between the parentheses in Eq. (7.41) may be neglected, and Eq. (7.41) reduces to

$$C_s = \frac{C_{w,TWA} R_s t}{V_s} \tag{7.42}$$

where $C_{w,TWA}$ is the TWA concentration during the exposure.

Static exposures have been used in the calibration of SPMDs and similar samplers [9,11,28,59,61] and also is the typical calibration scenario in SPME research [36,60,62]. Equilibration times obtained with static exposures are sometimes erroneously assumed to also apply to field exposures [59,61]. Equation (7.39) shows that the evolution of analyte concentrations in the samplers follows first-order kinetics, with a rate constant that is dependent on the water volume, among other factors. High rate constants can be found when the water volume is small compared with the sorption capacity of the sampler ($V_w \ll K_{sw} V_s$). In this case, the rate constant is approximately equal to R_s/V_w. However, the water volume in the field is essentially infinite ($V_w \gg K_{sw} V_s$), and the rate constant for the attainment of equilibrium equals $R_s/(K_{sw} V_s)$ in that case. The intuitive explanation of short equilibration times that may be observed in static exposure designs is that both the accumulation in the sampler and the depletion of the water favour the attainment of equilibrium [63]. By contrast, depletion of the water phase in the field is insignificant.

7.9.2 Static renewal design

In static renewal designs, the exposure water is refreshed batchwise [41,54]. This design may be used when static or continuous flow exposure designs are not an option. This may occur, for example, when a static exposure would result in an excessive depletion of the water phase, or when problems occur in maintaining stable aqueous concentrations during flow-through exposures. Aqueous concentrations should be measured at least at the beginning and at the end of each renewal period, in order to estimate their average. Uptake curves may be generated when it can be assumed that the amounts removed from the water are absorbed by the sampler (i.e. loss terms like evaporation

and wall sorption, as well as sorption on to dissolved/particulate matter can be neglected) and that the average aqueous concentrations do not vary greatly among renewals. Even then, the mathematical modelling of such data is not so easy, except for the case of kinetic sampling over the entire exposure period (Eq. (7.42)).

7.9.3 Continuous flow design

Continuous flow designs aim at preventing depletion of the water phase during the exposure by ensuring a constant supply of freshly contaminated water to the exposure chamber. As with the static and static renewal designs, sorption to dissolved/particulate matter should be negligible in order to prevent overestimating C_w. However, sorption to the equipment used in the exposure system has no detrimental effect, provided that the equipment has equilibrated with the water. Stable aqueous concentrations can be maintained during the entire exposure if the flushing rate (Q: volume per unit time) of the exposure chamber is much larger than the total sampling rate of all samplers [30]

$$Q \gg nR_s \tag{7.43}$$

where R_s is the sampling rate per sampler and n the total number of samplers in the exposure system. For example, an exposure system that contains five passive samplers that have a sampling rate for a particular compound of 4 L day^{-1} would require a flushing rate at the beginning of the experiment, that is much higher than 20 L day^{-1}. Such a set-up would therefore require a flushing rate of at least 100 L day^{-1} of water with dissolved organic carbon (DOC) levels that are low enough to ensure that contaminant sorption to DOC is insignificant. With the gradual removal of samplers during the experiment, the flushing rate may be reduced, provided that the hydrodynamic conditions in the exposure chamber can be kept constant, e.g. by additional stirring or by recirculation pumping. Because sampling rates are linearly proportional to the sampler surface, the use of smaller samplers may help to reduce the water demand. It should be realised in this case, however, that for WBL-controlled uptake the sampling rate may be a weak function of the sampler length (Eq. (7.22)).

Mixing of stock solutions in methanol or acetone is the most widely used method for preparing contaminated water needed in the exposure experiments [2,6,32], but generator column techniques based on C_{18}-coated silica [28,30] or permeation through a dialysis membrane [64] have also been used.

When constant aqueous concentrations can be maintained during the entire experiment, sampling rates and sampler–water partition coefficients may be obtained by curve fitting of Eq. (7.12). In case the extent of equilibrium attained is insufficient to estimate K_{sw}, the linear uptake equation (Eq. (7.13)) should be used. Decision methods for selecting the correct model are discussed elsewhere [28,65].

Slightly more complicated models should be used when aqueous concentrations are not sufficiently constant during the exposure. Suppose that the aqueous concentrations can be described by a second-order polynomial in time

$$C_w(t) = C_0 + C_1 t + C_2 t^2 \tag{7.44}$$

the solution to the differential equation (Eq. (7.2)) can be found as [66]

$$\frac{C_s}{K_{sw}} = \left(C_0 - \frac{C_1}{k_e} + \frac{2C_2}{k_e^2}\right)[1 - \exp(-k_e t)] + \left(C_1 - \frac{2C_2}{k_e}\right)t + C_2 t^2 \tag{7.45}$$

where k_e is given by Eq. (7.11). The solution for constant concentrations (Eq. (7.12)) and aqueous concentrations that vary linearly with time [30] can be seen to be special cases of Eq. (7.45).

7.9.4 *In situ* calibration

The evaluation of dissipation rate constants of PRCs has been used as a method for calibrating the uptake rates of PSDs *in situ* [2,11,65,67–69]. When PRCs are selected that do not occur in the environment in significant amounts (e.g. ^{13}C-labelled PCBs or perdeuterated PAHs), their dissipation rate constants can be estimated from the rearranged Eq. (7.14)

$$k_e = -\frac{\ln(C/C_0)}{t} \tag{7.46}$$

where C_0 is the PRC concentration at $t = 0$. Consequently, the sampling rate of this PRC can be obtained from the rearranged Eq. (7.11)

$$R_s = k_e K_{sw} V_s \tag{7.47}$$

PRCs can be used only if their dissipation rate is large enough to quantify the difference in PRC concentration at the beginning and at the end of the exposure. Analytical precision is the controlling factor in this case. For compounds with large dissipation rates, detection limits may be an issue. As a result, PRC-derived sampling rates can be obtained only for compounds that span a 1.5 log units wide range in log K_{ow}. In the case of SPMDs, this range spans log K_{ow} values between 4.5 and 6, but for PSDs

with smaller sorption capacities, these values may be shifted towards the higher K_{ow} end.

Extrapolation of PRC-based sampling rates to compounds with much lower log K_{ow} values is not so critical, because these compounds will have attained a substantial, if not complete, degree of equilibrium, and Eq. (7.15) is quite insensitive to uncertainties in sampling rates for this group of compounds. However, uncertainty exists on the question of how PRC-based sampling rates should be extrapolated to the high log K_{ow} range. Huckins *et al*. [11] defined the exposure adjustment factor (EAF) as the ratio of the (PRC-based) sampling rate in the field and the sampling rate of compounds with the same physicochemical properties obtained during laboratory calibration studies

$$\mathrm{EAF} = \frac{R_{s,field}}{R_{s,lab}} \tag{7.48}$$

These authors showed that the EAF is only a weak function of log K_{ow}, and that PRCs may be used to reduce the effect of exposure conditions on sampling rates from 3- to 10-fold to about 2-fold. The EAF approach has recently been generalised [3]. An alternative method of using PRC-based sampling rates to estimate R_s values of more highly hydrophobic compounds is based on the assumption that the conductivity of the WBL is proportional to $D_w^{2/3}$ [3,30,69]. Since D_w is a weak function of molecular size, R_s can be estimated from [3]

$$R_s = R_{sPRC}\left(\frac{V_{PRC}}{V}\right)^{0.39} \tag{7.49}$$

where V_{PRC} and V are the LeBas molar volumes of PRC and analyte respectively. The PRC should be subject to WBL-controlled kinetics, in this case. Experimental sampling rates for WBL-controlled uptake decrease much stronger with molecular size than indicated by Eq. (7.49), but this decrease may well be caused by the overestimation of concentrations of dissolved analyte, due to sorption to DOC [3,5,30]. However, to date, experimental proof of this assumption is not available.

7.10 CONCLUSION AND OUTLOOK

Considerable progress has been made in understanding the factors that control hydrophobic organic contaminant uptake by passive samplers.

- Transfer through the water boundary layer generally is the rate-limiting step for the uptake of highly hydrophobic compounds. As a

result, the sampling rates (R_s) for these compounds depend on the hydrodynamic conditions at the exposure site. Unfortunately, sampling rates for these compounds are difficult to estimate from the local flow velocities and turbulence intensities, and *in situ* calibration techniques based on the dissipation of performance reference compounds (PRCs) are necessary.

- Diffusion through the membrane is the rate-limiting step for compounds with low membrane–water partition coefficients (K_{mw}). Sampling rates for these compounds are only dependent on temperature, and sampling rates obtained in the laboratory can be applied in the field.
- Attempts have been made to eliminate the flow-dependency of sampling rates for highly hydrophobic compounds, by adding additional transport barriers in the sampler and by using more polar membranes. These attempts have been unsuccessful due to a dramatic drop in sampling rates, resulting in detectability problems.
- The dissipation of PRCs allows for estimating sampling rates *in situ*. This technique is hampered by the limited range of log K_{ow} values ($4.5 < \log K_{ow} < 6$) for which dissipation rate constants can be estimated. Model calculations are presently used to extrapolate PRC-based sampling rates into the high log K_{ow} range, but the experimental evidence in support of these models is scarce, and more research in this area is needed. In addition, reliable experimental values of the sampler–water partition coefficients for PRCs are still missing.

Much less is known about samplers for hydrophilic contaminants. The models that have been developed for hydrophobic samplers are useful for understanding the functioning of hydrophilic samplers as well, but some important differences between the sampling of hydrophobic and hydrophilic contaminants are worth noting. First, reliable K_{mw} values for hydrophilic contaminants are missing. Experimental K_{mw} values as well as models that can be used to predict these values from the contaminant's molecular properties are needed. Second, sorption of hydrophilic compounds to the membrane and the central sorption phase involves surface interactions and non-linear sorption isotherms. This may result in anisotropic exchange and competition for sorption sites. Third, the sampling rates that can be obtained for hydrophilic compounds are much lower than for hydrophobic substances, which results in high detection limits. Although a number of different membranes have been tested already, the selection of other membrane

types may yield somewhat higher sampling rates. Assessing these issues is a major challenge for the near future.

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Chapter 9

Monitoring of priority pollutants in water using Chemcatcher passive sampling devices

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9.1 INTRODUCTION

In recent years, a number of alternative methods of monitoring water quality has been developed to complement and/or replace spot sampling methods that provide only an instantaneous estimate of the concentration of pollutants at the time and point of sampling. Amongst these alternative technologies are passive sampling devices that use a diffusion membrane to separate a receiving phase (with a high affinity for the pollutants to be monitored) from the aqueous environment.

Over the last decade, a range of low-cost passive sampling devices, incorporating a polymeric membrane and a sorbent receiving phase held in an inert plastic body, for monitoring polar contaminants (e.g. triazine pesticides), non-polar organic pollutants (e.g. polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs)), organometallic compounds (e.g. organotin compounds) and heavy metals (e.g. copper, lead, mercury and zinc) in aquatic environments has been developed in our laboratory. The performance of the sampling devices for the various groups of target analytes was optimised by an appropriate selection of combinations of various sorbent receiving phases and polymeric membranes.

9.2 CONCEPT OF CHEMCATCHER

The design of this passive sampling device was developed to provide a single low-cost sampler body that could house a range of combinations of receiving phases and diffusion membranes as appropriate for the

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wide range of classes of pollutants in the aquatic environment. Analytes permeate through the membrane, across a fixed diffusion gap to the receiving phase, where they are retained. Accumulation rates and selectivity are regulated by the choice of both the diffusion-limiting membrane and the solid-phase receiving material. One objective of this design was to overcome some of the problems associated with some of the other currently used passive sampling techniques. A range of solid-phase extraction materials bound to an inert polymeric disk matrix was used as a receiving phase for the accumulation of contaminants from water. This is advantageous as there is no risk of leakage or loss of receiving phase into the aquatic environment. The receiving phase consists of a chromatographic (for organic and organometallic analytes) or chelating (inorganic analytes) receiving phase separated from the aqueous environment by means of a diffusion membrane. These receiving phases have the advantage that they are relatively easy to extract to provide clean samples for chemical analysis.

9.2.1 Receiving phases

The accumulation of organic analytes by a passive sampler occurs as a result of absorption or adsorption of compounds from an unfavourable (bulk water phase) to a more favourable medium (receiving phase). The driving force of this process is determined by the difference between chemical potentials of an analyte in the two media. The Chemcatcher passive sampling system uses a receiving phase based on a solid sorbent immobilised in a polymeric matrix in the form of a disk, and this overcomes a number of problems associated with the use of liquid receiving phases. Not only is the system physically robust but because the receiving phase can be selected from a wide range of commercially available phases, there is potential for increasing the range of analytes sampled or for making the sampling system selective. Substances accumulate from the external aqueous environment into the receiving phase until equilibrium is achieved. This process is fully reversible for receiving phase materials based on sub-cooled liquids (e.g. low-density polyethylene (LDPE) or polydimethylsiloxane (PDMS)). However, sorption is often not fully reversible for solid sorbent materials.

In the simplest case, capacity of a receiving phase accumulating a chemical from water is defined as a product of its affinity for an analyte, given by its distribution coefficient between the receiving phase and water K_{DW}, and the volume of receiving phase V_D.

TABLE 9.1
Chemcatcher configurations for integrative sampling of various pollutant classes

Pollutant class	Receiving phase	Diffusion membrane
Hydrophobic organic compounds (log $K_{OW} > 3$)	C_{18} Empore^{TM} disk	Non-porous low-density polyethylene (LDPE)
Hydrophilic organic compounds (log $K_{OW} < 3$)	C_{18} Empore^{TM} disk	Microporous polysulfone (PS)
	SDB-RPS Empore^{TM} disk	Microporous polyethersulfone (PES)
Metals	Chelating Empore^{TM} disk	Microporous cellulose acetate (CA)
Mercury	Chelating Empore^{TM} disk	Microporous polyethersulfone (PES)
Organotin compounds	C_{18} Empore^{TM} disk	Microporous cellulose acetate (CA)

Empore^{TM} extraction disks were selected as convenient receiving phases for use in the Chemcatcher samplers. They are available as standard 47-mm diameter sorbent particle loaded disks. The particles are held together within an inert matrix made of polytetrafluoroethylene (PTFE) (90% sorbent: 10% PTFE, by weight). The variety of sorbent materials used in the Empore^{TM} disk technology enabled the selection of suitable receiving phases for all classes of pollutants under investigation, including polar and non-polar organic analytes, organometallic compounds and metals (Table 9.1). A further advantage is the availability of published extraction protocols for a number of analytes and a simple analyte elution with consistent recoveries. Moreover, procedures enabling the disks to be loaded (using procedures developed for solid-phase extraction) in a reproducible manner with internal standards or performance reference compounds (PRCs) by filtering an aqueous standard solution through the disk were developed [1].

9.2.2 Diffusion membranes

Two types of polymeric membranes have been tested for construction of Chemcatcher samplers; non-porous membranes including LDPE and

microporous membranes including glass fibre, nylon, polycarbonate, PTFE, polyvinylidenedifluoride (PVDF), cellulose acetate (CA), polysulfone (PS), polyethersulfone (PES) and regenerated cellulose. The membranes separate the sorption phase from the bulk water phase, and reduce the flux to the sorption phase. The membrane acts as a semi-permeable barrier between the receiving phase and the aqueous environment. The dissolved analytes can pass through to the receiving phase, while particulates, microorganisms and macromolecules with a size greater than the exclusion limit cannot permeate. Without the protection of the membrane, there is a risk of deterioration of the receiving phase disks in the aqueous environment due to biofouling. The criteria for selecting an optimum membrane for sampling a specific group of analytes have been discussed in Chapter 7.

The physical strengths, handling properties and chemical resistance of membrane materials were assessed during the initial evaluation. These tests were followed by accumulation studies of test analytes in prototype devices fitted with different membranes in a flow-through system. The latter studies were designed to determine the conductivity to mass transfer of membranes for a broad range of organic and organometallic pollutants and metal ions. Differences in conductivity of various membrane materials are shown in Fig. 9.1. In this first evaluation stage, optimum combinations of diffusion membrane/receiving phase systems were selected for a comprehensive evaluation, including calibration in the laboratory and testing in the field (Table 9.1).

PS and PES membranes were selected for sampler devices designed to sample polar organic pollutants ($\log K_{OW} < 3$) and mercury. These membranes have a high degree of physical strength and good antifouling properties, due to their low surface energy that prevents adsorption of macromolecules to the surface. Polar molecules readily diffuse through the 0.2-μm wide water-filled pores. In contrast, more hydrophobic compounds sorb to the polymer matrix of the membrane. Due to low diffusivity in the polymer matrix, conductivity of the membrane decreases dramatically with increasing hydrophobicity of sampled compounds. CA was selected as a material suitable for construction of Chemcatcher samplers for inorganic ions and organotin compounds, due to their optimum diffusion through the water-filled membrane pores, combined with negligible adsorption to the membrane material.

The non-porous LDPE allows permeation of hydrophobic analytes ($\log K_{OW} > 3$–4), due to the favourable combination of high membrane/water partitioning coefficients and membrane diffusivities for those compounds (see Chapter 7). On the other hand, the membrane has a

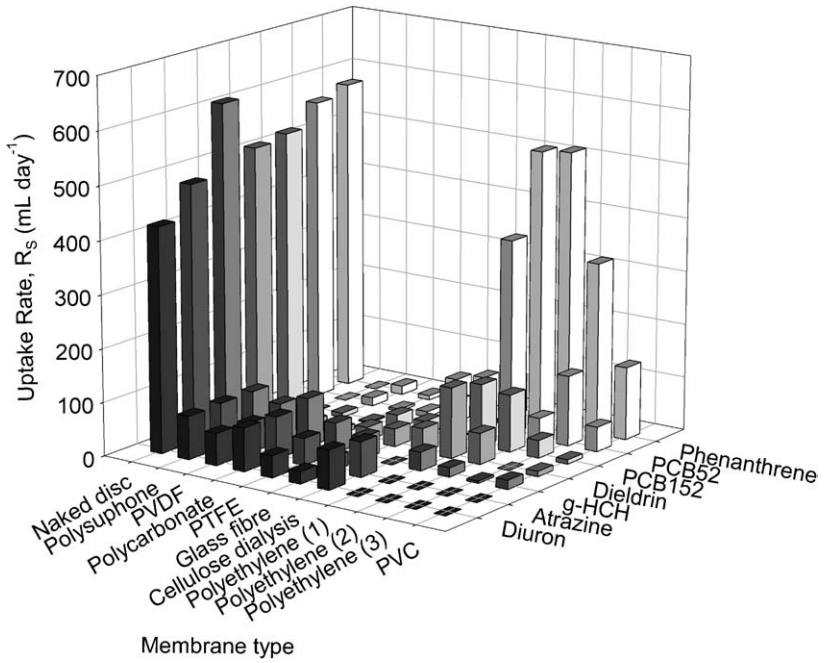

Fig. 9.1. The effect of diffusion membrane materials on the patterns of uptake of seven organic compounds. The exposure was performed at constant analyte concentration in water at 11°C in a flow-through tank. A 47-mm C_{18} Empore™ disk was used as receiving phase in all cases.

high resistance to mass transfer of more polar compounds and completely excludes the permeation of ions and molecules with effective diameter larger than 1 nm.This material was used in the Chemcatcher designed to sample non-polar organic pollutants.

9.2.3 Sampler body

9.2.3.1 Reusable sampler body prototype

The principles of Fickian diffusion state that the flux of a substance to the receiving phase is proportional to the surface area over which diffusion takes place and is inversely proportional to the diffusion path length. Therefore, if passive sampling obeys Fickian diffusion, the physical dimensions of the sampler body significantly affect the sampling rate for analytes. During the development phase, the design of the Chemcatcher body was optimised in terms of both construction materials and sampler geometry.

In the evaluation stage, PTFE was selected as a construction material for the sampler body. Its advantage is a low sorption capacity for most environmental pollutants. Moreover, PTFE is denser than water and is not buoyant in the sampled environment, making it easy to deploy this prototype in the field by suspending it from a wire or a string.

The system was constructed to fit a 47-mm Empore^{TM} disk as the receiving phase, with the chosen diffusion membrane material being laid directly on its surface. Both were supported by means of a 50-mm rigid PTFE backing plate (Fig. 9.2). The active surface area of the Chemcatcher sampler is 17.5 cm^2. To seal the sampler, a sleeve open at the back was screwed into place to hold the individual body sections together. In addition, a sealing plate allowed the system to be filled with water and sealed during storage and transport. Thus, the sampler body also acts as a container for storage and transport. The PTFE body could be reused several times, but only after a thorough cleaning involving a multi-step washing procedure.

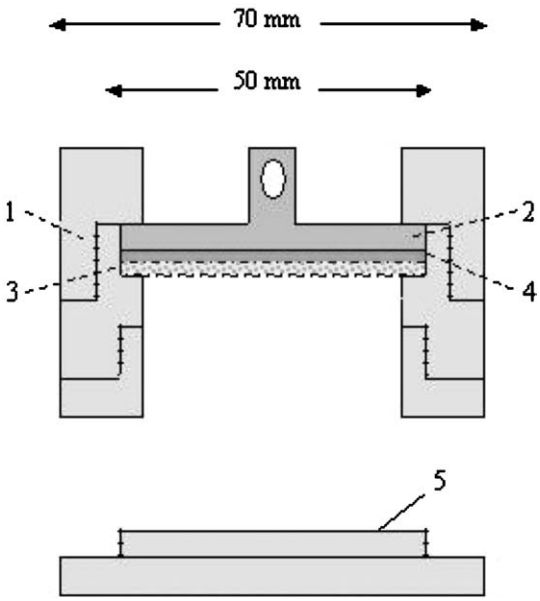

Fig. 9.2. Schematic diagram of the prototype Chemcatcher device, used during the sampler development. The PTFE body parts (components 1 and 4) support the receiving phase (component 2) and the diffusion membrane (component 3) and sealed them in place. The sampler is sealed by means of a screw cap (component 5) for storage and transport.

In the early stages of development [2], a protective steel mesh was used to protect the surface of the membrane. However, the use of a mesh was later abandoned, because it proved to accumulate particulate matter in the field and also to provide shelter for colonising organisms that cause fouling or degradation of the membrane.

9.2.3.2 Disposable sampler body prototype

In subsequent performance tests, the uptake kinetics of many analytes were shown to be controlled by diffusion in the aqueous boundary layer on the membrane surface. The resistance to mass transfer of the boundary layer depends on hydrodynamic conditions in the membrane vicinity. These are significantly affected by the construction geometry of the sampler body. The membrane and receiving phase of the first-generation Chemcatcher prototype were located inside a 20-mm deep depression in the sampler body. This sampler design effectively buffers the effect of fluctuating flow on the sampler performance. However, it also effectively reduces convective transport of analytes to the sampler membrane, causing reduced sampling rates (i.e. the rate at which the sampler accumulates chemicals). For an optimum sampler performance, high sampling rates are essential, especially for sampling non-polar chemicals, due to their extremely low concentrations in the water column. In order to increase sampling rates, the geometry of the body was further refined in the latest version of Chemcatcher body prototype by reducing the depth of the cavity to a minimum (Fig. 9.3). In comparison with the first-generation prototype, the second-generation sampler collects analytes with increased sampling rates. Tests showed that the sampling rate for non-polar compounds ($\log K_{OW} > 3$–4), which are accumulated under aqueous boundary layer control, was increased by a factor of 2. This provides improved sensitivity, but also increased variation of sampling rates in response to fluctuations in turbulence (water flow).

In the latest design, the Chemcatcher body is made of mouldable plastic materials. The body consists of three components (two body parts and a lid for storage and transport), which are clipped together (Fig. 9.3). This makes the sampler assembly and disassembly faster than it was in the first-generation prototype, where assembly was made using screw threads. This sampler body prototype was designed as a disposable device for a single field deployment. This removes difficulties connected with cleaning procedures and accompanying quality control measures required for use in trace analysis. The plastic material can be recycled.

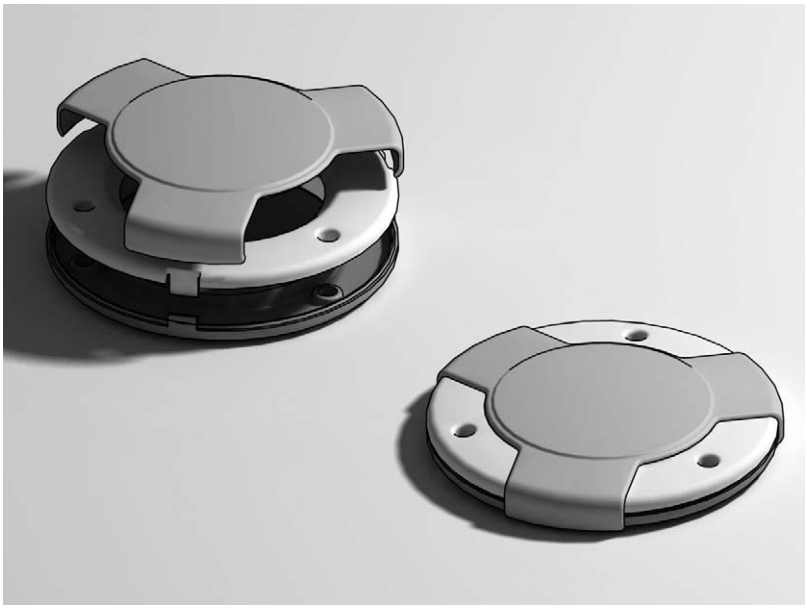

Fig. 9.3. Views of the disposable Chemcatcher sampler.

Depending on the nature (temperature, turbulence, presence of suspended solids) of the environment to be sampled and on the target analyte properties, a sampler design can be selected to provide an optimum performance.

9.3 THEORY

The general theory of passive sampling is described in Chapter 7, and this is applicable to the various Chemcatcher designs. In summary, mass transfer of a chemical into the sampler involves several diffusion and interfacial mass transport steps across the various barriers that may be present; i.e. the stagnant aqueous boundary layer, possibly a biofilm, the diffusion membrane, the inner fluid (liquid or gaseous) phase, and the receiving phase. In the initial stages of exposure, analyte uptake is expected to be linear or time-integrative after steady-state flux of chemicals into the sampler has been achieved [3,4]. Under these conditions, the amount of a chemical in the receiving phase is directly proportional to the product of the concentration in the surrounding water (C_W) and the exposure time (t). For practical purposes, uptake in

the linear phase can be described by

$$m_D(t) = m_0 + C_W R_S t \quad (9.1)$$

where m_D is the amount of analyte accumulated in the receiving phase, m_0 is the initial amount of analyte in the receiving phase, and R_S is the sampling rate of the system:

$$R_S = k_{ov} A \quad (9.2)$$

where k_{ov} (m s^{-1}) is the overall mass transfer coefficient and A (m^2) is the surface area of the membrane. The uptake of an analyte is linear and integrative approximately until the concentration factor of the sampler ($m_D(t)/C_W$) reaches half saturation. The sampling rate of an individual chemical can be determined experimentally under fixed conditions at constant analyte concentration. Under environmental conditions, when the water concentration changes during the exposure, the term C_W represents a time-weighted average (TWA) concentration during the deployment period.

9.4 CALIBRATION

The sampling rate depends on the physicochemical properties of the analyte, the environmental conditions and the sampler design. To enable measurement of TWA water concentrations of a range of pollutants, the Chemcatcher sampler was calibrated in flow-through tank studies under controlled conditions of temperature and water turbulence. Concentrations of the analytes in water (C_W) and the amounts accumulated in the receiving disk (m_D) were measured regularly during the exposure. In each experiment, passive samplers were exposed for up to 14 days in a constant concentration of analyte. Each factor (temperature and stirring speed (turbulence)) was tested at three levels. The calibration experiments were designed to characterise the effect of physicochemical properties, temperature and hydrodynamics on kinetic and thermodynamic parameters characterising the exchange of analytes between the sampler and water. So far, calibration data have been reported for the non-polar Chemcatcher [1,5] and calibration data for other Chemcatcher designs will be reported shortly [6,7].

9.5 SAMPLING OF HYDROPHOBIC ORGANIC CONTAMINANTS

Kingston *et al*. [2] designed one of the Chemcatcher prototypes for the sampling of non-polar organic compounds with log K_{OW} values greater

than 3. This system uses a 47-mm C_{18} Empore^{TM} disk as the receiving phase and a 35-μm thick LDPE diffusion membrane. The C_{18} Empore^{TM} disk has a very high affinity and capacity for the sampled hydrophobic organic pollutants. LDPE is a non-porous material, even though transient cavities with diameters approaching about 1 nm are formed by random thermal motions of the polymer chains. The thermally mediated transport corridors of the polyethylene exclude large molecules, as well as those that are adsorbed on sediments or colloidal materials such as humic acids. Only truly dissolved and non-ionised contaminants are sequestered.

Recently, the optimisation of this sampler design has been reported [8]. This involved the improvement of sampling characteristics including the enhanced sampling kinetics and precision by decreasing the internal sampler resistance to mass transfer of hydrophobic organic chemicals ($\log K_{OW} > 5$). This was achieved by adding a small volume of *n*-octanol, a solvent with high permeability (solubility × diffusivity) for target analytes, to the interstitial space between the receiving sorbent phase and the polyethylene diffusion membrane. The use of *n*-octanol as an interstitial phase resulted in an approximately 20-fold increase in sampling rates compared with those observed with water as the interstitial phase [8].

