Environmental Science
Processes & Impacts

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

rsc.li/process-impacts

Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Characterisation and comparison of the uptake of ionizable and polar pesticides, pharmaceuticals and personal care products by POCIS and Chemcatchers

S.L. Kaserzon[a]*, D.W. Hawker[b], K. Kennedy[a], M. Bartkow[c], S. Carter[d], K. Booij[e] and J.F. Mueller[a]

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Growing concern about the environmental impact of ionizable and polar organic chemicals such as pesticides, pharmaceuticals and personal care products has lead to the inclusion of some in legislative and regulatory frameworks. It is expected that future monitoring requirements for these chemicals in aquatic environments will increase, along with the need for low cost monitoring and risk assessment strategies. In this study the uptake of 13 neutral and 6 ionizable pesticides, pharmaceuticals and personal care products by modified POCIS (with Strata^{TM}-X sorbent) and Chemcatchers^{TM} (SDB-RPS or SDB-XC) was investigated under controlled conditions at pH = 6.5 for 26 days. The modified POCIS and Chemcatcher^{TM} (SDB-RPS) samplers exhibited similar performance with the uptake of the majority of the 19 chemicals of interest categorised as linear over the 26-day deployment. Only a few ionized herbicides (picloram and dicamba) and triclosan showed negligible accumulation. Chemcatcher^{TM} with SDB-XC sorbent performed relatively poorly with only carbamazepine having a linear accumulation profile, and 8 compounds showing no measurable accumulation. Differences in the uptake behavior of chemicals were not easily explained by their physico-chemical properties, strengthening the requirement for detailed calibration data. PES membranes accumulated significant amount of some compounds (i.e. triclosan and diuron), even after extended deployment (i.e. 26 days). At present there is no way to predict which compounds will demonstrate this behavior. Increasing membrane pore size from 0.2 to 0.45 µm for Chemcatcher^{TM} (SBD-RPS) caused an average increase in R_s of 24%.

Environmental impact This study provides new data on the sampling behavior of ionizable (*n*=6) and polar (*n*=13) organic chemicals of environmental relevance with POCIS (with Strata^{TM}-X sorbent) and Chemcatchers^{TM} (with SDB-RPS and XC extraction disks). Sampling rates normalised on surface area were of similar magnitude (~1.6 L dm^{-2} d^{-1}), but were uncorrelated among sampler/sorbent types, indicating that sorbent type and sampler layout can have a pronounced effect on the sampling rates. Membrane pore size had a minor (~24%) effect on the sampling rates. A small number of chemicals were significantly accumulated in PES membranes.

Introduction

Ionizable and polar organic chemicals such as many pesticides, pharmaceuticals and personal care products (PPCPs) have emerged as a major group of environmental pollutants. Some have acidic or basic functional groups that may become ionized at ambient pH.[1] Widespread contamination from these chemicals in aqueous environments results from numerous urban and agricultural applications and subsequent release or discharge.[2,3] Some polar organic chemicals persist after wastewater treatment processes resulting in their continuous release into the aquatic environment.[4,5] Recent studies suggest that while these chemicals are generally present at trace (low ng L^{-1}) levels and present little risk of acute toxicity,[6] some compounds can show chronic effects at these levels.[2,4,5] Thus, growing concern about the environmental impact of these chemicals has lead to the inclusion of some in legislative and regulatory frameworks.[7] It is expected that future monitoring requirements for ionizable and polar organic chemicals in aquatic environments will increase, along with the need for low cost monitoring and risk assessment strategies.[1,4,8,9]

Passive sampling tools have become increasingly important in environmental monitoring, enabling *in situ* extraction and accumulation of chemicals, as well as providing relatively low detection limits and time-integrated estimates of environmental concentrations.[10,11] The Polar Organic Chemical Integrative Sampler (POCIS)[12] and Chemcatcher^{TM} [13] have emerged in recent years as effective passive sampling tools for polar organic chemicals.[9,14-22] With both samplers, neutral as well as cation and anion exchanging commercial solid phase extraction (SPE) sorbents can be used to accumulate analytes, potentially extending their usefulness to ionizable compounds. With POCIS, examples of these sorbents include Oasis™ HLB, MCX, WAX and Strata-XAW™, and Chemcatchers^{TM} contain a poly(styrene-divinylbenzene) reversed phase copolymer extraction disk with (SDB-RPS) or without (SDB-XC) sulfonic acid moieties.

The design of POCIS necessarily includes a polyethersulfone (PES) membrane that covers the sorbent phase while Chemcatcher^{TM} samplers often incorporate them as well[22-26] to reduce sampling rates (R_s) and to exclude particles.[27] PES membranes of different pore sizes (typically 0.1 µm with POCIS, and 0.2 or 0.45 µm with Chemcatcher^{TM}) have been used.[12,23,25,28]

R_s and sorbent-water sorption coefficient (K_{sw}) values are now available for a growing number of chemicals, especially with POCIS.[1,14,17,25,28] Morin et al.[14] investigated uptake kinetics and sampling rates for 56 polar organic chemicals and reported that 13 ionized and polar chemicals showed negligible, no or low accumulation with POCIS containing Oasis^{TM} HLB. A study with POCIS using Oasis^{TM} HLB, MAX and MCX suggested that the use of ion exchange sorbents holds little advantage over the traditionally used mixed mode sorbent (Oasis^{TM} HLB) for monitoring a range of (21) PPCPs.[29] Fauvelle et al.[24] however demonstrated that the anion exchange sorbent Oasis^{TM} MAX provided a higher sorption capacity and therefore was more suitable for anionic herbicides, when compared to Oasis^{TM} HLB. Studies with Chemcatcher^{TM} comparing SDB-RPS versus SDB-XC Empore^{TM} disks for the sampling of 10 herbicides and 2 pharmaceuticals revealed similar sampling performance, but with SDB-RPS proving more advantageous for hydrophilic compounds.[16]

A side by side comparison of POCIS and Chemcatcher^{TM} has previously only been undertaken by Vermeirssen et al.[30] with results suggesting R_s for these samplers were well correlated ($r^2 = 0.68$) for twenty two pesticides and PPCPs investigated. However only three of these compounds were ionized under the experimental conditions employed and the main focus of this study was chemical transport kinetics over the PES membrane itself.

