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Determination of the uptake and release rates of multifamilies of endocrine disruptor compounds on the polar C18 Chemcatcher. Three potential performance reference compounds to monitor polar pollutants in surface water by integrative sampling

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ABSTRACT

The uptake kinetics of 27 emerging pollutants on the polar C18 Chemcatcher have been investigated. This investigation determined the sampling rates of 20 compounds, including 16 endocrine disruptors and 4 pharmaceuticals, which were used as overall pollution indicators. Calibrations were completed in a 50-L flow-through microcosm with continuous renewal of tap water spiked with approximately 3 μg/L of each pollutant and with sampling times at 1, 3, 6 and 12 h and 1, 3, 7, 14, 21 and 28 days. Exponential regressions for the accumulation kinetics were plotted to confirm the maximum linear uptake times for each molecule using the half time of equilibrium ($t_{1/2}$) criteria. Of the compounds tested, 17 were accumulated linearly for up to 14 or 21 days with an R^2 above 0.98 for linear correlations. The evaluation of the release kinetics of a C18 Chemcatcher spiked with 20 deuterated compounds identified 3 potential performance reference compounds (PRCs) with exponential desorption rates showing relatively good isotropic exchange.

1. Introduction

The need for data that measure environmental concentrations of multiple emerging pollutants in water is expressed by the increasing number of available multiresidue analytical methods [1–4]. Such methods coupled to offline extractions such as solid phase extraction (SPE) enable the detection and quantification of multifamilies of pollutants at the sub-ng/L level, which is consistent with levels found in the environment [5,6]. These methods allow for the punctual quantification of pollution. The results may vary depending on the sampling conditions; factors that may affect these levels include recent rainfall, overload at a waste water treatment plant or a recent field spreading of manure or waste water treatment plant sludges. Samples, therefore, should be collected as often as possible to account for these variations; barriers to such frequent sampling include analytical time restraints, costs, and the available resources.

Recently, systems known as passive or integrative samplers have been developed to optimize water sampling by mimicking the accumulation of hydrophobic substances in living organisms. Semipermeable membrane devices (SPMDs) were designed to mimic the accumulation of hydrophobic substances with an octanol–water partitioning coefficient log(K_{ow}) ranging from 3 to 10 [7]. Such systems are based on an equilibrium state between the receiving phase, which uses a high-purity triolein, and the environment, which is air or water. In 1999, Alvarez et al. [8] developed polar organic chemical integrative samplers (POCIS) to monitor polar and hydrophilic compounds in water using polymeric receiving phases. These systems are based on adsorption phenomena and accumulate pollutants during an integrative phase that must be determined during calibration [9,10]. The extant literature presents the sampling rates of only some pharmaceuticals and pesticides [10–13] for POCIS in their pharmaceutical or pesticide configurations. A newer integrative sampler, the Chemcatcher, was developed in 2000 to monitor polar or hydrophobic compounds in water depending on its configuration [13,14]. This passive sampler is composed of a polytetrafluoroethylene (PTFE) or polycarbonate body containing one receiving media covered by a polyethersulfone (PES) diffusion membrane. In its polar configuration, the accumulation can be performed using various adsorption

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phases: C18 [15], SDB-RPS [16], SDB-XC [17] or any other SPE phase available as SPE disks.

All of these passive samplers are calibrated in the laboratory under specific conditions for the pH, temperature, conductivity, salinity and flow velocity [18]. In real exposure conditions, such parameters cannot be reproduced: biofilms accumulate on the diffusion membranes and induce variations between laboratory and in situ calibrations on SPMDs [19] and on POCIS [20]. To be able to correlate sampling rates regardless of the exposure conditions, an approach using performance reference compounds (PRCs) has been applied and validated for the SPMDs [19,21]. Theoretically, this approach cannot be transferred to Chemcatcher and POCIS. A molecule needs to meet three criteria to be used as a PRC: it must have isotropic exchange as well as first-order adsorption and desorption kinetics. These criteria are not analogous for POCIS or the Chemcatcher principally due to differences between the adsorption and desorption mechanisms on SPE phases compared to the solute partitioning that occurs in SPMDs [9]. Studies still look for molecules that could be used as PRCs that have anisotropic exchange mechanisms and show relatively good desorption. Metolachlor, simazine, isoproturon, deethylatrazine (DEA), deisopropylatrazine-d5 (DIA-d5) and atrazine have been evaluated as potential PRCs for pharmaceutical POCIS [22,23]. DIA-d5 exhibited a good exponential desorption correlation and has been field-tested. Currently, DIA-d5 is the only potential PRC reported for pharmaceutical POCIS. The possibility of using PRCs for Chemcatcher has been evaluated and validated for its hydrophobic configuration due to the presence of a small layer of saturated n-octanol [24]. Concerning the polar configuration of Chemcatcher, only one potential PRC has been found when using SDB-RPS SPE disks as receiving phase – diuron d6 [25] – and only one has been found when using the C18 SPE disks – dimethylphthalate [26] – reported by Shaw et al. [25].

In this context, the aim of this work was first to evaluate the adsorption of 27 endocrine disruptors and pharmaceuticals on the polar C18 Chemcatcher, to determine their linear uptake phases and to calculate their sampling rates. Afterwards, the applicability of the PRC approach to the polar C18 Chemcatcher was evaluated by studying the desorption of the 20 available deuterated compounds. More precisely, the evaluation of these release kinetics identified 3 potential PRCs with exponential desorption and relatively good isotropic exchange.

