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## Calibration of Chemcatcher® passive sampler for selected highly hydrophobic organic substances under fresh and sea water conditions†

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This study presents sampling rates ( $R_s$ ) of the nonpolar Chemcatcher® for selected polybrominated diphenylethers (PBDEs), polychlorinated biphenyls (PCBs) and organochlorine pesticides measured in two calibration experiments with fresh water and salt water (2.5% NaCl), respectively. The uptake experiments were performed with samplers on a carousel in a flow-through tank system at constant concentration of test substances and a temperature of 13 °C. It was found that the linear flow velocity at the sampler surface calculated based on the rotation speed of the carousel ( $0.4 \text{ m s}^{-1}$ ) disagreed with the actual measured velocity using a vane anemometer ( $0.11 \text{ m s}^{-1}$ ). The sampling rates  $R_s$  of the test compounds were in the range of  $0.15$  to  $0.89 \text{ L d}^{-1}$  and were slightly lower in salt water than in fresh water, showing the minor effect of the salt matrix on the uptake of highly hydrophobic organic compounds. Five performance reference compounds (PRC) were also tested during the tank experiments. A higher offload of PRCs was found in salt water (with elimination rates between  $0.034 \text{ d}^{-1}$  and  $0.051 \text{ d}^{-1}$ ) compared to fresh water (elimination rates between  $0.017 \text{ d}^{-1}$  and  $0.028 \text{ d}^{-1}$ ). Our study demonstrates the suitability of the Chemcatcher® device for time-integrated monitoring of highly hydrophobic micropollutants dissolved in fresh and salt water down to the lower ng-per-litre range.

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### Water impact

Water monitoring of priority organic pollutants as required *e.g.* under the European Water Framework Directive include polybrominated diphenylethers (PBDEs) and DDT and its metabolites. This is a challenging task because of their low concentration in the water phase. Passive samplers accumulate such aqueous micro-pollutants and can, after calibration, be used to determine time-weighted average water concentrations for periods of weeks to months. The paper describes calibration experiments with the non-polar Chemcatcher as passive sampler for selected PBDEs, DDT and its metabolites, and some polychlorinated biphenyls in order to determine the sampler uptake rates in fresh and salt water. The results are useful for monitoring tasks in different aqueous environments.

## 1. Introduction

### 1.1 General facts

Contaminants show great distribution variability in natural aqueous environments due to their diverse chemical characteristics, different input pathways or their continuous remobilization from sediments caused by anthropogenic activities. To ensure compliance with the European Water Framework

Directive (WFD),<sup>1</sup> knowledge of contaminant concentration is mandatory. This requires accurate monitoring efforts with sufficient coverage regarding time scale and a close-meshed monitoring network. The current monitoring approaches are, however, often limited to low frequency spot sampling, which provides only snapshot information about the current contamination status, in particular, when working in dynamic environments. One solution could be the use of time-integrated sampling approaches, namely passive sampling. In comparison to conventional spot sampling the application of passive samplers allows for the detection of very low analyte concentrations.<sup>2</sup> Moreover, the determination of time-weighted average concentration of pollutants makes passive sampling more representative than spot sampling strategies. In addition, passive sampling provides information about the bioavailability of target pollutants.<sup>3</sup> For these reasons, passive samplers are becoming increasingly important. In 2011 the European

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Commission approved a guidance document of the task group on chemical monitoring where passive sampling techniques were named as alternative monitoring tools under the WFD regulations.<sup>4</sup> In June 2011 an ISO standard<sup>5</sup> was published to give guidance for passive sampling in surface waters which can help to broaden the acceptance of passive sampling devices among water management authorities.

Many passive sampling systems have been developed for sampling organic and inorganic substances and some of them are commercially available. The most widely used and investigated passive sampling system is the semi-permeable membrane devices (SPMD)<sup>6,7</sup> for lipophilic substances, the diffusive gradients in thin films (DGT) for metal and metal species<sup>8</sup> and the polar organic chemical integrative sampler (POCIS) for polar organic substances.<sup>9</sup> Other passive sampling systems for collecting nonpolar contaminants were developed, such as the membrane-enclosed sorptive coating (MESCO),<sup>10,11</sup> low-density polyethylene membrane<sup>12</sup> or the Chemcatcher®.<sup>13</sup>

The aim of this study was to test experimentally the influence of dissolved salts on the uptake of nonpolar substances using the Chemcatcher.