Knowledge gaps remain concerning the understanding of uptake and sorption mechanisms for these important aquatic contaminants with aquatic passive samplers.[4,9] Therefore the aims of this current study were firstly to compare and characterise the behavior of ionizable and neutral pesticides and PPCPs in terms of transport kinetics, solute-sorbent binding and solute-membrane binding with different sorbents (POCIS containing Strata-X™ and Chemcatcher^{TM} passive samplers containing Empore^{TM} SDB-XC and SDB-RPS). A second aim was to investigate the role of PES membranes on chemical accumulation and transport with these samplers by determining the mass distribution between the sorbent and membrane, as well as the effect of membrane pore size. To this end, chemical and sampler specific uptake parameters were determined (i.e. R_s, half-times to equilibrium ($t_{1/2}$), K_{sw} and PES membrane-water sorption coefficients (K_{mw})). Nineteen cationic, anionic and polar pesticides and PPCPs (log K_{ow} range -0.07 to 4.76) were chosen, representing a suite of compounds frequently encountered in marine and freshwater environments.[31,32]

Materials and methods

Chemicals, materials and reagents. Physico-chemical properties of the 13 pesticides and 6 PPCPs investigated in this work are listed in Table 1. Recovery standards used were caffeine-d_3, carbamazepine-d_{10}, hydrochlorothiazide-^{13}C-d_2, and 2,4-D-$^{13}C_6$. Internal standards used for analysis were acetyl sulfamethoxazole-d_5 and dichlorophenylacetic acid. All chemicals and standards were purchased from Novachem Pty Ltd. (Victoria, Australia). A stock solution containing ~ 1000 µg L^{-1} of all chemicals was prepared in methanol (MeOH). Working solutions and spiking mixtures were prepared by dilution of the stock in MeOH. All standards and solutions were stored at 4 °C. HPLC grade MeOH, acetone and acetonitrile (ACN) were purchased from Merck, Germany. Ultra pure water was used in sampler construction, sample cleanup and chemical analysis (HI-PURE water system, Permutit, Australia).

Calibration study – experimental design. Chemcatchers^{TM} and modified POCIS (the latter within stainless steel cages) were concurrently deployed in a staggered consecutive deployment design from 1 to 26 days (Supporting Information (SI) Fig. S1) on a stainless steel rotor (set to 11 rpm) in a1400 L water tank (SI Fig. S2), containing potable water from Brisbane, Australia, as detailed earlier.[19,34] The water in the tank was spiked with an aliquot of the stock solution, mixed and then left for 2 hours to equilibrate (resulting in concentrations of 270 ± 50 ng L^{-1}; Table 1). The water in the tank was removed and replaced, using the same protocol as described above, on days 3, 10 and 17 (static renewal) to ensure minimal depletion of the chemicals. Grab samples (1 L) were collected daily, with two grab samples collected on days when the water was exchanged (before and after exchange). The tank remained covered with a stainless steel lid throughout the course of the study.

The water flow over the samplers was estimated to be 0.23 ± 0.04 m s^{-1} using co-deployed passive flow monitors (PFMs).[35] Temperature was recorded every 20 minutes using a submersible data recorder (Thermochron i-button, Dallas, USA) and averaged 27 ^{o}C. The pH of the water was measured daily and averaged 6.5 ± 0.2 while salinity was determined to be 0.4 g kg^{-1}. This pH is within the pH range of most natural freshwaters in Australia (pH 6.5 – 8).[36]

Grab samples. Two separate 40 mL portions of each grab sample were used for analysis of neutral and ionized compounds respectively. Prior to extraction, all samples and blanks were spiked with recovery standards (8 ng). Extraction was performed using preconditioned 6 mL, 200 mg Strata-X™ SPE cartridges (Phenomenex, Sydney, Australia). Cartridges used for extraction of neutral chemicals were pre-loaded with 2 mL MeOH followed by 1 mL ultra pure water and those used for extraction of ionic compounds pre-loaded with 2 mL MeOH containing 0.12% HCl. All cartridges were eluted with 2 mL MeOH followed by 1.5 mL ACN and 1.5 mL acetone. Final extracts were evaporated to near dryness and reconstituted in 10% ACN: ultra pure water and spiked with internal standards (4 ng). Extracts were stored at 4 °C until analysis by LC-MS.

Preparation and extraction of passive samplers. Four passive sampler configurations were deployed concurrently in the tank system (with a maximum of 3 samplers from each configuration). The three Chemcatcher^{TM} configurations comprised (i) Empore^{TM} SDB-RPS extraction disk covered by a 0.2 µm pore size PES membrane (ii) Empore^{TM} SDB-RPS extraction disk covered by a 0.45 µm pore size PES membrane and (iii) Empore^{TM} SDB-XC extraction disk covered by a 0.45 µm pore size PES membrane. One modified POCIS configuration was deployed using Strata-X^{TM} as the sorbent phase between two 0.45 µm pore size PES membranes.

Chemcatcher^{TM} Samplers. SDB–RPS and SDB-XC Empore^{TM} disks (ED) (47 mm; 3M, Brisbane, Australia) were conditioned by soaking in 25 mL MeOH (30 min) then 20 mL ultra pure water (5 min). Assembled Chemcatchers^{TM} (exposed surface area 15.9 cm^2) were stored at 4 °C prior to and after exposure. After deployment, disks were removed and spiked with recovery standards (8 ng) and placed in an ultrasonic bath with either 5 mL MeOH followed 3 mL ACN and 3 mL acetone (for SDB-RPS) or 2 x 5 mL MeOH (for SDB-XC). Extracts were evaporated under a gentle stream of nitrogen to 0.5 mL, then reconstituted to 1 mL in 10% ACN: ultra pure water. Internal standards (4 ng) were added prior to analysis by LC-MS.

Modified POCIS Samplers. Modified POCIS passive samplers were constructed as described previously[19] with the exception of the sorbent phase used. To extend the duration of the kinetic/linear uptake stage, the modified POCIS contained an increased sorbent mass (viz. 600 mg Strata-X^{TM}) and reduced surface area (16 cm^2) compared with the standard POCIS “pharmaceutical” configuration (i.e. 200 mg Oasis HLB and 41 cm^2 surface area). The sorbent in the modified POCIS was packed very tightly (i.e. to maximum capacity) which prevented shifting of the sorbent during deployment. Prior to exposure, each assembled POCIS was conditioned in a 100 mL beaker using 20 mL of MeOH followed by 40 mL water (10 minutes for each solvent). Individual POCIS were sealed in solvent rinsed aluminium foil and stored at 4 °C prior to and after exposure. Each POCIS was disassembled and the sorbent transferred while moist, using a stainless steel spatula, into a pre-cleaned empty 6 mL SPE cartridge with a 20 µm glass fibre frit. Recovery standards (8 ng) were spiked onto the sorbent. After 1 h, samples were eluted on an SPE manifold under vacuum with 5 mL MeOH, 3 mL ACN and 3 mL acetone. The eluate was reduced under a gentle stream of nitrogen to about 0.1 mL, and made up to a final volume of 0.5 mL ultra pure water with 10% ACN. Internal standards (4 ng) were spiked prior to analysis by LC- MS (as described above).