2. Experimental

2.1. Chemicals and materials

Acetonitrile LC/MS Chromasolv grade, methanol, ammonium acetate puriss. p.a. for mass spectroscopy ≥99.0% and formic acid puriss. p.a. eluent additive for LC–MS ~98% were purchased from Fluka (Saint Quentin Falavier, France). Endocrine disruptor-quality water was obtained using a MilliQ® Gradient A10 system equipped with an EDS-PAK cartridge and a 0.2 μm Millipak® 40 filter from Merck-Millipore (St. Quentin Yvelines, France). All analytical standards were purchased from Sigma–Aldrich (St. Quentin Fallavier, France): 2.4-dichlorophenoxyacetic acid (2.4D), acetochlore (Ace), alachlore (Ala), atrazine (Atra), carbendazim (Carb), diuron (Diu), iprodion (Ipr), procholraz (Pro), thiram (Thi), estrone (E1), 17β-estradiol (βE2), megestrol acetate (MegA), progesterone (P), testosterone (T), 2.4-dichlorophenol (2.4DCP), 4-n-nonylphenol (nNP), 4-n-octylphenol (nOP), 4-nonylphenol technical (mixture of branched and linear 4-nonylphenol, tNP), resorcinol (Res), 4-tert-butylphenol (tBP), 4-tert-octylphenol (tOP), 3.4-dichloraniline (3.4D), carbamazepine (Carba), diclofenac sodium salt (Diclof) and ibuprofen (Ibu). All deuterated compounds were purchased from CIL Cluzeau (St. Foy la Grande, France): Ibuprofen-d3, diclofenac d4 sodium salt and carbendazim d4. C18 SPE Empore disks were purchased from Sigma–Aldrich, and polyether sulfone (PES) SUPOR 200 (pore diameter: 0.2 μm; thickness: 145 μm) hydrophilic membranes were ordered from Pall (St. Germain-en-Laye, France). Exponential regressions for the desorption study and linear regressions for the accumulation study were calculated using MS Office Excel 2007 regressions. Nonlinear regressions for the accumulation study on samplers were performed using Addinsoft XLStat 2011 software for MS Office Excel.

2.2. HPLC–MS/MS quantification and validation of the method

The HPLC system used for this study was an Agilent 1200 RRLC with a G1312B Binary Pump SL, a G1369A autosampler, a G1315B column heater and a G1316C photodiode array detector (Agilent Technologies, Avondale, USA). The detection was performed on a triple quadrupole 3200 QTrap from ABSciex (ABSciex, CA, USA) used in its scheduled MRM mode. The list of the followed transitions is shown in Table 1.

The separation was accomplished on a (100 mm × 2.1 mm) Kinetex XB-C18 Core Shell with 1.7 μm diameter particles. A multilinear gradient with 0.1 mmol/L of ammonium acetate in endocrine disruptor-quality water and acetonitrile was used for the separation of the negative ionizable compounds. A second multistep gradient was developed for the positive ionizable compounds using endocrine disruptor-quality water with 0.01% (v/v) of formic acid and acetonitrile.

To confirm the robustness of the calibration and desorption studies, a validation of the analytical method was performed. Standards were diluted in endocrine disruptor-quality water to mimic the injection of water samples from calibration experiments and the eluates from samplers after treatment. Calibration with triplicate injections and 5 injections of one concentration at approximately the expected limit of quantifications were performed over 3 days with independent standards each day. This protocol enabled the estimations of the intraday instrumental relative standard deviation and the intraday relative standard deviation of sample preparations and to verify the linearity of the method by statistical means.

2.3. Spiking of the samplers

The preparation procedure for the Empore C18 SPE disks used for the Chemcatcher includes a conditioning step with 50 mL of methanol followed by 25 mL of MilliQ water. This protocol has been modified [25] to spike the SDB-RPS SPE Empore disks with 250 mL of water containing 1 μg of potential PRCs. In this study, C18 SPE disks were spiked by percolating 200 mL of a standard solution of deuterated compounds at 1.5 μg/L in MilliQ water. Thus, each Chemcatcher was spiked at 0.3 μg of each deuterated compound. Spiked quality control samplers were prepared concurrently and were stored during all of the experiment at 6 °C. Quality control samplers were disassembled, and SPE disks were extracted and analyzed after the exposure period.

2.4. In laboratory adsorption and desorption experiments

Adsorption and desorption studies on the Chemcatcher were performed with the CEMAGREF Lyon using large flow-through microcosms inspired by the system described by Mazzella et al. [22].

During the calibration of the samplers, two 50 L glass aquaria were equipped with peristaltic pumps and Versilic or Tygon tubing to ensure continuous flow and renewal of spiked water (Fig. 1). Water was fortified in a mixing chamber with tap water pumped

Table 1
First transitions followed in MRM mode, retention time (R_t), declustering potential (DP) and collision energy (CE) for selected compounds.

Ionization mode	Compound	R_t (min)	Precursor (m/z)	Product (m/z)	DP (V)	CE (V)
ESI +	Carbendazim	2.5	192.2	160.2	36	25
	Carbamazepine	3.9	237.2	194.1	41	25
	Thiram	4.2	241.1	88.0	21	17
	Atrazine	4.3	216.2	174.1	41	23
	3.4-Dichloroaniline	4.3	162.1	127.0	46	27
	Diuron	4.3	233.1	71.9	41	31
	Testosterone	4.7	289.3	97.1	46	31
	Linuron	4.9	249.1	160.0	36	23
	Diclofenac	5.5	296.0	214.2	31	41
	Iprodion	5.7	330.1	245.2	21	19
	Alachlore	5.8	270.2	238.2	21	15
	Prochloraz	5.8	376.1	308.2	21	17
	Acetochlore	5.8	270.2	224.2	21	13
	Progesterone	6.1	315.4	97.1	66	31
	Megestrol acetate	6.1	385.3	325.4	41	19
	4-Methylbenzylidene camphor	7.9	255.3	105.1	41	45
ESI –	Resorcinol	1.3	109.0	65.1	−30	−18
	2.4-Dichlorophenoxyacetic acid	4.0	218.9	160.9	−20	−16
	Bisphenol A	5.1	226.9	133.0	−40	−36
	2.4-Dichlorophenol	5.2	160.9	124.9	−35	−22
	β-Estradiol	5.3	271.1	145.2	−75	−52
	Estrone	5.5	269.1	145.1	−70	−48
	4-t-Butylphenol	5.6	149.0	132.9	−40	−28
	4-tert-Octylphenol	7.1	205.1	133.0	−45	−36
	4-tert-Nonylphenol	7.7	219.1	133.0	−45	−44
	4-n-Octylphenol	7.7	205.2	106.1	−40	−28
	4-n-Nonylphenol	8.2	219.1	106.0	−50	−28