The present paper shows the results of two different calibration experiments for the Chemcatcher® with a C<sub>18</sub> Empore™ disk as receiving phase and a low-density polyethylene membrane as diffusion-limiting barrier for nonpolar substances, including polybrominated diphenylethers (PBDEs), polychlorinated biphenyls (PCBs) and organochlorine pesticides. The calibration experiments were conducted in a laboratory flow-through system with a carousel made from polytetrafluoroethylene (PTFE), described previously by Vrana, *et al.*<sup>14</sup> The samplers were exposed for 14 days, in spiked fresh water and in 2.5% salt water simulating Northern Sea conditions. Moreover, the applicability of various performance reference compounds was tested.

## 2. Theory

The mass transfer of an analyte from water to the sampler includes diffusion and 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 a *n*-octanol-saturated C<sub>18</sub>Empore™ disk.<sup>15</sup> The accumulation of pollutants in the receiving phase of a passive sampler follows 1st-order kinetics:<sup>16</sup>

$$m_{s(t)} = m_0 + (c_w K_{sw} V_s - m_0) \times \left[ 1 - \exp\left(-\frac{k_{ov} A}{K_{sw} V_s} t\right) \right] \quad (1)$$

where  $m_{s(t)}$  [kg] is the mass of substance in the receiving phase,  $m_0$  [kg] the substance mass in the receiving phase at the start of exposure,  $c_w$  [kg m<sup>-3</sup>] the water concentration during the exposure time,  $K_{sw}$  [L kg<sup>-1</sup>] the receiving phase-water distribution coefficient,  $V_s$  [m<sup>3</sup>] the volume of the receiving phase,  $k_{ov}$  [m s<sup>-1</sup>] the overall mass transfer coefficient,  $A$  [m<sup>2</sup>] the membrane surface area, and  $t$  [s] the exposure time.

The coefficient of the exponential function can be combined to the constant  $k_{ex}$  [s<sup>-1</sup>], which is defined as the overall exchange rate. Its relation to the so-called sampling rate  $R_s$  [m<sup>3</sup> s<sup>-1</sup>], which represents formally an equivalent volume of water extracted by the sampler per unit of time is given in eqn (2).

$$k_{ex} = \frac{k_{ov} A}{K_{sw} V_s} = \frac{R_s}{K_{sw} V_s} \quad (2)$$

The accumulation of substances can be approximately regarded as linear until the amount of analyte reaches half of its equilibrium level:<sup>17</sup>

$$t_{\frac{1}{2}} = \frac{\ln 2}{k_{ex}} \quad (3)$$

With substances similar to the target analytes such as deuterated or isotope-labelled substances, the overall exchange rate  $k_{ex}$  can be estimated. By using such performance reference compounds (PRCs), the influence of biofouling, temperature, water flow and other environmental parameters can be approximately taken into account and a field sampling rate  $R_{s-f}$  can be calculated.

The experimental PRC exchange rate can be determined by eqn (4):

$$m_{PRC}(t) = m_{0PRC} \times \exp(-k_{ex} t) \quad (4)$$

where  $m_{PRC}$  is the mass of PRC in the receiving phase [ng] and  $m_{0PRC}$  the amount of PRC added to the receiving phase before exposure (this amount is known).

With the help of the experimental exchange rate, the field sampling rate  $R_{s-f}$  can be adjusted, when the PRC has similar physicochemical properties as the monitored compound:<sup>16</sup>

$$R_{s-f} = R_{s-CAL} \frac{k_{ex-f}}{k_{ex-CAL}}, \quad (5)$$

where  $k_{ex-CAL}$  is the experimental exchange rate of a PRC, which is determined in the laboratory,  $k_{ex-f}$  is the exchange rate of a PRC observed under field conditions and  $R_{s-CAL}$  is the sampling rate determined in the laboratory using eqn (4).

## 3. Material and methods

### 3.1. Physicochemical properties of substances

The WFD include PBDE 47, 100 and total DDT (sum of *p,p'*-DDT; *o,p'*-DDT; *p,p'*-DDD and *p,p'*-DDE) as priority substances. The European Union defines environmental quality standards in water for these compounds in a recent directive.<sup>18</sup> Some important physicochemical properties of all test substances are summarized in Table 1.