PES Membranes. PES membranes (47 mm diameter; PALL Supor®, Melbourne, Australia) with 147 µm thickness and a pore size of 0.2 µm (used on Chemcatcher^{TM} with SDB-RPS) or 140 µm thickness and a pore size of 0.45 µm (used with all sampler configurations including Chemcatcher^{TM} (SDB-RPS)) to facilitate sampler comparison) were employed. Membranes were cleaned before use in 200 mL MeOH for 20 minutes followed by 400 mL of water for 5 minutes. PES membranes were collected from all samplers deployed for 1, 7, 13 and 26 days. Extraction followed the same procedure as the extraction of the sorbent of the respective passive sampler (with the exception of PES deployed with POCIS that were extracted in an ultrasonic bath).

LC-MS analysis. Analysis of both passive and grab sample extracts was conducted by Queensland Health Forensic and Scientific Services (QHFSS), a National Association of Testing Authorities accredited laboratory. Samples were analysed by HPLC/tandem Mass Spectrometry using an AB/Sciex API4000Q mass spectrometer equipped with an electrospray (TurboV) interface (MDS Sciex, Concord, Ontario, Canada). Analytical details are found in SI (SI Text S1). QA/QC details (i.e. results from replicate and control grab water samples and passive sampler fabrication controls (i.e. non-exposed samplers)) are found in SI (SI Text S2, Tables S1-S4).

Data modelling. The accumulation of ionizable and polar organic chemicals in the sorbent of Chemcatcher^{TM} and POCIS samplers was analysed using a one compartment, first order kinetic model (Eq. 1).[10,37]

$$C_\mathrm{s} = K_\mathrm{sw} C_\mathrm{w} \left[1 - \exp\left(-\frac{R_\mathrm{s}\, t}{m_\mathrm{s} K_\mathrm{sw}}\right)\right] \tag{1}$$

where C_s is analyte concentration in the sorbent, K_{sw} the sorbent-water sorption coefficient, C_w the concentration in water, R_s the initial sampling rate (at $t = 0$), and m_s the mass of sorbent.

When sampling is conducted over relatively short time-spans, Eq. (1) can be reduced to the linear approximation model, Eq. (2)

$$C_\mathrm{s} = \frac{C_\mathrm{w} R_\mathrm{s} t}{m_\mathrm{s}} \tag{2}$$

Based on Eq. (1), the half-life time to equilibrium ($t_{½}$) is calculated by

$$t_{1/2} = \frac{\ln(2)\, m_\mathrm{s}\, K_\mathrm{sw}}{R_\mathrm{s}} \tag{3}$$

The sorption coefficient between the PES membrane and water (K_{mw}) was calculated from the ratio of average analyte concentration in the PES membrane (C_m) to the average concentration in the water.

Values of K_{sw} were estimated for compounds whose accumulation was fit to Eq. (1) by unweighted nonlinear least squares regression (GraphPad Prism 5, GraphPad Software, Inc., San Diego, USA). R_s data were estimated from Eq. (1) for analytes that reached the curvilinear or equilibrium stages of accumulation and from Eq. (2) for analytes that remained in the linear accumulation mode throughout the 26 d calibration study (using unweighted nonlinear least squares regression and linear regression, respectively (GraphPad Prism 5).

Results and discussion

Uptake of ionizable and polar organic chemicals by POCIS and Chemcatcher^{TM}. Concentrations of target analytes in the water tank (C_w) determined by daily grab samples were stable for most chemicals (Table 1).

Coefficients of variation (CV) ranged from 10 – 33% for the 19 chemicals. Uptake of most analytes over 26 days exposure by modified POCIS and Chemcatcher^{TM} samplers was either nonlinear (with the accumulation profile being fit to Eq. 1) or linear (Eq. 2). However, negligible accumulation was observed for dicamba, picloram and triclosam in all samplers, and for many other

Table 1. Physico-chemical properties, average exposure C_w, mean recoveries and LOQs of the target compounds.

Compound	Classification	Molar mass (g mol^{-1})	Log K_{ow}	pKa[a]	Log D_{ow}[a] (pH 6.5)	% speciation Negative (-) / Postive(+) Neutral (N)[b]	C_w (ng L^{-1}) (n=37) Ave	S.D	CV%	Mean recovery %	LOQ (µg L^{-1})
Pesticides											
Neutral chemicals											
Ametryn	methylthiotriazine herbicide	227.	2.98			*N*	275	63	23	90	0.002
Bromacil	uracil herbicide	261	2.11			*N*	325	63	19	94	0.006
Diuron	phenylurea herbicide	233	2.68			*N*	332	65	20	94	0.01
Fluometuron	phenylurea herbicide	232	2.42			*N*	299	60	20	89	0.022
Prometryn	triazine herbicide	241	3.51			*N*	266	68	25	85	0.003
Tebuthiuron	urea herbicide	228	1.78			*N*	282	57	20	92	0.003
Terbutryn	triazine herbicide	241	3.74			*N*	245	63	26	82	0.006
Ionised chemicals											
2,4-D	phenoxyacetic herbicide	221	2.81	2.73	-0.96	>99% -	241	53	22	81	0.003
Dicamba	benzoic acid herbicide	221	2.21	1.97	-2.32	>99% -	280	36	13	87	0.004
Haloxyfop	phenoxy herbicide	362	3.38	2.90	-0.22	>99% -	303	68	23	66	0.003
Picloram	pyridine herbicide	219	1.90	2.30	-2.30	>99% -	206	31	15	94	0.019
Triclopyr	pyridine herbicide	256	2.53	3.97	0	>99% -	237	68	29	86	0.009
PPCP's											
Neutral chemicals											
Caffeine	stimulant	194	-0.07			*N*	284	40	14	102	0.013
Carbamazepine	anticonvulsive	236	2.45			*N*	300	31	10	104	0.004
Dapsone	antibacterial	248	0.97			*N*	228	65	29	74	0.003
DEET	repellent	191	2.18			*N*	279	72	26	77	0.005
Hydrochlorothiazide	diuretic	298	-0.07	7.90	-0.09	4% -	261	41	16	99	0.006
Triclosan	antibacterial, antifungal	290	4.76	7.80	4.74	5% -	101	33	33	84	0.01
Ionised chemicals											
Codeine	analgesic	299	1.20	8.21	-0.52	98% +	231	73	32	66	0.033

Dicamba (3,6-dichloro-2-methoxybenzoic acid), MCPA (2-Methyl-4-chlorophenoxyacetic acid), 2,4-D (2,4-Dichlorophenoxyacetic acid), DEET (N,N-Diethyl-m-toluamide).