at 35 L/day and standard pollutant solutions were injected by a syringe pusher at 1.05 mL/day. The content of the mixing chamber was then transferred to the 2 exposure aquaria at 10 cm/s in front of the samplers using the peristaltic pump. The final concentration of pollutants in the aquaria was approximately 3 μg/L. Samplers were exposed in the dark, and the temperature was maintained at 20 °C. The dissolved organic carbon (DOC), temperature, flow velocity, pH and conductivity were controlled during the experiment. Concentrations in the aquaria and the contents of the syringe were analyzed at each sampling day. Three Chemcatcher were taken at 1, 3, 6 and 12 h and 1, 3, 7, 14, 21 and 28 days for the calibration study.

For the desorption study, spiked Chemcatchers were exposed in the dark for 3, 7, 14, 21 and 28 days in two aquaria with a continuous flow of tap water. The same parameters followed in the adsorption study were also controlled during this experiment.

2.5. Extraction and recoveries

After exposure, the Chemcatchers were shortly rinsed with endocrine disruptor-quality water upon opening the lid. Once the Chemcatcher was disassembled, the PES membrane was stored in aluminum foil at 6 °C, and the SPE disk was mounted on an Empore filtration system to be dried under vacuum. The dried C18 Empore disk was then transferred to a glass test tube containing 10 mL of Chromasolv-grade acetonitrile for 20 min and was agitated using a vortex. The SPE disk was then transferred to a second glass test tube with clean steel tweezers for 10 min of extraction in Chromasolv-grade methanol. The methanol and acetonitrile from the two test tubes were mixed before being separated into two aliquots. One aliquot was stored at −26 °C, and the other one was evaporated to dryness under a nitrogen stream at 40 °C. Samples were dissolved in 2 mL of 80:20 (v/v) acetonitrile:endocrine disruptor-quality water before being diluted at least 100 times in

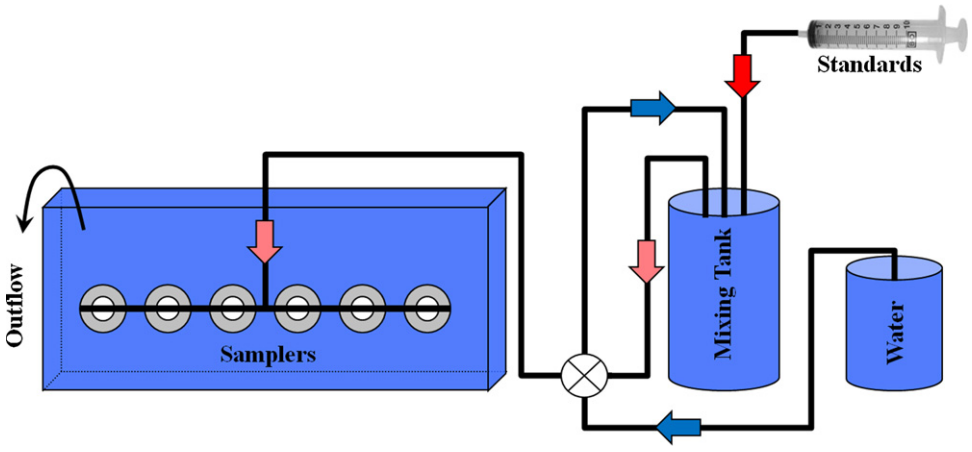

Fig. 1. A 50 L flow-through microcosm used for the kinetic study of the polar C18 Chemcatcher.

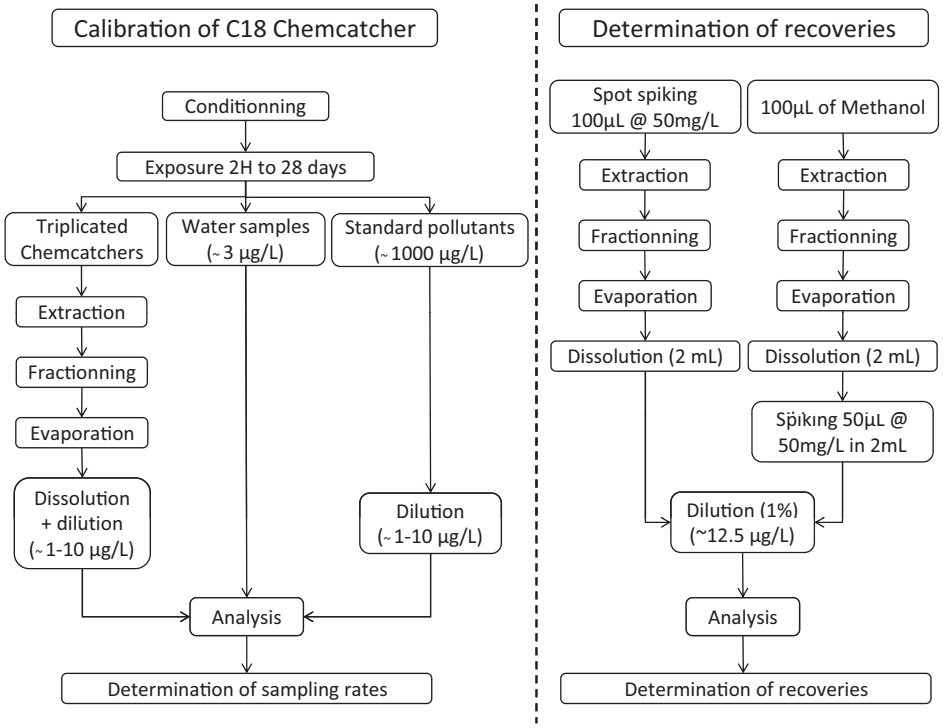

Fig. 2. Scheme of the whole experiment to determine the uptake and release rates of selected pollutants on the polar C18 Chemcatcher.