9.5.1 Calibration data

Calibration data for the non-polar Chemcatcher were obtained in laboratory experiments designed to measure the uptake of target analytes (sampling rate; R_S) and offloading of PRCs (elimination rate constants; k_e) at different combinations of temperature and hydrodynamic conditions in a full factorial design. The calibration data were gathered in order to determine the sampling parameters and to observe how they are affected by environmental conditions to enable a more precise measurement of TWA concentrations of non-polar priority pollutants in the field [1].

Over the range of controlled laboratory conditions (temperature and turbulence), the magnitude of R_S values of hydrophobic chemicals spanned over two orders of magnitude (i.e. from $0.008\,L\,day^{-1}$ up to $1.380\,L\,day^{-1}$). The sampling rate is strongly affected by the physicochemical properties of the compounds. Among the non-polar priority pollutants, the highest sampling rates were observed for small, moderately hydrophobic compounds: anthracene, phenanthrene, fluoranthene and pyrene. The lowest sampling rates were measured for

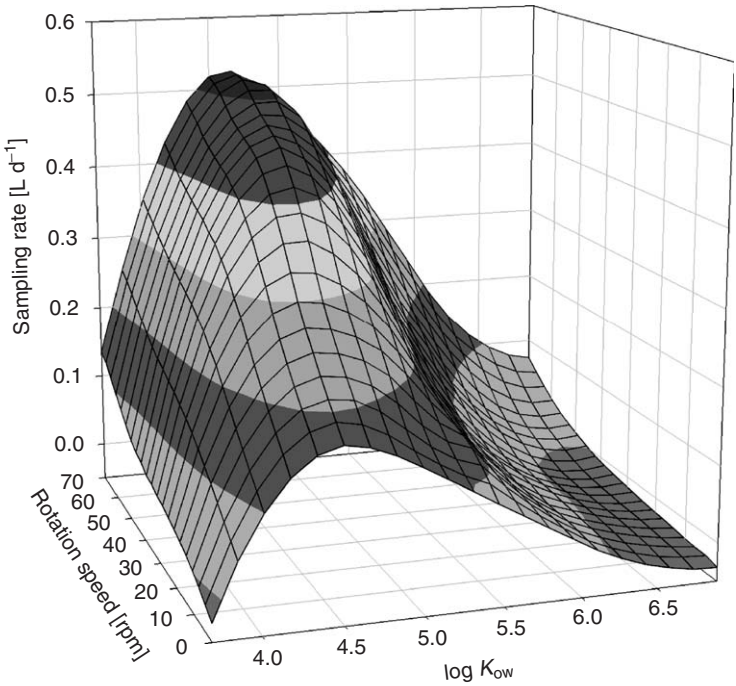

Fig. 9.4. Effect of water turbulence (expressed as rotation speed of a carousel device loaded with samplers) and log K_{OW} on the sampling rates for a range of non-polar organic compounds in the Chemcatcher at 11°C.

indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene and benzo[g,h,i]perylene; large and extremely hydrophobic compounds. The typical dependence of sampling rates on hydrophobicity is shown in Fig. 9.4.

Sampling rates increase with the increasing temperature, and the temperature dependence of the sampling rate R_S can be described by an Arrhenius-type equation. The mean activation energy for all of the hydrophobic analytes under investigation was 93 kJ mol^{-1}. This corresponds to an increase in sampling/offload rate of a factor of 5.2 over the temperature range 6–18°C. For comparison, Huckins *et al*. [9] calculated from the literature data available for semipermeable membrane devices (SPMDs) an average activation energy of 37 kJ mol^{-1}. Thus, the effect of temperature on the Chemcatcher uptake kinetics appears to be more significant than that on SPMD sampling rates.

With the exception of the moderately hydrophobic lindane (log $K_{OW} = 3.7$), a significant increase in sampling rate with increasing flow velocity was observed for all compounds under investigation (Fig. 9.4). This corresponds well with the theory of diffusion through two films in

series [10,11], which predicts a switch in the overall mass transfer to the aqueous boundary layer control for hydrophobic compounds. A similar effect of hydrodynamics has been observed and explained for SPMDs [12].

9.5.2 Performance reference compound concept

Figure 9.5 shows that for a range of environmental conditions (temperatures and water flow rates) there is a good correlation between uptake kinetics (sampling rate R_S) of analytes and offload kinetic parameters (elimination rate constant k_e) of their deuterated analogues (used as PRCs). This demonstrates isotropy of the uptake (absorption) onto and the offload (desorption) from the sampler for a range of hydrophobic analytes. Thus, the PRC concept can be applied to the measurement of *in situ* exchange kinetics in the field.

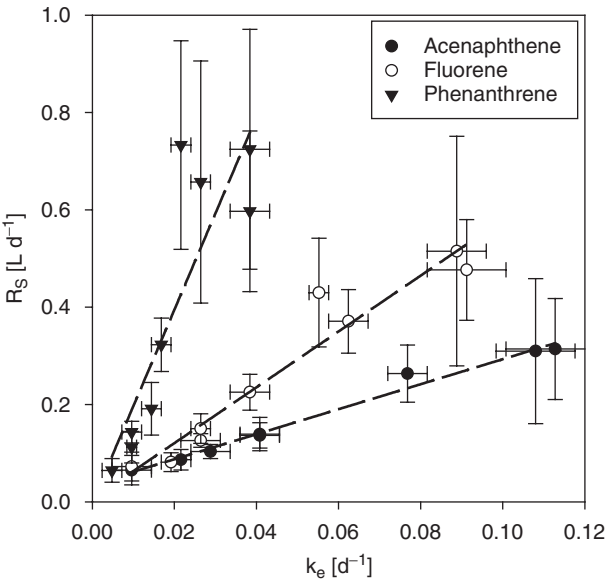

Fig. 9.5. The correlation between the sampling rates R_S of three polycyclic aromatic hydrocarbons and the elimination rate constants k_e of their perdeuterated analogues demonstrates the isotropic exchange kinetics for the non-polar Chemcatcher sampler variant. The data represent laboratory flow-through exposures performed at various combinations of water temperature and turbulence. Reproduced from Ref. [1] with permission from Elsevier.

9.5.3 Non-polar Chemcatcher/water distribution coefficients

Assuming isotropy of the exchange kinetics of the chemicals under investigation, and the validity of the model used to describe the kinetics, the value of the receiving phase water distribution coefficient K_{DW} can be calculated as the ratio of the absorption and desorption transport parameters for a particular compound (see also Chapter 7):

$$K_{DW} = \frac{R_S}{k_e V_D} \tag{9.3}$$

The experimental evidence indicates that K_{DW} values are not significantly affected by temperature in the range 6–18°C. This enables the derivation of an empirical equation to calculate the distribution coefficient K_{DW} of a compound between the non-polar Chemcatcher sampler and water using the *n*-octanol–water partition coefficient:

$$\log K_{DW} = 1.382 \ \log K_{OW} - 1.77 \quad (r = 0.97, s = 0.13, n = 31) \tag{9.4}$$

Huckins *et al.* [9] have shown that for SPMDs, the log K_{OW} versus log SPMD/water partition coefficient plot for compounds with log $K_{OW} > 5.0$ deviated from linearity. This phenomenon has also been observed for plots of log bioconcentration factor versus log K_{OW} [13]. It has not yet been demonstrated whether or not a deviation from linearity occurs for very hydrophobic compounds in the non-polar Chemcatcher.

9.5.4 Empirical uptake rate model

It is convenient to derive an empirical equation for the *in situ* estimation of sampling rates for use in the interpretation of results obtained with the Chemcatcher passive sampler in field studies. Huckins *et al.* [9,14] showed that for SPMDs, differences in exposure conditions cause sampling rates to be shifted by a constant factor for all compounds. A similar observation was made for the non-polar Chemcatcher. Log R_S versus log K_{OW} plots from all calibration studies for the Chemcatcher have very similar shapes, but show a varying offset for the different exposure conditions (combinations of water temperature and turbulence). A nonlinear regression analysis of log-transformed sampling rates R_S on a third-order polynomial function of log K_{OW} from all calibration studies enabled the derivation of an empirical model that can be used to calculate the sampling rate as a function of hydrophobicity.

This relationship is applicable within the range of log K_{OW} 3.7 to 6.8 and for a range of exposure conditions (temperatures between 6 and 18°C and water turbulence (stirring speeds from 0 to 70 rpm)):

$$\log R_S = P + 22.755\ \log K_{OW} - 4.061\ \log^2 K_{OW} + 0.2318\ \log^3 K_{OW}$$
$$(r = 0.92, s = 0.22, n = 134) \tag{9.5}$$

The relative ratios of sampling rates of any two compounds within the calibration range are constant for a broad range of exposure conditions. The knowledge of the parameter P is sufficient to characterise the effect of varying environmental conditions on the absolute magnitude of the sampling rates. The standard deviation of the fit (0.22 log units) corresponds to an uncertainty factor of approximately 1.7, which is relatively low considering the large differences in exposure conditions tested. Information on concentrations, that are accurate within a factor of 2, is still highly relevant for environmental risk assessment purposes.

9.5.5 Estimation of *in situ* TWA concentrations

An algorithm has been derived to calculate TWA water concentrations from the amounts of analytes accumulated in non-polar Chemcatcher samplers during field deployment [5]. This involves the characterisation of *in situ* exchange kinetics, using PRCs. The PRC elimination rate constant k_e is calculated using two points: amount of PRC in a sampler prior to and after a field exposure. Isotropic first-order exchange kinetics are assumed. Sampling rates R_S of PRCs are calculated using Eqs. (9.3) and (9.4). The PRC-derived sampling rates are then fitted to Eq. (9.5), using the exposure-specific effect P as the only adjustable parameter. The sampling rates of individual compounds are then estimated from Eq. (9.5) with the optimised value of parameter P. TWA concentrations of target analytes at the sampling site can be estimated from concentrations in the exposed samplers using the rearranged Eq. (9.1):

$$C_W = \frac{m_D(t) - m_{Df}}{R_S t} \tag{9.6}$$

where C_W represents the TWA water concentration during the deployment period, $m_D(t)$ is the analyte mass found in the sampler after field exposure, m_{Df} is the average mass of analyte found in the field blank, R_S is the estimate of the *in situ* sampling rate derived as described above and t equals exposure time.

9.6 SAMPLING OF HYDROPHILIC ORGANIC CONTAMINANTS

9.6.1 Integrative sampler

Kingston *et al.* [2] designed a Chemcatcher prototype for integrative sampling of polar organic compounds with log K_{OW} values lower than 3 over long exposure times. This system uses a 47-mm C_{18} Empore^{TM} disk as the receiving phase and a 100-μm thick PES diffusion membrane. The C_{18} Empore^{TM} disk, used as a receiving phase in this Chemcatcher prototype, has been shown to have a high affinity and capacity for many organic pollutants. The octadecyl functional groups bonded to the silica surface provide mainly non-polar interactions with hydrophobic molecules. However, a fraction of the silica material has non-substituted silanol groups with a high affinity for molecules with polar functional groups. These interactions involve mainly hydrogen bonding or dipole–dipole interactions. Thus, this sorbent disk exhibits can retain analytes with a broad range of physicochemical properties.

As described earlier, PES is a porous membrane with a high permeability for polar organic chemicals. This material has also been used in other passive samplers, e.g. polar organic chemical integrative samplers (POCIS) [15] (also see Chapter 8).

Retention of some polar compounds on C_{18} Empore^{TM} disks is stronger than one would expect from their hydrophobicity. This high receiving phase affinity permits the sampling of pollutants over a prolonged period without reaching the saturation of the sorbent material. On the other hand, this high affinity complicates the selection of compounds with a medium sampler fugacity that could be used as PRCs, since offloading rates are extremely low and it is not possible to measure *in situ* analyte exchange kinetics. This is shown in Fig. 9.6. Linear uptake of atrazine (a compound with relatively low hydrophobicity: log $K_{OW} = 2.61$) into the Chemcatcher was observed during a period of 14 days under a range of exposure conditions. No significant elimination of D_5-atrazine, loaded onto the Empore^{TM} disk prior to exposure, was observed over this period. This demonstrates an ideal performance of this variant of Chemcatcher as an integrative sampler for polar compounds. However, it is impossible to see whether the uptake kinetics of atrazine was correlated with the elimination kinetics of D_5-atrazine. Thus this compound cannot be used as a PRC in the time scale of a typical field exposure. Several other compounds, including D_5-atrazine, D_{10}-chlorpyrifos, D_8-naphthalene, D_{10}-simazine and D_{14}-trifluralin, were tested and none was identified to be suitable as a potential PRC.

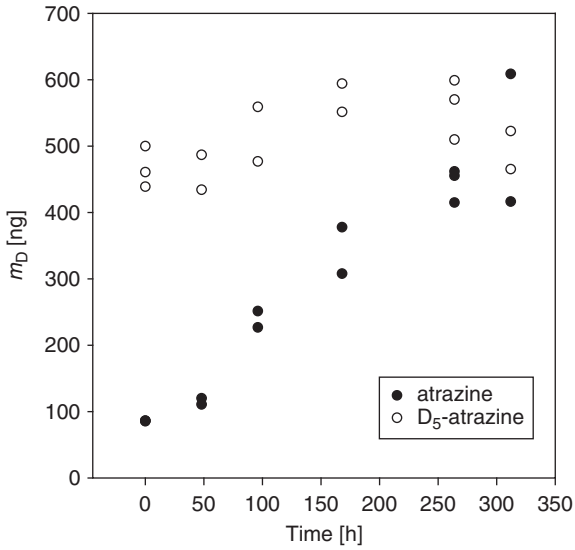

Fig. 9.6. Uptake of atrazine in the Chemcatcher prototype fitted with C_{18} Empore^{TM} disk and a polyethersulfone membrane in a flow-through laboratory exposure (14 days). No significant elimination of D_5-atrazine, loaded onto the Empore^{TM} disk prior to exposure was observed. Data are presented from an exposure conducted at 4°C in turbulent water (rotation speed 70 rpm). The aqueous concentration of atrazine was held constant at 1 μg L^{-1}, and the water-exchange rate in the flow-through system was 50 L day^{-1}.

Calibration data for the polar variant of Chemcatcher were obtained in laboratory experiments in a similar experimental set up as described in Section 9.5.1. Experiments were designed to determine sampling rates R_S of a selected number of triazine and phenylurea herbicides for various combinations of temperature and hydrodynamic conditions. An example of sampling rates of the triazine herbicides is shown in Fig. 9.7.

The sampling rates increase with increasing temperature, and the activation energy for the triazine herbicides under investigation (simazine and atrazine) was 130 kJ mol^{-1}. This would correspond to an increase in R_S of nearly a factor 10 over the temperature range 6–18°C. Thus, the temperature dependence of sampling rate for devices fitted with PES membranes seems to be greater than for those fitted with LDPE membranes. On the other hand, the observed effect of hydrodynamic conditions on sampler performance was only moderate.

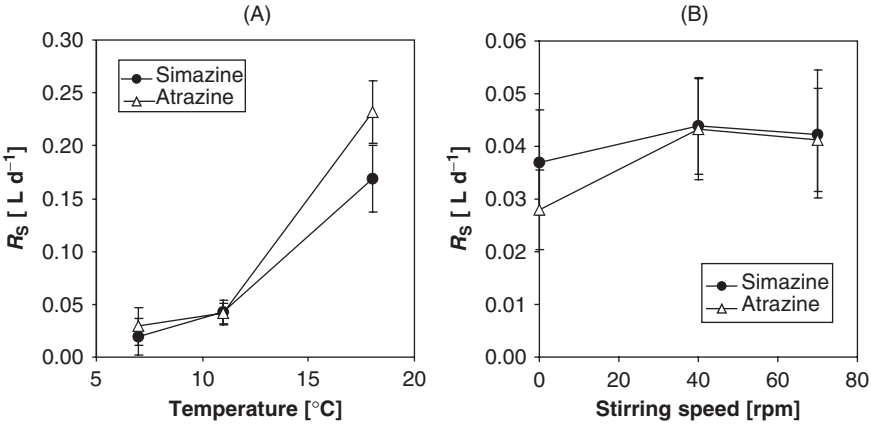

Fig. 9.7. Effect of temperature (A: measured in turbulent water) and water turbulence (B: expressed as rotation speed of a carousel device loaded with samplers; measured at 11°C) on the sampling rate of the polar Chemcatcher for triazines.

9.6.2 Short pollution event detector

Many pesticides, some of which are polar molecules, are released at high concentrations into streams and rivers in episodic events, such as field runoff after pesticide spraying, heavy rain and storm events, or during wastewater discharge. These events usually last only a few hours and in order for these compounds to be detected by passive samplers, a device with a short response time is required. However, the device fitted with a PES membrane, although ideal for long-term monitoring, has a lag phase of several hours that represents the time necessary for the analytes to diffuse through the membrane to reach the receiving phase. The lag phase of the device can be predicted using a theoretical model for the mass flux through a plane sheet with constant concentration on both sides of the sheet, as outlined in Chapter 7. Since the PES membrane is discarded before analysis (only the receiving phase is analysed), the lag time for passage through the membrane has to be taken into account.

Shaw and Müller [16] suggested the use of a device fitted with only an Empore^{TM} disk receiving phase (without a diffusion membrane) to reduce the response time and make the sampler more reactive to accidental pollution events. The naked Empore^{TM} disks deployed in stainless steel cages secured between two squares of wire mesh that

allowed the disks to be exposed on both surfaces. Later, Stephens *et al*. [17] used a device with a naked Empore™ disk fitted in the Chemcatcher PTFE body, and accumulation in such a device is shown in Fig. 9.1. Such samplers have a very short lag phase that represents only the time taken for the analyte to diffuse across the aqueous boundary layer. The analyte sampling rates are higher than in devices fitted with PES membranes as the resistance to mass transfer is lower in absence of the membrane. The disadvantage of such device is a fast equilibration of the sampling device with the water phase, which restricts to a few days the time over which the sampler operates in time-integrative mode. Moreover, because the main barrier to the mass transfer is the aqueous boundary layer, the sampling kinetics of such devices are sensitive to changing hydrodynamic conditions [18,19]. Potentially, problems may arise with sample clean-up due to fouling of the receiving phase during a direct contact with sampled water in the field. More work is required to minimise the uncertainty caused by sampling rate fluctuations with degree of water turbulence. Nevertheless, this approach is very useful for detecting and semi-quantitative evaluation of short pollution events.

9.7 SAMPLING OF METALS

A Chemcatcher variant based on diffusion through a porous CA membrane to a receiving phase, where the analyte is removed by chelation in a chelating Empore™ disk has been developed for monitoring metals [19]. Uptake rates to the receiving phase were determined in both batch and flow-through laboratory exposures for different metal ions. Sampling rates were found to be diffusion controlled and inversely related to pH. The uptake rate can be used for calculating the diffusion coefficients for specific compounds under defined laboratory conditions [19]. *In situ* deployment of the passive sampler was demonstrated to provide metal concentrations, corresponding to the electrochemically available fraction of total metal [20].

Laboratory handling procedures were developed that enabled a direct analysis of the accumulated metals on the receiving membrane by laser ablation inductively coupled plasma mass spectrometry [20]. In a later study, a calibration database of R_S values for five metals for independently varied temperature and turbulence conditions was established in an experimental setup similar to that described in Section 9.5.1 [6]. R_S for cadmium, copper, nickel and zinc were within

the same order of magnitude (50–150 mL day^{-1}) and showed similar variations with temperature and turbulence. Somewhat lower sampling rates (12–17 mL day^{-1}) were measured for lead. Both changes in temperature and turbulence were shown to have a significant effect on sampling rates of metal ions [6].

9.8 SAMPLING OF ORGANOMETALLIC COMPOUNDS

Another version of Chemcatcher has been developed for the measurement of the TWA concentrations of organotin compounds (monobutyltin, dibutyltin, tributyltin and triphenyltin) in water. The receiving phase is a C_{18} Empore^{TM} disk and the diffusion membrane is CA. The effects of environmental variables (pH, salinity and biofouling) that could influence accumulation in receiving phase have been evaluated in the laboratory. Linear uptake was observed for at least for 14 days of exposure at constant aqueous concentration of analytes. Compound-specific sampling rates varied between 0.063 and 0.038 L day^{-1} [7].

9.9 FIELD APPLICATIONS

9.9.1 Pan-European field trials to compare the performances of the Chemcatcher and spot sampling in monitoring the quality of river water

In 2004, field performance of the non-polar Chemcatcher was tested in a field trial in rivers in four European countries (the Czech Republic, Finland, The Netherlands and Norway). The sampler exposure was repeated twice at each of the four sampling sites, once in spring and once in autumn. The uptake of selected organic priority pollutants (PAHs and OCPs) in the Chemcatchers during deployment periods up to 28 days were compared with the contaminant levels found in extracts from filtered spot samples of water collected regularly over the exposure period. The resulting dataset provides a solid basis for the evaluation of the passive sampling method for hydrophobic chemicals with log K_{OW} from 3 to 7. The main objective of the study was to evaluate the ability of non-polar Chemcatcher samplers to estimate TWA concentrations of selected PAHs and OCPs under various exposure conditions (contaminant spectrum, temperature, water turbulence and fouling).

For practical estimation of the chemical exchange kinetics between Chemcatcher and water, the PRC approach was successfully applied and validated. The coefficients of variation of the two-point estimate of

the PRC overall exchange rate constants k_e ranged from 1% to 34% and the precision was sufficient to allow significant k_e estimates for a number of PRCs in each of the individual field studies. The PRC offload data confirmed that the chemical exchange kinetics are site specific and depend significantly on exposure conditions, including temperature, turbulence and biofouling. The knowledge of PRC offload kinetics in combination with laboratory-derived Chemcatcher calibration data enabled estimation of *in situ* sampling rates for the whole range of target analytes that were expected to be found in the monitored rivers. The compound-specific sampling rates ranged from 0.003 to 0.424 L day^{-1}. Maximum *in situ* sampling rates were measured for compounds with moderate hydrophobicity (log K_{OW} 4–6). The method sensitivity decreased for very hydrophobic (log $K_{OW} > 6$) compounds. The examination of the site-specific exchange kinetics of PRCs indicated in eight field exposures for European rivers that the uptake remained linear for up to 28 days for compounds with log $K_{OW} > 4.3$ at all sampling sites.

Heavy biofouling of the samplers was observed at all four sampling sites. This may be the reason for the deterioration of the exchange kinetics of the samplers with increasing time. Confocal laser microscopy was used to obtain semi-quantitative measure (film thickness and density) of the biofilm layer.

Method detection limits of target analytes in sampler extracts ranged from 0.2 to 10 ng per sampler. Instrumental method detection limits can be translated into site-specific minimum detectable water concentrations of 0.1–138 ng L^{-1} on the basis of compound-specific *in situ* sampling rates over a 14- or 28-day exposure period. The lowest detection limits were achieved for compounds with a favourable combination of a low instrument detection limit and high sampling rate. This was the case for the OCPs including dieldrin, α-endosulfan, hexachlorobenzene, lindane and pentachlorobenzene, as well as for PAHs with less than five aromatic rings.

Mean masses of PAHs found in Chemcatchers exposed in the field ranged between one and tens of ng per sampler. Compounds with two, three and four aromatic rings per molecule dominated the PAH spectrum. These are more water soluble than the heavier PAHs, and are thus likely to be present in water at higher concentrations. Moreover, the sampling performance characteristics of the Chemcatcher favour the uptake of compounds with moderate hydrophobicity. The concentrations of analytes found in Chemcatcher extracts were converted into the corresponding TWA aqueous concentrations, using the calculated *in situ* sampling rates. The estimated TWA concentrations of individual

truly dissolved PAHs at the sampling sites ranged between the detection limit and 60.3 ng L^{-1}. The estimated TWA concentrations of individual truly dissolved OCPs ranged between the detection limit and 3.4 ng L^{-1}.

The TWA concentrations estimated from the passive sampler data were compared with concentrations of analytes determined from filtered water samples to assess the performance of Chemcatcher. When comparing the TWA concentrations calculated from spot samples and passive samplers, it is important to consider the differences in contaminant fractions in water that are measured using the two methods. TWA concentrations estimated using passive samplers reflect the truly dissolved concentrations and do not account for the pollutants bound to particles and colloids in water. Water samples filtered through 0.45-μm pore size filters still contain a contaminant fraction that is bound to dissolved organic material (DOM) present in water. The truly dissolved fraction of hydrophobic analytes in water will depend on the level and quality of DOM, which may fluctuate during the sampling period. Unfortunately, there is a lack of equipment that is suitable for routine measurements of dissolved concentrations at a reasonable cost. The comparison was limited to cases where a particular analyte was detected in both the spot samples and the passive samplers. With a few exceptions (namely hexachlorobenzene and lindane) a comparison with spot samples was possible for the pesticides and for the PAHs with a maximum of four aromatic rings per molecule. The difference in water concentrations calculated using both methods never exceeded one order of magnitude.

9.9.2 Monitoring pesticide runoff in Brittany, France

In 2005, Schäfer *et al*. [21] used Chemcatcher fitted with naked SDB-XC Empore™ disks to investigate whether they can be applied to monitor field runoff of ecotoxicologically relevant pesticides in current use. The field study was performed in Brittany, in the North-western France, a region with intensive agriculture and pesticide usage. Between 1 and 3 samplers were deployed for 10–13 days at each of the 16 small streams. The target analytes were mainly polar or moderately polar pesticides with log K_{OW} values between 1.4 and 4.13. These belonged to multiple classes of pesticides: chloracetanilide herbicides (alachlor, acetochlor), the phenylurea herbicide linuron, the oxadiazolone herbicide oxadiazon, carbamate insecticides (pirimicarb, carbofuran), the organophosphate insecticide chlorfenvinphos, the organochlorine insecticide

endosulfan, the pyperidine fungicide fenpropidin and the conazole fungicide tebuconazole. A significant accumulation of all compounds except fenpropidin, chlorfenvinphos and α-endosulfan was observed in the devices. These results indicate the potential utility of these samplers in providing semi-quantitative or qualitative data on compounds present in episodic events, and the utility of the SDB-XC Empore™ disks for sequestering polar compounds. This phase may be more useful than the C_{18} disks described for the polar variant of the Chemcatcher, and further work in this area is ongoing.

9.9.3 Field trial in the River Meuse in The Netherlands

A field test of the wide range of passive sampling devices presently available was conducted at RIZA's monitoring station at Eijsden (NL) in April 2005 as part of the Screening method for Water data InFormation in support of the implementation of the Water Framework Directive (SWIFT-WFD) project. The aim of this trial was to evaluate the suitability of passive samplers for monitoring water quality to meet the requirements of the European Union's Water Framework Directive (WFD) legislation. The trial was designed to provide data on the robustness and utility of this technology in order to strengthen the case for its introduction into monitoring programmes.

Passive samplers for metals, polar and non-polar organic pollutants were deployed for overlapping periods of 7, 14 and 21 or 28 days in the River Meuse. Chemcatchers with different configurations were tested alongside SPMD, membrane-enclosed sorptive coating (MESCO), POCIS and DGT. TWA concentrations obtained were compared with those obtained from conventional spot sampling and analysis by an accredited laboratory. In addition, since the field deployment was undertaken at RIZA's monitoring station, concentrations from continuous monitoring for organic contaminants and composite sampling for metals were available for further comparisons.

It was therefore possible to evaluate information provided by the passive samplers alongside that from *in situ*, spot and composite sampling for the monitoring of metals in water. TWA zinc concentrations measured with Chemcatcher were calculated from the masses of zinc accumulated over exposures of 7, 14 and 21 days and available calibration data. These were compared with spot sampling and weekly composite sampling conducted to determine total and filtered (0.45 μm) fractions of zinc (Fig. 9.8). TWA concentrations measured with the Chemcatcher for 7-, 14- and 21-day exposures are generally in good

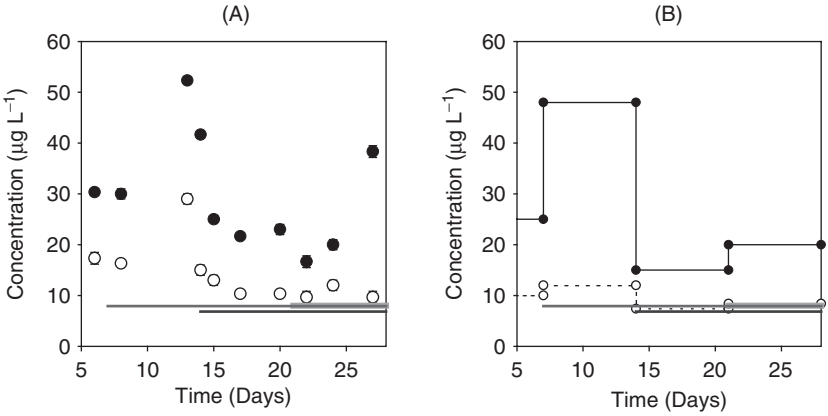

Fig. 9.8. Comparison of TWA zinc concentrations obtained for exposures of 7, 14 and 21 days of the Chemcatcher in the River Meuse with spot sampling (A) and composite sampling (B). Both sets of water samples were analysed without (•) and with filtration (o) to 0.45 μm.