[a] Values taken from PhysProp Database via EpiSuite (http://www.epa.gov/opptintr/exposure/pubs/episuitedl.htm)

[b] Neutral speciation (N) means > 50% exists as neutral species

* log D_{ow} determined via

$\log D_{ow}$ (acid) = $\log K_{ow} - \log(1+10^{pH-pKa})$

$\log D_{ow}$ (base) = $\log K_{ow} - \log(1+10^{pKa-pH})$

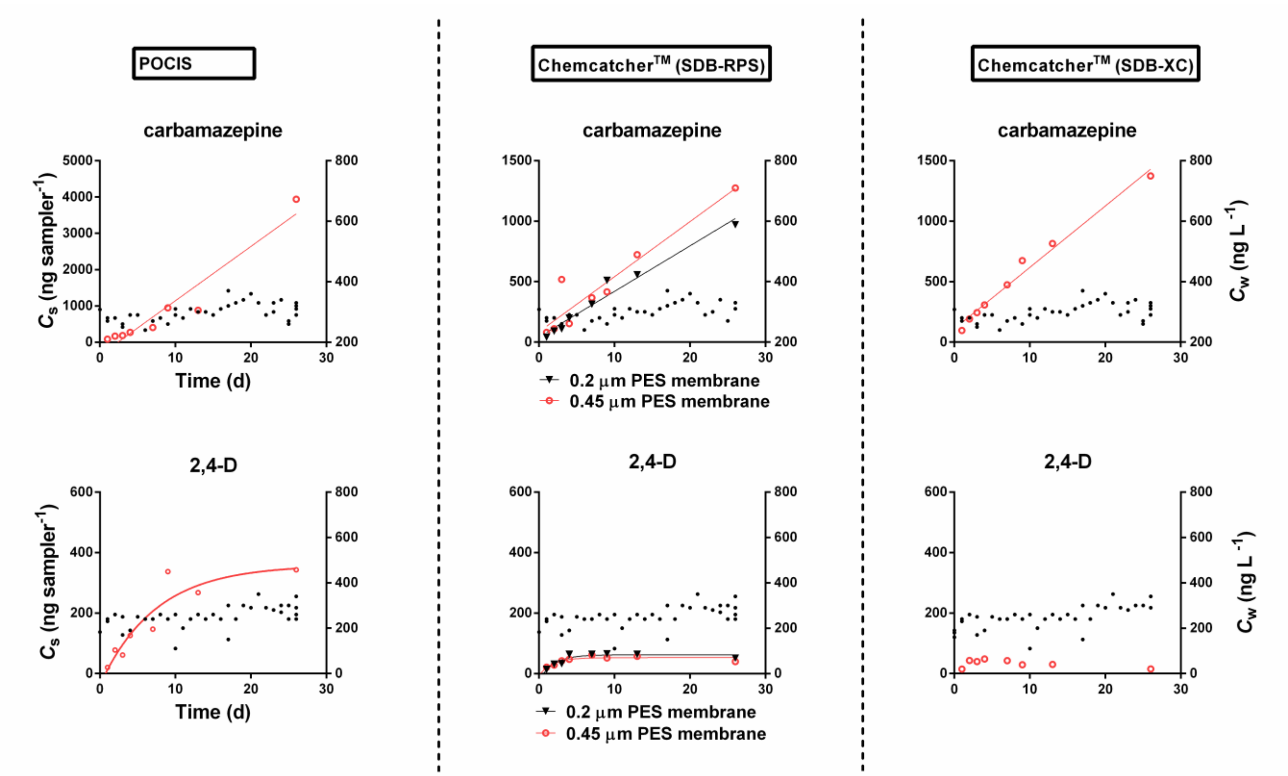

Figure 1. Linear accumulation of carbamazepine with modified POCIS and Chemcatchers$^{\mathrm{TM}}$ containing SDB-RPS Empore$^{\mathrm{TM}}$ disks (with 0.2 and 0.45 µm PES membranes) and SDB-XC Empore$^{\mathrm{TM}}$ together with nonlinear and negligible (SDB-XC) accumulation of 2,4-D with these samplers. Black dots represent water concentrations.

compounds in Chemcatcher$^{\mathrm{TM}}$ equipped with SDB-XC extraction disks (Fig. 1, SI Fig. S3).

The modified POCIS and Chemcatcher$^{\mathrm{TM}}$ (SDB-RPS) (0.2 µm PES) samplers exhibited similar performance with the uptake of 12 and 10, respectively, out of the 19 analytes categorised as having linear uptake ($r^2 > 0.80$) over the 26 day exposure. A poorer linear fit was observed for diuron with the Chemcatcher (SDB-RPS) with the larger pore size membrane (0.45 µm), due to an outlier in the uptake profile at t = 3 d (SI Fig. S3). Those compounds showing linear accumulation in both POCIS and Chemcatcher$^{\mathrm{TM}}$ (SDB-RPS) were mainly neutral pesticides and PPCPs, but uptake of codeine, an important pharmaceutical that is positively charged at pH = 6.5 also demonstrated linearity. Uptake for most of the other ionic polar organic chemicals was nonlinear.

The herbicides picloram and dicamba, both benzoic acid derivatives, and the antibacterial and antifungal agent triclosan however showed very little accumulation (< 26, 14 and 9 ng sampler^{-1}, respectively) with both modified POCIS and Chemcatcher$^{\mathrm{TM}}$ (SDB-RPS) samplers (Table 2, SI Figs. S3). These herbicides are negatively charged at pH = 6.5 while triclosan is a hydroxylated diphenyl ether and primarily neutral at this pH. Reduced accumulation of certain analytes by passive samplers has been observed previously. In one study authors reported that five chemicals (which included polar, nonpolar, neutral and ionized ones) showed low or no accumulation in POCIS with Oasis$^{\mathrm{TM}}$ HLB.[14] In another study, Fauvelle et al.[24] found no accumulation of dicamba in POCIS with Oasis$^{\mathrm{TM}}$ HLB.

The polymeric materials used with the samplers in this work (Strata-X$^{\mathrm{TM}}$ with POCIS and SDB-RPS with Chemcatcher$^{\mathrm{TM}}$) are styrene-divinylbenzene copolymers that contain pyrrolidone and sulfonic acid functional groups, respectively. These modifications have been designed to increase the hydrophilicity of these sorbents that would otherwise be hydrophobic in nature.[38] Such sorbents can retain ionizable and polar organic chemicals through a number of mechanisms including π-π bonding, hydrogen bonding, as well as van der Waals and Coulomb interactions, depending on the sorbate's size, structure and charge. Bäuerlein et al.[39] showed that Van der Waals interactions were the predominant factor governing sorption of neutral polar organic chemicals investigated on the sorbent Oasis$^{\mathrm{TM}}$ HLB (equivalent to the Strata-X$^{\mathrm{TM}}$ used here).

The SDB-RPS sorbent is regarded as having a mixed mode of action including acting as a cation exchange material due to ionization of the sulfonic acid groups.[40] However the similarity in behaviour, particularly with anionic sorbates, between this sorbent and Strata-X^{TM} which is positively charged, would suggest coulombic repulsion is relatively unimportant and that other mechanisms determine the extent of sorption.