endocrine disruptor-quality water. A scheme of the overall analytical procedure used for the experiment is synthesized in Fig. 2.

Recoveries have been calculated comparing the extractions of six C18 SPE disks spiked with 100 μL standard solution at 50 mg/L to extractions of two blank C18 SPE disks spiked after extraction with 50 μL of the same solution. All molecules yielded recoveries above 70% with standard deviations between 3 and 14% except for 3.4D ($60 \pm 6\%$), Carb ($63 \pm 6\%$) and alkylphenols (53–70%). The recoveries calculated for the 2.4DCP were below 30%.

3. Uptake and release kinetics theory

The polar C18 Chemcatcher was built with one receiving phase, a C18 SPE disk, and one diffusion membrane in PES (polyether sulfone) with 0.2 μm pore diameters and a typical thickness of 145 μm. The Chemcatcher body used in this study is the second design and is manufactured in polycarbonate instead of the old version, which was manufactured in PTFE. The influence of this change in the Chemcatcher's design, mainly the reduction in the depth of the sampler's cavity, has been studied for hydrophobic organic pollutants in water [27]. This reduction should slightly decrease the sensitivity to the fluctuating flow and increase the uptake rates. This increase can be explained by the inversely proportional relationship between the diffusion path length and the rate of diffusion from the water to the adsorption phase. Such comparison between the two systems has not been studied for polar compounds.

3.1. Uptake rates and the calibration of samplers

The theory describing the accumulation of organic pollutants in equilibrium passive samplers such as semipermeable membrane devices (SPMDs) or integrative samplers such as POCIS has been well described [28,9,10]. The models developed for such samplers, built with receiving phases and diffusion membranes, can be used for the uptake of polar and non-polar organic pollutants on the Chemcatcher [24].

The overall equation describing the accumulation of the pollutant concentration in the sampler C_S (measured in ng/g) (Eq. (1)) has been established for SPMD [29] and represents a solution of first-order exchange kinetics (Fig. 3).

Overall expression for concentration in a passive sampler device as a function of time:

$$C_S = K_{SW} C_W (1 - \exp(-k_e t)) \quad (1)$$

where K_{SW} is the partitioning coefficient of sampler/water ($L\,g^{-1}$); t is the time of exposure; k_e is the desorption rate constant (day^{-1}).

Eq. (1) can be simplified to Eq. (2) for the linear phase of integrative samplers when the concentration of the pollutant in water can be expressed as a time-weighted average $C_W = C_{W,TWA}$ (measured in μg/L). In the case of diffusion membrane-covered samplers such as Chemcatcher, which are controlled by the external aqueous boundary layer, the concentration in the sampler can be expressed as a linear function of time (Eq. (2′)). Eq. (2) and (2′) are valid until the

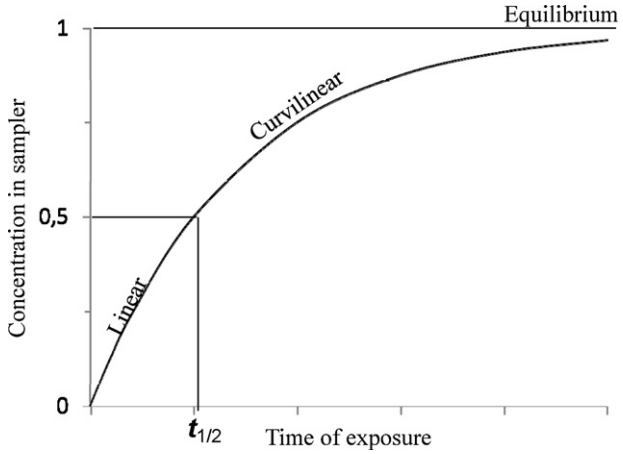

Fig. 3. Theoretical accumulation curve of passive sampler devices for first-order exchange kinetics.

system reaches the equilibrium half-time, i.e., the time needed for the sampler to accumulate half of the equilibrium concentration: $t_{1/2} = \ln(2)/k_e$ in days.

Simplification of Eq. (1) in the case of an integrative or linear accumulating device:

$$C_S = k_u C_W t \quad (2)$$

where k_u is the uptake rate constant ($L\,day^{-1}\,g^{-1}$).

Modification of Eq. (2) in the case of a linear accumulating sampler under water boundary layer control

$$C_S = \left(\frac{R_S}{M_S}\right) C_W t \quad (2')$$

where M_S is the mass of adsorption phase (g); R_S is the sampling rate (L/day).

The sampler needs to be calibrated to determine the half time of equilibrium and the sampling rate for each molecule. With these values, the time-weighted average concentrations of the pollutant in water during in situ exposure campaigns can be calculated. There are two different conditions typically used to determine the uptake rates for the calibration of POCIS or Chemcatcher. The first method uses mechanical or magnetic agitation and alters the concentration by punctual renewal of the pollutants to mimic variations in exposure concentrations [30,12]. The second method uses flow-through systems with a constant concentration of pollutant during the exposure and continuous flow [22,31] to calibrate the passive sampler with a constant $C_{W,TWA}$ (μg/L) term in Eq. (2′). In each case, sampling rates are calculated using Eq. (2″) by expressing R_S (L/day) as a function of the concentration in the sampler (C_S in μg/g), the mass of adsorption phase (M_S in g), the concentration of exposure (C_W in μg/L) and the exposure time (days).