TABLE 9.2

Comparison of mean zinc concentrations measured with the Chemcatcher and spot sampling (with and without filtration) for exposure times of 7, 14 and 21 days

Exposure (days)	TWA concentration (μg L^{-1})		Spot sampling dissolved concentration (μg L^{-1})	
	Mean	Std dev.	Mean	Std dev.
7	8.0	1.8	10.5	1.3
14	6.9	1.7	10.9	1.4
21	7.9	2.4	13.9	6.2

agreement with those determined by spot and composite sampling. While Chemcatcher-measured zinc concentrations are similar to mean dissolved concentrations from spot sampling for 7- and 14-day exposures, the precision of the measurement appears lower (Table 9.2). Higher fluctuations in concentrations observed during the 21-day exposure resulted in a significant loss of precision for spot sampling, while lower precision for Chemcatcher may have resulted from environmental impacts such as biofouling. However, it remains difficult to judge the accuracy of each of these methods in determining the TWA labile fraction of zinc. Slight underestimation of time-integrated filtered concentration

of zinc by the Chemcatcher may be the result of the uncertainty or bias from the calibration data used or due to a fraction of filtered zinc not available for uptake by the Chemcatcher. The time-integrated nature of *in situ* sampling is likely to offer more representative information than that provided by infrequent spot samples, and should be useful in assessing long-term trends in contaminant levels.

9.9.4 Field trial in the estuary of the River Ribble in the United Kingdom

A field trial was conducted as part of the SWIFT-WFD project in the United Kingdom Pilot River Basin, the Ribble catchment. Pressure points along the Ribble estuary were identified, and a risk assessment was then effected. A trial was then designed to be carried out in October 2005, and passive samplers were selected to monitor some of the contaminants that might be present as a result of past and present industrial activity, including boat building, shipping and oil drilling. These pollutants potentially included metals (e.g. cadmium and mercury), organotin compounds (MBT, DBT and TBT) and PAHs. Chemcatchers for polar, non-polar organic pollutants, metals and organotins were deployed along with other sampling devices over a 5-week period. A number of sampling sites was selected along the estuary including Preston docks and a control site upstream of the tidal area. One aim of this trial was to demonstrate the value of these tools in comparison with standard monitoring methods used in the estuary. The estuary was an aggressive environment with high tidal flows, and episodic storm events carrying debris down the river. Some of the sampling devices were lost because of physical damage in which the moorings were dislodged and swept away. However, sufficient deployment rigs survived to allow the measurement of pollutants at four sites over the deployment period. An example that illustrates the utility of the samplers is provided by the measurements of TWA concentrations of cadmium along the estuary (Fig. 9.9). Masses of cadmium accumulated in the Chemcatchers were generally low. Concentrations upstream of the tidal area, in Preston docks and downstream of the dock appeared similar while the concentration in one sampler from the site in mid-estuary was significantly higher. Despite possible error in the estimation of uptake rates, R_S due to the uncertainty in the levels of turbulence at the different sites, the Chemcatcher samplers yielded more useful information than that provided by the routine spot sampling carried out over the period of the trial.

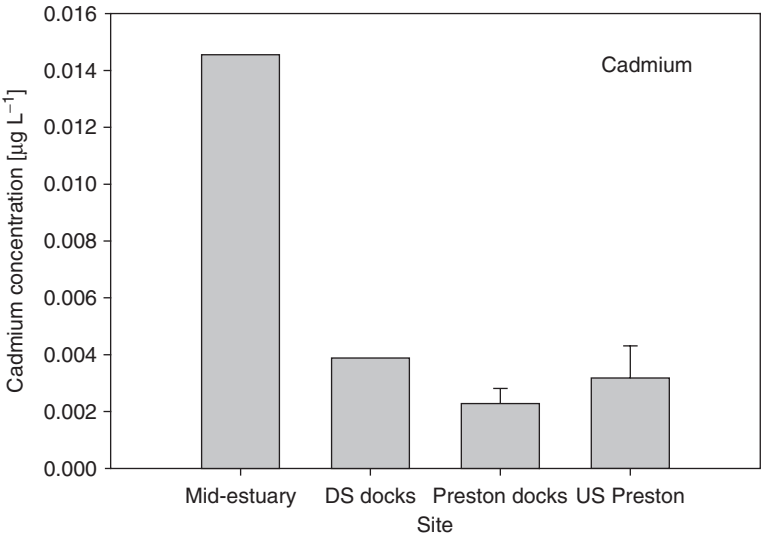

Fig. 9.9. TWA cadmium concentrations measured using the Chemcatcher passive sampler at various sites along the Ribble estuary. Data for the mid-estuary and DS docks sites are from a single sampler and data shown for Preston docks and upstream of Preston are the mean of two measurements (DS: downstream; US: upstream).

The standard monitoring by the Environment Agency for England and Wales was conducted on two occasions during the trial. Cadmium concentrations were found below limits of detection (LOD: 0.04 $\mu g\,L^{-1}$) for all sites monitored. This is in agreement with concentrations measured with Chemcatcher and emphasises the advantage of *in situ* time-integrative sampling over spot sampling in term of detection limits, since useful data that could be used in determining trends were obtained. This contrasts with the spot sampling where only categorical information (not detected) was obtained.

9.10 COMPARISON OF THE PERFORMANCE OF THE CHEMCATCHER WITH THAT OF OTHER SAMPLING DEVICES

The performances of passive samplers can be compared for a range of classes of pollutants, and evaluated alongside other methodologies. For example, calibration data for hydrophobic organic pollutants are available in the literature for SPMDs [22] and the MESCO sampling devices [23,24]. These devices differ in their design geometry and the materials

used in their construction. However, the sampling rate is directly proportional to the sampler functional surface area. Consequently, the highest sampling rates will be achieved with passive samplers having the largest surface area, such as the standard size SPMDs (450 cm^2 in comparison to 17.5 cm^2 for the Chemcatcher). It is therefore necessary to compare the performances on a surface area specific basis, i.e. with sampling rates expressed as volume of water cleared for a chemical, per unit time and unit surface area ($L\,day^{-1}\,cm^{-2}$). In making this comparison it is necessary to take into account reported variations in sampling rates with exposure conditions. Although the most calibration studies reported in the literature were performed in flow-through systems, they were not all conducted under identical conditions (temperature and turbulence). However, if these limitations are taken into account an approximate comparison of sampling rates can be made. The surface-specific sampling rates of three passive sampling devices (MESCO, SPMD and non-polar Chemcatcher) are similar for PAHs compounds with three and four aromatic rings, and range from 5 to 13 $mL\,day^{-1}\,cm^{-2}$. This indicates that the uptake of these compounds by the three different samplers is governed overall by a similar mass transfer process; this is most likely to be diffusion across the aqueous boundary layer.

A similar comparison can be made for the polar variant of Chemcatcher and the POCIS. The surface area of the standard configuration of POCIS is 41 cm^2 (see Chapter 8), in comparison with 17.5 cm^2 for the Chemcatcher. The two samplers are fitted with similar diffusion membrane materials, both are made of PES. The surface-specific sampling rates at room temperature for atrazine and simazine were approximately a factor 2 higher for the Chemcatcher than those reported by Alvarez (Table 8.4 in Chapter 8). This is a reasonable agreement, and the observed difference may be caused by differences in the calibration conditions for the two sets of samplers.

While for the metal version of Chemcatcher, uptake is limited by diffusion in water across the boundary layer and the CA membrane, for the DGT it is restricted by metal diffusion across the hydrogel and only minor effects of the boundary layer are reported [25]. For both samplers, free ions and organic/inorganic metal complexes are able to dissociate within the time required to cross the diffusion layers will accumulate and therefore the TWA concentration will be representative of these fractions. A major difference between these devices is the procedure for the calculation of TWA concentrations. While laboratory-based calibration data are used to calculate TWA concentrations with

the Chemcatcher, concentrations for DGT are obtained using known metal diffusivities for the hydrogel layer measured in the laboratory.

In order to evaluate the performance of the Chemcatcher and the DGT when responding to simulated peaks of metal concentrations, a 5-day tank experiment was conducted using Meuse river water. TWA concentrations were measured and compared with the equivalent concentrations from unfiltered, filtered (0.45 μm) and ultra-filtered (5 kDa) spot samples. Figure 9.10 shows a comparison of TWA concentrations measured by the Chemcatcher and the DGT, relative to spot sampling concentrations. While for Cd and Ni, the Chemcatcher slightly underestimates TWA concentrations, the DGT is in better agreement with filtered fractions of these metals. Similar results are obtained for both samplers for Zn and closest agreement is with the filtered fraction. For Cu, both samplers underestimate the filtered concentration while clearly overestimating the ultra-filtered fraction. Generally, results appear in agreement with the speciation of these metals under those conditions. Overall, TWA concentrations obtained using the Chemcatcher appear to have a slight bias as most data points are below the 1:1 relationship. This may be related to the selection of laboratory

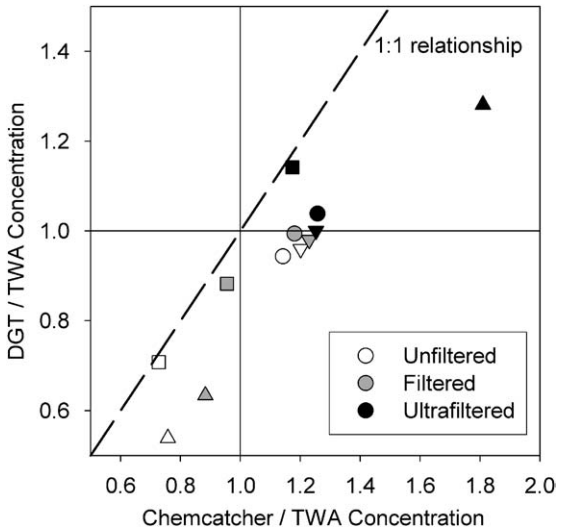

Fig. 9.10. Comparison of TWA Cd (O), Cu (Δ), Ni (▽) and Zn (□) concentrations measured by Chemcatcher and DGT relative to TWA concentrations (unfiltered, filtered (0.45 μm) and ultra-filtered (5 kDa)) measured by spot sampling during a 5-day long tank experiment with spiked metals simulating fluctuating concentrations in natural Meuse river water.

calibration data for set levels of temperature and turbulence that differ slightly from conditions observed during the experiment.

9.11 FUTURE TRENDS

The advantage of passive sampling over classical spot sampling is that it provides a measure of average conditions in a body of water over extended periods of time. This gives a more representative picture of water quality than a few instantaneous measurements of pollutant levels taken at intervals over a year. Monitoring programmes based on passive sampling will therefore provide better information on which to assess long-term trends in pollutant concentrations. For metal samplers, it is possible to obtain extra information on speciation that is pertinent to their bioavailability and potential toxicity [26,27] and hence underpin robust risk analysis. In order to facilitate recognition of the value of passive sampling, and its potential for underpinning legislation it is essential to demonstrate the validity of the method, and to develop standards for use in this field. One national standard (BSI PAS 61) [28] is available, and this covers the preparation, field deployment in surface waters and preparation for analysis of passive samplers. It is also important, however, to recognise the limitations of passive samplers, and to address some of the challenges laid down by these. One important challenge is the assessment of the impact of biofouling of the diffusion membrane on uptake rates. A further challenge is to develop sampler designs that can be used to detect and quantify peaks of concentrations during short but significant pollution events. This may be especially important for the measurement of, for example, intermittent industrial releases that may otherwise not be detected. Currently, it is difficult to assess whether an observed accumulation in a sampler is the result of a transient event or a lower but more constant concentration. In order to be able to interpret passive sampler data, particularly over the short-term deployments needed to detect peak episodic events, a better knowledge of observed lag phases between the appearance of a peak of contaminant concentration in water and its detection by a passive sampling device will be required to allow a clearer interpretation of passive sampling data.

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Chapter 10

Membrane-enclosed sorptive coating for the monitoring of organic compounds in water

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10.1 INTRODUCTION

Membrane-enclosed sorptive coating (MESCO) denotes the recently developed miniaturised passive sampling devices consisting of a membrane which encloses polydimethylsiloxane (PDMS) coatings or coarse silicone material (embedded in a fluid) as the collecting phase for organic compounds.[1] The general advantages of the MESCO samplers are (i) the simple and loss-free separation of the collector phase; (ii) its processing without further clean-up steps by direct thermal desorption or solvent microextraction; (iii) the possibility to spike the collecting phase before deployment with so-called performance reference compounds (PRCs) and (iv) that, in addition to chemical target or non-target analysis, the collecting phase can also be subject to biological effect screening (after digestion using an appropriate solvent).

In our work we took advantage of commercially available PDMS coatings or silicone materials as the collecting phase. PDMS is recommended as a receiving phase in extraction and thermodesorption as it has a number of benefits compared with other sorbents [1]. The predominant mechanism of analyte extraction into PDMS/silicone phase is absorptive partitioning which has the advantage that displacement effects of the analytes (competitive enrichment), characteristic for adsorbents, play no role.

[1]When neat silicone material is used as collecting phase instead of a sorptive coating, one can take the abbreviation MESCO also for membrane-enclosed silicone collector.

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The chapter gives an overview of theoretical aspects and design of the different MESCO sampler formats for water monitoring[2] and summarises our efforts to calibrate the samplers for several priority pollutants in laboratory studies and to test them under field conditions.

10.2 PASSIVE UPTAKE MODEL FOR MESCO SAMPLER

It has been shown that the amount of the chemical accumulated in the MESCO sampler from water with constant chemical composition can be described by the following equation [2]:

$$m_S(t) = m_0 + (C_W K_{SW} V_S - m_0)\left[1 - \exp\left(-\frac{k_{ov} A \alpha}{K_{SW} V_S} t\right)\right] \tag{10.1}$$

where m_S is the mass of analyte in the receiving phase (PDMS), m_0 is the amount of analyte in the sampler at the start of the exposure, C_W represents the water concentration during the deployment period, K_{SW} is the receiving phase/water distribution coefficient, V_S is the volume of the receiving phase, k_{ov} is the overall mass transfer coefficient, A is the membrane surface area, α is the pore area of the membrane as fraction of total membrane area (membrane porosity) and t equals time. α will be set to 1 for non-porous membranes. The coefficient in the exponential function is referred to as the overall exchange rate constant k_e:

$$k_e = \frac{k_{ov} A \alpha}{K_{SW} V_S} = \frac{R_S}{K_{SW} V_S} \tag{10.2}$$

where R_S is the sampling rate, expressing equivalent volume of water cleared of chemical per unit of time in the linear (integrative) uptake phase.

Adding standards (i.e. PRCs) to the receiving phase prior to exposure of the passive sampler has been suggested as a means to calibrate the exchange rates *in situ* [3,4]. When PRCs are used that are not present in water ($C_W = 0$), Eq. (10.1) reduces to

$$m_S(t) = m_0 \exp(-k_e t) \tag{10.3}$$

which is a one-parameter equation, because the amount of PRC added to the MESCO sampler (m_0) is known.

[2]Some other MESCO variants designed for monitoring semi-volatile organic compounds in air are described in Chapter 5.

10.3 DESIGN OF THE DIFFERENT MESCO FORMATS

10.3.1 PDMS-coated fibre enclosed in an LDPE membrane

As a precursor of the MESCO [5] we tested membrane bags (13×2.5 cm) of 100 μm thick low-density polyethylene (LDPE) tubing (Polymer-Synthesewerk Rheinberg, Germany), heat-sealed at both ends, in combination with a 100 μm PDMS-coated SPME fibre (Supelco, Deisenhofen, Germany) as collector phase ($V_S = 0.68$ μL) and 25 mL of a 40/60 isopropanol/water mixture (v/v) as inner fluid. LDPE is the membrane material also used in construction of SPMDs [6] and the PDMS-coated fibre is a rational tool for solid-phase microextraction of analytes from aqueous samples, and provides high enrichment factors for more hydrophobic substances [7]. Figure 10.1 shows the design of this permeation sampler. The coil spring (of stainless steel) prevents the fibre coating from a direct contact with the membrane. A serious shortcoming of this sampler is that the polymer-coated quartz glass fibre tip is fragile and difficult to handle during removal from and re-inserting into the steel needle of the commercial SPME syringe device.

10.3.2 PDMS-coated stir bar enclosed in a dialysis membrane bag (MESCO I)

This type, first described by Vrana *et al*. in 2001 [2,8], uses the PDMS-coated stir bar as collector phase. The stir bar is known under the trademark Twister^{TM} (Gerstel, Mülheim/Ruhr, Germany) and is commonly used for solvent-free microextraction using the same principle as

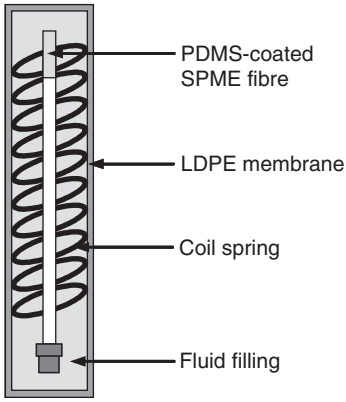

Fig. 10.1. Construction of MESCO precursor [5].

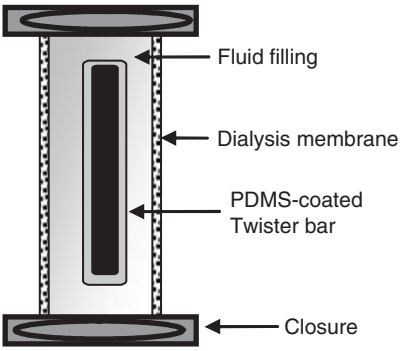

Fig. 10.2. Diagram of MESCO I [2].

an SPME fibre, but with a larger extraction capacity. Figure 10.2 shows a diagram of the sampler. Specifically, we tested dialysis membrane bags made of regenerated cellulose (Spectra/Por 6) with molecular weight cut-off of 1 kDa (3×1.8 cm), sealed at each end with a 35 mm Spectra/Por closure, in combination with Twister bars of 15 mm length coated with a 500-μm-thick layer of PDMS ($V_S = 24\,\mu L$) and 3 mL bi-distilled water as membrane bag filling. Regenerated cellulose is a porous hydrophilic membrane material that enables widening the applicability to a broader polarity range of pollutants, including low-hydrophobic substances ($\log K_{OW} < 4$). Unfortunately, this material has relatively low chemical and thermal stability and is subject to microbial degradation, which potentially leads to the damage of the sampler in natural surface waters during prolonged exposure of several weeks.

10.3.3 Silicone material enclosed in an LDPE membrane (MESCO II)

This sampler type combines [8,9] the advantages of a high-capacity collector phase with that of a more stable membrane material, LDPE. These membranes are hydrophobic, resistant to solvents and biodegradation and they can be heat-sealed. Furthermore, the relatively expensive and fragile Twister bar is substituted by a cheap silicone material (pieces of a tube or rod) as collector phase. Figure 10.3 shows the schematic design of the sampler. Additional investigations have shown the usefulness of these materials for an effective pre-concentration of several classes of persistent organic pollutants from water samples and the applicability of thermodesorption–GC–MS analogously to the processing of Twister bars [9,10]. The significantly enhanced volume of the collector phase

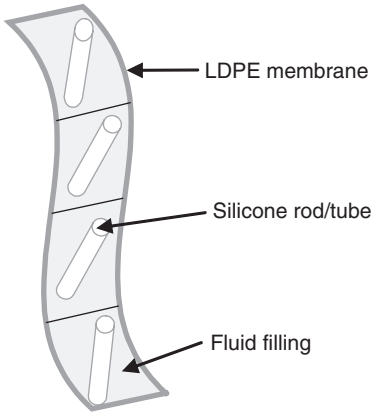

Fig. 10.3. Schematic design of MESCO II [8].

($>100\,\mu L$) increases the maximum exposure time of the passive sampler in the field. A practical drawback of silicone tubes, when used as collecting phase in combination with water as fluid filling, is that remaining water droplets (inside the tube) can disrupt the GC–MS analysis.

Since 2004 we have focused our work on improvement of the promising MESCO II format with silicone rods enclosed. Several thicknesses of LDPE membrane were tested as well as other membrane materials, such as the dense polypropylene bag, usually used for membrane-assisted solvent extraction of water samples in the laboratory [11]. Interestingly, it turns out in a preliminary laboratory study that this latter material is not useful for MESCO devices because it obviously prevents the transfer of substances to the inner receiving phase (silicone rod).

10.4 LABORATORY-DERIVED SAMPLING RATES OF THE VARIOUS MESCO FORMATS

The performance of the PDMS-coated fibre in LDPE membrane bag (MESCO precursor) was tested by time-dependent exposure in a flow-through system [2] at 19°C (upstream flow: 36 $L\,h^{-1}$; nominal water concentration for each test substance: 50 $ng\,L^{-1}$; exposure times: up to 360 h). The sampling rates obtained are summarised in the second column of Table 10.1 (for details of SPME fibre desorption and gas chromatographic analysis see Ref. [7]).

MESCO I samplers were also tested in this flow-through apparatus (under the same conditions as above; see Ref. [2] for experimental

TABLE 10.1

Sampling rates (R_S) of the two early MESCO formats in comparison with that of a standard SPMD for selected priority pollutants

Substance	R_S of SPMD ($mL\,h^{-1}$)[a]	R_S of MESCO precursor ($mL\,h^{-1}$)[b]	R_S of MESCO I ($mL\,h^{-1}$)[b]
α-HCH[c]	108	0.0005	0.40
Hexachlorobenzene	58	0.0022	0.25
Anthracene	150	0.0014	0.22
Fluoranthene	188	0.0015	0.25
Pyrene	217	0.0012	0.27
Benzo[a]anthracene	133	0.0009	0.37
PCB 28[c]	350	0.0070	0.15
PCB 52	258	0.0088	0.15
PCB 101	258	0.0063	0.13
PCB 138	200	0.0046	0.09
PCB 153	133	0.0031	0.10

[a]At 18°C for α-HCH, hexachlorobenzene and the polyaromatic hydrocarbons, at 12°C for PCBs; taken from Ref. [12].
[b]At 19°C.
[c]Substance abbreviations: HCH—hexachlorocyclohexane; PCB—polychlorinated biphenyl.

details). The determined sampling rates are given in the last column of Table 10.1.

Due to its much larger sampling capacity, the standard SPMD (of 450 cm^2 surface area) has up to five orders of magnitude higher sampling rates than the MESCO formats tested. But one should bear in mind that the substances trapped in the PDMS coating (of an SPME fibre or a Twister bar) are, in contrast to that sampled using an SPMD, transferred quantitatively to the injector of the analytical instrument. This prevents, at similar sampling sensitivity, possible volumetric dilution errors but has on the other hand the disadvantage of having only ''one shot'' per sampler specimen that can be overcome only by multiple exposure of samplers (as a MESCO string). Further flow-through calibration experiments showed that the sampling rates in MESCO I were not significantly affected by the flow velocity, within the tested range of exposure conditions [2,13].

Different configurations of the MESCO II sampler were exposed to spiked water in a similar flow-through system at 14°C (upstream flow: 60 $L\,h^{-1}$; nominal concentration: 50 $ng\,L^{-1}$ for each test chemical; exposure times: up to 176/236 h). The membrane bags (5 cm × 3 cm) consisted of 100 μm thick LDPE tubing (Polymer-Synthesewerk Rheinberg,

Germany). Four cm long pieces of silicone tube (with 3.6 mm O.D., 3.0 mm I.D.; Reichelt, Heidelberg, Germany) or 4-cm-long pieces of silicone rod (2.0 mm O.D., Goodfellow, Bad Nauheim, Germany) were used as collector phase. The silicone material was embedded in 8 mL water in one series of experiments or in air for another series (see Ref. [9] for further experimental details). The sampling rates calculated from the accumulated analyte mass are given in Table 10.2. Remarkably higher R_S values (in the same order of magnitude as those obtained for MESCO I) were obtained with air as fluid filling of the membrane bags. This can be explained by a detailed consideration of the mass-transfer resistances [9]. Tube and rod material yielded similar results but the variances in R_S were lower for the tube-containing sampler.

Recently, we determined preliminary sampling rates for new MESCO II sampler formats in rapid semi-continuous batch extraction tests [14]. These consisted of lay-flat membrane strips, 15×3 cm of the 100 μm thick membrane or 8×4 cm of that with 50 μm wall thickness. The strips were segmented by heat-sealing into four or two uniform parts, respectively. Each segment (2 cm long) contained a 15 mm long piece of pre-conditioned SR ''embedded'' in air. Such an SR piece is equivalent to 47 μL of receiving phase. These data are given in Table 10.2. There is a reasonably good agreement with R_S values obtained in the previous study. Additional flow-through experiments are in progress to investigate the influence of temperature and water flow on the sampling rates of these inexpensive MESCO variants and to test the applicability of the PRC concept for R_S adjustment to varying sampling conditions.

10.5 FIELD APPLICATION OF MESCO SAMPLERS

10.5.1 A case study with MESCO I for monitoring of persistent organic pollutants in surface water

10.5.1.1 Sampling site

To assess the performance of MESCO for monitoring persistent organic pollutants (POPs) in the field, samplers were exposed in water at a site located in the river Weisse Elster at the locality Halle-Burgholz in Saxony-Anhalt, Germany, close to the confluence of the River Weisse Elster with the River Saale (51°25′10″N; 11°59′47″E, estimated using Google Earth). Three MESCOs were deployed at the sampling site for 28 days during summer 2002 (24th July–21st August). The last two weeks of sampler exposure coincided with the major flood that occurred

TABLE 10.2

Sampling rates (R_S) of different MESCO II configurations (SR—silicone rod; ST—silicone tube) for selected priority pollutants determined in various laboratory experiments

Substance	R_S of SR+water in 100 µm LDPE[a] ($mL\,h^{-1}$)	R_S of ST+water in 100 µm LDPE[a] ($mL\,h^{-1}$)	R_S of ST+air in 100 µm LDPE[a] ($mL\,h^{-1}$)	R_S of SR+air in 100 µm LDPE[b] ($mL\,h^{-1}$)	R_S of SR+air in 50 µm LDPE[b] ($mL\,h^{-1}$)
α-HCH[c]	0.28	0.18	0.14	0.031[d]	0.039[d]
1,2,3,4-TCB[c]	*not det.*[e]	*not det.*[e]	*not det.*[e]	1.47	0.61
Pentachlorobenzene	0.21	0.19	4.30	1.30	2.24
Hexachlorobenzene	0.09	0.06	0.90	0.65	0.87
Naphthalene	*not det.*[e]	*not det.*[e]	*not det.*[e]	0.13[d]	*not det.*[e]
Acenaphthylene	0.51	0.73	1.40	0.07[d]	*not det.*[e]
Acenaphthene	0.48	0.67	2.23	0.35	*not det.*[e]
Fluorene	0.75	1.34	1.88	0.49	*not det.*[e]
Phenanthrene	0.26	0.27	0.93	0.63	0.72
Anthracene	0.13	0.26	0.99	0.40	0.83
Fluoranthene	0.04	0.06	0.12	0.33	0.26
Pyrene	0.03	0.03	0.10	0.26	0.23
PCB 28[c]	0.06	0.06	0.92	0.74	0.63
PCB 52	0.03	0.04	0.62	0.66	4.12[f]
PCB 101	0.004	*not det.*[e]	*not det.*[e]	0.39	*not det.*[e]
PCB 138	*not det.*[e]	*not det.*[e]	*not det.*[e]	0.14	0.05
PCB 153	*not det.*[e]	*not det.*[e]	*not det.*[e]	0.15	0.05

[a]Determined in a flow-through apparatus with a nominal analyte concentration of $50\,ng\,L^{-1}$ at 14°C [9].
[b]Determined in serial batch extraction tests with a nominal analyte concentration of $25\,ng\,L^{-1}$ at room temperature [14].
[c]Substance abbreviations: HCH—hexachlorocyclohexane; TCB—tetrachlorobenzene; PCB—polychlorinated biphenyl.
[d]Distribution constant ($K_{SW} = C_{MESCO}(eq.)/C_{W}(eq.)$) calculated by assuming that $C_{W}(eq.) = 25\,ng\,L^{-1}$.
[e]Not determined.
[f]Potential outlier.

in the river basins of Elbe and Danube in Central Europe in August 2002. A local flood event was observed also at the Weisse Elster, accompanied with the rise in water level up to 2 m against the typical summer average. The samplers were retrieved after the flood wave retreated. During the exposure, the water temperature at the sampling site varied from 19 to 22°C.

10.5.1.2 Target pollutants

The analytes included several groups of POPs: γ-hexachlorocyclohexane (γ-HCH), hexachlorobenzene (HCB), 2,2′-bis(4-chlorophenyl)-1,1′-dichloroethylene (DDE), selected polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). The K_{SW} values, needed in further data evaluation, were approximated by PDMS/water distribution coefficients from the literature and were reported previously [13].

10.5.1.3 Sampler preparation

MESCO I preparation has been described in detail elsewhere [2,13]. Briefly, the cleaned and conditioned Twister stir bar was pre-loaded with six PRCs: $^2H_{10}$-biphenyl (D_{10}-BIP), $^2H_{10}$-phenanthrene (D_{10}-PHE), $^2H_{10}$-anthracene (D_{10}-ANT), $^2H_{10}$-fluoranthene (D_{10}-FLT), $^2H_{10}$-pyrene (D_{10}-PYR) and $^2H_{12}$-benzo[a]anthracene (D_{12}-BaA). This was performed by stirring the Twister bar for 30 min at 1000 min^{-1} at room temperature in 25 mL of solution containing 1 $\mu g L^{-1}$ of each PRC. For sampler assembly, the Twister bar was placed inside a dialysis membrane bag. The bag was filled with 3 mL of bi-distilled water and sealed at each end with 35 mm Spectra Por closures.