Very different behavior was observed with the other passive sampler configuration investigated (Chemcatcher^{TM} (SDB-XC)). Only one compound, carbamapezine, exhibited linear uptake, 10 pesticides and PPCPs showed nonlinear uptake and 8 demonstrated negligible accumulation with this sorbent (Table 2, SI Fig. S3). The latter group included the compounds showing little accumulation with the other passive sampler configurations but additionally included fully ionized pesticides (2,4-D and triclopyr) and the neutral compounds caffeine, dapsone, hydrochlorthiazide. SDB-XC is a styrene-divinylbenzene copolymer, but unlike the others under consideration, contains no polar or ionizable functional groups and is hydrophobic. This material has been used for sampling of polar analytes, but not ionizable ones.[26,41] Results presented in this work show that SDB-RPS and Strata^{TM}-X exhibited better accumulation of analytes and are therefore superior to SDB-XC for sampling the polar and ionizable pesticides and PPCPs investigated here.

Time-weighted average (TWA) concentrations of environmental contaminants may be estimated from passive samplers during the integrative stage of sampling (i.e. with linear accumulation of chemicals).[10] Linearity of uptake is reliant on a combination of compound property, exposure time, exposure conditions, and the sampler design. The $t_{1/2}$ values were longest with the modified POCIS, ranging from 4 – 12 days, compared with 1 – 9 days for Chemcatcher^{TM} (SDB-RPS) and 2 – 8 days for Chemcatcher^{TM} (SDB-XC) (Table 2).

The duration of the $t_{1/2}$ time period may be extended by increasing the sorbent's mass-to-surface area ratio. The half-life time for 2,4-D uptake by POCIS observed in a previous study (3 days)[24] was shorter than in the present study (~ 7 days), which can be attributed to the higher sorbent mass and reduced surface area employed in the present study (600 mg and 16 cm^2 vs. 200 mg and 41 cm^2 in standard POCIS).

Relationship between R_s and chemical properties. Sampling rates per unit surface area (R_s/A) are shown in Table 2 with a number reported here for the first time (7 with POCIS, 8 with Chemcatcher^{TM} (SDB-RPS) and 9 with Chemcatcher^{TM} (SDB-XC)). Remaining data are within the range of values reported in the literature regardless of differences in sampler configurations (SI Table S5). For POCIS, area normalised R_s values ranged between 0.57 – 2.6 L dm^{-2} d^{-1} in this study (for dapsone – carbamezapine) compared with 0.10 – 1.2 L dm^{-2} d^{-1} (caffeine – carbamazepine) in other studies for the compounds of interest. With Chemcatcher^{TM} (SDB-RPS) using 0.2 μm PES, R_s values ranged between 0.32 – 1.2 L dm^{-2} d^{-1} in this study (prometryn – dapsone) and between 0.05 – 8.3 L dm^{-2} d^{-1} (diuron – fluometuron) in studies reported in the literature. For Chemcatcher^{TM} (SDB-XC), those R_s/A values that could be determined ranged between 1.2 – 4.9 L dm^{-2} d^{-1} (carbamazepine – DEET) compared with 0.15 – 4.7 L dm^{-2} d^{-1} (diuron - terbutryn) in various studies reported in the literature.

No correlation was observed between R_s values determined with the modified POCIS and Chemcatcher^{TM} (SDB-RPS; 0.2 or 0.45 μm pore size) for the chemicals in this study (SI Fig. S4). This is in contrast to observations by Vermeirssen et al.[30] who found the R_s of 22 polar and ionizable chemicals with POCIS and Chemcatcher^{TM} (SDB-RPS) to be correlated (r^2 = 0.68). However this involved deployment of both samplers in similar housings (using metal stainless steel rings) while in the present study the typical teflon Chemcatcher^{TM} housing was used.[13] Differences in the resistance to mass transfer at the water boundary layer (WBL) and/or within the membrane between the POCIS (PES - Strata^{TM}-X) and Chemcatchers^{TM} (PES- SDB-RPS) may be responsible for the lack of correlation observed here.

Relationships between chemical R_s and log D_{ow}, molar mass or K_{sw} showed no clear trends with any sampler configuration (SI Figs. S5, S6, S7). So far, attempts to correlate R_s with the physico-chemical properties of target compounds have been met with varying success and an overall mechanistic uptake model is lacking.[4] This implies that compound-specific calibration data are needed for the full range of exposure conditions (flow, temperature and salinity among others) that can be encountered in the environment.

Effect of PES membrane on accumulation of ionizable and polar organic chemicals. Measured PES membrane-water sorption coefficients (expressed as log K_{mw}) were in the range 1.6 – 4.6 (hydrochlothiazide – triclosan) (SI Table S6). It should be noted that these sorption coefficients were estimated from the transient concentrations in the membrane and the water during the exposures and are not strictly equilibrium values. However, estimated log K_{mw} values were similar to those of Vermeirssen et al. [30], with an average difference of 0.09 log units. High K_{mw} values may cause a delay in compound transfer to the sorbent, but this was not observed for any compounds in this study. Some chemicals showed no (e.g. dicamba) or very little accumulation in PES (e.g. carbamazepine, caffeine and hydrochlorthiazide (SI Fig. S8, S9). For these compounds, less than 30% of the amount in the sampler was found in the membrane even at the shortest exposure time and swift transfer to the sorbent phase was observed. Other compounds showed a greater affinity for the PES membrane. Triclosan and diuron had by far the highest accumulation in PES. Almost 100% of the triclosan was found in the membrane, even after 26 days sampler deployment. Consequently we also observed little transfer of triclosan from the membrane to the sorbent and sampling was categorized as unsuccessful considering sorbent only (SI Figs. S3). Triclosan is the subject of increasing scrutiny due to its widespread use, incomplete removal during conventional wastewater treatment and potential for conversion into dioxin congeners.[42] Low mass balances of this compound have previously been noted with calibration of POCIS. This has been attributed to poor recoveries from the sorbent and/or degradation of sorbed triclosan, compromising derived TWAs.[17] Results presented here suggest it may be due to all the triclosan being found in the membrane.

A high proportion of diuron accumulation in PES was also noted, with approximately 60% accumulated in PES and 40% in the sorbent at day 26 (SI Fig. S9). This result is in agreement with two previous studies that have reported high diuron accumulation in PES.[26,30] To demonstrate the effect of this, an R_s value for diuron (for

Table 2. Surface area normalized sampling rates (R_s/A), sorbent-water sorption coefficients (K_{sw}) and half-time to equilibrium ($t_{1/2}$) of ionizable and polar contaminants by POCIS and Chemcatcher^{TM}.