Expression derived from Eq. (2′) used to calculate the sampling rate of a molecule on a water boundary layer-controlled integrative sampler:

$$R_S = \frac{C_S M_S}{C_{W,TWA} t} \quad (2'')$$

3.2. Release rates and the evaluation of potential PRCs

Multiple factors during the in situ exposure could induce variations between the calculated uptake rates and the rates observed in real conditions. Influences such as the concentration of pollutants, the pH, the salinity, the temperature and the flow are often studied [30,18]. The formation of biofilms during the exposure in real surface water has been reported as a highly influential factor on sampling rates in the case of SPMDs [19]. All of these parameters impact sampling rates; for example, changes in the pH or salinity induced a 12% maximal variation in the calculated sampling rates in a study by Zhang et al. [18].

The sampling rates obtained in a laboratory can be corrected for the real exposure conditions by using performance reference compounds with SPMDs. The comparison of the desorption rates from a laboratory ($k_{e,PRC}$) and from in situ exposures ($k_{e,expo}$) enables the calculation of an exposure adjustment factor equal to the ratio $k_{e,expo}/k_{e,PRC}$ [32]. Eq. (3) is used to calculate those desorption rate constants from experimental studies and real in situ exposure. To ensure that PRCs can correct for the variations in exposure parameters, both adsorption and desorption mechanisms must have first-order kinetics. Moreover, isotropic exchanges of analytes require verification [19].

Equation of the desorption of a potential PRC on a passive sampler:

$$C_{t,PRC} = C_{0,PRC}\ \exp(-k_{e,PRC} t) \quad (3)$$

4. Results and discussion

4.1. Validation of the analytical method

A multi-residue analytical approach has been undertaken to develop an LC–MS/MS method for the analysis of 27 selected endocrine disruptors and pharmaceuticals. Two methods have been optimized corresponding to two ionization modes. The first method in positive ionization mode has been developed to quantify 16 compounds (see Table 1 for MRM transition) in less than 9 min. The elution is performed using a multi-linear gradient with water that had been acidified using formic acid and acetonitrile. The second method, developed for the analysis of the 11 negative ionizable compounds, uses a multistep gradient with 0.1 mM ammonium acetate in water and acetonitrile. Those LC–MS/MS methods have been validated for direct injections of 100 μL standard solutions in water using a method inspired by ICH recommendations [33]. Calibrations at 7 concentrations have been performed over three days with three independent series of standard solutions to validate these methods. The intraday RSD of the system and the interday RSD of the preparation step and analytical step were calculated. Linearity has also been verified using statistical means. Limits of detection (LODs) and quantification (LOQs) have been determined using S/N = 3 and S/N = 10, respectively. Five replicated injections of 100 μL of three independent standard solutions were used to evaluate the LOD and LOQ. The concentrations used to determine LODs and LOQs of the analytical methods were approximately 20 ng/L for the positive ionizable compounds and approximately 450 ng/L for the negative compounds. These results are provided in Table 2.

The method developed for positive ionizable compounds showed very good linearity from 0.4 to 20 μg/L for all molecules except diuron, linuron, testosterone, and carbamazepine, which had two linear domains. The calculated Fisher ratios for all of the positive ionizable compounds were between 0.09 and 2.10 when using 7 concentrations with three independent solutions. Compared to the tabulated value for the Fisher ratio: 2.96 for a 5% risk and 5 and 14 degrees of freedom, the obtained values validate the linearity of the calibration for all molecules [34]. Similar results were observed for the 4 molecules that showed 2 linearity domains. Intraday relative standard deviations ($n = 3$) calculated for each concentration level were good for all compounds (<20%). Interday relative standard deviations ($n = 9$) were also good (<20%).

Negative ionizable compounds gave relatively good intraday and interday relative standard deviations (<30%) except for 2.4-dichlorophenol, 4-n-nonylphenol and 4-tert-butylphenol. This method also obtained good linear relationships ($R^2 > 0.992$) for concentrations ranging from 1 to 20 μg/L. The calculated Fisher ratios were between 0.05 and 0.34 for all of the molecules with 6 calibration levels independently prepared in triplicate. Linearity was validated using the tabulated Fisher ratio value equal to 3.26 for 4 and 12 degrees of freedom and for a 5% risk.

These methods were validated to be able to precisely measure the MDL and MQL in real-surface water samples. Instead of saying that the molecule has not been found during the exposure, we would like to pinpoint the limit of quantification of the exposure and analysis method of pollutants accumulated during the exposure.

4.2. Uptake of selected compounds on a C18 Chemcatcher

Calibration of the samplers has been performed with continuous renewal of spiked tap water in 50 L aquaria for 28 days of exposure with 10 sampling times: 1, 3, 6 and 12 h and 1, 3, 7, 14, 21 and 28 days (Fig. 1).

Table 2
Validation of LC–MS/MS method: mean values ($n = 18$) of intraday and interday relative standard deviations for 0.5–20 μg/L; correlation coefficient for linear regression (R^2) plotted for concentration ranging from 0.5 to 20 μg/L.