### 3.2 Material and chemicals

The Chemcatcher® body parts were provided by the University of Portsmouth, UK. C<sub>18</sub> Empore® disks (47 mm diameter)

**Table 1** Physicochemical properties of test substances

Substance	Melting point[°C]	Water solubility [mg L <sup>-1</sup> ]	log <i>K</i> <sub>ow</sub>
PCB 28	57.5	0.012 (ref. 26)	5.87 (ref. 19)
PCB 52	87	0.011 (ref. 26)	5.97 (ref. 19)
PCB 101	77	0.07 (ref. 26)	6.38 (ref. 19)
PCB 153	103	0.0009 (ref. 26)	6.58 (ref. 19)
PBDE 47	83.8	0.015 (ref. 27)	6.81 ± 0.08 (ref. 20) 6.77–7.49 (ref. 21 and 22)
PBDE 100	102	0.04 (ref. 27)	7.24 ± 0.16 (ref. 20) 7.66–8.38 (ref. 21 and 22)
<i>p,p'</i> -DDT	108.5	0.001–0.14 (ref. 26)	6.19 (ref. 23)
<i>o,p'</i> -DDT	74	0.026–0.085 (ref. 26)	5.53 (ref. 24) 6.53 (ref. 25)
<i>p,p'</i> -DDE	89	0.001–0.12 (ref. 26)	5.69 (ref. 23)
<i>o,p'</i> -DDE	76.5	0.14 (ref. 26)	5.43 (ref. 24) 6.47 (ref. 25)
<i>p,p'</i> -DDD	109.5	0.0002–0.0009 (ref. 26)	6.16 (ref. 19)
<i>o,p'</i> -DDD	77	0.1 (ref. 26)	4.87 (ref. 24) 6.42 (ref. 25)

were purchased from Varian Inc., Walton-on-Thames, UK. LDPE membrane material (40 µm thick) was obtained from Fisher Scientific, Loughborough, UK. Polydimethylsiloxane (PDMS)-Twister™ (10 mm long, coated with PDMS, 0.5 mm film thickness) were provided by Gerstel, Mülheim, Germany. The solvents (HPLC grade quality or higher) dichloromethane, ethylacetate, isopropyl alcohol, trimethylpentane, methanol and *n*-octanol were purchased from Merck, Darmstadt, Germany. All PCB standards were obtained from Dr. Ehrenstorfer, Augsburg, Germany. PBDE standards were obtained from Chiron AS, Trondheim, Norway. DDT and its metabolites were purchased from Riedel-de Haën®, Seelze, Germany. All labeled standards were obtained from Cambridge Isotope Laboratories (Andover, MA, USA). Salt for the calibration experiment was purchased in the form of table salt (99.8% NaCl, no additives) from the European Salt Company (Hannover, Germany).

### 3.3 Evaluation of the analyte recovery

To determine the loss of substances during the extraction method, described in 3.4, a recovery experiment was conducted. 400 µL of a standard solution (1 ng µL<sup>-1</sup>) including each test compound was added to each of six Empore disks. After air drying, 1 mL methanol in acetone (45% v/v) was carefully dropped on each disk, following the extraction method described in section 3.4. Finally the extracts were measured together with external calibration standards using GC-MS.

### 3.4 Preparation and processing of the sampler

The Chemcatcher® device was used with the reusable body made from polytetrafluoroethylene (PTFE) as described by Kingston *et al.*<sup>13</sup> The non-polar Chemcatcher type imbeds a C<sub>18</sub>-Empore disk as the receiving phase which is covered by

low-density polyethylene (LDPE) as the diffusion-limiting membrane. Before exposure, the receiving phases were conditioned by soaking overnight in methanol and after passing 50 mL of methanol and 150 mL tap-water through the disk. PRCs were loaded on the Empore disk by filtration of an aqueous solution of 250 mL containing 2 µg of PCB 202, PCB 54, D<sub>10</sub>-Benz(a)anthracene, <sup>13</sup>C<sub>6</sub>-HCB and D<sub>10</sub>-Fluoranthene.<sup>28</sup> The diffusion membrane soaked overnight in *n*-hexane. Before assembly the Empore Disk was applied on the lower part of the Chemcatcher housing and 1 mL of *n*-octanol in methanol (45% v/v) was added between the receiving phase and the diffusion-limiting membrane, to minimize the initial resistance between this layers for ensuring higher sampling rates.<sup>15</sup> After exposure the Chemcatcher® body was rinsed with tap-water and the body carefully disassembled. The C<sub>18</sub> disk was taken out of the PTFE-body, dried under vacuum and extracted with 5 mL of acetone in an ultrasonic bath followed by 5 mL of mixture of ethylacetate and isooctane (1/1). The combined extract was passed over a NaSO<sub>4</sub> cartridge to remove water traces. Finally the extract was evaporated under nitrogen. Approximately 450 µL of the extract remained as a result of the low volatility of *n*-octanol. Afterwards the extract was transferred to a 2 mL vial and 50 µL of 10 ng µL<sup>-1</sup> internal standard D10-anthracene was added to the sample.