	POCIS (0.45 μm PES)						Chemcatcher^{TM} SDB-RPS (0.2 μm PES)						Chemcatcher^{TM} SDB-RPS (0.45 μm PES)						Chemcatcher^{TM} SDB-XC (0.45 μm PES)					
Compound	R_s / A (L dm^{-2} d^{-1})		K_{sw} (L kg^{-1})		$t_{1/2}$	Uptake*	R_s / A (L dm^{-2} d^{-1})		K_{sw} (L kg^{-1})		$t_{1/2}$	Uptake*	R_s / A (L dm^{-2} d^{-1})		K_{sw} (L kg^{-1})		$t_{1/2}$	Uptake*	R_s / A (L dm^{-2} d^{-1})		K_{sw} (L kg^{-1})		$t_{1/2}$	Uptake*
	estimate	*S.D*	*estimate*	*S.D*	*(d^{-1})*		*estimate*	*S.D*	*estimate*	*S.D*	*(d^{-1})*		*estimate*	*S.D*	*estimate*	*S.D*	*(d^{-1})*		*estimate*	*S.D*	*estimate*	*S.D*	*(d^{-1})*	
2,4-D	1.05	0.4	1570	310	6.5	NL	0.63*	0.19	260	25	1.8	NL	0.93*	0.26	290	20	1.4	NL						N
Haloxyfop	1.5*	0.43	4145	740	12	NL	1.02*	0.35	1550	265	6.6	NL	1.19*	0.35	1870	280	6.8	NL	2.38*	0.96	2260	385	4.1	NL
Triclopyr	1.69*	0.41	1470	145	3.8	NL	1.05*	0.59	385	60	1.6	NL	1.47*	0.77	435	60	1.3	NL						N
Hydrochlorothiazide	1.11	0.28	1890	250	7.4	NL	0.56*	0.09	980	85	7.6	NL	0.81*	0.13	550	30	3	NL						N
Ametryn	1.29*	0.07				L	0.35	0.02				L	0.5	0.05				L	4.27*	2.22	2250	390	2.3	NL
Bromacil	1.77*	0.06				L	0.78*	0.05				L	0.86*	0.1				L	4.23*	1.65	2240	290	2.3	NL
Diuron	1.02	0.04				L	0.44	0.01				L	0.72	0.14				L	1.75	0.84	2150	480	5.3	NL
Fluometuron	1.82*	0.08				L	0.73	0.04				L	0.85	0.1				L	3.2*	0.88	2680	300	3.7	NL
Prometryn	1.48	0.08				L	0.32	0.02				L	0.48	0.04				L	3.89*	2.34	2120	430	2.4	NL
Tebuthiuron	1.71*	0.07				L	0.69	0.04				L	0.8	0.07				L	2.32*	0.69	2880	400	5.4	NL
Terbutryn	1.86	0.09				L	0.41	0.04				L	0.62	0.06				L	2.88	1.7	3210	845	4.8	NL
Caffeine	0.75	0.1				L	0.9	0.12	1840	130	8.9	NL	1.1	0.32	1840	275	7.3	NL						N
Carbamazepine	2.64	0.29				L	0.85	0.04				L	1.07	0.1				L	1.21*	0.06				L
Dapsone	0.57*	0.06				L	1.22*	0.13	2500	145	9	NL	1.08*	0.56	2270	660	9.2	NL						N
DEET	2.12	0.13				L	0.72*	0.03				L	0.93*	0.14				L	4.92*	2	3040	440	2.7	NL
Codeine	1.96	0.23				L	0.42*	0.03				L	1.21*	0.13				L	1.77*	1.35	3400	1530	8.4	NL
Dicamba						N						N						N						N
Picloram						N						N						N						N
Triclosan						N						N						N						N

L = linear accumulation over 26 days. NL = Non-linear accumulation. N = negligible accumulation.

* R_s for which literature data was not available

Chemcatcher^{TM} (SDB-RPS) containing 0.2 µm pore size PES) taking membrane accumulation into account is 80% higher than when only sorbent is considered. No relationship was observed between accumulation of chemicals in PES (relative to the whole sampler) and their log K_{ow}, log D_{ow}, molar mass or K_{mw} (data not shown).

Increasing the membrane pore size from 0.2 to 0.45 µm with Chemcatchers^{TM} (SDB-RPS) caused 24 ± 16% increase in R_s (n = 16, Table 2, Fig. 2). This effect of PES pore size on R_s values for ionizable and polar organic chemicals will be reflected in derived TWA values (Eq. 2). Hence pore size needs to be taken into account when comparing data from or undertaking calibration with POCIS and Chemcatchers^{TM}. No trend was identified between the percentage reduction of R_s values and compound hydrophobicity (log K_{ow} or log D_{ow}), size or charge.

The mass transfer coefficient through the PES membrane (k_m) is given by

$$k_m = \varphi D/(\theta^2 d) \quad (4)$$

where φ = porosity, D = diffusion coefficient in water, θ = is pore tortuosity and d = membrane thickness.

It is reasonable to assume that differences exist in porosity and tortuosity (φ and θ) between the 0.2 and 0.45 µm pore size PES membranes that bring about small changes in k_m. Results from this comparison suggest at least partial membrane control for accumulation of these compounds with Chemcatcher^{TM}. Analyte transfer through the PES can occur through a biphasic pathway across the water filled pores and the polymer matrix. The flux of analytes will depend on the relative magnitude of both pathways. Most chemicals showed rapid transfer to the sorbent. In the case of diffusion through the membrane pores only, R_s/A can be estimated. If we assume $\varphi = 0.7$, $\theta = 1.2$, d = 140 µm and $D = 5 \cdot 10^{-10}$ m^2 s^{-1}, this results in an estimation of k_m = 1.5 dm d^{-1} or 1.5 L dm^{-2} d^{-1}. This is similar to the observed R_s/A for POCIS (1.5 ± 0.5 L dm^{-2} d^{-1}), Chemcatcher^{TM} (SDB-RPS; with 0.45 µm PES) (0.9 ± 0.3 L dm^{-2} d^{-1}) and Chemcatcher^{TM} SDB-XC (1.8 ± 0.8 L dm^{-2} d^{-1}). Although Eq. (4) predicts R_s/A to the correct order of magnitude, we acknowledge that it does not explain the appreciable differences in sampling rates between the different sampler designs, which were all fitted with the same membrane. Nor does it explain the lack of correlation between R_s/A for POCIS and Chemcatcher^{TM}. Clearly, the effect of the sorbent type on the uptake kinetics is insufficiently understood.