Four control samplers were prepared together with the three field-deployed samplers; these were stored in the laboratory at −20°C until analysis. Controls were processed exactly as deployed samplers and were used to define contamination during preparation and storage, and to determine nominal PRC concentrations in MESCO samplers.

10.5.1.4 Sampler deployment and retrieval

On the day of deployment, MESCOs were freshly prepared in the laboratory and transported to the field in amber glass jars filled with bi-distilled water to prevent drying of the dialysis membrane during transport. At the sampling site, MESCOs were removed from the jars and placed into a protective deployment device designed for sampling using SPMDs. The deployment device was a canister made of perforated stainless steel sheet (5 mm openings), containing five racks designed for holding standard length SPMDs. One of these carriers was used to hold

the MESCOs. Three SPMDs with standard configuration (2.54 × 91.4 cm, 75–90 μm membrane thickness, total mass 4.3 g each) were exposed next to MESCOs, in the same deployment device. Before exposure, SPMDs were spiked with PRCs (10 μg/SPMD of each standard) as described earlier [15]. The deployment device protected MESCOs and SPMDs from abrasion and the sequestered pollutants from sunlight. The canister was held at depth of approximately 1 m below surface using a buoy, rope and anchor, and was secured to the shore with a rope.

On day 28, samplers were removed from the deployment device and checked visually for mechanical damage. Although disintegration (mechanical or biological degradation) of the cellulose bags occurred during the exposure of MESCOs, the Twister bars were found to be intact, sticking by their magnets to the inner surface of the deployment canister. The Twister bars were dried using a soft paper tissue, transferred using clean forceps to GC vials (2 mL), sealed and transported to the laboratory in a portable icebox (on ice and in darkness) and stored at −20°C till analysis. Field exposed samplers were analysed together with the control samplers.

10.5.1.5 Sampler processing and analysis

The quantification of the compounds accumulated during field exposure on Twister bars of the MESCO samplers was carried out as described previously [2,13]. Briefly, analyses were performed on an Agilent Technologies (Palo Alto, CA, USA) GC 6890 with MSD 5973N system equipped with a Gerstel (Mülheim/Ruhr, Germany) thermodesorption system TDS A and a cold injection system CIS-4 from Gerstel with an empty liner that was used for cryofocusing the analytes prior to the transfer onto the analytical column. The single ion monitoring (SIM) mode of the mass selective detector applying one or two characteristic ions per compound was chosen for the detection. Quantification of target substances sorbed on Twister bars was accomplished using a five-point external standard curve. Method quantification limit for the analytes under investigation ranged from 1 to 5 pg per Twister.

Details of SPMD processing were described earlier [15,16]. SPMD data evaluation was performed using the empirical uptake model derived by Huckins *et al*. [17].

10.5.1.6 Accumulated amount of water pollutants

Table 10.3 shows the mass of each target analyte accumulated in the MESCOs during a 28-day field deployment. Quantifiable amounts of all target analytes were found in field-exposed samplers. Control blanks

TABLE 10.3

Average mass of pollutants (in pg per Twister bar) determined in the control MESCOs (m_0) and in the field-exposed MESCOs (m_S; $n = 3$), and *in situ* aqueous concentrations of organic analytes estimated from MESCO (C_W)

Compound	m_0 (pg)	CV[a] ($n = 4$) (%)	m_s (pg)	CV ($n = 3$) (%)	k_e (day^{-1})	C_W ($ng\,L^{-1}$)
HCB	1	13	79	2	0.085	0.14
γ-HCH	1.8		1695	27	0.130	182
p,p'-DDE	<1		132	8	0.069	0.03
PCB 28	1	16	62	7	0.077	0.05
PCB 52	<1		43	6	0.072	0.02
PCB 101	<1		27	12	0.065	0.004
PCB 138	<1		33	5	0.062	0.003
PCB 153	<1		22	9	0.062	0.002
PCB 180	<1		8	10	0.064	0.001
Acenaphthylene	4	45	124	11	0.107	2.16
Acenaphthene	10	10	1172	3	0.102	12.2
Fluorene	18	9	1128	4	0.100	9.76
Anthracene	8	30	1494	9	0.094	7.03
Phenanthrene	62	30	3128	7	0.094	15.4
Fluoranthene	13	30	3135	8	0.079	2.86
Pyrene	13	15	3302	8	0.076	2.16
Benzo[a]anthracene	2	76	1185	3	0.069	0.32
Chrysene	4	42	967	2	0.063	0.10
Benzo[b]fluoranthene	<5		450	1	0.071	0.15
Benzo[k]fluoranthene	<5		244	3	0.068	0.06
Benzo[a]pyrene	<5		455	4	0.067	0.09
Indeno[1,2,3-cd]pyrene	<5		121	7	0.087	0.29
Dibenzo[a,h]anthracene	<5		46	10	0.084	0.03
Benzo[g,h,i]perylene	<5		115	10	0.076	0.20

The samplers were exposed 28 days in August 2002 at a site in the river Weisse Elster in Saxony-Anhalt, Germany.
[a]CV, coefficient of variation or relative standard deviation of multiple samples.

contained quantifiable amounts of lindane, PCB 28 and PAHs with up to four aromatic rings. Nevertheless, analyte levels found in field exposed samplers were in all cases significantly higher than those in control blanks. The variation of the masses recovered from three replicate field exposed devices ranged from 1% (benzo[b]fluoranthene) to 27% (lindane). This is an excellent precision despite the degradation of the protective cellulose membranes of the MESCOs during exposure.

10.5.1.7 In situ exchange kinetics from PRC offload

Our previous investigations have shown that both uptake and elimination of a particular compound in MESCO I are characterised by the same exchange rate constant k_e, according to Eq. (10.1) [13]. The use of PRCs allowed a two-point estimation of the first-order exchange rate constants k_e. These were calculated from the rearranged Eq. (10.3) using mean values (from replicate samples) of the PRC amounts found in field exposed samplers (m_S) and in the controls (m_0) and exposure time of 28 days:

$$k_e = \frac{\ln(m_0/m_S)}{t} \tag{10.4}$$

The calculated k_e values ranged from 0.072 day^{-1} (D_{10}-PYR) to 0.126 day^{-1} (D_{10}-BIP). Student's t-test ($\alpha = 0.05$) was performed to ensure that changes in PRC residue concentrations were statistically significant, according to the law of error propagation. This was the case for all PRCs excepting D_{12}-BaA with no significant offload during exposure.

The field-derived k_e values were two to three times higher than those reported in a laboratory calibration study [13]. This indicates faster exchange kinetics at the sampling site than those observed under laboratory conditions. The temperature at the sampling site during the field study was similar to that in the calibration study. Although this investigation [13] indicated that the flow velocity had no significant effect on the exchange kinetics, this was tested only at low velocities. The flow around the cage with samplers in the field was much faster than the simulated flow in the calibration apparatus, and the increased water turbulence might have affected the analyte mass transfer between water body and samplers, despite the buffering effect of the protective cage. The elevated exchange kinetics can also be explained by degradation of cellulose membranes during the field exposure, resulting in a significant loss of resistance to analyte exchange between Twister and water.

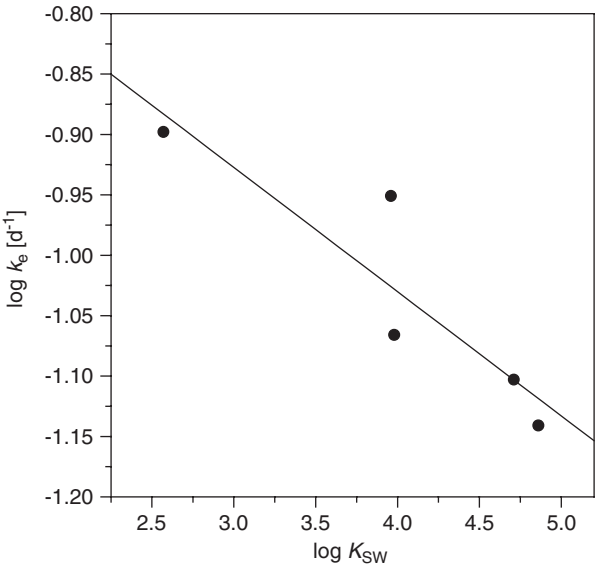

Fig. 10.4. Correlation between estimated *in situ* exchange rate constants k_e and PDMS/water distribution constant K_{SW}. The sampling using MESCO I was performed in August 2002 in the river Weisse Elster near confluence with River Saale.

The substance-specific k_e values were estimated from the linear correlation between log k_e and log K_{SW} (Fig. 10.4):

$$\log k_e = -0.6187 - 0.1029 \log K_{SW}$$
$$(n = 5, s = 0.05, r = 0.904) \qquad (10.5)$$

The estimated *in situ* k_e values of target analytes are shown in Table 10.3.

10.5.1.8 Sampling-mode considerations

The knowledge of *in situ* k_e values enables to estimate the percentage of sampler saturation with target analytes after 28 days of exposure, when a constant pollutant concentration in the river water is assumed. This can be calculated as $(1-\exp(-k_e\ t)) \times 100\%$ and shows that the accumulated concentrations of target analytes approached 83–97% of partitioning equilibrium, determined by the magnitude of the PDMS/water distribution constant K_{SW} (Fig. 10.5). The sampler exposure seems to have exceeded the maximum time period allowing time-weighted average (TWA) sampling, which lasts approximately until the sampler approaches

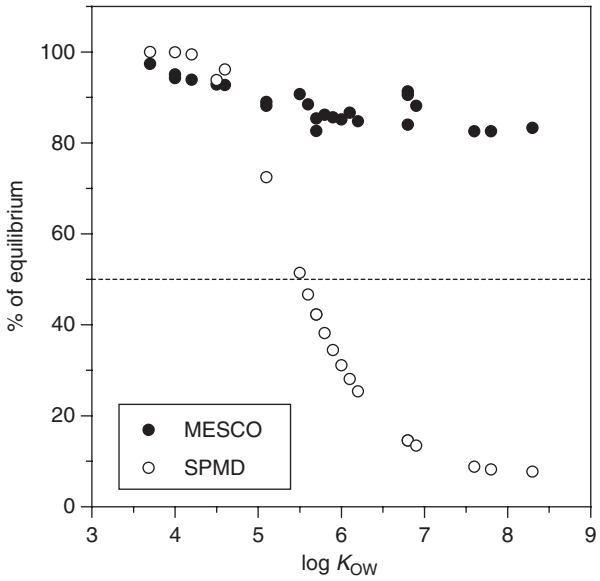

Fig. 10.5. Percentage of target–analyte equilibration between passive samplers and water as dependent from their hydrophobicity (expressed as log K_{OW}) after 28 days of field exposure in the river Weisse Elster. The dashed line indicates the maximum limit of saturation (50%) permitting a time-integrative sampling.

half-saturation. The prolonged field exposure was due to the flood event that made it impossible to retrieve the samplers any earlier.

A comparison of percentage of sampler saturation with target analytes in MESCO and a standard-size SPMD shows that after 28 days of exposure, partitioning equilibrium was reached in both samplers for compounds with log $K_{OW} < 4.5$ (Fig. 10.5). Compounds with log $K_{OW} > 5.5$ have not exceeded half-saturation in SPMDs. This indicates that SPMDs sampled those compounds in time-integrative mode.

In contrast, all compounds have likely exceeded the half-saturation in MESCO samplers (Fig. 10.5). Thus, after 28 days, MESCO was in the curvilinear or equilibrium sampling phase. This is caused by the fact that MESCO has much lower absorption capacity than SPMD, due to its very small receiving-phase volume. The calculation of saturation halftime $t_{1/2} = \ln 2/k_e$ shows that the MESCO remained in the linear or integrative uptake phase during the first two weeks of exposure for most of the analytes under investigation. This information is valuable for further method validation, indicating that field exposures using MESCO I in warm and turbulent water should not exceed two weeks,

if the study is aimed the estimation of TWA concentrations. Two weeks seems to be also a compromise time period during which no degradation of the cellulose membrane is expected.

10.5.1.9 Estimate of ambient aqueous concentrations

As a consequence of the different exchange kinetics between the field study and laboratory experiments, a direct application of laboratory-derived calibration data for calculation of ambient aqueous concentrations of target analytes was not appropriate in this particular case. Nevertheless, the calculation of aqueous concentrations was performed using Eq. (10.1), knowing the necessary substance-specific parameters k_e and K_{SW}:

$$C_W = \frac{m_s - m_0}{K_{SW} V_S [1 - \exp(-k_e t)]} \tag{10.6}$$

The estimated aqueous concentrations are shown in Table 10.3. They range from $1\,\mathrm{pg\,L^{-1}}$ (PCB 180) to more than $180\,\mathrm{ng\,L^{-1}}$ (lindane), demonstrating that MESCO allows for *in situ* measurement of very low contaminant levels. It is important to stress that the calculated aqueous concentrations are an estimate of the truly dissolved fraction present in water as shown by Garcia-Falcon *et al*. [18]. The sampling-mode considerations indicate that the calculated values in this particular study did not provide an accurate TWA concentration estimate, nevertheless, MESCO I has a great potential for time-integrative sampling, provided the deployment period is restricted to a shorter time.

10.5.1.10 Comparison of MESCO I with SPMD

Figure 10.6 shows a comparison of aqueous concentrations of PAHs estimated from analyte amounts accumulated in MESCOs and SPMDs during a 28-day field deployment. Both methods provide information on a dissolved fraction of analytes, enabling a direct comparison of results obtained using the two approaches. Aqueous concentrations estimated using both methods showed similar patterns, with higher levels of less hydrophobic light PAHs (with four and less aromatic rings) and low concentrations of more hydrophobic, heavy (less water soluble PAHs with five and more aromatic rings). MESCO-derived aqueous concentrations of light PAHs were higher than those derived from SPMDs. The opposite trend was observed for heavy PAHs.

There may be various sources of differences in absolute values calculated using the two methods. First, neither of the two methods provided accurate estimates of TWA concentrations for light PAHs, because both samplers nearly approached partitioning equilibrium. Thus, values

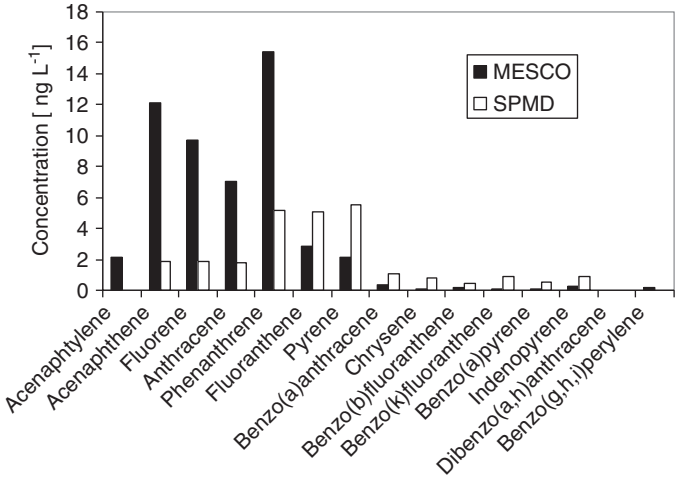

Fig. 10.6. Comparison of aqueous concentrations of PAHs at the sampling site in the river Weisse Elster (August 2002), estimated using two passive sampling approaches.

calculated for these compounds reflect also short-term (from the last week of exposure or so) fluctuations in concentrations, rather than the representative time-weighted mean. Further, SPMD-derived concentrations of heavy PAHs provide a qualitatively better estimate of TWA than those derived from MESCO (see Section 10.5.1.9). Finally, calculations of MESCO-derived concentrations relied on accuracy of K_{SW} values reported in literature. There is only a limited number of studies that provide these values and relatively high risk that some of them may be biased.

Nevertheless, we believe that the two passive sampling methods provide a more representative picture of the water quality than occasional spot sampling. Moreover, with the use of MESCO II devices some disadvantages of the foregoing MESCO format (underestimation of very hydrophobic compounds, possible disintegration of sampler due to membrane degradation during longer exposure) can be prevented although this, in turn, sets other restrictions, especially with respect to more polar target substances which will not be accumulated due to their low permeability in the non-porous and hydrophobic LDPE membrane envelope.

10.5.2 Field trials with MESCO II—first results

Since 2004, water monitoring using MESCO II strips (SR+air) alongside other passive samplers (SPMDs, bare silicone rods and Chemcatcher)

was carried out at several sites in three rivers in Germany (Elbe, Saale, Mulde) and additionally in the Spittelwasser creek, a tributary to the Mulde river near Bitterfeld, an area heavily polluted by chemical industry during the last 100 years. The major goal of these trials was to test the field performance of MESCO II devices under different ambient conditions (regarding water flow and temperature, hydrochemistry and biological activity). Similar to the Twister bars, the silicone rod pieces were spiked with PRCs before sampler assembly in order to adjust the laboratory-derived sampling rates to *in situ* conditions. The data evaluation for these field campaigns is still under way.

As an example we present results obtained for HCB in the Spittelwasser near Jessnitz (at the site 51°41′28″N; 12°17′25″E, estimated using Google Earth) during Summer 2005. MESCO II strips with 50 and 100 μm LPDE membrane thickness, respectively, were tested in two different deployment devices, i.e. in a wide-mesh protective grid and in a long narrow perforated cage as used for SPMDs. The samplers were exposed for 28 days and TWA concentrations were estimated from the amounts accumulated using the sampling rates listed in Table 10.2. Figure 10.7 shows the TWA concentrations against snapshot results obtained every two weeks from grab samples pre-concentrated by SPME and analysed using GC-MS (for analytical details see Ref. [14]). The correspondence between the results of the different sampling strategies is remarkable, especially if one bears in mind that the evaluation of MESCO data is based on preliminary sampling rates from a rapid semi-continuous laboratory calibration test. Figure 10.7 also shows a slight influence of hydrodynamics on the HCB accumulation. Reduced flow in the cage seemed to have lowered the substance uptake into MESCO samplers. This aspect is currently under investigation in flow-through experiments.

Also from another monitoring exercise, the field trial in the Meuse river in Eijsden (The Netherlands) which was organised in April–May 2005 within the framework of the EU project SWIFT-WFD [19], interesting results are expected on the field performance of MESCO I and II devices in comparison to other passive sampler formats that were applied [20].

Currently, field trials are in progress in the region of Bitterfeld (Saxony-Anhalt, Germany) with miniaturised MESCO II strips for time-integrative and depth-oriented monitoring of groundwater wells. The first results show that silicone rods enclosed in LDPE membrane are even able to accumulate volatile organic compounds such as 1,4-dichlorobenzene over several weeks. A comparison of substance amounts accumulated with the water concentrations obtained from parallel exposed passive diffusion

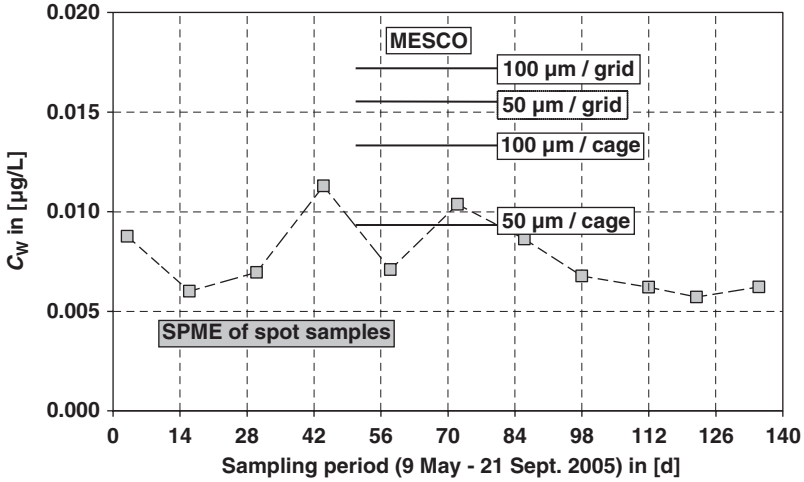

Fig. 10.7. Comparison of aqueous concentrations of HCB in the Spittelwasser creek (Summer 2005), obtained from analyses of snapshot samples and from passive sampling with MESCO II samplers made using different LDPE membranes (either 100 or 50 µm thick), deployed in wide-mesh protective stainless steel grids or in perforated cages as usually used for SPMDs, respectively.

bags [21] will allow the estimation of *in situ* sampling rates and/or distribution constants for such analytes with the MESCO II sampler. More work is needed, both in field and laboratory, to screen the spectrum of more volatile compounds to be monitored and to determine the period for time-integrative sampling.

ACKNOWLEDGMENTS

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29 Passive sampling: chemical analysis and toxicological profiling

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29.1 Introduction

Organic pollutants are often present in the water column at trace concentrations that are difficult to detect when conventional low volume spot sampling of water is applied. The scope of the sampling campaign performed using passive samplers was the screening of trace organic pollutants and their toxic potentials in the water column of the Danube, as well as the assessment of their spatial distribution along the river.

Freely dissolved concentrations of priority substances in the water phase (c_{free}) can be derived from the uptake of these substances by passive samplers, and because accumulated contaminants represent a large water volume, low limits of quantification can be obtained. C_{free} is a more stable parameter than a concentration measured in whole water as the level is not influenced by variable amounts of the substance bound to dissolved and suspended particulate organic matter. Thus, it is very suitable for assessment of trends. C_{free} is further considered to play a key role in chemical uptake by aquatic organisms. It is proportional to the chemical activity (Mayer et al., 2003) and if in equilibrium with surrounding environmental compartments it also represents chemical activity of those environmental compartments, including the biota at the base of the food chain (Reichenberg and Mayer, 2006).

We used an "active" passive sampling system (APS) for temporally and spatially integrative sampling of trace organic pollutants. APS is used in a concept similar to that of a Ferry-Box ("Website of the European Ferrybox Community," 2014) to obtain a representative picture of pollution situation along defined stretches or transects of large water bodies including rivers, lakes or seas. The uptake principle in the APS remains the same as in classical static passive sampling and the monitoring results can be evaluated using usual passive sampler calibration parameters. The APS enhances the uptake rate of contaminants into passive samplers, thereby allowing to drastically reduce the exposure time needed for accumulation of sufficient chemicals for analysis.

The application of temporal- and spatial- integrative passive sampling approach resulted in samples that provide a representative picture of pollution situation in eight defined stretches of the Danube River.

29.2 Methods

29.2.1 Passive samplers

Three types of passive samplers were applied: two partitioning samplers for hydrophobic compounds (silicone rubber (SR) and low density polyethylene (LDPE) sheets), and an adsorption sampler for polar compounds based on styrene-divinylbenzene solid phase extraction disks, SDB-RPS Empore disks (ED), respectively.

The SR sampler consisted of a single Altesil® SR sheet with dimensions 14×28 cm and 0.5 mm thickness. The mass of a sampler was cca 23 g and the surface area exposed to water was 392 cm^2 (one side of the sheet). SR samplers (except those intended for the ecotoxicological analysis) were spiked

prior to exposure with a number of Performance Reference Compounds (PRCs) that are partially released during exposure. The residual concentration of PRC is compared with the initial amount of PRCs analysed in samplers that have not been exposed.

The LDPE sampler consisted of two strips 4×28 cm and 80 µm thickness (cut from 2.5 cm wide lay-flat LDPE tubing from Brentwood Plastics Inc, St. Louis, USA). LDPE samplers were also spiked with PRCs and were used for chemical analysis only.

The ED sampler consisted of 10 solid phase extraction disks Empore® SDB-RPS with 47 mm diameter. The mass of a sampler was cca 3.2 g and the surface area exposed to water was 173 cm^2. Before exposure samplers were pre-conditioned and kept immersed in MilliQ water until exposure. These samplers were not spiked with PRCs.

29.2.2 Sampling operation

The "active" passive sampling system was installed on board of the expedition ship Argus to obtain enhanced passive sampler uptake rates in order to achieve sufficient sensitivity despite the short time available for sampling.

The APS device consists of a rectangular stainless steel plate box. During operation the box remained open from two sides and it was fully immersed in water. One end of the box was connected to a submersible pump (cca 9 m^3 h^{-1}) that forced water at high flow velocity (1-2 m s^{-1}) through the exposure chamber. A submersible temperature and light intensity logger was attached to the box during the entire cruise. Two parallel APS devices were in operation during each sampling period. The samplers exposed in one device were used for chemical analysis, and those from the other one for ecotoxicological analysis, respectively.

The APS device was deployed on the frontal deck of the Argus. For sampling, the device was immersed in a flow-through system that consisted of a 600 l stainless steel tank. The river water in the tank was exchanged at a rate cca 3 m^3 h^{-1} by a high performance pump. The water intake to the chamber was by a vertical steel pipe positioned in front of the ship. The water sampling depth was cca 0.5 m below the water level.

The device was operated only during the cruising of the ship or when the ship anchored outside harbours (e.g. for sampling) in areas not visibly impacted by point sources of pollution, e.g. discharge pipes, industrial areas next to the river, oil film visible on the water surface. The device was switched off before the ship entered harbours and switched on again when the cruise resumed. Samplers were mounted to the APS device just before exposure and removed immediately after recovery. The recovered samplers were placed back into their storage containers. They were stored in a refrigerator at 4°C on board of the ship and transported to the processing laboratory once per week, where they were stored in a freezer at -20°C.

Each individual water sampling period took approximately 5 days. During this period ship moved downstream along a defined stretch. The obtained sample contained water pollutants integrated in time and space along that stretch. Samplers were exchanged every 5 days, which resulted in total of eight samples of each type (SR, LDPE and ED) representing eight stretches of the Danube (Table 89). Sampling periods were planned so that exposure was avoided during days when ships stopped in harbours for one day or longer.

Table 89: River stretches sampled with passive samplers deployed from the Argus ship

Stretch number	Stretch start and end	River km	Dates of cruise	Mean water temperature [°C]	Exposure time [d]	Volume extracted by SR [l][1]
1[2]	Regensburg-Passau	2375-2225	13.8.-16.8.	-	-	-
2	Passau-Bratislava	2203-1852	17.8.-22.8.	21.3	2.0	169
3	Bratislava-Budapest	1852-1632	22.8.-26.8.	22.0	1.2	84
4	Budapest-Vukovar	1648-1297	26.8.-2.9.	21.9	1.7	139
5	Vukovar-Belgrade	1297-1154	2.9.-6.9.	22.8	1.6	133
6	Belgrade-Turnu-Severin	1154-930	6.9.-10.9.	22.1	2.0	139
7	Turnu-Severin-Ruse	930-495	11.9.-17.9.	21.9	2.0	129
8	Ruse-Braila	495-170	17.9.-21.9.	19.2	1.4	79
9	Braila-Tulcea	170-71	21.9.-26.9.	18.7	1.3	72

[1] Volume of water extracted by the SR sampler during exposure; it is calculated for a model compound with molecular mass of 300.
[2]The stretch from Regensburg to Passau was not sampled due to initial technical difficulties with sampler installation.

29.2.3 Sample processing

SR samplers (except those intended for the ecotoxicological analysis) were spiked with recovery internal standards. Compounds sorbed in the SR sheet were extracted for 8 hours in methanol using Soxhlet extraction. The volume of the extract was reduced using Kuderna-Danish (K-D) apparatus and under nitrogen flow to a volume of 2 ml. For ecotoxicological analyses, the sample in methanol was divided to aliquots for different types of bioassays. For chemical analyses, a 20% aliquot of the sample was used for instrumental analysis by LC/MS methods. The remaining 80% aliquot of samples for chemical analysis was azeotropically transferred to hexane using K-D apparatus. Aliquots of the extract were divided into vials for different types of GC/MS analysis. The extract aliquots for analysis of PAHs were further cleaned-up by a silica gel column clean up step using diethylether/acetone elution. The extract aliquots for analysis of organochlorine compounds (OCs), PCBs, BDE and PRCs were purified by a cleanup using activated silica gel modified with sulphuric acid. Following cleanup, addition of internal standards and volume reduction using a K-D apparatus, samples were analysed using a GC-MS/MS method for indicator PCBs, BDEs, OCPs and PRCs.

LDPE samplers, including trip controls, were extracted twice by soaking overnight with *n*-pentane (100 ml). Recovery standards (deuterated PAHs and PCBs that do not occur in the environment) were added to the extraction jar during the first extraction. The volume of pentane was reduced to 2 ml by a gentle stream of nitrogen at room temperature.

Extracts were split into two, with one fraction kept for non-target screening. For target analyses, extracts were first split into two equal fractions by volume. One fraction received a general clean-up using gel permeation chromatography (GPC). This post GPC sample was again split into two equal fractions by volume; the first of these was reduced in volume using nitrogen and analysed for PAH; the second received treatment with 2 × 1 ml concentrated sulphuric acid, was reduced in volume, and analysed for PCBs and OCs (Allan et al., 2013).

For non-target analyses, the extracts from samplers without PRCs were reduced by a gentle stream of nitrogen to 50-100 µl, with no clean up in order to preserve the integrity of the samples as much as possible. The extracts were stored at -20 °C until analysis by gas chromatography coupled to high resolution time of flight mass spectrometry (GC-HR ToFMS).