### 3.5 Extraction of test-substances from water

As described by De la Cal *et al.*<sup>29</sup> there is a problem associated with the extraction of PBDEs and DDX from water using solid phase extraction (SPE) with C18 cartridges. For this reason it was decided to use the Gerstel-PDMS-Twister™ for extracting the analytes from water samples.

The Twister™ provides evidence of accumulation of trace organic substances in aqueous media by employing the concept of stir bar sorptive extraction.<sup>30</sup> The Twister absorbs the analytes according to their partition coefficient between aqueous sample and Twister receiving phase. The water concentration during the flow-through exposure experiments was set to 25 ng L<sup>-1</sup> by continuous injection of appropriate volume of spiking solution. During the experiments samples of 200 mL of the effluent from the tank were collected daily and were stirred after adding 40 mL methanol at 1200 U min<sup>-1</sup> for 16 h with a PDMS-Twister™. Addition of methanol increases the extraction recovery, as a result of the decreasing absorption of the analytes on the glass ware.<sup>31</sup> It is known, that the presence of methanol influences the distribution coefficient between the aqueous and extraction phase,<sup>32</sup> demanding an external calibration using the same extractions method to graduate the effect of methanol. After extraction the Twister™ was measured with thermodesorption-GC-MS together with an external calibration. The external calibration was accomplished first with Twisters in spiked tap water (+20% methanol) and second in spiked tap water with 2.5% salt content (+20% methanol) over a concentration range of 1.6 ng L<sup>-1</sup> to 35 ng L<sup>-1</sup>. Each

water sample was taken and extracted in duplicate and every calibration level in triplicate. The analytical performances of the Twister were evaluated for both matrices (tap water and 25 PSU NaCl). The LOD and LOQ are shown in Table S1.†

### 3.6 Experimental setup of Chemcatcher calibration

Two 14-day calibration experiments were included in the study. Each experiment employed a constant concentration flow-through exposure system. The experimental setup is shown in Fig. 1. Using a flow-through exposure system the passive samplers could be calibrated under controlled condition of temperature, water flow, salinity and analyte concentration. The experimental setup consisted of a 20 L glass tank with an overflow to waste. The tank contained a Teflon carousel, described by Vrana *et al.*<sup>14</sup> with places for 14 samplers and twist controlled by a RZA 2051 electronic stirrer (Heidolph Instruments GmbH & Co.KG, Schwabach, Germany). The water was stirred at 40 rpm. The water turbulences were measured by a MiniAir20 (Schiltknecht Messtechnik AG, Gossau, Schweiz). To obtain a constant analyte concentration in the exposure system test analytes, dissolved in methanol, were pumped by a micro pump (ProMinent®, Heidelberg, Germany). The fresh water was pumped by ProMinert Gamma 5 with 5 L h<sup>-1</sup> in the tank. For generating salt water (2.5%/25 PSU) NaCl content) two peristaltic pumps were used, one for pumping tap water with 4 L h<sup>-1</sup> and the second peristaltic pump for adding with 1 L h<sup>-1</sup> high concentrated salt solution (12.5% NaCl). The experiments were done in a chromatographic refrigerator TC 105-1 from Tritec

(Hannover/Germany) at a constant temperature of 13 °C (ESI† Fig. S1). The content of the salinity was measured with a density meter (Anton Paar DMA48, Graz, Austria). Before the start of the calibration, the experimental setup was running 48 h without sampler to stabilize the concentration of the test substances and to equilibrate the system. At the beginning of each experiment, 12 Chemcatcher®, prepared and spiked with PRC, were placed in the flow-through system on the carousel. After defined time periods two samplers were removed. Additionally three Chemcatcher controls were analyzed to determine initial contamination from assembly processes and background contamination during sampler handling as well as the initial PRC concentration before exposure.