Compound	Intraday RSD (%)	Interday RSD (%)	R^2	LOQ (ng/L)	Compound	Intraday RSD (%)	Intraday RSD (%)	R^2	LOQ (ng/L)
2.4D	2.5	4.1	1.0000	17.0[b]	4MBC	1.7	7.4	0.9986	14.5[a]
Ace	3.2	6.9	0.9991	9.50[a]	P	2.4	5.3	0.9995	5.00[a]
Ala	3.2	6.8	0.9978	4.50[a]	T	4.4	5.1	0.9963	4.00[a]
Atra	2.4	4.9	0.9985	2.00[a]	E1	3.2	4.5	1.0000	18.0[b]
Carb	2.0	4.5	0.9983	1.00[a]	βE2	7.8	8.7	0.9987	185[b]
Diu	3.6	4.8	0.9982	8.50[a]	2.4 DCP	18	20	0.9989	580[b]
Ipr	4.3	11	0.9994	11.0[a]	BPA	4.7	7.5	0.9999	40.0[b]
Lin	3.8	4.4	0.9995	15.3[a]	nOP	10	19	0.9965	310[b]
Pro	3.4	9.0	0.9998	2.00[a]	nNP	21	37	0 .9929	360[b]
Thi	5.4	16	0.9940	2.50[a]	Res	5.4	6.5	0.9999	275[b]
MegA	2.1	5.3	0.9994	4.50[a]	tBP	18	10	0.9989	490[b]
3.4D	2.7	8.2	0.9986	5.40[a]	tOP	7.6	12	0.9994	260[b]
Carba	3.6	4.2	0.9962	1.50[a]	tNP	8.6	18	0.9981	95.0[b]
Diclof	3.4	9.2	0.9989	2.00[a]					

[a] Limits of quantification measured using S/N = 10 for 100 μL of standard solution in MilliQ water around 20 ng/L.
[b] Limits of quantification measured using S/N = 10 for 100 μL of standard solution in MilliQ water around 450 ng/L.

During the 28 days of exposure, the C18 SPE disks of the PES membrane-covered Chemcatcher accumulated 20 of the 27 selected compounds. All of these molecules showed excellent fit with the exponential solution of first-order accumulation (Eq. (1)) with correlation coefficients over 0.976. Among these 20 molecules, 12 pesticides, hormones, pharmaceutics and bisphenol A were accumulated with a good linear correlation ($0.985 < R^2 < 0.999$) after 21 days of exposure (Table 3). As shown in Table 3, 5 compounds, linuron, prochloraz, E1, βE2 and 4-tert-octyphenol, showed a linear uptake for up to 14 days of exposure with an R^2 between 0.968 and 0.998. Finally the uptake of three molecules, carbendazim (Fig. S1 in Supplementary material), diclofenac and ibuprofen, presented linear and curvilinear accumulation phases and seemed to reach the equilibrium state after 7 or 14 days. These 20 molecules showed excellent correlations to the exponential and the linear uptake models, as theoretically described. In all cases, the equilibrium half-time was a sufficient discriminatory criterion between the linear and exponential phases of accumulation.

Thiram, one of the 7 molecules that were not accumulated, was not detected on samplers probably due to its degradation during the exposure time. Its degradation half-time (DT50) in water by photolysis is approximately 0.4 days at pH 5 at 25 °C and by hydrolysis 3.5 days at pH 7 at 25 °C [35]. Resorcinol may not accumulate on the C18 SPE disks due to its very high polarity ($\log(K_{ow}) = 0.80$, which was calculated with the ALOGPS 2.1 program [36]). However, n-octylphenol, branched and linear nonylphenol may have not been detected on the C18 SPE disk due to a combination of their poor ionization in mass-spectrometry and a hydrophobicity that was too high ($5 < \log(K_{ow}) < 6$).

The UV filter (4MBC) and the prochloraz showed small lag times during the first hours of exposure as the values quantified for the first samplings (1, 3, 6 and 12 h) seem to accumulate more weakly than the overall linear uptake (Fig. S2 in Supplementary material). Integrative samplers are constructed with diffusion membranes, and their uptake is under the control of the water boundary layer. Thus, the lag time is the time required for the pollutants to cross those barriers before being accumulated in the receiving phase. Shaw et al. [25] observed a 1-day lag time for the uptake of diuron on an SDB-RPS Chemcatcher using the same PES diffusion membranes. During the calibration, no such lag time was observed for diuron (Fig. 4). This discrepancy may be due to a difference in the geometry of the Chemcatcher body if Shaw et al. used the PTFE body instead of the polycarbonate one used in this study. The new polycarbonate body has been developed to optimize sampling rates

Table 3
Calibration of the polar C18 Chemcatcher: correlation coefficient (R^2) and calculated $t_{1/2}$ from non linear regression realized using XLStats software; linear regression correlation coefficient, maximal time of exposure observed (linear uptake) and calculated sampling rates.

	Non linear regression		Linear regression		
	R^2	$t_{1/2}$ (day)	R^2	Linear uptake (day)	R_S (L/day)
4MBC	0.9928	330	0.9934	21	0.091
Ace	0.9957	315	0.9962	21	0.081
Ala	0.9975	267	0.9979	21	0.066
Atra	0.9944	61	0.9937	21	0.076
Carb	0.9972	4	0.9961	3	0.072
Diu	0.9979	193	0.9978	21	0.077
Ipr	0.9869	47	0.9846	21	0.007
Lin	0.9872	630	0.9982	14	0.052
Pro	0.9782	770	0.9983	14	0.045
MegA	0.9925	58	0.9915	21	0.114
P	0.9900	385	0.9904	21	0.062
T	0.9985	224	0.9988	21	0.109
3.4D	0.9989	198	0.9992	21	0.005
Carba	0.9988	41	0.9976	21	0.101
Diclof	0.9834	3	0.9976	3	0.107
BPA	0.9955	22	0.9943	21	0.104
E1	0.9760	20	0.9677	14	0.127
βE2	0.9838	18	0.9842	14	0.162
tOP	0.9882	14	0.9882	14	0.022
Ibu	0.9968	2	0.9870	3	0.079