ED samplers for chemical analysis (but not those for ecotoxicological analysis) were spiked with RIS (C_{13} caffeine, C_{13} triclosan, M8PFOA, M8PFOS, D_{13}-alachlor, D_6-diuron, D_{10}-simazine, deuterated EE_2, n-nonylphenol). All samplers where then freeze dried for 24 hours in the original containers that were used for sample storage and transport. The disks were extracted three times by overnight (12 h) slow shaking at room temperature with 70 ml acetone. Combined extracts were reduced by vacuum rotary evaporation. After removal of particles by filtration through a layer of anhydrous Na_2SO_4 the extract was further reduced in volume to cca 1 ml. The acetone extract was transferred to methanol by

addition of methanol (20 ml) and subsequent evaporation and a nitrogen flow to further reduce in volume to 2 ml. Aliquots of the extract were divided into vials for different types of analysis.

29.2.4 Sample analysis

29.2.4.1 Analysis of hydrophobic compounds

SR and LDPE sampler extracts were analysed using a GC-MS/MS (GC 7890 / MS-MS Triple Quadrupole 7000B (Agilent), equipped with an HT8 SGE Analytical Science column for PCBs and OCs. PAHs were analysed using GC 7890 / MS5975 (Agilent) equipped with a J&W Scientific fused silica column DB-5MS column. PBDEs were analysed by a GC equipped with a 15m × 0.25 mm × 0.10 µm RTX-1614 column (Restek, USA) HRMS (AutoSpec Premier) was operated in EI+ mode at the resolution of >10 000.

29.2.4.2 Analysis of polar compounds

Polar pesticides and pharmaceuticals were analysed by liquid chromatography (Waters Acquity) with MS detection (Waters Xevo TQ-S). Analytes were separated on reverse phase column (Waters Acquity UPLC BEH-C18) using gradient elution with methanol and water, both with 0.1% formic acid. Eluting analytes were ionized using electrospray in positive mode and detected in MRM mode.

29.2.4.3 Toxicological profiling

For toxicological profiling, a battery of bioassays has been established. The same tests are employed for assessment of toxic potential of samples from high volume active sampling (Chapter 27). The set consists of eight assays provided by four laboratories (INERIS, RECETOX, RWTH, and University of Queensland (UQ)). The selected bioassays cover several important steps in the toxicity pathway including induction of xenobiotic metabolism, specific and reactive modes of toxic action, activation of adaptive stress response pathways. The diverse modes of action provide broad range of information on toxic potential.

Specifically, there are assays for assessment of endocrine disruptive potential (anti-)estrogenicity (MELN) and (anti-)androgenicity (MDA-kb2), activation of receptors for xenobiotics (CAFLUX and HG5LN-hPXR), immune response (NF-κB-bla THP-1), mutagenicity and DNA damage –related apoptosis (Ames fluctuation assay and p53-bla HCT-116, resp.) and detection of response to oxidative stress (ARE-bla Hep G2). The model cell lines are exposed to dilution series of the ED and SR extracts to describe dose-response relationship of the effects. The potentials are quantified in comparison with negative control and positive control describing the effect of a model chemical with known toxic potency specific for each of the bioassay endpoints.

Table 90: List of bioassays employed in the toxicological profiling of passive sampler extracts

Laboratory	Bioassay	Endpoint
INERIS	MELN	Binding to and activation of human estrogen receptor (ER)[1]
	HG5LN-hPXR	Binding to and activation of the human pregnane X receptor (PXR)[2]
RECETOX	CAFLUX	Binding to and activation of aryl hydrocarbon receptor (AhR)[3]
	MDA-kb2	Binding to and activation or inhibition of activity of human androgen receptor (AR)[4]
RWTH	Ames fluctuation assay	Assessment of mutagenic activity in Salmonella typhimurium after metabolic activation of compounds with S9 liver fraction[5]
UQ	p53-bla HCT-116	Assessment of p53-mediated apoptosis rate in response to DNA damage[6]
	ARE-bla Hep G2	Induction of the Nrf-2-mediated oxidative stress pathway[7]
	NF-κB-bla THP-1	Induction of inflammatory response[8]

[1](Balaguer et al., 1999), [2](Lemaire et al., 2006), [3](Aarts et al., 1998), [4](Wilson et al., 2002), [5](Reifferscheid et al., 2012), [6](Yeh et al., 2014), [7](http://tools.lifetechnologies.com/content/sfs/manuals/cellsensor_AREblaHepG2_man.pdf, n.d.), [8]("http://tools.lifetechnologies.com/content/sfs/manuals/CellSensor_NFkBbla_THP1_man.pdf," n.d.)

29.2.5 QA/QC

The applied quality control measures included the analysis of procedural solvent blanks, fabrication controls, field controls and matrix spikes.

29.2.6 Data analysis

Dissolved water concentrations of were calculated from analyte amounts accumulated in SR and LDPE samplers, the in situ sampling rate (*R*s) of the compounds and their sampler-water partition coefficients (Smedes et al., 2009) as described in Smedes and Booij (2012). Sampling rates were estimated from dissipation of PRCs from samplers during exposure using methods described by Booij and Smedes (2010).

For ED samplers calibration data are not available so far. For compounds under investigation we assumed an integrative uptake with a constant sampling rate. Identification of pollutant gradients along the Danube was performed based on the amount of a compound sampled by the ED in individual stretches, normalised to an average sampler exposure time (1.6 days).

29.3 Results

29.3.1 Analysis of hydrophobic compounds- use of silicone rubber samplers

SR samplers were deployed at 8 successive Danube stretches to characterise the spatial variability of hydrophobic compounds in the water column of the river.

29.3.1.1 Polychlorinated biphenyls and brominated diphenyl ethers

Calculated dissolved PCB concentrations were in sub ng l^{-1} range (Figure 150). Sums of 6 indicator PCB congeners ranged from 158 to 369 pg l^{-1}. Over the set of PCBs investigated there is a decrease in free dissolved concentration as hydrophobicity increases. The highest spatial variability is observed for the more water soluble congeners PCB28, 52 and 101. There was no clear spatial trend of PCB contamination along the river.

Concentrations of freely dissolved PBDEs (referring to the sum of the concentrations of congener numbers 28, 47, 99, 100, 153 and 154) were below the limit of quantification of 3 pg l^{-1} with the exception of the stretch Passau to Bratislava, where the summed concentration of the 6 congeners was 12 pg l^{-1}. Measurement of such low concentrations would require longer exposure times for integrative sampling, which was not available during the JDS3 cruise. A parallel 43 day sampling using a caged SR sampler statically deployed at a sampling site downstream Bratislava in the period August-October 2013 provided a concentration estimate of 2 pg l^{-1} for the sum of 6 PBDE congeners (Vrana, unpublished data).

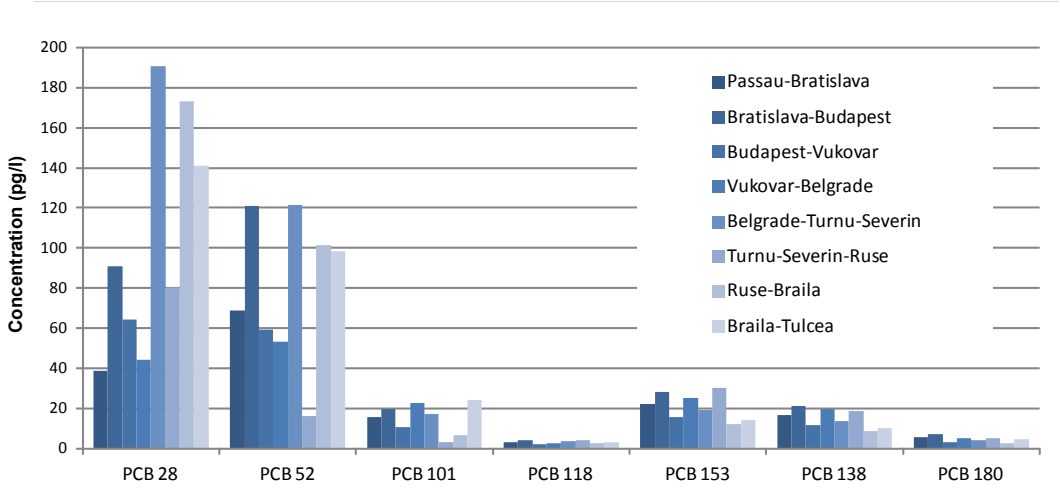

Figure 150: Free dissolved concentration of PCBs measured by SR samplers in 8 Danube stretches

29.3.1.2 Organochlorine compounds

The free dissolved concentrations of OCs were in sub ng l^{-1} range (Figure 151).The highest concentration of pentachlorobenzene (PeCB) up to 96 pg l^{-1} was observed in the stretch between Budapest and Belgrade whereas the highest level of hexachlorobenzene (HCB) of 97 pg l^{-1} was measured in the lowest Danube stretch between Ruse and Tulcea. The spatial variability of PeCB concentration was higher than that of HCB. Among the hexachlorocyclohexane (HCH) congeners, only β-HCH is reported because of low extraction recovery of the remaining isomers. There is an increasing trend of β-HCH concentration along the river, ranging between 9 pg l^{-1} in the upper stretches and 259 pg l^{-1} in the river delta area, respectively. The same spatial trend can be observed also for the sum of total DDT (given as sum of 4 isomers according to the Directive 2008/105/EC) as well as for p,p`-DDT. Concentrations of p,p`-DDT (1-21 pg l^{-1}) comprised only 2-7% of the total DDT, which indicates no current use of DDT in the Danube catchment. In the delta area concentration of DDT metabolites reach levels up to 864 pg l^{-1}.

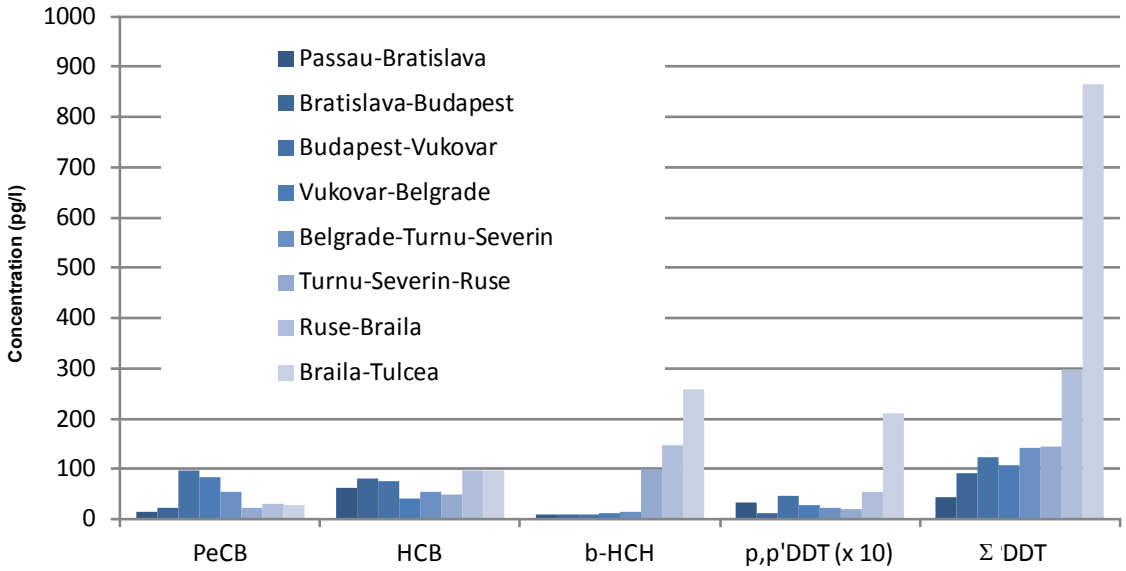

Figure 151: Free dissolved concentration of OCPs measured by SR samplers in 8 Danube stretches

29.3.1.3 Polycyclic aromatic hydrocarbons

Summed concentrations (Σ16 US EPA PAHs) of free dissolved PAHs in the water column ranged between 10.6 ng l^{-1} in stretch 7 and 45.1 ng l^{-1} in stretch 4, respectively. Summed concentrations were largely composed of PAHs with up to 4 aromatic rings. As for PCBs there is a strong decrease of free dissolved concentration with increasing compound hydrophobicity (Figure 152). Concentrations of compounds with 6 aromatic rings were mostly below the limit of quantification (tens of pg l^{-1}). Elevated PAH concentrations were observed in the stretches 4 and 5 (Budapest to Vukovar) and stretch 5 (Vukovar to Belgrade) with distinct pollutant patterns, which indicates different sources of PAHs along those river stretches. Concentrations of individual PAHs measured in stretch 2 (Passau to Bratislava) are within the concentration range that was measured in that stretch in spring till autumn 2011 using SPMD passive samplers (Vrana et al., 2014). This indicates that free dissolved PAH concentrations and their patterns in that Danube stretch in the summer period remained stable over a period of several years. A comparison with free dissolved concentrations measured using passive sampling in other European rivers (Vrana et al., 2014) shows that the concentrations of PAHs in the Danube is comparable to about 10 times lower.

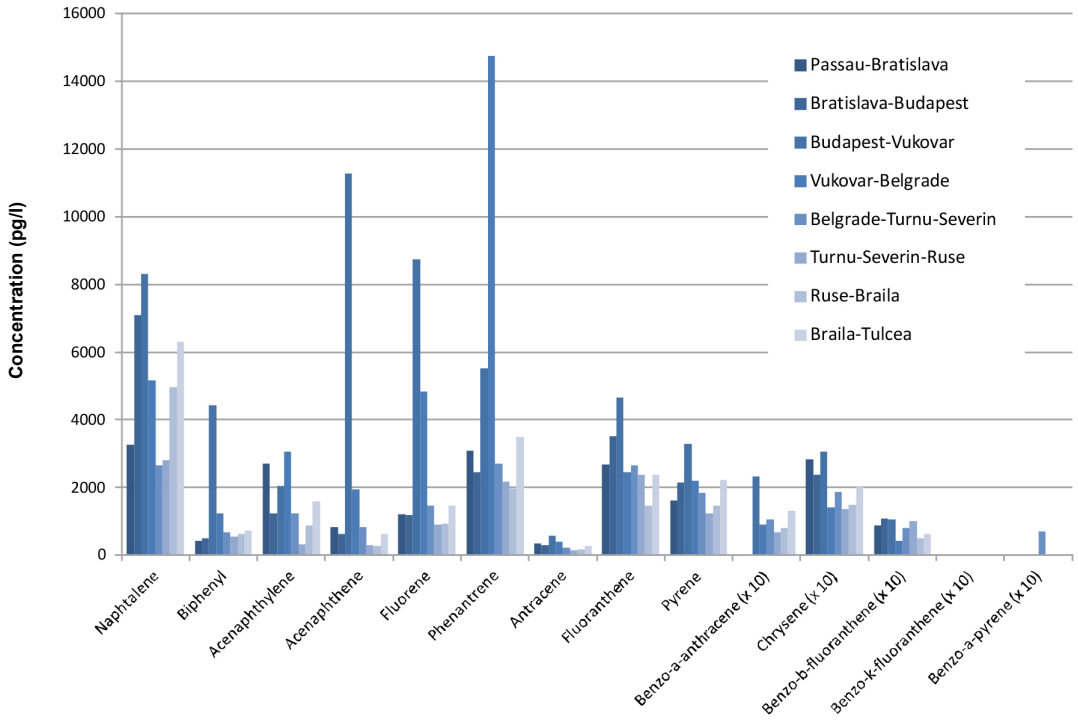

Figure 152: Free dissolved concentration of PAHs measured by SR samplers in 8 Danube stretches

29.3.1.4 Alkylphenols

The highest concentrations of free dissolved 4-nonylphenol (4-NP; 9.2 ng l^{-1}) and that of 4-tert-octylphenol (4-t-OP; 0.36 ng l^{-1}) was observed in the stretch between Vukovar and Belgrade (Figure 153). Concentration of 4-t-OP was on average 50 times lower than that of 4-NP.

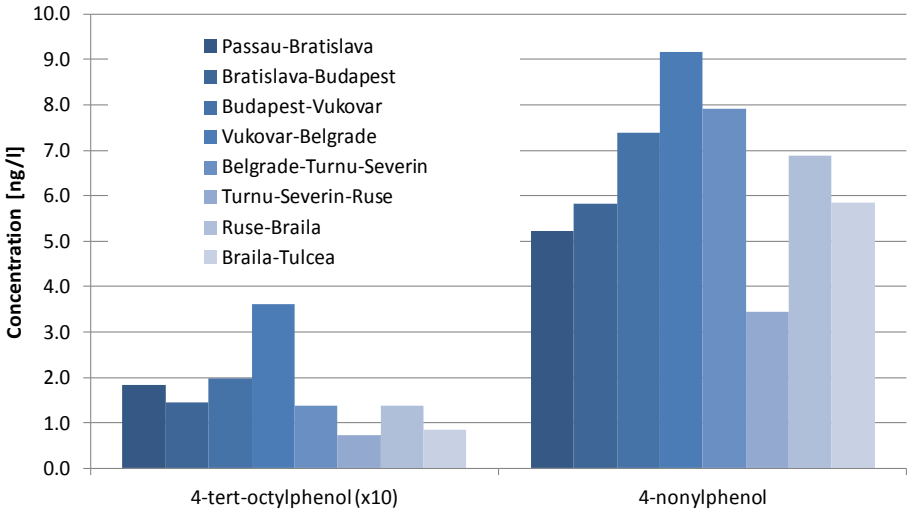

Figure 153: Free dissolved concentration of alkylphenols measured by SR samplers in 8 Danube stretches

29.3.2 Analysis of polar compounds – use of Empore disk samplers

29.3.2.1 Polar pesticides

A suite of 40 polar pesticides was analysed in extracts from the ED samplers. Results of analysis of five WFD priority pollutant polar pesticides, namely alachlor, atrazine, diuron, isoproturon and simazine are shown in Figure 154. Alachlor and diuron were present at concentrations less than or close to limit of quantification, which roughly corresponds to concentrations less than 100 pg l^{-1} in water. Estimated concentrations of atrazine, simazine and isoproturon in water were in the order of units of ng l^{-1} with the maxima of these pesticides in the stretch from Ruse to Braila. The results indicate that concentrations of the priority polar pesticides were far below their EQS values. It has to be noted that the main period of pesticide application is April-July and therefore the JDS results are not representative for the application season of these compounds.

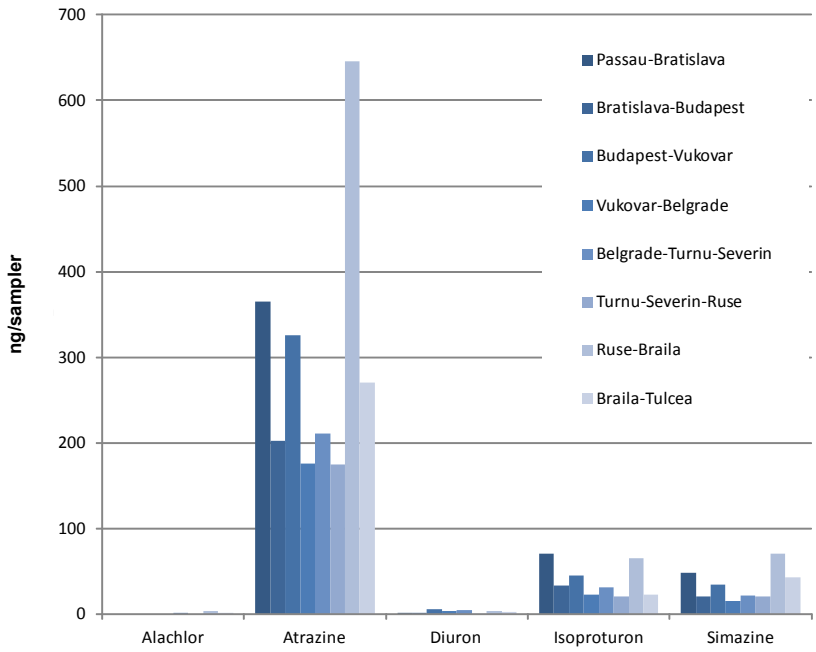

Figure 154: Spatial variability of WFD priority pollutant polar pesticides in the water column measured by ED samplers in 8 Danube stretches. Data is expressed as amount of compound taken up by an integrative sampler during an average sampler exposure (1.6 days)

29.3.2.2 Alkylphenols

The longitudinal relative concentration profile of alkylphenols in the Danube, measured by ED samplers (Figure 155), was similar to that reported by SR samplers. The highest concentrations of both 4-t-OP and 4-NP, but also of bisphenol A was measured in the stretch from Vukovar to Belgrade. In ED samplers concentration of 4-t-OP was on average 40 times lower than that of 4-NP.

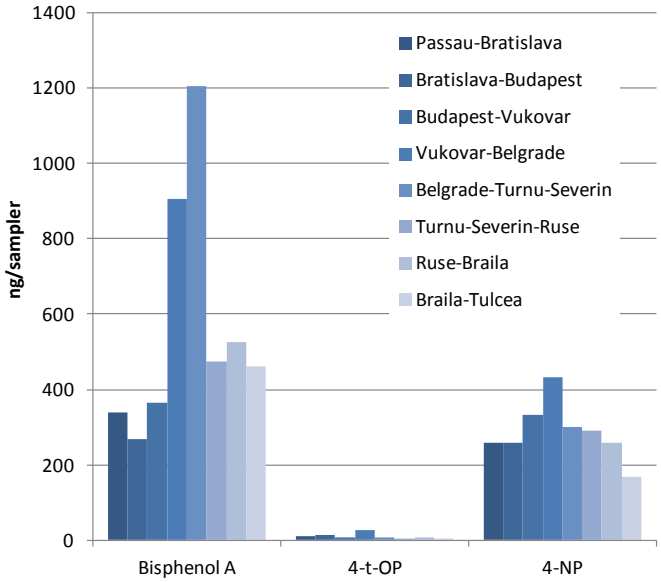

Figure 155: Spatial variability of alkylphenols in the water column measured by ED samplers in 8 Danube stretches. Data is expressed as amount of compound taken up by an integrative sampler during an average sampler exposure (1.6 days)

29.3.2.3 Pharmaceuticals

Results of analysis of caffeine and two pharmaceuticals, carbamazepine and diclofenac in extracts from the ED samplers are shown in Figure 156. The trend of caffeine concentration in the water column along the river was similar to that of bisphenol A. Estimated caffeine concentration levels were up to several tens of ng l-1 with the maximum observed concentration in the stretch from Vukovar to Belgrade. For comparison, analyses of caffeine in discrete spot samples taken collected the cruise and analysed by ELISA showed median concentration in Danube of 93 ng l-1 (Chapter 26). Estimated concentrations of carbamazepine along the river were in units of ng l-1 and less variable than that of caffeine. In agreement with the measurements made during JDS2 diclofenac was present at concentrations less than or close to limit of quantification, which can be explained by the biodegradability of this compound (Loos et al., 2008).

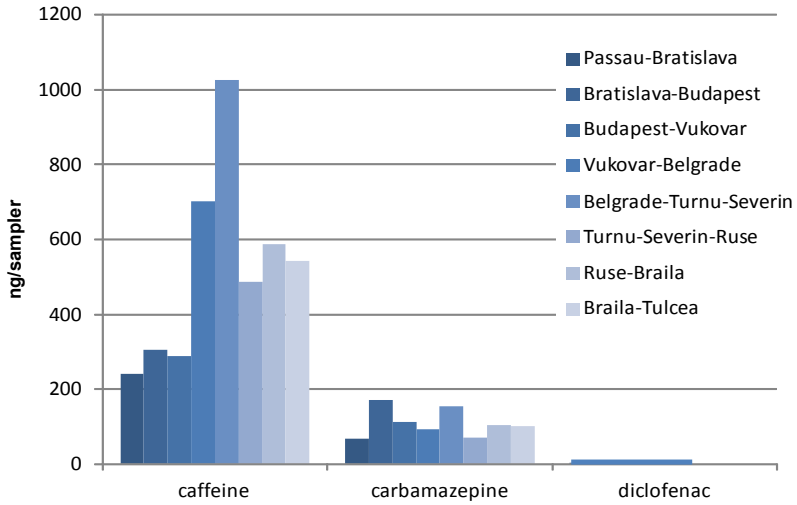

Figure 156: Spatial variability of caffeine and selected pharmaceuticals in the water column measured by ED samplers in 8 Danube stretches. Data is expressed as amount of compound taken up by an integrative sampler during an average sampler exposure (1.6 days)

29.3.3 Toxicological profiling

Selected toxic/bioactive potentials (see Table 90) of extracts of SR and ED passive samples are currently under evaluation. Preliminary results indicate that SR extracts contain significant amounts of dioxin-like compounds assessed by CAFLUX bioassay (Figure 157). Estimated toxic equivalents (bioTEQ) of samples recalculated for the sampled volume are between 6-10 pg l^{-1}. MELN bioassay has indicated estrogenic activity in SR samples. The specific estrogenic potential needs to be quantified yet. Available data from HG5LN-hPXR bioassay show that some SR extracts can significantly activate pregnane X receptor, but not the androgenic receptor. Negative results have been obtained in case of mutagenicity of SR extracts in Ames assay. Preliminary data indicate that at least some of the ED samples possess quantifiable estrogenic and PXR-related potential significantly higher than field blank samples.

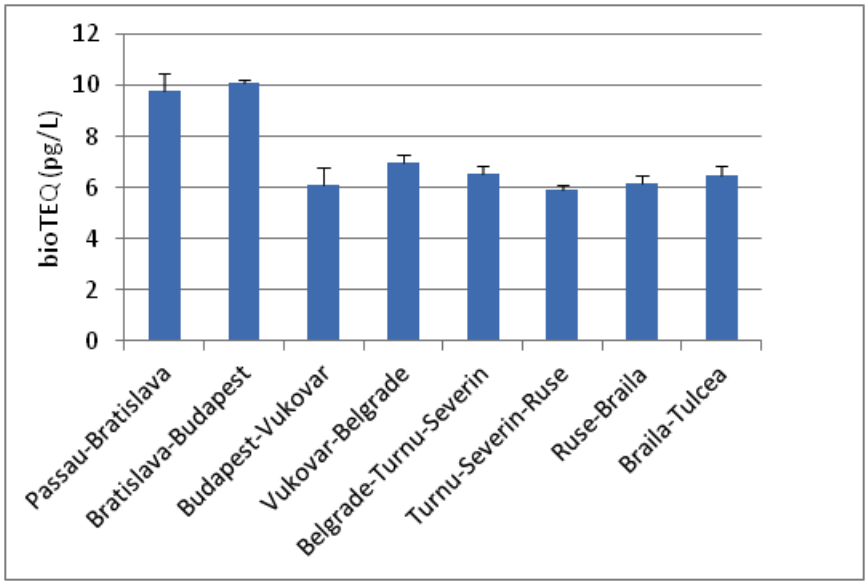

Figure 157: Estimate of toxic equivalent of TCDD in the water column measured by SR samplers in eight Danube stretches determined in CAFLUX bioassay

29.4 Conclusions

Despite the low or sub- ng l^{-1} concentrations of most organic pollutants present in the free dissolved phase, passive sampling enabled to clearly identify spatial gradients of a broad range of organic pollutants in the water column, including PCBs, OCs, PAHs, alkylphenols, selected polar pesticides and pharmaceuticals. In many cases, the integrative character of passive sampling allowed measurement of compounds down to pg l^{-1} levels where methods based on low volume spot sampling of water applied in the previous JDS2 survey failed to detect them (Sengl, 2008).

Passive samplers in most cases confirmed similar spatial distribution of pollutants along the river, as was observed in JDS2. The highest levels of PAHs, alkylphenols and caffeine in passive samplers were observed in the Danube stretches between Budapest and Belgrade. In agreement with JDS2, the downstream profile of PCBs and HCB showed a low variability and did not suggest particular emission maxima (Umlauf et al., 2008). In accordance with the findings during the JDS1 and JDS2, the downstream profile of β-HCH, DDT and its metabolites displays a sharp increase in the water column downstream Braila towards the Black Sea (Umlauf et al., 2008). The low percentage of p,p`-DDT of the total DDT concentration indicates that there was no current use of DDT in the area. The levels of priority pollutant polar pesticides alachlor, atrazine, diuron, isoproturon and simazine were comparable with the levels found in water samples during JDS2 and well below their respective EQS values (Loos et al., 2008).

Whereas data from spot sampling reflects the pollution at the individual JDS sampling sites at a single moment of time, passive samplers continuously sampled pollutants for several days, including river

stretches between individual JDS sampling sites. Thus, the information provided by spot sampling and passive sampling should be considered as complementary.

Finally, the combination of passive samplers with bioassays presents a very promising approach for detection of various trace organic pollutants and toxic potentials along the river and for identification of areas of concern for further investigation.

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29.6 Acknowledgments

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Príloha 33

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NORMAN
Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances

Passive sampling of emerging pollutants in the aquatic environment: state of the art and perspectives
Position Paper

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This document has been written as a follow-up to the expert group meeting organised by the NORMAN association on 27th May 2009 in Prague. It reflects the position of the NORMAN association experts and invited speakers on the topic of passive sampling and its application in the monitoring of emerging pollutants in aquatic environment.

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Executive Summary

Passive samplers represent an innovative monitoring tool for the time-integrated measurement of bioavailable contaminants in water and sediment. Passive sampling technology is proving to be a reliable, robust and cost-effective tool that could be used in monitoring programmes across Europe. These devices are now being considered as a part of an emerging strategy for monitoring a range of priority and emerging pollutants.