In cases where accumulation in membranes is appreciable, the use of models that incorporate a separate membrane compartment are desirable to account for the entire flux with samplers.[30] However, the complexity of parameterising such a model that would include mass transfer coefficients of the WBL, the membrane and the sorbent (k_w, k_m and k_s) is considerable. As shown above, our present knowledge is incomplete and the development of such models is presently not achievable. Some simplification may be possible with samplers having a hydrogel layer in place of a (PES) membrane. This layer reduces the effects of external hydrodynamics on chemical uptake by providing a constant diffusion layer that relies on measurable diffusion coefficients.[43]

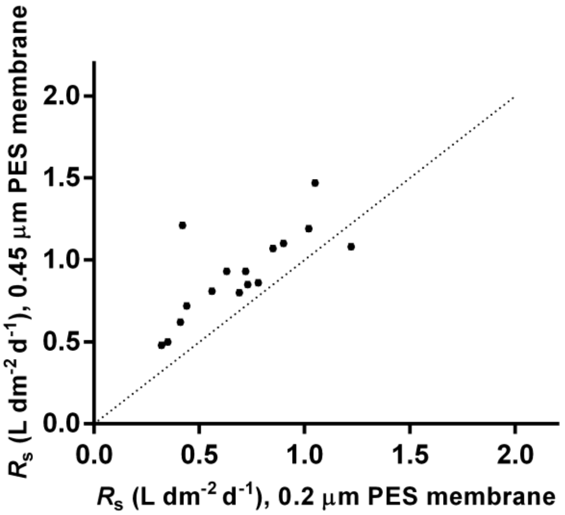

Figure 2. Sampling rates (R_s; L dm^{-2} d^{-1}) for Chemcatchers^{TM} (SDB-RPS) deployed using PES membranes with 0.2 vs. 0.45 µm pore size. Dotted line represents a 1:1 relationship.

Conclusions

Uptake of 13 neutral and 6 ionizable pesticides, pharmaceuticals and personal care products by modified POCIS (with Strata^{TM}-X sorbent) and Chemcatchers^{TM} (SDB-RPS or SDB-XC) was investigated under controlled conditions at pH = 6.5 for 26 days. Linear accumulation was observed over this time period with POCIS and Chemcatcher^{TM} (SDB-RPS) for 12 and 10 of the ionizable and polar pesticides and PPCPs, respectively. Most anionic compounds attained partial or complete equilibrium. Surface area normalized sampling rates (R_s/A) ranged between 0.32 – 4.9 L dm^{-2} d^{-1} (prometryn – DEET). For chemicals that approached equilibrium, sorbent–water sorption coefficients were 260 – 4100 L kg^{-1} (2,4-D – haloxyfop) and half- times to equilibrium 1.3 – 12 days (triclopyr – haloxyfop). With the unfunctionalised styrene-divinylbenzene sorbent of Chemcatcher^{TM} (SDB-XC), linear accumulation was found only for carbamazepine. Triclosan and the anionic herbicides picloram and dicamba showed negligible uptake in all samplers. For Chemcatcher^{TM} SDB-RPS with triclosan, diuron and 2,4-D > 50% of the compound was retained by the PES membrane (0.2 µm pore size) after 26 days deployment. Increasing membrane pore size from 0.2 to 0.45 µm for Chemcatcher^{TM} (SBD-RPS) caused a slight increase in Rs of 24%. Overall, results from the work described in this thesis show that the passive sampling technologies investigated can be useful as part of a suite of monitoring tools for most of the ionizable and polar analytes of interest.

Acknowledgements

This research was funded by the Australian Research Council's Linkage Projects scheme (LPO883675), with industry partner support of SEQWater, NMI, DW WA, EPA Victoria, EPA South Australia, Office of Environment and Heritage NSW, Brisbane City Council, GBRMPA, DERM, Queensland Health Forensic and Scientific Services (QHFSS), Griffith University and The University of Queensland (UQ). Sarit Kaserzon is also supported by a top-up scholarship from Water RA. Jochen Mueller is funded by an ARC

Future Fellowship (FF 120100546). The authors thank Chris Paxman, Amy Heffernan, Jake O'Brien, Phong Thai and Kristie Thompson, Entox for providing laboratory and sampling support. The National Research Centre for Environmental Toxicology (Entox) is a joint venture of UQ and QHFSS.

Notes and references

[a]The University of Queensland, The National Research Centre for Environmental Toxicology, 39 Kessels Rd., Coopers Plains QLD 4108, Australia
[b]Griffith University, School of Environment, Nathan QLD 4111, Australia
[c]SEQWater, PO Box 16146, City East QLD 4002, Australia
[d]Queensland Health Forensic and Scientific Services, Coopers Plains QLD 4108, Australia
[e]NIOZ Royal Netherlands Institute for Sea Research, P.O. Box 59, 1790 AB Texel, The Netherlands

Electronic Supplementary Information (ESI) is available on; mass spectrometry analysis details (Text S1); QA/QC procedures (Text S2); Analyte concentrations in duplicate and in blank grab water samples (SI Tables S1-S3); Amount of analytes in sample blanks (Table S4); Literature value R_s (Table S5); log K_{mw} values for POCIS and Chemcatchers^{TM} (Table S6); Experimental timeline (Fig. S1); Photograph of sampler deployment (Fig. S2); Analyte accumulation profiles with POCIS and Chemcatchers^{TM} (Fig. S3); R_s/A for target chemicals with POCIS vs. Chemcatchers^{TM} (Fig S4); R_s/A for chemicals vs. Log D_{ow}, molar mass and log K_{sw} for POCIS and Chemcatchers^{TM} (Fig. S5-S7); Analyte accumulation in PES (0.2 µm pore size) from Chemcatcher^{TM} (SDB-RPS) (Fig. S8); Percent accumulation in PES membranes (0.2 µm pore size) (Fig. S9); log K_{mw} vs. log D_{ow} and molar mass for POCIS and Chemcatchers^{TM} (Fig. S10). See DOI: 10.1039/b000000x/