### 3.7 Instrumental analysis

The Chemcatcher® samples were measured by using an Agilent 6890N gas chromatograph, Agilent Technologies, Waldbronn, Germany, with an HP-5MS-ultraInert column (15 m × 0, 25 mm × 0, 25 mm) associated with an Agilent 5975C mass spectrometer. 1 µL of sample was injected with pulsed splitless mode. The oven program started at 140 °C for 2 min, heating 2 °C per minute to 170 °C, hold 2 minute, then heating 15 °C per minute to end at 320 °C.

The Twister™ were measured directly after thermodesorption by GC-MS using a Gerstel Twister™ Desorption Unit linked to an Agilent 6890N gas chromatograph with a HP-5MS-ultraInert column (15 m × 0, 25 mm × 0, 25 mm) with a oven program, beginning at 60 °C for 2 minute, heating 10 °C to 310 °C, held for 5 min. The gas chromatograph was coupled with an Agilent 5973 mass spectrometer.

### 3.8 Data processing

The accurate *n*-octanol extract volume was calculated from the external calibration with the standard component D<sub>10</sub>-anthracene and its known internal standard concentration (added to the extract before volume reduction). The mass of the individual test compounds extracted from the Empore disk were calculated using eqn (6), where  $c_{\text{sample}}$  is the analyzed specific analyte sample concentration,  $V_{\text{sample}}$  is the accurate sample volume and  $f_e$  specific analyte recovery (determined in 4.1). The accumulated masses of test substances on the receiving phases were plotted by linear regression model using eqn (7):<sup>33</sup>

$$m_s(t) = \frac{c_{\text{Sample}} \times V_{\text{Sample}}}{f_e} \quad (6)$$

$$m_s(t) = m_o + c_w R_s t \quad (7)$$

with  $c_w$  as average of the water concentration in the exposure system determined by Twister™ measurements. The standard derivation of the sampling rate was calculated by the law of error propagation (eqn (8)), where  $b$  is the value of the

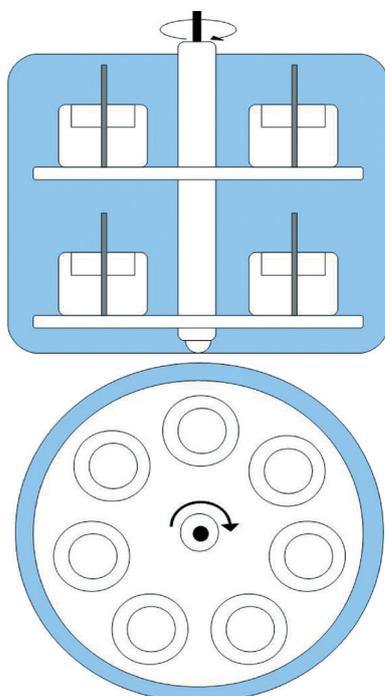


Fig. 1 Exposure tank and carousel device used in calibration experiments.

slope of the linear regression curve,  $s_b$  is the standard derivation of the slope and  $s_{c_w}$  the standard derivation of the tank water concentration of the analytes.

$$S_{R_s} = R_s \sqrt{\frac{S_{c_w}^2}{C_w^2} + \frac{S_b^2}{b^2}} \quad (8)$$

## 4. Results and discussion

### 4.1 Analyte recovery

A recovery experiment was conducted to determine the loss of selected compounds during the extraction method. For this propose the Empore disk was spiked with 400  $\mu\text{L}$  of a standard solution (1 ng  $\mu\text{L}^{-1}$  of each test substance). Afterwards it was handled as a sample described above. The analyte recovery of spiked  $C_{18}$ -Empore disk (see 3.5) was between 34.55% for  $p,p'$ -DDT to 137% for PBDE 100. As a result of the low recovery of  $p,p'$ -DDT, this analyte was removed from all following considerations. The summary of all measured analyte recovery is shown in Table 2. The value of extraction recovery was used later to calculate the correct mass of the test substances on the Empore Disk in the calibration experiments using eqn (6).

### 4.2 Concentration of test substances in water during the experiments

The analyte concentration resided in the range from 9.73 ng  $\text{L}^{-1}$  to 18.38 ng  $\text{L}^{-1}$  during the calibration experiment with tap water and between 13.14 ng  $\text{L}^{-1}$  and 18.38 ng  $\text{L}^{-1}$  for the salt water experiment. The respective coefficient of variation was between 1.90 ng  $\text{L}^{-1}$  and 5.00 ng  $\text{L}^{-1}$  and between 1.13 and 5.65, respectively. The highest variation was reported for PBDE 47 and PBDE 100 in the tap water calibration experiment and for PBDE 100 and PCB 153 in the 2.5% NaCl content calibration experiment. Both experiments indicated less analyte water concentration than expected. The lower analyte water concentration is likely the result of reduced pumped volume of the chemical pump or increased pumped volume of the water pump. Overall the analyte water concentration was less for all test substances than

expected, but quite stable on this level during the individual calibration experiments.