Passive sampling is based on the deployment *in-situ*, or use in the laboratory, of non-mechanical devices of simple construction capable of accumulating contaminants dissolved in water or sediment pore water. Such accumulation occurs via diffusion, typically over periods of days to weeks. Contaminants accumulated in exposed samplers are subsequently extracted and their concentration levels measured, allowing the quantification of time-weighted average (TWA) concentrations in water or equilibrium pore water concentrations in sediment. These devices can be deployed in most aquatic conditions (fresh and saline) and associated water treatment facilities, thus making them ideal for monitoring across the entire water cycle and even in remote areas with minimal infrastructure. Passive sampling can also be employed in batch sediment extractions to provide estimates of contaminant concentrations in pore water or assessment of bioavailable concentrations of contaminants in sediment.

In 2009, the NORMAN association organised a meeting of experts in the field of passive sampling. As a result of this meeting a position paper was produced, which reflects the view of the experts on the topic of passive sampling and its application in the monitoring of emerging pollutants in the aquatic environment and indicates future research and development needs in this area.

The position paper discusses functional principles of passive samplers and problems associated with the effects of environmental variables (temperature, water turbulence and sampler fouling) on their performance. Further, it lists the established or expected/potential performance of passive samplers for monitoring of the most discussed groups of emerging substances (such as cyanobacterial toxins, antifouling agents, brominated flame retardants, endocrine disrupting compounds, fluorinated surfactants, organosiloxanes, pharmaceuticals, polar pesticides, sunscreen filters etc.) and availability of calibration data that enable estimation of TWA concentrations. The document also shows the applicability of the passive sampling concept in risk-oriented monitoring of emerging substances in sediments and in determination of the bioaccumulative exposure of organisms. The great potential of this technology in combination with toxicological assays to determine the biological relevance of mixtures of toxicants with specific modes of action, and present at low concentrations, is also demonstrated.

If passive sampling is to become accepted and used in a regulatory context for monitoring water quality across Europe, then there is a need for the development of improved validation methods and setting-up of the appropriate quality control and quality assurance schemes for the technology. Successful demonstration of the performance of passive samplers alongside conventional sampling schemes, and inter-laboratory studies that demonstrate reproducibility of data produced by different designs of passive samplers, are urgently needed to facilitate the acceptance of passive sampling in routine regulatory monitoring programmes in the future.

I. Introduction

Improvements in analytical methods, primarily the introduction of more sensitive and specific mass spectrometry techniques, have increased awareness of the presence of emerging substances from many sources at trace levels (low ng L^{-1}) in the aquatic environment [1]. These substances include industrial chemicals and products, consumer products such as pharmaceuticals (both prescription and non-prescription drugs) and personal-care products, pesticides, natural bioactive compounds such as cyanotoxins and hormones, and metabolites of all these chemicals. Previous research focused mainly on non-polar and mono-polar compounds such as PCBs (polychlorinated biphenyls), PAHs (polycyclic aromatic hydrocarbons), chlorinated solvents, or chlorinated pesticides such as DDT or lindane. More recently attention has turned to the modern polyfunctional and often ionisable pesticides, biocides, drugs and personal care products. Currently there is a lack of knowledge regarding the fate and effects of many chemicals released into the environment either as products or accidentally. Although most of these compounds are present in the environment at low concentrations, many of them raise considerable toxicological concerns, particularly when present as components of complex mixtures [2].

Exposure assessment in the aquatic environment is based primarily on analytical measurements of chemical compounds in samples from various environmental compartments – water, sediments, soils, air – as well as from organisms from different trophic levels within a food chain [2]. Understanding and quantification of processes which emerging compounds can undergo in the environment, such as adsorption and partitioning between solid and aqueous phases, formation of complexes in solution as well as abiotic and biological transformation, are also urgently required. Both effective sampling and analytical methods are therefore essential to obtain reliable data on the concentrations, speciation and fate of these compounds in the aquatic environment.

While a lot of effort has been put into research and development of increasingly sensitive instrumental analytical methods for the measurement of emerging substances in various matrices in the aquatic environment, less interest has been paid to the development of suitable sampling techniques. Until recently, sampling methods for emerging substances were the same as those routinely used for monitoring priority pollutants in the aquatic environment. These are based on periodic collection of spot or grab bottle samples of water. The subsequent laboratory analysis of the sample provides a snapshot of the levels of pollutants at the time of sampling. There are, however, drawbacks to this approach in environments where contaminant concentrations vary over time, and where episodic pollution events such as spills or storm water runoff can easily be missed. This problem is particularly relevant to polar (hydrophilic) emerging substances. The residence times of these compounds in aquatic systems are generally lower than those of hydrophobic organic compounds. However, the presence of these more hydrophilic compounds in these systems (wastewater, surface water) may occur as a result of relatively episodic events (frequent, short duration and high concentration peaks). Thus, there is an urgent need for the development of suitable sampling and analytical methods capable of detecting and identifying contaminants in an integrative manner for an adequate assessment of the environmental risk posed by emerging substances.

One solution to this problem is to increase the frequency of sampling or to install automatic sampling systems that can collect numerous water samples over a given period. For example, the pooling of samples collected hourly into a 24 h composite sample, or

continuous on-line monitoring for specific sets of compounds can be used to provide representative data. These methods are both costly and in many cases impractical, since a secure site and additional infrastructure or personnel are required to protect, operate and maintain the mechanical automatic sampling devices. Over the last decade alternative methods for monitoring water quality have been sought to overcome some of the difficulties. A developing alternative strategy to these traditional sampling methods is to employ passive sampling devices that can be deployed over extended time periods (days to weeks) to provide time-weighted average (TWA) concentrations [3,4].

Passive sampling is a relatively easily applied sampling technique, based on the use of non-mechanical samplers of simple construction, often consisting of a single polymeric sorbing phase. In most cases these samplers do not require any external energy source to function. These devices can be deployed in most aquatic conditions (fresh and saline) and associated water treatment facilities, thus making them ideal for monitoring across the entire water cycle and even in remote areas with minimal infrastructure. Furthermore, these samplers assist with the sensitivity of subsequent analytical methods as they pre-concentrate and preserve chemicals sampled within these polymeric receiving phases. This enables improved sensitivity for a greater range of compounds and improved stability of chemicals within the sample without additional treatment (e.g. pH adjustment) unlike more traditional grab sampling techniques. In some cases, the use of passive samplers can also help to reduce or even eliminate the use of excessive volumes of toxic extraction solvents.

Passive samplers have been used for environmental monitoring since the 1970s, when the first samplers for the assessment of ambient air quality and workplace exposures to potentially hazardous air pollutants were developed and applied. To date, a number of sampler designs are commercially available and there are now established standards and official methods (e.g. ASTM, EPA, NIOSH, CEN and ISO protocols) for the use of these devices, which form part of legal frameworks. More recently, worldwide monitoring networks have been set up using passive air samplers to monitor persistent organic pollutants on a global scale [5,6].

In contrast, the application of passive samplers in monitoring water quality is some way behind the situation for air, and the technologies available for monitoring soils and sediments are even further from recognition. Since the introduction of the semi-permeable membrane device (SPMD), designed at USGS by Huckins et al. [7] in the early 1990s, passive samplers have become widely used for monitoring persistent organic pollutants and other non-polar organic compounds in the aquatic environment. Nearly ten years later, the passive sampling technology suitable for sampling hydrophilic organic compounds including modern pesticides, pharmaceuticals and personal care products has been reported in the work of Alvarez (POCIS sampler) [8] and Kingston et al. (Chemcatcher concept) [9]. Since then, the number of publications on development, performance optimisation and field application of passive samplers for emerging substances has grown rapidly.

A number of recent reviews have been published describing the design, calibration procedures, figures of merit and applications of the different devices for monitoring the aquatic environment [3,10,11,12]. Booij summarised in a report for the ICES Marine Chemistry Working Group the established or expected/potential performance of various passive samplers of compounds that are listed under WFD and other directives or conventions [13]. Recently, several review papers addressing passive sampling of emerging pollutants have been published [14,15]. In addition, a book describing the SPMD [16] and a

general text describing many passive sampling techniques for environmental monitoring [17] are available.

II. Concept of passive sampling

Passive sampling is based on the deployment *in-situ* or use in the laboratory of devices capable of accumulating contaminants dissolved in water or sediment pore water. Such accumulation occurs via diffusion, typically over periods of days to weeks. Contaminants accumulated in exposed samplers are subsequently extracted and their concentration levels measured, allowing the quantification of TWA concentrations in water or equilibrium pore water concentrations in sediment. It enables temporally-representative sampling or sampling of the truly dissolved concentration of contaminants in water or aquatic sediments. Even for those chemicals that are present at extremely low concentrations in the dissolved phase and are primarily accumulated in biota via the dietary uptake, passive samplers generally extract sufficient amounts of residues for analysis. Passive sampling can also be employed in batch sediment extractions under laboratory conditions to provide estimates of contaminant concentrations in pore water or assessment of bioavailable fraction of contaminant in sediment [18,19].
Passive sampling is based on the diffusion of analyte molecules from the sampled environmental medium (water or sediment pore water) to a receiving phase in the sampling device. The diffusion occurs as a result of a difference between chemical potentials of the analyte in the two media (Figure 1). The net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system, or until the sampling is stopped. The mass of chemical sorbed in the sampler following a given exposure period is initially proportional to the TWA concentration in the environmental medium to which the sampler was exposed (integrative samplers) and subsequently once equilibrium is achieved to the concentration in the environmental medium with which the device is at thermodynamic equilibrium (equilibrium samplers). The main advantage of kinetic or **integrative sampling** is that even contaminants from episodic events commonly not detected with spot sampling are collected by the sampler. This permits the measurement of time weighted average (TWA) contaminant concentrations over extended time periods using a single sample (extract from the passive sampler). This gives a more representative picture of contaminant levels than that obtained with the use of infrequent spot samples. To achieve **equilibrium sampling**, for a given sampler the sampling period needs to be sufficiently long to establish thermodynamic equilibrium between the water and the sorbent phase of the sampler. To achieve equilibrium within reasonable sampling periods samplers of relatively low capacity for the analytes of interest or with modified surface area to volume ratios may be required [20]. Application of the sampler-water distribution coefficient then enables the calculation of the analyte concentration in the sampled medium.

Analytes are accumulated in a suitable sorbent material within the passive sampler, known as a receiving phase. This can be a solvent, chemical reagent, absorbent polymer or a porous adsorbent material. Whereas most samplers of hydrophobic compounds are based on diffusion and absorption in non-porous polymers, most samplers of polar organic compounds (i.e. majority of emerging compounds) and metals are based on diffusion through porous membranes and sorption to selective **adsorbent materials**. The difference in selection of materials applied in sampler construction results in different sorption phenomena that define the driving force of the sampling process (Figure 2). In general, accumulation of hydrophilic organic compounds to porous adsorbents is more complex than absorption and

dissolution of hydrophobic chemicals in non-porous polymers (polyethylene or polydimethylsiloxane). This is because adsorption distribution coefficients (unlike partition coefficients in solvents and sub-cooled liquid polymers) described by sorption isotherms can be concentration-dependent. Competitive adsorption of analytes and possible interferences are also possible. The polar organic compounds are mainly retained by specific interactions with functional groups at the surface of the adsorbent. Although the use of adsorptive polymers with specific interactions is preferred in certain cases, the risk always exists of saturating the fixed number of superficial bonding sites when these polymers are applied to a complex sample matrix. Finally, many compounds may speciate into multiple forms depending on their pK_a parameters and the pH of the sampled medium. Where a sorbent phase only accumulates a single form of a specific compound such as the neutral species, these phenomena will also influence the observed uptake. Sampling description is thereby complicated by the presence of several species with different diffusion and sorption properties that may dynamically change during the sampling process, depending on a milieu of properties of both the sampled medium, the receiving phase and of the individual compound.

Recently, a novel absorptive equilibirum passive sampler for polar organic compounds has been reported by Magnér et al. [21]. This is based on a plastic material, polyethylene-co-vinyl acetate-co-carbon monoxide (PEVAC). This receiving phase operates as a homogenous, non-porous liquid in which the analytes are retained by dissolution rather than by specific interactions with the surface of the polymer. The PEVAC material showed enhanced sorption of several polar pesticides and pharmaceuticals compared to the silicone material. Identification of suitable absorbent polymer materials with high retention capacity of polar compounds presents a promising approach in future development of passive sampling technology and may replace currently used complex adsorption-based samplers for which data conversion into aqueous concentrations is often difficult.

For devices that operate in the kinetic or integrative mode, the sampling rate is given by the product of the overall analyte mass transfer coefficient and the active surface area of the sampler (R_S = k_o A). Sampling rate may be interpreted as the volume of water cleared of analyte per unit of exposure time (e.g. mL h^{-1} or L day^{-1}) by the device and is independent of the analyte concentration in the sampled medium. It can be affected and modulated by the analyte diffusion and partition properties in the media along the diffusional path, and is determined in laboratory calibration studies.

Often the main barrier to mass transfer is the water boundary layer (WBL) located at the external surface of the sampler. In such a case the sampling rate is significantly affected by environmental variables such as water temperature, turbulence and biofouling. If laboratory calibration data is to be used for calculation of TWA concentrations, the effect of these variables has to be either controlled or quantified. For samplers used to measure concentrations of non-polar organic analytes, one method of overcoming some of the problems associated with the impact of fluctuating *in situ* environmental conditions (temperature and turbulence) on sampling rate is the use of performance reference compounds (PRCs) [22]. These are analytically non-interfering compounds (typically deuterium or ^{13}C labelled analogues of the compounds to be measured) and are loaded onto the receiving phase of the sampler prior to deployment. These PRCs are eliminated from the receiving phase during the deployment period. Where the kinetics of uptake and elimination are isotropic, that is the rate constants for the elimination of the PRCs are affected by environmental variables in a manner similar to the uptake rates of pollutants, these elimination rate constants can be used to correct the sampling rates of pollutants in field

deployments. There is also some evidence that the elimination rate constants of PRCs can be used to compensate for the impact of biofouling on uptake; however, more work is needed in this area [23,24,25].

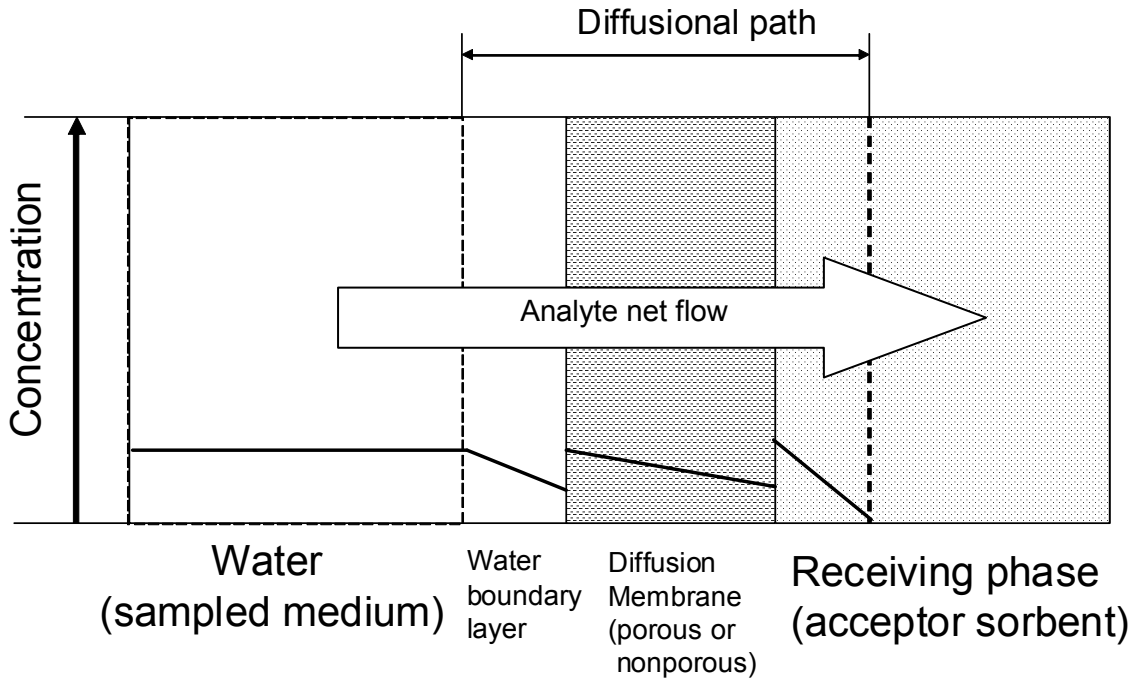

Figure1. *Functional principle of a passive sampling device, showing the concentration profile of a compound during diffusion and accumulation from bulk of the sampled medium to the sorbent (receiving phase) through a permeable (porous or non-porous) membrane. High affinity to the sorbent inside the sampler drives the diffusion of analyte molecules from the sampled medium into the sampler until the thermodynamic equilibrium is established. (adapted from Mills et al. [14]).*

The correction for the effect of environmental variables in samplers where the sequestration process depends on adsorption of the analyte presents one of the major challenges in the development of the technology. In many cases, uptake of analytes (polar organic compounds and metals) into these devices is WBL-controlled and thus sensitive to changes in flow turbulence. The PRC concept cannot, however, be generally used to correct calibration data for changes in field conditions because of the complex character of the desorption kinetics that may not be isotropic with the adsorption [26]. Mazzella et al. [27] and Budzinski et al. [28] have recently demonstrated isotropic exchange in certain exposure scenarios, but this concept still remains to be fully explored. In cases where PRC loss is not isotropic with uptake of target analytes, an alternative *in situ* calibration approach is to load PRCs into co-deployed sampling phases from which elimination is observed and which may subsequently be related to uptake. An *in situ* calibration technique, using PRC-loaded absorbent polydimethylsiloxane (PDMS) disks deployed alongside the Empore^{TM} adsorbent disk samplers as a surrogate calibration phase, has been proposed by Shaw et al. [26] and shows promise for future applications. Alternatively a passive flow monitor based on dissolution gypsum has been developed which may predict the sampling rate in response to *in situ* flow conditions [29]. Differences in mass transfer in absorption- and adsorption-based samplers are illustrated in Figure 3.

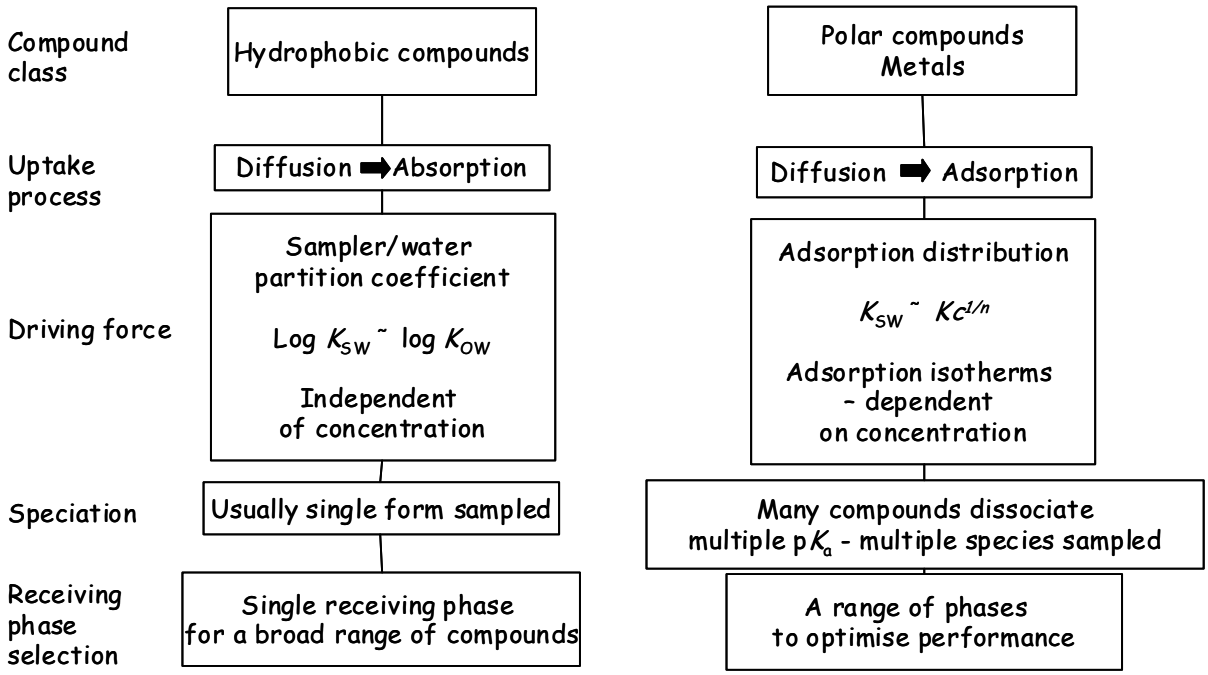

Figure 2. *Differences in passive sampling in (left) absorption- and (right) adsorption- based samplers. The majority of emerging substances are polar or semi-hydrophobic. Thus, the use of adsorbent-based samplers presents the most suitable sampling approach for these compounds.*

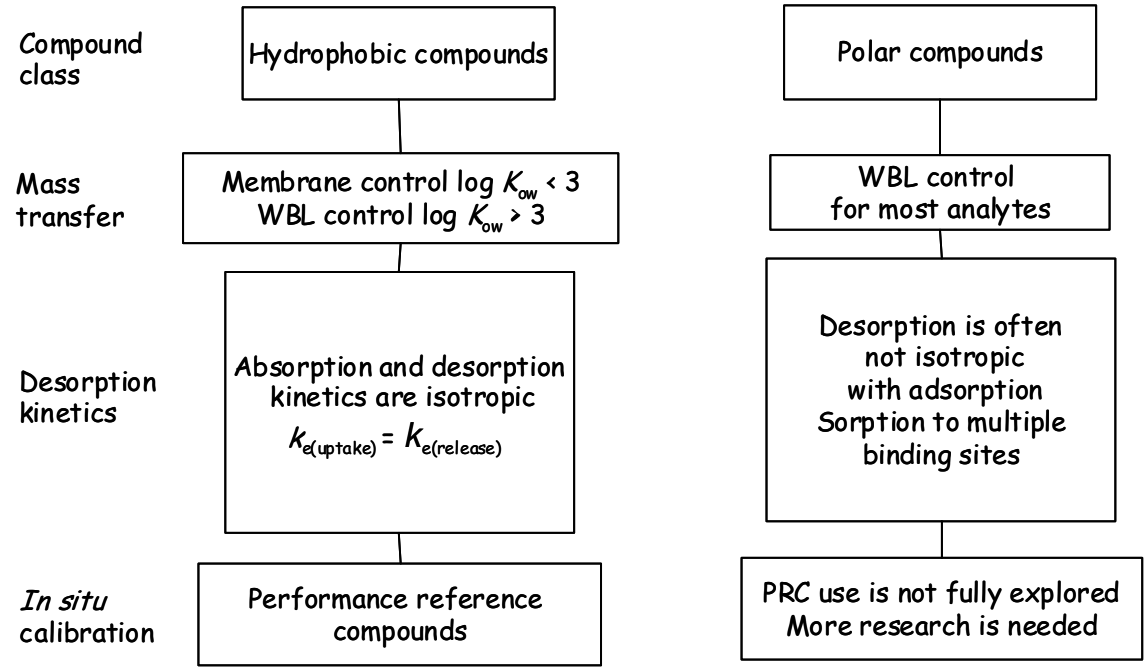

Figure 3. *Differences in mass transfer in (left) absorption- and (right) adsorption-based samplers*

III. Applications in aquatic monitoring of emerging compounds

A detailed description of sampler designs available for monitoring emerging polar organic compounds has recently been published by Söderström et al. [15]. Applications of passive samplers for some important groups of emerging substances are discussed in the following section. Table 1 lists the most discussed emerging pollutants in the aquatic environment, the established or expected/potential performance of passive samplers of these compounds and availability of calibration data that enable calculation of TWA concentrations.

III.1. Algal toxins

Algal toxins are a group of natural products which may occur in fresh, brackish and marine waters. However, possibly because of anthropogenic eutrophication and global climate changes, and subsequent blooms of potentially toxin-producing cyanobacteria, the incidence of contamination of water bodies with these compounds seems to have increased over recent years[30]. Algal toxins are structurally, functionally and phylogenetically diverse group of compounds with variable chemical and toxicological characteristics. These pollutants may cause serious health problems as documented by cases of human and animal intoxications as well as by the results of laboratory studies [30]. Based on the toxicity data, the World Health Organization (WHO) suggested the tolerable daily intake (TDI) value for microcystin-LR (a widespread hepatotoxin produced by cyanobacteria) is 0.04 μg kg^{-1} body weight, and corresponding safety guideline value 1.0 μg L^{-1} is recommended for drinking waters. There are no obligatory guidelines for other cyanobacterial and algal toxins. However the presence of these compounds in water is highly undesirable and tools for proper monitoring are necessary.

Owing to the quite high spatial and temporal variability of the occurrence and subsequent development of algal blooms, and hence potentially of co-occurring toxin production, passive samplers may prove to be a useful tool for monitoring of natural toxins. The first use of integrative passive sampling for algal toxins was described in the work of MacKenzie et al. They developed a passive sampler (SPATT bag) based on synthetic resin enclosed in porous sachets and used it for monitoring a group of marine toxins known as paralytic shellfish poisons [31]. The device was designed as an early warning of developing cyanobacterial blooms to protect consumers and prevent the harvesting of contaminated seafood products. This work was continued by other authors. Fux et al. evaluated various sorbents in the SPATT system [32]. Rundberget et al. redesigned the device and used it for monitoring of various natural toxins on the southern coast of Norway [33]. Shea et al. described the development of a monophasic device for monitoring of brevetoxins, highly toxic compounds produce during red tide events. Devices constructed of polydimethylsiloxane sheets were successfully used for integrative sampling [34]. Kohoutek et al. employed POCIS for the monitoring of microcystins in freshwater. The study was focused on evaluation of various configurations of the sampling device [35], and described calibration procedures and monitoring of the toxins under conditions of natural algal blooms. Concentrations of toxins obtained by passive sampling correlated well with the overall concentration of dissolved microcystins, demonstrating the suitability of passive sampling for the determination of TWA concentrations [35].

III.2.Antifouling compounds – organotins

Due to their bioaccumulation potential and toxicity, organo-metallic substances are considered as emerging pollutants of concern. In some cases organo-metallic compounds

(e.g. some organic forms of tin) are more toxic than inorganic complexes or free forms of the parent metal. Passive sampling devices have been used to measure a number of organo-metallic species, including those of lead, mercury and tin.

Følsvik et al. [36,37] reported the use of SPMDs for monitoring organotin compounds using SPMDs. Both dibutyl- and tributyltin were accumulated by the devices, but no accumulation of monobutyltin was observed during several weeks of SPMD exposure in a Norwegian fjord. Using this method, it was possible to identify concentration gradients of organotin compounds at the sampling site. Later, a variant of the Chemcatcher® sampler was developed and calibrated for the measurement of the TWA concentration of organotin compounds. [38,39]. Using gas chromatography (GC) with either ICP-MS or flame photometric detection, favourable limits of quantification for the device (14-day deployment) for the different organotin compounds in water were in the range of 0.8–25 ng L^{-1}, and once accumulated in the receiving phase the compounds were stable over prolonged periods [39].

III.3. Brominated flame retardants

Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants in products such as furniture, textiles, plastics, paints and electronic appliances. Due to their extreme hydrophobicity (log K_{ow} values 4–10), these compounds are dissolved in the aqueous phase at extremely low (sub-ppb) concentrations. Nevertheless, because of their possible environmental risks due to their persistence and bioaccumulation, the inclusion of certain PBDE congeners in monitoring programmes is justified. Booij et al. [40] used SPMDs for sampling and *in situ* pre-concentration of PBDEs from water at several sampling stations in the Scheldt estuary and the North Sea along the Dutch coast. The application of integrative sampling enabled the back-calculation of extremely low concentrations (in range 0.1-5 pg L^{-1}) of PBDE congeners in water from SPMD-accumulated amounts. Rayne and Ikonomou [41] employed SPMDs for sampling PBDEs in water in the Fraser River near Vancouver, Canada. The concentrations of PBDE found in SPMDs, their physicochemical properties, and their SPMD uptake parameters were used in an aquatic transport model to reconstruct the patterns of PBDE in pollution sources. The reconstructed patterns of accumulation in SPMDs closely approximated the composition of known technical mixtures of PBDEs.

III.4. Endocrine disrupting compounds

Over the last two decades the presence in the environment of endocrine disrupting compounds, such as those which mimic or block the action of endogenous hormones on steroid (oestrogen and androgen) receptors and subsequently alter the normal functioning of the endocrine system in wildlife and humans, has emerged as a major environmental issue [42,43]. Natural oestrogens (such as oestrone, E1, and 17-β oestradiol, E2) and synthetic oestrogens (e.g. 17-α-ethinyloestradiol, EE2, the active component of oral contraceptives) are very powerful endocrine disruptors. They derive mainly from excreta of humans and livestock [44]. Anthropogenic industrial chemicals such as nonylphenol (NP), bisphenol A (BPA) and phtalates are, however also known to influence the hormonal system of aquatic organisms. Wastewater treatment plants are important sources of pollution, since many endocrine disrupting compounds are not fully removed by the treatment processes. Several studies have demonstrated applicability of passive samplers for integrative sampling of these compounds during exposure periods up to several weeks [126,128,129,142]. For many compounds, calibration data that enable quantitative translation of amounts accumulated by the sampler into TWA concentrations are available (Table 1).