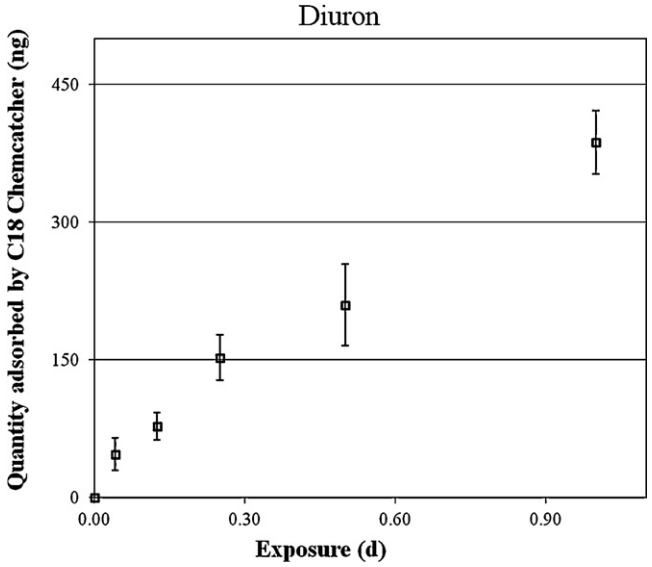

Fig. 4. Accumulation of diuron on the C18 Chemcatcher using a PES membrane for short periods of time (<3 days).

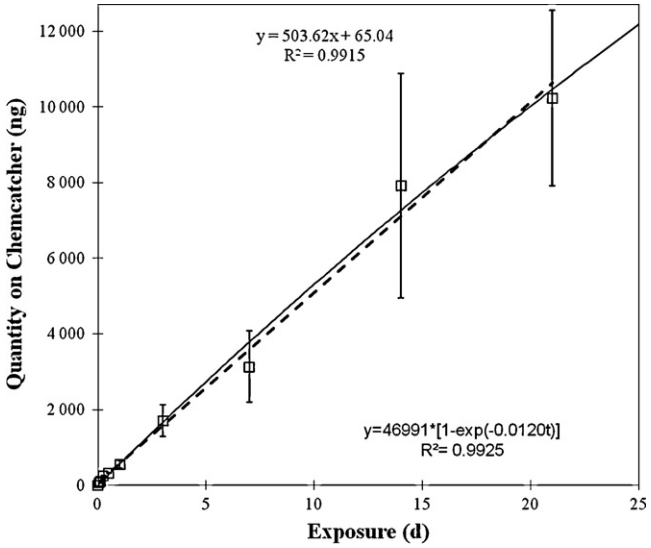

Fig. 5. Comparison of nonlinear and linear regressions for the accumulation of megestrol acetate on the polar C18 Chemcatcher.

by reducing the depth of the cavity containing the diffusion membrane and the receiving phase. Thus, the resistance to mass transfer in the water boundary layer has been modified, and the lag times may be reduced.

4.3. Calculated sampling rates

The uptake study allowed us to calculate sampling rates for the linear phase of all of the molecules accumulated on the C18

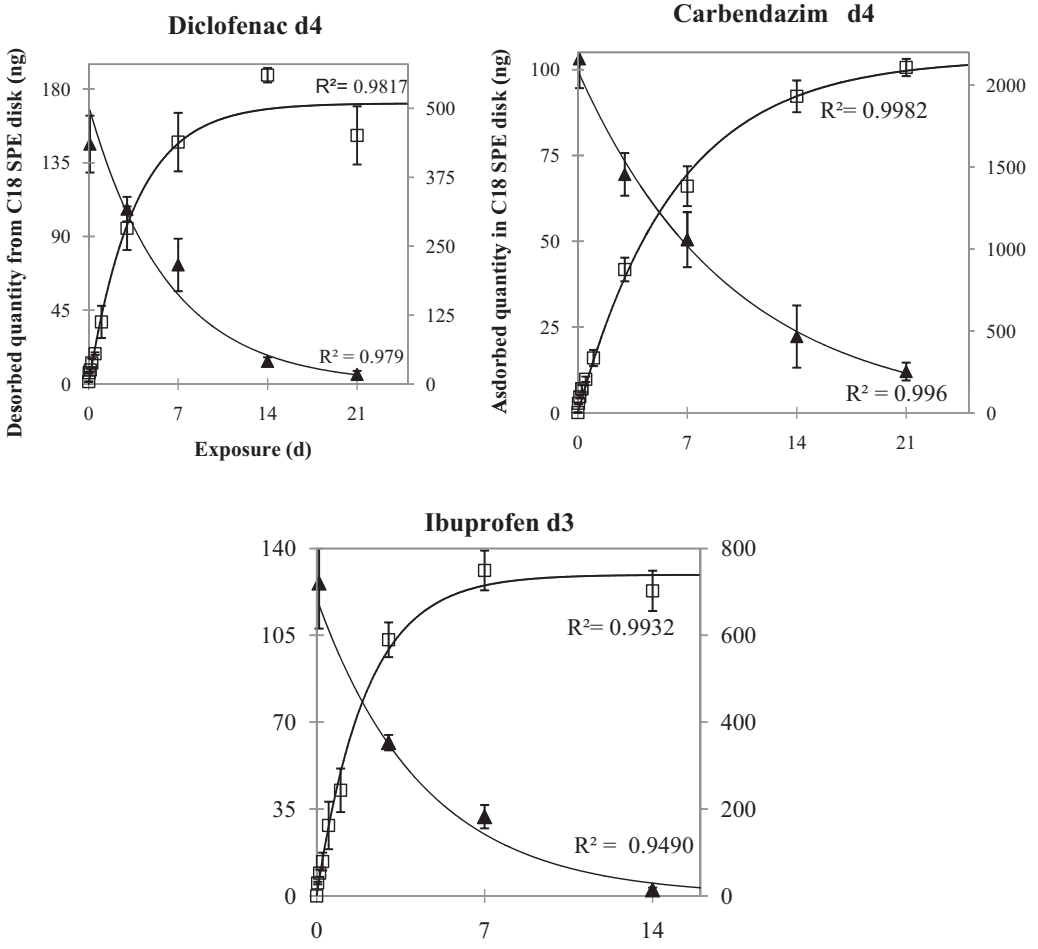

Fig. 6. Uptake (open squares) and desorption (full triangles) of three potential PRCs for the C18 Chemcatcher: deuterated diclofenac, carbendazim and ibuprofen. The solid line displays the correlation with the models.