1. H. Soderstrom, R.H. Lindberg, J. Fick, *J. Chromatogr. A.*, 2009, **1216**, 623-630.
2. S.R. Hughes, P. Kay, L.E. Brown, *Environ. Sci. Technol.*, 2012, **47**, 661−677.
3. G.A. Mills, B. Vrana, I.J. Allan, D.A. Alvarez, J.N. Huckins, R. Greenwood, *Anal. Bioanal. Chem.*, 2007, **387**, 1153-1157.
4. C. Harman, I.J. Allan, E.L.M. Vermeirssen, *Environ. Toxicol. Chem.*, 2012, **31**, 2724-2738.
5. M. Claessens, L. Vanhaecke, K. Wille, C.R. Janssen, *Mar. Pollut. Bull.*, 2013, **71**, 41-50.
6. T.L. ter Laak, M. van der Aa, C.J. Houtman, P.G. Stoks, A.P. van Wezel, *Environ. Int.*, 2010, **36**, 403-409.
7. European Commission, *Directive of the European Parliament and of the council. 2012. Available from:* http://ec.europa.eu/environment/water/water-dangersub/pdf/com_2011_876.pdf. 2012.
8. I.J. Allan, B. Vrana, R. Greenwood, G.A. Mills, B. Roig, C.A. Gonzalez, *Talanta*, 2006, **69**, 302-322.
9. R. Greenwood, G.A. Mills, B. Vrana, *TrAC-Trend. Anal. Chem.*, 2006, **25**, 751-754.
10. K. Booij, B. Vrana, J.N. Huckins, In *Passive Sampling Techniques in Environmental Monitoring*, Comprehensive Analytical Chemistry, 48; R. Greenwood, G. Mills, B. Vrana, Eds.; Elsevier: Amsterdam, 2007; pp 141−169.
11. D.A. Alvarez, J.N. Huckins, J.D. Petty , T.L. Jones-Lepp, F. Stuer-Lauridsen, D.T. Getting, J.P. Goddard, A. Gravell, In *Passive Sampling Techniques in Environmental Monitoring*, Comprehensive Analytical Chemistry, 48; R. Greenwood, G. Mills, B. Vrana, Eds.; Elsevier: Amsterdam, 2007; pp 171-197.
12. D.A. Alvarez, 1999, University of Missouri-Columbia: Columbia, MO, USA.
13. J.K. Kingston, R. Greenwood, G.A. Mills, G.M. Morrison, L.B. Persson, *J. Environ. Monit.*, 2000, **2**, 487-495.
14. N. Morin, J. Camilleri, C. Cren-Olive, M. Coquery, C. Miege, *Talanta*, 2013, **109**, 61-73.
15. C. Harman, M. Reid, K.V. Thomas, *Environ. Sci. Technol.*, 2011, **45**, 5676-5682.
16. E.L.M. Vermeirssen, N. Bramaz, J. Hollender, H. Singer, B.I. Escher, *Water Res.*, 2009, **43**, 903.
17. S.L. Macleod, E.L. McClure, C.S. Wong, *Environ. Toxicol. Chem.*, 2007, **26**, 2517.
18. M. Shaw, M.J. Furnas, K. Fabricius, D. Haynes, S. Carter, G. Eaglesham, J.F. Mueller, *Mar. Pollut. Bull.*, 2010, **60**, 113-122.
19. S.L. Kaserzon, K. Kennedy, D.W. Hawker, J. Thompson, S. Carter, A. Roach, K. Booij, J.F. Mueller, *Environ. Sci. Technol.*, 2012, **46**, 4985-4993.
20. R. Greenwood, G.A. Mills, B. Vrana, I. Allan, R. Aguilar-Martínez, G. Morrison, In *Passive Sampling Techniques in Environmental Monitoring*, Comprehensive Analytical Chemistry, 48; R. Greenwood, G. Mills, B. Vrana, Eds.; Elsevier: Amsterdam, 2007; pp 199-229.
21. D.A. Alvarez, J.D. Petty, J.N. Huckins, T.L. Jones-Lepp, D.T. Getting, J.P. Goddard, S.E. Manahan, *Environ. Toxicol. Chem.*, 2004, **23**, 1640-1648.
22. H.X. Li, E.L.M. Vermeirssen, P.A. Helm, C.D. Metcalfe, *Environ. Toxicol. Chem.*, 2010, **29**, 2461–2469.
23. S.L. Kaserzon, E.L.M. Vermeirssen, D.W. Hawker, K. Kennedy, C. Bentley, J. Thompson, K. Booij, J.F. Mueller, *Environ. Pollut.*, 2013, **177**, 58-63.
24. V. Fauvelle, N. Mazzella, F. Delmas, K. Madarassou, M. Eon, H. Budzinski, *Environ. Sci. Technol.*, 2012, **46**, 13344-13353.
25. E.L.M. Vermeirssen, C. Dietschweiler, B.I. Escher, J. van der Voet, J. Hollender, *Anal. Bioanal. Chem.*, 2013, **405**, 5225-5236.
26. A.T.K. Tran, R.V. Hyne, P. Doble, *Environ. Toxicol. Chem.*, 2007, **26**, 435-443.
27. B.S. Stephens, A.P. Kapernick, G. Eaglesham, J.F. Mueller, *Mar. Pollut. Bul.*, 2009, **58**, 1116-1122.
28. M. Shaw, G. Eaglesham, J.F. Mueller, *Chemosphere*, 2009, **75**, 1-7.
29. H.X. Li, P.A. Helm, G. Paterson, C.D. Metcalfe, *Chemosphere*, 2011, **83**, 271-280.
30. E.L.M Vermeirssen, C. Dietschweiler, B.I. Escher, J. van der Voet, J. Hollender, *Environ. Sci. Technol.*, 2012, **46**, 6759−6766.
31. A.T.K. Tran, R.V. Hyne, P. Doble, *Chemosphere*, 2007, **67**, 944-953.
32. K. Kennedy, M. Devlin, C. Bentley, K. Lee-Chue, C. Paxman, S. Carter, S.E. Lewis, J. Brodie, E. Guy, S. Vardy,

K.C. Martin, A. Jones, R. Packett, J.F. Mueller, *Mar. Pollut. Bull.*, 2012, **64**, 1495-1507.

33. G.A. Mills, R. Greenwood, B. Vrana, I. Allan, T. Ocelka, *J. Environ. Monit.*, 2011, **13**, 2979-2982.
34. B.S. Stephens, A. Kapernick, G. Eaglesham, J.F. Mueller, *Environ. Sci. Technol.*, 2005, **39**, 8891-8897.
35. D.S. O'Brien, B. Chiswell, J.F. Mueller, *J. Environ. Monit.*, 2009, **11**, 212-219.
36. NHMRC, *Australian Drinking Water Guidelines 6 2011. https://www.nhmrc.gov.au/_files_nhmrc/publications/attachments/eh52_aust_drinking_water_guidelines_update_131216.pdf*,. 2013. p. 197.
37. J.N. Huckins, I. Petty, C. Orazio, J. Lebo, R. Clark, V. Gibson, W.R. Gala, K. Echols, *Environ. Sci. Technol.*, 1999, **33**, 3918-3923.
38. N. Fontanals, R.M. Marcé, F. Borrull, *J. Chromatogr. A.*, 2007, **1152**, 14-31.
39. P.S. Bäuerlein, J.E. Mansell, T.L. ter Laak, P. de Voogt, *Environ. Sci. Technol.* 2012, **46**, 954-961.
40. S. Croubels, H. Vermeersch, P. De Backer, M.D.F Santos, J.P. Remon, C. Van Peteghem, *J. Chromatogr. B.*,1998, **708**, 145-152.
41. R.B. Schafer, A. Paschke, B. Vrana, R. Mueller, M. Liess, *Water Res.*, 2008, **42**, 2707-2717.
42. L. Sanchez-Prado, M. Llompart, M. Lores, C. García-Jares, J.M. Bayona, R. Cela, *Chemosphere*, 2006, **65**, 1338-1347.
43. C.E. Chen, H. Zhang, K.C. Jones, *J. Environ. Monit.* 2012, **14**, 1523-1530.