III.5. Fluorinated *surfactants*

Fluorinated surfactants (also referred to as poly- and perfluoroalkyl compounds, including perfluoroalkyl carboxylic acids, perfluoroalkyl sulfonates, fluorotelomeric acids, alcohols, etc.) have been used for decades to make stain repellents that are widely applied to fabrics, carpets and paper. They are still used in the manufacture of paints, adhesives, waxes, polishes, metal coatings, electronics and caulks. Due to concern over their persistence and global occurrence in humans and wildlife, two of these fluorinated surfactants, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) are within the family of compounds currently attracting the greatest attention as emerging pollutants.[45] It is difficult to identify the origin of pollution by fluorinated surfactants found in wastewater. Although no quantitative studies aimed at monitoring of these substances with passive sampling methods have been reported, Casey et al. [46] reported identification of these compounds in POCIS extracts at levels above associated controls. Recently, Günther et al. described the application of a passive sampler based on active carbon adsorbent [47]. Further research in development of passive samplers suitable for monitoring of these compounds in water is needed.

III.6. Organosiloxanes

Another important class of emerging pollutants is the organosiloxanes. These polymers comprise a backbone of alternating silicon-oxygen units with organic side chains attached to each silicon atom. Over the last 30 years organosiloxanes (silicones), both cyclic and linear forms, have been extensively used in a number of consumer products. These include for example anti-perspirants, and hair and skin care items. It has been estimated that in the USA adult women are exposed to up to 307 mg of organosiloxanes daily [48]. The most commonly used organosiloxane is decamethylcyclopentasiloxane (abbreviated to D_5) although others such as octamethylcyclotetrasiloxane (D_4) and their linear versions can be used in products [48]. These compounds have unusual physico-chemical properties combining high hydrophobicity (e.g. D_5 has a log K_{ow} of 6-8, depending on the literature reference used)) with a high Henry's Law constant and low water solubility [49]. Owing to these properties, most (c. 90%) of the organosiloxanes used in personal protection products are expected to be evaporated to the atmosphere during and after use, with the remainder being discharged into the wastewater. Several organosiloxanes are under assessment for classification as very persistent and very bioaccumulative in the environment. Hence there is an urgent need for monitoring levels of these compounds in different environmental compartments.

Analytically, siloxanes are difficult to measure at trace levels as they are ubiquitous atmospheric environmental contaminants, they are contained in sample vial caps, septa, gas chromatographic columns and they give problems of cross-contamination by laboratory workers using personal care products containing these substances. The maintenance of good procedural blanks and rigorous quality assurance and quality control measures are needed to ensure confidence in any quantitative results. For these reasons reliable environmental monitoring data are sparse. Most analytical methods for both cyclic and linear siloxanes employ headspace gas chromatography/mass spectrometry techniques [49], although large volume direct injection methods using *n*-hexane have also proved to be useful [50]. Sparham et al. [49] have recently analysed D_5 in the Rivers Great Ouse and Nene, UK (concentration range < 10-29 ng L^{-1}) and in treated wastewater (concentration range 31-400 ng L^{-1}). There are few other quantitative studies for D_5 and the other organosiloxanes of environmental concern.

Owing to the low concentrations of organosiloxanes found in the aquatic environment, the use of passive samplers in monitoring campaigns may offer the opportunity to pre-concentrate these compounds prior to instrumental analysis. To date, however, there is little experience of their use with this class of pollutants. Work in this area is being undertaken by researchers (Mills and Greenwood) at the University of Portsmouth, Portsmouth, UK. Preliminary findings show that pre-cleaned thin sheets of low density polyethylene (LDPE) membrane can be effectively used as passive samplers for D_4 and D_5. Work is currently being undertaken to identify PRCs that are suitable for use with the samplers and that are appropriate for the organosiloxanes of major environmental concern. Polydimethylsiloxane (PDMS) sheets cannot be used for this purpose because of background contamination with these smaller siloxane polymers. This makes it difficult to obtain good procedural blanks. Even with extensive washing it is still hard to remove all traces of D_4 and D_5 from these materials. Other polymers such as polyethylene terephthalate (PET), polyoxymethylene (POM), polytetrafluoroethylene (PTFE) and polycarbonate could potentially be used as either equilibrium or kinetic samplers for these compounds. Because the organosiloxanes are volatile, care must be taken during field deployments not to lose the sequestered analytes during retrieval and transport of samplers and in subsequent laboratory processing. Extensive QA and QC procedures must also be employed. Data from the Portsmouth group on the initial field use of the LDPE samplers for measuring this class of compounds are expected in 2011.

III.7. Pharmaceuticals

Concern over pharmaceutical residues (and personal care products) entering the aquatic environment has been growing since the mid-1990s. Both classes of compounds enter the environment largely as a result of human use, although some come from veterinary use. Several studies have reported the presence of a wide range of these chemicals at ng L^{-1} and sub ng L^{-1} concentrations in various water bodies. A complex mixture of chemicals is often present comprising the parent molecule, associated metabolites and environmental degradation products. Some of these substances may subsequently enter the food chain. The biological effects of pharmaceutical residues on aquatic organisms have been reviewed recently [51].

Effluent from wastewater treatment works is the most common source of pharmaceutical residues in streams and rivers. Some of these chemicals are resistant to treatment. Often the treatment process can break down conjugated drug metabolites to release the parent molecule back into the environment. A range of tertiary treatment processes (e.g. chlorination, ozonation and UV light) can be employed to reduce these levels, but these are expensive to operate continuously at the treatment plant.

Pharmaceuticals have a wide range of physico-chemical properties and concentrations in the aquatic environment and this can make their measurement challenging. Many drugs are either weak acids or bases with pK_a values in the range 4-10. The degree of ionisation will therefore differ in different water bodies that have pH values typically over the range 5.5-8.4 (i.e. from soft to hard fresh water and sea water). Likewise, these substances have a range of log K_{ow} values, but most are considered polar compounds. In some cases the chirality of the drug molecule also needs to be considered. Most compounds of environmental concern can be analysed using LC/MS/MS instrumental methods after extraction and concentration. Typically a wide range of analytes can be separated and quantified at the trace level in a single analysis.

There is a need to obtain reliable data on the fate of pharmaceuticals in the aquatic environment. These data can then be used to develop appropriate models and assist in the risk assessment process. As most discharges of these substances are sporadic and seasonal it is difficult to obtain such information using spot or grab sampling alone. Passive sampling therefore offers a number of opportunities in this area and this has been summarised by Mills et al. [14]. Recently, Söderström et al. [15] reviewed performance characteristics of samplers suitable for monitoring pharmaceuticals and other polar organic pollutants in the aquatic environment.

Two types of passive sampler (polar version of the Chemcatcher and POCIS) have been used for measuring TWA concentrations of pharmaceuticals (and some personal care products). The devices use either an immobilised (Chemcatcher) or loose (POCIS) receiving phase. The Chemcatcher uses a 47 mm Empore^{TM} disk, usually based on divinylbenzene co-polymer chemistry, although ion-exchange (both anion and cation) receiving phases can be used for certain classes of analyte. The POCIS uses a commercially available solid-phase extraction adsorbent (typically c. 200 mg Oasis HLB) that is specially designed to sequester pharmaceuticals. The same diffusion-limiting membrane (polyethersulphone) is used in both devices. This membrane has a low surface energy and this can limit biofouling of its surface during field use. The uptake rates of the two devices for these more polar analytes are low (typically less than 1 L d^{-1}) compared with the sampling of non-polar compounds by, for example, SPMDs. This can limit their usefulness in some applications, but – unlike non-polar compounds – polar compounds are usually present at higher concentrations, so that sampling rates below 1 L d^{-1} are not an obstacle.

Although a number of laboratory and field studies have been carried out using the POCIS, there is an urgent need for reliable calibration data (Table 1). In many cases different calibration systems (e.g. flow through and static with renewal) [52] and different water turbulences and temperatures have been used and this increased the variation in the data obtained. Much of the field data reported is therefore either qualitative (presence or absence of a pollutant) or semi-quantitative (amount extracted from the receiving phase) rather than using uptake rates to calculate actual water concentrations (ng L^{-1}).

III.8. Polar pesticides

Use of pesticides can have unintended effects on the environment. Over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species, including non-target species, air, water, bottom sediments, and food [53]. There are four major routes through which pesticides reach water, including: spray-drift outside of the intended application area, percolation, or leaching, through soil column, with water runoff or concomitant soil erosion, or through accidental or negligent releases [54]. There is an increased demand for environmental monitoring of pesticides because some of them are either already identified as priority substances under the Water Framework Directive (e.g. atrazine, simazine, diuron, isoproturon), or may become priority substances in the future or are relevant as river basin-specific pollutants in selected European regions [55]. An EU “Thematic Strategy on the Sustainable Use of Pesticides” calls for environmental monitoring to be done for other new pesticides in order to verify whether the concentrations in the aquatic environment are “safe” [56].

The first passive sampler reported for this chemical class was the POCIS [57,58]. Typically, for sampling of polar pesticides POCIS remains in the time-integrative mode for exposure periods of up to several weeks. This sampler has found application in integrative sampling of

a wide range of polar pesticides and, for many of them, calibration data are available that enable quantitative translation of amounts accumulated by the sampler into TWA concentrations (Table 1).

Polar pesticides are often released at high concentrations into streams and rivers in episodic events. These events usually last only a few hours and for these compounds to be detected by passive samplers, a device with a short response time is required. But passive sampling devices fitted with microporous membranes (e.g. polyethersulphone membrane in POCIS), although ideal for long-term monitoring [59], have a lag-phase of several hours which represents the time necessary for the analytes to diffuse through the membrane to reach the receiving phase [24]. In situations where detection of short pollution events in the monitored water body is required, a long lag-phase of the sampling device presents a potential disadvantage. Shaw and Mueller [60] suggested the use of a device fitted with an Empore^{TM} disk bonded polymeric sorbent as receiving phase (without a diffusion limiting membrane) to reduce the response time and make the sampler more reactive to sudden pollution events [61]. The disadvantage of such devices is a fast equilibration of the sampling devices with the water phase, which restricts to a few days the time over which the samplers operate in time-integrative mode. Comparison of the performance of two different types of Empore^{TM} disks as passive samplers showed that the styrene-divinylbenzene-reverse phase sulfonated (SDB-RPS) Empore^{TM} disk had better performance as sorbent phase for very polar compounds compared to C18 [62].

III.9. Sunscreen and ultra-violet filters

The analysis of sunscreens/organic ultra-violet (UV) filters in water has increased substantially in the last two years. Due to their use in a variety of personal care products, these compounds can enter the aquatic environment indirectly from showering, washing clothes, via wastewater treatment plants and also directly from recreational activities.

In one of the first studies, Poiger et al. [63] detected four organic UV filters (80-950 ng SPMD^{-1}) in SPMDs deployed at Lakes Zurich and Greifensee, Switzerland. SPMD-derived water concentrations were in the range of 1-10 ng L^{-1} and corresponded well with those determined in spot samples of water. In a later study, Balmer et al. [64] investigated the occurrence of four important organic UV filter compounds in water, wastewater and fish from various Swiss lakes. Data from passive sampling using SPMDs supported the presence of these UV filters in lakes and rivers and suggested some potential for accumulation of these compounds in biota. Recently, Fent and Zenker et al. [65,66] demonstrated the applicability of the POCIS sampler for monitoring oestrogenic UV filters in surface water. They found that processing of POCIS samples with subsequent instrumental measurements was much less time consuming than processing of fish samples for environmental monitoring. Hydrophilic compounds like benzophenone-4 which do not accumulate in fish lipids could also easily be determined using the POCIS sampler.

IV. Application in sediment monitoring

Until recently sediment monitoring has relied on the determination of total or normalised contaminant concentrations. This approach, however, does not distinguish between freely dissolved and bound molecules and aims to assess the presence of chemicals rather than their activity and availability [67]. Since many laboratory and field studies have demonstrated that biological effects in benthic organisms are not generally related to the total concentration

of contaminants in sediments, alternative and more representative measures of the bioavailable fraction of contaminants in sediments are required [68]. In addition, it has been shown that traditional empirical models tend to overestimate pore water concentrations.

Application of passive sampling to sediment monitoring can be undertaken *in situ* with buried passive samplers or in batch experiments in the laboratory following grab sampling or coring (and sectioning). Passive samplers can be used to:

- Determine freely dissolved contaminant concentrations in pore water;
- Estimate sediment-pore water partition coefficients for contaminants of interest;
- Measure contaminant desorption rates;
- Estimate the fraction of contaminants available for desorption within a relatively short time scale or fraction effectively contributing to the partitioning with pore water and/or biota;
- Measure surface water/pore water activity or fugacity ratios to estimate whether sediments act as a source or sink for contamination in the overlying water;
- Measure the total contaminant amount in sediment that is available for release to the aqueous phase within a given time.

The most commonly used passive sampling approach is based on the principle that the passive sampler is exposed to a sediment sample until a thermodynamic equilibrium between the two phases is established. According to partition theory, the concentration of a compound in the sampler is directly proportional (by the equilibrium partitioning coefficient between sampler and water) to the freely dissolved concentration of sampled compounds in pore water. Because this concentration is considered to be the driving force for the uptake of the contaminants by aquatic organisms, the bioavailability of a substance can be directly assessed using passive samplers. However, depending on sampler characteristics (e.g. surface area and volume), equilibrium may not be established for the most hydrophobic compounds during exposure and therefore performance reference compounds (such as used for surface water deployments) can be used to quantify sampler-pore water exchange kinetics and dissolved concentrations in such situations [67,69].

In all cases it is absolutely crucial to select an appropriate combination of sampler and sediment volumes in order to avoid significant depletion of the pore water phase. The true freely dissolved concentration of contaminant in pore water can be determined when the sampler's sorption capacity is kept well below that of the sediment sample to avoid depletion during the extraction [20,70,71]. When the sorption capacity of sampler to sediment is kept high, samplers can be used to measure the total contaminant amount in sediment that is available for release to the aqueous phase within a given time. This represents the fraction available to take part in partitioning with sediment organisms. The contaminants remaining in the sediment following such extraction can be considered effectively unavailable [72]. This fraction can also be estimated by repeated/successive extractions of the sediment with an adsorbent phase such as Tenax [73,74]. Such procedures also enable the quantification of contaminant desorption rates.

The concentration difference between the *in situ* deployed samplers from the sediment and those from the overlying water give direct information on the fugacity difference between sediment and water, and on the direction of the contaminant diffusion at the sediment−water interface as well [20,71,75]. This enables identification of sites where remedial treatment of sediment may be appropriate. Other parameters, such as sedimentation rates and the spatial

resolution of sediment sampling close to the sediment-water interface, are crucial for such measurements.

For metals, the technique of diffusive gradients in thin films (DGT) provides an important contribution to understanding processes that metals undergo in sediments. DGT provide measurements in sediments that can be reported either as the mean flux of labile metal species to the device during the deployment time, or as the mean interfacial concentration in pore water. For a given device and deployment time, the interfacial concentration can be related directly to the effective concentration of labile metal [76]. This concentration represents the supply of metal to any sink, be it DGT or an organism that comes from both diffusion in solution and release from the solid phase. The primary use of DGT in sediments has been to investigate the distribution of solutes (metals) at high spatial resolution and to interpret the dynamics of the pollutant release from sediment [76]. Pore water concentration profiles with a fine resolution can be obtained by deploying DGT probes vertically in sediment and across the sediment–water interface. Modelling of metal accumulation in DGT with increasing exposure time can allow the estimation of sediment–water partition coefficients for metals of interest.

It is crucial that the risk assessments of contaminants in sediment are as reliable as possible. It is widely accepted that it is the dissolved fraction of pollutants that is available for interaction with biological tissues and that can thereby cause bioaccumulation and/or biological effects. Several studies have shown that biota concentrations, calculated from partition coefficients based on classical equilibrium partition theory, are often orders of magnitude higher than the actual measured concentration in the sediment-dwelling organisms. But, using the freely dissolved concentration derived from passive samplers, the calculated concentrations in biota are in good agreement with the actual measured values [77].The methodology using passive sampling is leading to a much better understanding of how hydrophobic contaminants interact with sediment. This will allow a better estimation of (bio)availability, as can be validated through comparison with uptake by organisms. Data obtained with passive samplers can be used in risk calculations for sediment-bound contaminants with regard to any need for remedial measures for contaminated sediments and these studies would be an important input with regard to environmental quality standards for contaminants in water proposed in the EU Water Framework Directive.

So far, the methodology of passive sampling in sediment has been tested and successfully validated in studies focused mainly on priority groups of contaminants that cause major environmental problems, such as polycyclic aromatic hydrocarbons or polychlorinated biphenyls. Nevertheless, this concept can also be successfully applied in risk-oriented monitoring of other groups of contaminants in sediments, including emerging substances. Further research is needed to develop novel solid phases with strong affinity to a broad range of compounds that may be found in sediments. These sampler materials should allow an easy extraction and analysis of accumulated substances [68].

V. Application in monitoring of contaminants in biota

Knowledge of dissolved phase chemical concentrations is a critical part of understanding how aqueous exposure levels relate to the concentrations of residues measured in organisms in various trophic levels of aquatic ecosystems. The freely dissolved concentrations of pollutants represent the driving force for bioconcentration. Thus, passive

samplers enable *in situ* determination of the bioaccumulative exposure of organisms at the lowest trophic level (filter feeders, e.g. mussels), in nearly all food chains, to hydrophobic organic compounds [78,79]. The estimation of bioaccumulation factors (BAFs) in certain species of concern (e.g. mussels) has also been demonstrated [79,80]. Moreover, since the contribution of dietary uptake for organic compounds with log K_{ow}s < 5.5 is generally very small, organism exposure assessment can be potentially extended to higher trophic levels for less hydrophobic compounds.

Bayen et al. [81] recently reviewed kinetic studies of the uptake of neutral non-polar chemicals from the aqueous phase into organisms (fish, bivalve, crustacean, insect, worm, algae, and protozoan) and passive samplers. They demonstrated that passive samplers are biomimetic when diffusional partitioning processes mediate concentrations in organisms of concern (i.e., when residue accumulation in organism tissues follows equilibrium partitioning theory). Huckins et al. [78] discussed in detail accumulation into the SPMD sampler compared with that into biomonitoring organisms.

The large number of variables, which potentially affects the accumulation of hydrophobic organic compounds in biota, suggests that it is unrealistic to expect any single passive sampler to be biomimetic of all biomonitoring organisms. Also, it is similarly unrealistic to expect that one or two species of biota mimic bioaccumulation in all organisms of concern. Variables affecting pollutant accumulation in passive samplers are limited to the sampler properties, physicochemical properties of the sampled chemical, exposure site conditions (e.g. temperature and turbulence, and exposure scenario factors such as the constancy of chemical concentrations during the exposure period). The ability to generate chemical-specific calibration data and then adjust these values to site-specific conditions (e.g. using PRCs) [22] means that analyte concentrations obtained using passive samplers are directly comparable across sampling sites.

There are some fundamental similarities in the characteristics and processes affecting the accumulation in biota and passive samplers, especially for hydrophobic organic compounds. Diffusion of non-polar compounds through non-porous polymers used in passive sampler construction mimics the diffusion across bio-membranes. Also, partitioning between the polymers, organism lipids and the exposure water is similar and can be described by the equilibrium partitioning theory. Finally, the surface-to-volume ratio appears to be a critical parameter for the uptake rate of the more hydrophobic chemicals, both for samplers and organisms.

Monitoring by passive samplers has some advantages over the use of biota. Passive samplers can be prepared to a standardised quality characterised by low initial concentration of contaminants, uniform composition, diffusion and sorption properties. In contrast, test organisms often contain background contamination levels and they are naturally variable in composition. As a result, variability of chemical analysis of biota or sediment is in most cases higher than that associated with analysis of passive samplers. Moreover, the simple polymeric matrix composition of passive samplers provides sample extracts that contain much less matrix interference in comparison with extracts from biota and sediment. Samplers can be applied in almost any environment with a broad range of water quality properties and even in very polluted sites where biomonitoring organisms may not survive. In contrast, biomonitoring organisms can be applied only within a certain geographical range and they do not tolerate extreme exposure conditions (e.g. temperature, pH, pollution, and salinity). The uptake process of pollutants in passive samplers is simple (by diffusion and sorption), whereas it is more complex in organisms since it includes bioconcentration, bioaccumulation

and metabolism. The complexity of these processes is increased by behavioural, physiological and anatomical characteristics of biomonitoring organisms.

The uptake capacity of polar organic compounds in biomonitoring organisms is in most cases low. Also, these compounds reach steady state within a short period of time, so that biological sampling of polar organic compounds has a very limited applicability [82]. In comparison with biomonitoring organisms, passive samplers demonstrate better retention of contaminants that are absorbed during peak exposure events. The amount of chemicals accumulated in passive samplers in most cases reflects the dissolved, readily bioavailable, concentration in sampled water, whereas the estimation of contaminant bioavailability from total amount found in an organism body may be difficult, owing to the presence of a non-incorporated portion of the pollutant in its intestines.

For metals, the DGT technique measures directly the variables needed to assess water quality. Uptake of trace metals across living membranes is determined by free ion concentrations when membrane transport is slow and by the total concentration of labile species when membrane transport is fast. Deployment of twin DGT devices with different diffusive gel layers can provide an *in situ* measurement of both labile inorganic and total labile species. Free ion activities can be calculated from labile (free and/or kinetically-labile species in solution) inorganic concentrations.

VI. Application in ecotoxicity assessment

Ecotoxicity assessments are an invaluable tool for the evaluation of water quality and in some countries ecotoxicity assessments are compulsory, for example, with direct toxicity assessments of effluents released to the environment [83]. One of the main advantages of ecotoxicity assessments is that they give an integrated picture of the total toxic burden of the complex mix of chemicals that are present in environmental samples. It is often the case that toxic substances cannot be identified and chemical monitoring methods cannot be targeted, but ecotoxicity assessments can still measure the effect of these unknowns in environmental samples. Such samples can be tested, either at the level of organisms (e.g. daphnids or fish embryos [83],[84]), at the level of cells (e.g. fish cell lines) [84] or at the sub-cellular level (e.g. specific binding of chemicals to receptors using reporter gene assays). An example of such a reporter assay comes from research on endocrine disruptors, where cells have been modified to express oestrogen receptors ([85],[86]). The binding of oestrogens – or oestrogen-like compounds – to the receptors leads to the production of an enzyme which in turn induces a colour change in the medium (or light emission) that can be quantified easily. Commonly, bioassays are applied to whole water samples, extracts of water samples or extracts of organism tissues. Applying the same bioassays to extracts of passive samplers is straightforward and an increasing number of studies have explored this.

VI.1. Passive samplers as mimics for bioconcentration

Combining bioassays with (grab) water samples has the same limitations (or advantages) as compared to combining chemical analyses with water samples. Grab samples give an accurate picture of the total concentration only at a certain point in time. Grab samples again provide data on toxic effects that relate only to the time of sampling. As an alternative, combining ecotoxicity assessments with monitoring of chemicals in biota, for example by analysing extracts of aquatic organisms, is certainly feasible, and produces more representative results than analysing grab samples, but has the same limitations associated

with monitoring of contaminants in biota as discussed in the previous section (i.e. section V.). Combining bioassays with passive sampling circumvents the limitations that are associated with grab samples and chemical monitoring in biota. Furthermore, a passive sampler mimics bioconcentration of freely dissolved chemicals over cell walls, membranes or a filter feeding apparatus or gills. Thus, testing passive sampler extracts in bioassays has a high relevance as this reflects exposure scenarios in the aquatic environment.

VI.2. Which passive sampler suits which bioassay?

Numerous biological assays have already been used successfully in combination with passive samplers. Many studies deal with quantification of environmental oestrogens with reporter gene assays in extracts from SPMDs ([87,88]), POCIS ([89],[90],[91],[92],[93],[94]) and Chemcatchers ([95]). An assay that covers compounds such as PAHs and dioxin-like compounds, the EROD assay, has been used with extracts from SPMDs ([87]) and in combination with the Toximeter ([96]). Several studies describe the use of Chemcatchers and POCIS to measure photosystem II (PS-II) inhibitors ([97],[98],[99],[100]). Microtox, a bacterial whole cell assay that is used to measure baseline toxicity, has also been used in combination with POCIS ([94],[100]), Chemcatcher ([98]) and SPMD ([101]) extracts. Muller et al. tested Chemcatchers extracts in the umuC assay, which is used to assess genotoxic effects in response to the presence of DNA-damaging chemicals within the sampled mixture. [98]. Mutagenicity has been assessed in extracts from SPMDs by Rastall et al. [87]. Shaw et al. used Chemcatchers in combination with two invertebrate bioassays, coral larval settlement and sea urchin larval development, in addition to bacterial luminescence and microalgal photosynthesis [102].

The above listing is certainly not complete but illustrates that the range of bioassays is very diverse, spans across organisational levels – from gene expression to whole organisms – and covers multiple modes of action. In addition, both relatively hydrophobic absorptive passive samplers and adsorptive samplers used to sample more polar chemicals have been used in combination with these multiple end-point bioassays. Although various combinations of passive sampler and bioassays have been explored, it is difficult to list fixed combinations for passive samplers and biotests. The reason for this is that the range of compounds that is targeted by bioassays is often very diverse and no single sampler can adequately target a set of chemicals with diverse physicochemical properties. This issue can be illustrated for an algal test that is used to quantify the effects of herbicides such as diuron and atrazine that inhibit PS-II. Log K_{ow} values for PS-II inhibitors range from below 1 (e.g. metamitron) to 4 (dipropetryn). Metabolites of these compounds can also be active PS-II inhibitors and may further extend the log K_{ow} range of possible PS-II inhibitors. Log K_{ow} ranges for compound classes targeted by other bioassays can be even larger; e.g. PCBs with log K_{ow} values up to 7 are oestrogenic whereas benzotriazole, with a log K_{ow} of 1.4, is anti-oestrogenic. As passive samplers usually target a range of log K_{ow} values spanning 2 to 3 orders of magnitude [87], it is clear that not all compounds that are active in a bioassay will be sampled in a similar, integrative fashion. Some toxic compounds may reach equilibrium well before others. Thus, even when the concentration ratios of various toxicants in the environment are constant, different integrative sampling windows of individual compounds will cause their concentration ratios in a passive sampler to vary over the deployment time of the sampler. In addition, different compounds with the same mode of action may have very different diffusion coefficients within a given sampler (or over a membrane that envelops the sampling phase), and thus behave differently in response to changing environmental conditions.

Although no single passive sampler covers all compounds that act on a certain organism or have a certain mode of action, this does not negate the rationale of combining passive samplers with ecotoxicity assessments. The use of bioassays is a more holistic approach to assessing the risk associated with exposure, since the technique provides a functional integrative assessment of mixture toxicity for chemicals accumulated by passive samplers to levels sufficient to induce a biological response. So, by combining passive sampling with bioassays it is possible to avoid intensive chemical analyses. However, when using a specific bioassay in a sampling campaign, one has to attempt to identify the main possible toxicants that may be present at the sampling locations and select a sampler that best covers the log K_{ows} of those toxicants.

VI.3. The link between biological and chemical analysis

It is common to express the effect of water samples in ecotoxicity tests as a dilution factor, i.e. at what dilution the sample still leads to a certain effect level in the bioassay [83]. The same approach can be used for a passive sampler and one can express the toxic effect in terms of a certain portion of a sampler extract [89]. An alternative approach was developed by Koči et al., a toxicity measure corrected for the volume sampled by a passive sampler (vtox [103]). Although these approaches are clearly informative, and one can classify more or less polluted sites and derive water quality criteria on this basis, it is difficult to compare chemical and biological analyses directly.

Another system to evaluate effects in bioassays is the toxic equivalent (TEQ) concept. It was first established for effects caused by dioxins and PCBs on the arylhydrocarbon receptor [104]. Subsequently, the concept has been applied to oestrogenic activity, phytotoxicity and other types of toxicity. In essence the TEQ concept revolves around comparing the dose response curve induced by a sample to the dose response induced by a reference compound (see [105]). The biological response to the sample can then be expressed in terms of an amount or concentration of the reference compound. This approach can then be complemented by testing many individual compounds in the bioassay to establish their dose-response curves; from these one can derive their potencies relative to the reference. When a set of compounds has been quantified in an environmental sample by means of chemical analysis, concentrations of these compounds can be multiplied by the potencies of the compounds and added together (assuming concentration addition applies) [106]. The sum of the individual chemicals signifies the toxicity based on chemical analysis and the minimum expected response of the environmental sample in the biological test. This approach is well established and many legal TEQ limits are in place for dioxin-like compounds (e.g. the EU limit for fish = 4 pg WHO-PCDD/F-TEQ /g fresh weight) [107].

Being able to relate results from a bioassay directly to those obtained by chemical analyses has the main advantage that one can assess whether most of the toxicity has been accounted for by the chemical analyses, or whether major toxicants have been missed. In passive sampling, linking biological analyses to chemical analyses has been done in several studies ([90],[92],[93],[97],[99]). Attention has focused on oestrogens, PAHs and herbicides and recently also on baseline toxicity ([100]).