Chemcatcher under the following calibration conditions: average water concentration 3 μg/L, $T = 21.2 \pm 0.1$ °C ($n = 13$), pH 8.1 ± 0.2 ($n = 13$), $\sigma = 393.5 \pm 4.9$ mS/cm ($n = 13$), DOC = 13.3 ± 2.2 mg/L and flow velocity measured at 10.3 ± 3.6 cm/s.

Using megestrol acetate as an example in Fig. 5, nonlinear regressions were plotted to confirm that they fit to the first-order accumulation kinetics and to determine the maximum exposure time for the linear uptake phase. Using a model consistent with the accumulation described in Eq. (1), the desorption constant (k_e) value was determined for each compound, and the equilibrium half-time ($t_{1/2} = \ln(2)/k_e$) was calculated. Linear regressions were then plotted to calculate the sampling rate R_S (Table 3), which is defined as the slope of the line divided by the average water concentration measured during the experiment.

The mass of sorbent (M_S in g) used in a C18 SPE disk is not precisely available in the literature or from the manufacturer; it has been estimated as approximately 90% of the total weight of the SPE disk [37]. Eq. (2′) is modified to express the mass of analyte (m_S measured in ng) as a function of the time: $m_S = R_S \times C_W \times t$. For the Chemcatcher, the sampling rate R_S (L/day) is calculated for the linear phase of accumulation using Eq. (4).

Expression of the sampling rate R_S used for the Chemcatcher:

$$R_S = \frac{m_S}{C_W t} \quad (4)$$

The $t_{1/2}$ value calculated from the nonlinear regression parameter k_e confirms the maximal time of exposure used for the linear regression to calculate the sampling rate of each molecule. For both nonlinear and linear regressions, good correlations were obtained.

The sampling rates calculated using Eq. (4) are consistent with the values observed in studies with similar exposure parameters for the PES membrane-covered polar Chemcatcher: with SDB-RPS disks [25] for atrazine (0.10 L/day) or diuron (0.08 L/day) or with SDB-XC disks [38] for acetochlor (0.35 L/day), alachlor (0.32 L/day) or linuron (0.12 L/day). Higher sampling rates were obtained for the Chemcatcher when diffusion membranes were not used for BPA (1.71 L/day) or tOP (2.78 L/day), but this configuration enabled linear accumulation for only 4 days [39]; this naked version of the Chemcatcher has been suggested for use when monitoring variations during short periods of time.

4.4. Release rates – potential PRCs for the C18 Chemcatcher

The desorption study undertaken with spiked samplers for 28 days in a continuous flow microcosm enabled us to look for potential PRCs on the C18 Chemcatcher.

Among the 20 available deuterated compounds of the selected molecules, only 3 showed good desorption after 14 days of exposure (80–100%): carbendazim-d4, diclofenac-d4 and ibuprofen-d3. Relative standard deviations ($n = 6$ or $n = 4$) were below 40% during the 14 days of exposure, which is consistent with the analytical method and the expected variations due to the spiking procedure of the Chemcatcher and the standard deviations obtained after the extraction step. The three molecules showed relatively good exponential correlations (triangles in Fig. 6), with R^2 values above 0.949 for 14 or 21 days of exposure, which correlates well with the theoretical equation (3). As observed by Greenwood et al. [37], atrazine-d5 did not desorb enough from pre-loaded C18 SPE disks to be considered a potential PRC for the C18 Chemcatcher.

As shown in Fig. 6, both the uptake and release of the 3 potential PRCs were consistent with first-order kinetics of accumulation (Eq. (1)) and desorption (Eq. (3)). Adsorption kinetics yielded an equilibrium half-time of approximately 2 or 3 days for the three molecules and a desorption half-time of approximately 3 days for ibuprofen or carbendazim and 4 days for diclofenac. Isotropic exchange is nearly verified, and first-order kinetics were observed for all of the 3 potential PRCs, whereas linear adsorption was compared to exponential desorption for the only potential PRC found on the polar Chemcatcher with a PES membrane-covered SDB-RPS Chemcatcher: diuron-d5 [25].

5. Conclusions

Integrative samplers are the most representative and cost-effective systems currently available to monitor pollutants in surface water over long periods of time. To adapt data obtained in laboratories during calibration to the real conditions during exposure in surface waters, these systems need a PRC approach. Currently, due to the difficulty of finding molecules that desorb from the SPE phases used, only one potential PRC has been reported on the C18 Chemcatcher and one on the SDB-RPS Chemcatcher [25]. This project enabled the evaluation of the uptake and release kinetics of 27 selected pollutants on the Chemcatcher using a well-defined and controlled exposure system and an optimized and validated multi-residue LC–MS/MS method. Isotropic exchange and first-order accumulation and desorption kinetics allowed the identification of 3 potential PRCs on the C18 Chemcatcher enabling the monitoring of 17 endocrine disruptor compounds and pharmaceuticals with linear accumulation phases up to 14 or 21 days. In future experiments, the calibrated samplers with potential PRCs will be exposed in real surface water to confirm laboratory results.

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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.chroma.2012.03.025.

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