VI.4. Identification of toxic compounds in passive samplers: effect-directed analysis

Effect-directed analysis (EDA) is another area where ecotoxicity assessments can be used [108]. In EDA, an environmental sample is fractionated chromatographically and next, the

various fractions are tested individually for toxic effects. Once toxicity has been detected in a fraction, this fraction can be analysed chemically to identify possible toxicants. This is a very powerful method for identifying major toxicants in a complex environmental sample, particularly when the bioassay data are expressed as TEQ to allow for direct comparisons between data from chemical and biological analyses.

The EDA approach has been applied frequently in sediments [68,109]. As yet, only one example comes from passive sampling. Rastall et al. [110] fractionated SPMD extracts and tested these for activity in a reporter gene assay for oestrogen receptor agonists. They found that oestrogens sampled by SPMDs cover a wide log K_{OW} range, but individual oestrogens could not be identified. This area is one where much progress can be made.

In a recent field study where POCIS were deployed for five weeks in treated sewage effluents, a toxic spill occurred at one of 21 sites. The toxic spill caused a fish kill in the receiving river, and the POCIS from this site recorded the highest baseline toxicity in a bacterial test [100]. Using chemical analyses of water samples taken directly following the fish kill, the toxicant(s) causing fish mortality could not be identified (A. Stockli, personal communication). Although EDA was not attempted with these POCIS, it clearly points to an effective use for passive samplers as monitors for such peak toxic events.

VI.5. How does the bioassay response in passive sampler extracts relate to sampler exposure conditions?

The rate at which a compound is sampled by a passive sampler depends on the properties of the compound, the properties of the sampler and the environmental conditions at the deployment site. For individual chemicals it is fairly straightforward to establish relationships between compound properties, environmental conditions and sampling rates [111]. In contrast, the response in bioassays is the sum of the effects caused by contributions from at best a few (for highly specific endpoints) to a large number of individual compounds. As the composition of the mixtures and the relative abundance of the toxicants can vary widely across sites, and over time, this poses certain limitations on how bioassay results can be interpreted with respect to varying environmental conditions. Interpretation can be even harder when a sampler includes a membrane. For example, it was shown that more polar compounds (log K_{OW} < 2) move more rapidly over a polyethersulphone membrane than less polar compounds (log K_{OW} > 3) into the SDB sampler phase in the Chemcatcher [99]. For short sampling windows, less polar compounds may be under-represented in the mixture of toxicants which will skew results. Thus, when combining bioassays and passive sampling one has to appreciate the uncertainties caused by the fact that the suites of target chemicals cover a wide range of physicochemical properties. As a result, different mixtures of chemicals with the same mode of toxic action will respond differently to varying exposure conditions.

VII. Quality assurance, quality control and normation

If passive sampling is to become accepted and used in a regulatory context for monitoring water quality across Europe, then there is a need for the development of improved validation methods and setting up of the appropriate quality control and quality assurance schemes for the technology. This would involve a set of activities (e.g. development of standard certified reference materials, setting-up of round robin exercises and the publication of standard methods) as those have been established for the validation of analytical techniques for the

measurement of various analytes of importance in different environmental matrices. There is also a need for associated accreditation schemes laboratories involved in passive sampler calibration measurements in the lab and those using passive samplers in the field.

The implementation of the above is not straightforward. For laboratory calibrations of the samplers, there is a need for large volumes of reference materials to be available. For field trials it may be possible to use reference sites that are well characterised and stable in chemical composition. An attempt to compare various water monitoring methods that could potentially be used in support of the Water Framework Directive was undertaken as part of a European Union-funded project [112] and the results of this activity have been summarized [113]. A number of field trials were undertaken in different water bodies across Europe and the results from these multiple comparisons indicated the potential utility of this approach. But these activities are expensive to develop and organize and therefore regulators and other end-users need to be convinced of the value of these alternative monitoring techniques so that they can support the provision of EU funding to enable this important research in support of policy and associated legislation.

Several interlaboratory field trials, where a range of passive sampling technologies will be evaluated at European riverine sites, are being set up in 2010. The first is being facilitated within the framework of AQUAREF (the organisation coordinating French laboratories involved in water monitoring) [114]. A call was made in early 2010 for the participation of research groups across Europe who are involved in either developing or using passive sampling technology. Several field sites were selected and include both surface water and a marine lagoon in France. This trial focuses on the monitoring of pesticides, PAHs and metals. The second exercise is being proposed by the NORMAN network, where the focus of this exercise will be on the application of passive sampling for monitoring pollutants of emerging concern. Further, an interlaboratory proficiency testing scheme aimed at the chemical analysis of a range of hydrophobic organic compounds and metals in two commercially available passive samplers has been launched recently in the Czech Republic. [115] The results of these exercises will be of value in demonstrating the future utility of the technology and will be helpful in the design of similar activities in the future.

Progress has been made on the normation of passive sampling methods. One of the deliverables of the European Union-funded project STAMPS [116] was the development of a British Standards Institution Publicly Available Specification [117]. This specification provides guidance for end-users on the preparation, deployment and associated quality assurance requirements for the use of passive samplers in surface waters. The specification is currently under consideration for development of a CEN/ISO standard [118].

VIII. Application of passive samplers in regulatory monitoring

"Emerging pollutants" can be defined as pollutants that are currently not included in routine monitoring programmes at the European level and which may be candidates for future regulation, depending on research on their (eco)toxicity, potential health effects and public perception and on monitoring data regarding their occurrence in the various environmental compartments. In many cases knowledge of their ambient and background levels in water, sediments and biota is still limited and even less is known of the long-term ecotoxicological effects of these emerging contaminants. At such an early stage, it is difficult if not impossible to derive appropriate environmental quality standards (EQS) for these chemicals without the use of significant safety factors. Therefore compliance testing against EQS values is not

often undertaken for these substances. Most monitoring programmes that include emerging pollutants are in general screening studies [119,120] aimed at obtaining additional information on the occurrence of these compounds in various aquatic environmental matrices, where they are likely to accumulate. Passive sampling may be favoured over matrices such as sediments and biota for such screening. It draws advantage from a simple matrix composition that enables simplified sample extraction, cleanup and the subsequent instrumental analysis. Moreover, field exposure of passive samplers in various matrices such as surface waters, wastewaters and sediment can be standardised. In addition, the use of, for example absorption-based samplers for the screening of non-ionic hydrophobic substances in water and sediments results in limits of detection which are generally substantially lower than those that can be achieved through bottle sampling [121]. Another factor to be taken into account in screening studies is the possible (mostly unknown) temporal variability in the concentration of emerging pollutants in water. Continuous monitoring possible with passive samplers can help in reducing the uncertainty associated with sampling when concentrations vary in time. For example, variable concentrations may be observed for emerging contaminants that are emitted in the urban environment and that can ultimately be released from sources such as landfill and wastewater effluents. This is, however, also valid for compliance monitoring of more conventional pollutants for which EQS have been derived and are in use (e.g. for the EU WFD). Despite the measurement of a different fraction of contaminants in water, passive samplers can be used to support data collected by infrequent bottle sampling [122,123] or through monitoring in biota. This allows continuous monitoring in conditions where this would not be feasible and improves the representativeness of the sampling. The integrative nature of passive sampling combined with extremely low limits of detection for non-ionic hydrophobic organic contaminants may represent the only acceptable way to monitor some of these substances in surface waters. Since passive sampling is based on the measurement of dissolved phase pollutants, further comparison with EQS based on “whole water” concentration values may require additional information to account for the fraction of contaminants associated with other phases such as dissolved organic carbon and suspended particulate matter. In the long term, such a strategy requires the development of water body-specific knowledge of contaminant speciation and partitioning. The additional information on non-dissolved fractions of compounds can be obtained in parallel representative measurements of these compounds in suspended particular matter or bottom sediments. The sum of the representative (e.g. TWA) contaminant concentration in the dissolved phase (provided by passive samplers) and that bound to colloids and particles (provided by sampling of suspended particulate matter) will provide the measure of total concentration that can be applied in compliance checking with EQS.

Moving towards an implementation of passive sampling for regulatory monitoring of emerging substances will require the identification of suitable material for accumulation of target compounds and an accurate characterisation and calibration of the devices. In this regulatory context, passive samplers may be applied to the monitoring of surface waters in both populated and remote areas and other aqueous matrices such as wastewaters and other effluents. Samplers can be deployed simultaneously in different media in order to detect gradients in chemical activity/concentration and understand fluxes of these emerging substances.

IX. Future trends

There are several future trends for the development of passive sampling techniques for emerging substances.

Novel materials will need to be tested as selective receiving phases (e.g. ionic liquids, molecularly imprinted polymers, and immuno-adsorbents), together with membrane materials that permit the selective diffusion of chemicals. Novel synthetic absorbent polymer materials with high retention capacity of polar organic compounds may enable the replacement of currently used adsorption-based samplers for which data conversion into aqueous concentrations is often difficult.

A major challenge in the future development of the technology is the calibration of devices to enable the quantification of the concentration of emerging substances present in water. In comparison with devices designed for sampling hydrophobic organic compounds, sampling of most emerging substances is more complex. In addition to the common factors (temperature, water turbulence and biofouling), other factors (e.g. salinity, DOC level, pH, and the presence of complex mixtures of contaminants) may significantly affect the performance of samplers of emerging substances and these need to be evaluated. There are several routes to reduce uncertainty associated with the passive sampler data. These include quantitative assessment, reduction or control of the known factors which impact on sampler performance. For samplers where analytes are accumulated in the receiving phase by absorption mechanisms, PRCs can be successfully employed for improving the accuracy of the measurement of TWA concentrations of contaminants in the field. However, further research is needed to understand accumulation kinetics in samplers fitted with adsorbent-type receiving phases. Mechanical control of constant water flow conditions around the receiving phase in the field enables sampling rates of WBL-controlled samplers that are unaffected by turbulence [124]. Such devices require an *in situ* use of rotors or pumps that force water motion around the sampling devices. Thus, they cannot be classified as true “passive samplers”. However, miniaturised devices that require only a low energy supply (e.g. batteries or solar cells) for the operation of pumps can be deployed in the same way as passive samplers.

Miniaturised devices present a further trend in technology development. Small samplers are usually less expensive to use because of the lower costs of materials needed for their preparation and the reduced equipment requirements for their deployment. Lower volumes of solvents and reagents are consumed during their subsequent processing. Small samplers also offer the advantage of easy transportation to and from the sampling site. As miniaturised devices should not deplete the bulk matrix, they can be used in situations where space, volume and the flow of water are limited; for example, in groundwater boreholes.

The ability to predict kinetic and thermodynamic uptake parameters for passive samplers using quantitative structure property relationship (QSPR) models describing interactions of sampled compounds with materials used in the construction of devices is also important. This may help to reduce the amount of required laboratory-based calibration experiments.

Development of biomimetic devices capable of simulating the accumulation of toxic chemicals in tissues of aquatic organisms will enable a reduction in the use of chemical monitoring in biota in routine monitoring programmes. It will also decrease the uncertainty

associated with the data obtained, as this is based on highly variable samples of biological material.

The combination of the deployment of passive samplers followed by the biological testing of sampler extracts with the aim of detecting and subsequently identifying toxicologically relevant compounds offers much potential. This approach can provide information concerning the relative toxicological significance of waterborne contaminants and hence help to improve risk assessments for different water bodies.

Finally, further development of QA/QC, method validation schemes, and standards for the use of passive sampling devices is urgently needed. Successful demonstration of the performance of passive samplers alongside conventional sampling schemes as well as inter-laboratory studies that demonstrate reproducibility of data produced by different designs of passive samplers will help to facilitate the acceptance of passive sampling in routine regulatory monitoring programmes in the future.

Table 1. List of most discussed emerging pollutants in the aquatic environment and the established or expected/potential performance of passive samplers of these compounds.

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
Natural products	Cyanotoxins	Microcystins	-	+	**d**	[125]
Antioxidants	Antioxidants	2,6-Di-tert-butylphenol	-	+		
		4-tert-Butylphenol	-	+		
		BHA	-	+		
		BHQ	-	+		
		BHT	-	+		
Antifouling compounds	Antifouling compounds	Irgarol	-	+	**d**	[9,99]
	Organotin compounds	Dibutyltin ion	-	+	**d**	[38,39]
		Monobutyltin ion	-	+	**d**	[38,39]
		Tetrabutyltin ion	-	+	**d**	[38,39]
		Diphenyltinion	-	+	**d**	[38,39]
		Triphenyltin ion	-	+	**d**	[38,39]
Detergents	Ethoxylates/ carboxylates of octyl/nonyl phenols	4-Nonylphenol di-ethoxylate (NPE2O)	-	+	**d**	[25,126, ,127]
		4-Nonylphenol mono-ethoxylate (NPE1O)	-	+	**d**	[25,126 ,127]
		4-Nonylphenoxy acetic acid (NPE1C)				

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		4-Nonylphenoxyethoxy acetic acid (NPE2C)				
		4-Octylphenol di-ethoxylate (OPE2O)	-	+	**d**	[25,126,127]
		4-Octylphenol mono-ethoxylate (OPE1O)	-	+	**d**	[25,126,127]
		4-Octylphenoxy acetic acid (OPE1C)				
		4-Octylphenoxyethoxy acetic acid (OPE2C)				
Disinfection by-products (drinking water)	Iodo-trihalomethanes		-			
	Bromoacids		-			
	Bromoacetonitriles		-			
	Bromoaldehydes		-			
	Haloacetic acids (chloro-, bromo-, iodo-)		-			
	Other disinfection by-products	Bromate				
		Cyanoformaldehyde				
		Decabromodiphenyl ethane				
		Hexabromocyclododecane (HBCD)	+	-		
		NDMA	+	-	**d**	
Plasticizers	Phthalates	Benzylbutylphthalate (BBP)	+	-		
		Diethylphthalate (DEP)	+	-		
		Dimetylphthalate (DMP)	+	-		
		Di-n-butylphthalate (DBP)	+	-		
		Di-n-octylphthalate (DOP)	+	-		
	Other	Bisphenol A	-	+	**d**	[25,128,142, 129]
		Triphenyl phosphate			**d**	
	Benzophenone derivatives	2,4-Dihydroxybenzophenone	-	+	**d**	[65]

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
Flame retardants	Brominated flame retardants	1,2,5,6,9,10-Hexabromocyclododecane (HBCD)	+	-		
		Tetrabromo bisphenol A (TBBPA)	+	-		
		Tetrabromo bisphenol A bis (2,3 dibromopropylether)	+	-		
		Hexabromocyclododecane (isomers)	+	-		
		Decabromodiphenyl ethane	+	-		
	Polybrominated diphenylethers	2,2',3,4,4',5',6-Heptabromodiphenyl ether (BDE 183)	+	-	**d**	
		2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153)	+	-	**d**	
		2,2',4,4',5,6'-Hexabromodiphenyl ether (BDE-154)	+	-	**d**	
		2,2',4,4',5-Pentabromodiphenyl ether (BDE-99)	+	-	**d**	
		2,2',4,4',6-Pentabromodiphenyl ether (BDE-100)	+	-	**d**	
		2,2',4,4'-Tetrabromodiphenyl ether (BDE-47)	+	-	**d**	
		2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether (BDE-209)	+	-	**d**	
		Technical Decabromodiphenyl ether	+	-	**d**	
		Technical Octabromodiphenyl ether	+	-	**d**	
		Technical Pentabromodiphenyl ether	+	-	**d**	
	Organo-phosphates	Tri-(dichlorisopropyl)-phosphate		+	p	[130]
		Triethylphosphate		+	p	
		Tri-n-butylphosphate		+	**d**	
		Triphenylphosphate		+	**d**	
		Tris(2-chloroethyl)-phosphate		+	p	
	Chlorinated paraffins	Long chain PCAs (lPCAs, C>17)	+	-	p	

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Medium chain PCAs (mPCAs, C14-17)	+	-	p	
		Technical PCA products	+	-	p	
Fragrances	Fragrances	Acetylcedrene		+	p	
		Benzylacetate		+	p	
		Benzylsalicylate		+	p	
		Camphor		+	p	
		g-Methylionone		+	p	
		Hexylcinnamaldehyde		+	p	
		Isoborneol		+	p	
		Isobornylacetate		+	p	
		Isoquinoline		+	p	
		d-Limonene		+	p	
		Methyldihydrojasmonate		+	p	
		Methylsalicylate	-	+	**d**	
		p-t-Bucinal		+	p	
		Terpineol		+	p	
	Nitro musks	Muskketone	+	-	**d**	
		Muskxylene	+	-	**d**	
		Musk ambrette	+		p	
	Macrocyclic musks					
	Polycyclic musks	AHTN (Tonalide)	+	-	**d**	
		Galaxolide	+	-	**d**	
		OTNE	+	-	**d**	
		AHDI (Phantolide)	+	-	**d**	
		ADBI (Celestolide)	+	-	**d**	
		ATII (Traseolide)	+	-	**d**	
Gasoline additives	Dialkyl ethers	Methyl-tert-butyl ether (MTBE)	-	-		
Indus-trial chemi-cals	Industrial chemicals	TCEP				
		Triphenyl phosphine oxide				
Perfluoro-alkylated substances	Perfluoroalkylated substances	Perfluorooctane sulfonate (PFOS)		+	p	
		Perfluorooctanoic acid (PFOA)		+	p	
Personal care products	Sun-screen agents	4-Methylbenzylidene camphor	+	+	**d**	

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Benzophenone	-	+	**d**	
		Benzophenone-3	-	+	**d**	
		Butyl methoxydibenzoyl-methane			p	
		Ethylhexyl methoxycinnamate	+	+		
		Eusolex				
		Homosalate				
		N,N-Diethyltoluamide	-	+	**d**	
		Octocrylene				
		Oxybenzone				
	Insect repellents	N,N-diethyl-m-toluamide (DEET)	-	+	**d**	
		Bayrepel				
	Carriers	Octamethylcyclotetrasiloxane (D4)	+	-	p	
		Decamethylcyclopentasiloxane (D5)	+	-	p	
		Dodecamethylcyclohexasiloxane (D6)	+	-	p	
		Hexamethyldisiloxane (HM or HMDS)	+	-	p	
		Octamethyltrisiloxane (MDM)	+	-	p	
		Decamethyltetrasiloxane (MD2M)	+	-	p	
		Dodecamethylpentasiloxane (MD3M)	+	-	p	
	Parabens (hydroxybenzoic acid esters)	Methyl-paraben	-	+	p	
		Ethyl-paraben	-	+	p	
		Propyl-paraben	-	+	p	
		Isobutyl-paraben	-	+	p	
Pesticides	Polar pesticides and their degradation products	Acetochlor	-	+	**d**	[26,131,132]
		Amitrole	-	+		
		Bentazone	-	+	**d**	
		Bromofos-ethyl	-	+		
		Carbazole	-	+		
		Carbendazim	-	+	**d**	[99]
		Carboxin	-	+		
		Glyphosate	-	+		
		Chloridazon	-	+	**d**	
		Clopyralid	-	+		
		Chlorpropham	-	+		
		Chlorpyrifos	-	+	**d**	[130]
		Chlorotoluron	-	+	**d**	
		2,4 D	-	+	**d**	[59]
		Dicamba	-	+	p	[59]

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Desethylterbutylazine	-	+	**d**	
		Desmedipham	-	+		
		Desmetryn	-	+		
		Diazinon	+	+	**d**	[99]
		Diclobenil	-	+		
		d-Dichlorvos	+	+	**d**	[57]
		Dinoterb	-	+		
		Endosulfan-sulfate	+	+	**d**	[133]
		Ethoprophos	-	+		
		Ethofumesate	-	+	**d**	
		Fluroxypyr	-	+		
		Heptenophos	-	+		
		Iodofenphos	-	+		
		Imidacloprid	-	+		
		MCPA	-	+	**d**	[59]
		MCPB	-	+	p	
		MCPP (Mecoprop)	-	+	p	[99]
		Metalaxyl	-	+	**d**	[27]
		Methomyl	-	+		
		Metamitron	-	+	**d**	
		Mevinphos	-	+		
		Phenmedipham	-	+		
		Prometryn	+	+	p	
		Prometon	-	+	**d**	
		Secbumeton	-	+		
		Terbutryn	+	+	p	[99]
		Terbutylazine	-	+	**d**	[134,99]
		Thiabendazyl	-	+	**d**	
		Triadimefon	-	+		
	Other pesticides	Cypermethrin	+	-	**d**	
		Deltamethrin	+	-	**d**	
		Permethrin	+	-	**d**	[135]
	New pesticides	Sulfonyl urea				
	Degradation products of pesticides	Desisopropylatrazine	-	+	**d**	[27]
		Desethylatrazine	-	+	**d**	[27,99]
Bio-cides	Biocides	Triclosan	+	+	**d**	[129,136]
		Methyltriclosan	+	+	**d**	[137]
Pharmaceuticals	Analgesic	Acetaminophen (paracetamol)	-	+	**d**	[129,138,139]
		Codeine	-	+	p	
		Hydrocodone	-	+		
	Anorexic	Fenfluramine	-	+	p	

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
	Anthelmintic	Ivermectin	-	+	p	
	Antibacterial	Amoxicillin	-	+	p	
		Ampicillin	-	+	p	
		Azithromycin	-	+	**d**	[128,140]
		Chloramphenicol	-	+	p	
		Chlortetracycline	-	+	p	
		Ciprofloxacin	-	+	p	
		Clarithromycin	-	+	**d**	[95,141]
		Cloxacillin	-	+	p	
		Danofloxacin	-	+	p	
		Dicloxacillin	-	+	p	
		Doxycycline (anhydrous)	-	+	p	
		Doxycycline (monohydrate)	-	+	p	
		Enoxacin	-	+	p	
		Enrofloxacin	-	+	p	
		Erythromycin	-	+	**d**	[141]
		Flumequine	-	+	p	
		Josamycin	-	+	p	
		Lincomycin	-	+	p	
		Methicillin	-	+	p	
		Minocycline	-	+	p	
		Norfloxacin	-	+	p	
		Novobiocin	-	+	p	
		Ofloxacin	-	+	p	
		Oleandomycin	-	+	p	
		Oxacillin	-	+	p	
		Oxytetracycline	-	+	**d**	
		Penicillin G	-	+	p	
		Penicillin V	-	+	p	
		Roxithromycin	-	+	**d**	[141]
		Spiramycin	-	+	p	
		Sulfadiazine	-	+	**d**	
		Sulfamerazine	-	+	**d**	[128]
		Sulfamethazine	-	+	**d**	[141]
		Sulfamethoxazole	-	+	**d**	[99,129]
		Sulfapyridine	-	+	**d**	[129,138, 141]
	Anticonvulsant	Carbamazepine	-	+	**d**	[95,129, 138,141]
		Primidone	-	+		
	Antidepressant	Tetracycline	-	+	**d**	
		Tiamulin	-	+		

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Citalopram	-	+		[129]
		Escitalopram	-	+		
		Sertraline	-	+	**d**	[129]
		Fluoxetine	-	+	**d**	[129,141, 140]
		Fluvoxamine	-	+		
		Paroxetine	-	+	**d**	[129]
	Antidiabetic	Glyburide (glibenclamid; glybenzcyclamide)	-	+		
		Metformin	-	+	p	
	Antiemetic	Diphenhydramine	-	+	**d**	
	Antihistaminic	Loratadine	-	+		
	Antihyperten-sive	Nadolol	-	+		
		Verapamil	-	+		
	Anti-inflammatory	Aceclofenac	-	+		
		Acemetacin	-	+		
		Acetylsalicylic acid (aspirin)	-	+	**d**	[138]
		Alclofenac	-	+		
		Diclofenac	-	+	**d**	[99,138, 141]
		Fenoprofen	-	+	**d**	[141]
		Fenoprofen calcium salt dihydrate	-	+		
		Ibuprofen	-	+	**d**	[129,138]
		Indomethacin	-	+	**d**	
		Ketoprofen	-	+	**d**	[138,141]
		Meclofenamic acid	-	+		
		Mefenamic acid	-	+		
		Naproxen	-	+	**d**	[129,138, 141]
		Phenylbutazone	-	+		
		Phenazone	-	+		
		Propyphenazone	-	+		
		Tolfenamic acid	-	+		
	Antimicrobial agent	Clotrimazole	-	+		
	Antineoplastic	Cyclophosphamide	-	+	p	
		Cyclophosphamide (anhydrous form)	-	+		
		Daunorubicin	-	+		
		Doxorubicin	-	+		
		Epirubicin	-	+		

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Fluorouracil	-	+		
		Ifosfamide	-	+	p	
	Antiulcerative	Famotidine	-	+		
		Lansoprazole	-	+		
		Omeprazole	-	+	**d**	[141,140]
		Ranitidine	-	+	p	
	Anxiolytic	Alprazolam	-	+	**d**	
		Bromazepam	-	+	**d**	
		Diazepam	-	+	**d**	[138]
		Lorazepam	-	+	p	
		Medazepam	-	+	p	
		Meprobamate	-	+	p	
		Nordiazepam	-	+	p	[138]
		Oxazepam	-	+	p	
		Temazepam	-	+	**d**	[141]
	Beta-Blockers	Acebutolol	-	+	p	
		Atenolol	-	+	**d**	[129,141]
		Betaxolol	-	+	p	
		Bisoprolol	-	+	p	
		Carazolol	-	+	p	
		Metoprolol	-	+	p	[129]
		Oxprenolol	-	+	p	
		Pindolol	-	+	p	
		Propranolol	-	+	**d**	[129,141]
		Sotalol	-	+	p	[129]
		Timolol	-	+	p	
	Blood viscosity agents	Pentoxifylline	-	+		
	Bronchodilators	Albuterol	-	+		
		Albuterol sulfate	-	+		
		Clenbuterol	-	+	**d**	[138]
		Fenoterol	-	+		
		Salbutamol	-	+	**d**	[138]
		Terbutaline	-	+	**d**	[138]
	Diuretic	Caffeine	-	+	**d**	[128, 129,138]
		Furosemide	-	+	p	
		Hydrochlorothiazide	-	+	**d**	[141]
	Lipid regulators	Bezafibrate	-	+		
		Clofibric acid	-	+	**d**	[141]
		Etofibrate	-	+		

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Fenofibrate	-	+		
		Fenofibric acid	-	+		
		Gemfibrozil	-	+	**d**	[129,138,141]
		Lovastatin	-	+		
		Mevastatin	-	+		
		Pravastatin	-	+		
		Simvastatin	-	+	p	
	Sedatives, hypnotics	Acecarbromal	-	+		
		Allobarbital	-	+		
		Amobarbital	-	+		
		Butalbital	-	+		
		Hexobarbital	-	+		
		Pentobarbital	-	+		
		Aprobarbital	-	+		
		Secobarbital sodium	-	+		
	Steroids and hormones	17-alpha-Oestradiol	-	+	**d**	[25,128,129,142]
		17-alpha-Ethinyloestradiol	-	+	**d**	[25,128]
		17-beta-Oestradiol	-	+	**d**	[25,128,129,,142]
		Beta-sitosterol	-	+	**d**	
		Cholesterol	-	+	**d**	
		Diethylstilbestrol	-	+	p	
		Oestriol	-	+	**d**	[142]
		Oestrone	-	+	**d**	[25,128,129]
		Oestrone 3-sulphate	-	+	p	
		Prednisolone	-	+	p	
		Dexamethasone	-	+	p	
		Bethametasone	-	+	p	
		Mestranol	-	+	**d**	
	Psychiatric drugs	Amitryptiline	-	+	**d**	[138]
		Doxepine	-	+	**d**	[138]
		Imapramine	-	+		
		Nordiazepam	-	+	**d**	[138]
		Zolpidem	-	+		
	X-ray contrast media	Diatrizoate	-	+		
		Iohexol	-	+		
		Iomeprol	-	+		
		Iopamidol	-	+		
		Iopromide	-	+		
Trace metals	Trace metals and their compounds	Tetramethyllead	+	-		
		Tetraethyllead	+	-		

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
	Benzotriazoles	4-Methyl-1H-benzotriazole	-	+	p	
		5-Methyl-1H-benzotriazole	-	+	**d**	
		5,6-Dimethyl-1-H-benzotriazole	-	+	p	
	Tolyltriazoles (TT)	Tolyltriazole 4-/5-Tolyltriazole (TTri)				
Wood preserva-tives	Phenols	para-Cresol	-	+	**d**	
Other	Drugs of abuse	Cocaine	-	+	p	
		Codeine	-	+	**d**	[141]
		Dihydrocodeine	-	+	p	
		Heroin	-	+	p	
		Hydrocodone	-	+	p	
		Morphine	-	+	p	
		Oxycodone	-	+	p	
	Benzothiazoles (BT)	Benzothiazole	-	+	**d**	
		2-Mercapto-benzothiazole	-	+	**d**	
		Benzothiazole sulfonic acid	-	+	p	
	Nicotine metabolite	Cotinine	-	+	**d**	[128]

The following considerations apply.

[a]potential of non-polar samplers: (e.g. SPMD, LDPE, silicone, non-polar Chemcatcher)

+ = log K_{ow} > 4; - = log K_{ow} < 3

[b]potential of hydrophilic samplers (POCIS, the hydrophilic version of Chemcatcher, Empore™ disks and others)

+ = log K_{ow} < 3 ; - = log K_{ow} >4

[c]stage of development:

d = performance has been demonstrated in the laboratory and/or in the field;

p = performance is likely to be good, but experimental evidence is not available.

[d]selected references are given to publications containing sampler calibration data

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