### 4.3 Measurement of flow velocity

In previous papers,<sup>14,33</sup> the linear velocity in the calibration tank system was calculated with eqn (9), where  $r$  is the radius of the circular path of the passive sampler on the carousel and  $f$  the rotation speed of the carousel

$$\omega = 2\pi r f \quad (9)$$

By using eqn (9) a linear flow velocity of 0.4 m  $\text{s}^{-1}$  for the passive samplers inside the flow-through system was estimated. But it could be seen that the water moved partly with the carousel in a round exposure tank system and as a consequence the velocity was expected to differ from the calculated value. Hence the flow velocity was measured with a MiniAir20 system directly. The MiniAir20 is a vane anemometer and can measure flow velocity of gaseous and liquid media. For a precise determination of the flow velocity, the sensor was held diagonally to the direction of rotation. This indicated that the velocity of the Chemcatcher was lower than the linear velocity measured with the sensor, as a result of the round tank design. The effective velocity was calculated by subtracting the calculated value (eqn (9)) from the measured velocity. The effective velocity results are shown in Fig. 2. The average of the effective velocity was

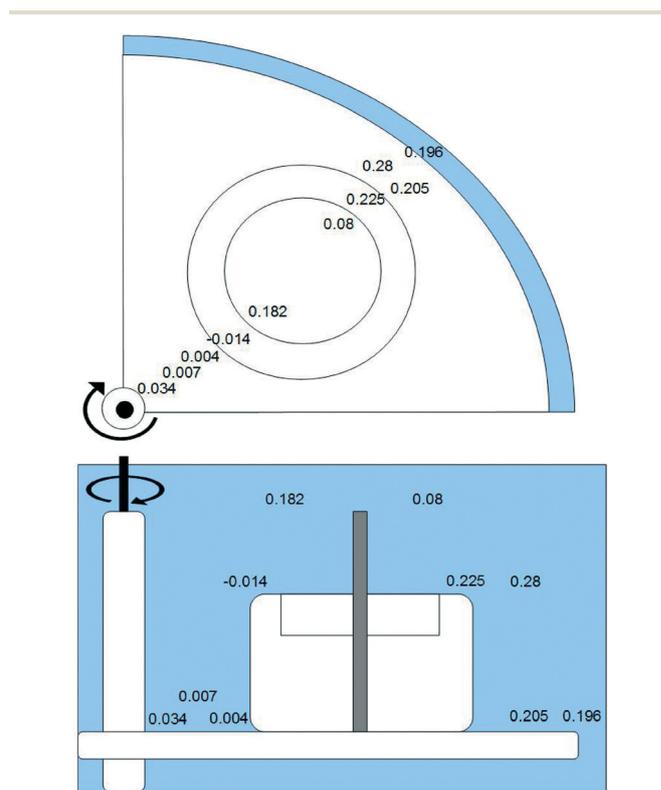


Fig. 2 Effective velocity [ $\text{m s}^{-1}$ ] measured with MiniAir20 in flow-through exposure tank system including 14 Chemcatcher.

Table 2 Analyte recovery of spiked  $C_{18}$ Empore disk with standard deviation ( $n = 6$ )

Substance	Recovery in %
PBDE 47	121.64 $\pm$ 17.76
PBDE 100	136.59 $\pm$ 18.79
PCB 28	60.76 $\pm$ 9.90
PCB 52	66.03 $\pm$ 10.44
PCB 101	72.76 $\pm$ 10.62
PCB 153	67.18 $\pm$ 10.62
$p,p'$ -DDT	34.55 $\pm$ 4.34
$o,p'$ -DDE	52.21 $\pm$ 9.63
$p,p'$ -DDE	50.99 $\pm$ 8.66
$o,p'$ -DDD	69.12 $\pm$ 11.62

$0.11 \text{ m s}^{-1}$  and thus much lower than the velocity estimated ( $0.4 \text{ m s}^{-1}$ ).

#### 4.4 Uptake kinetics

The suitability of the nonpolar version of the Chemcatcher® was tested in calibration experiments in fresh- and salt water. Both experiments were carried out at constant temperature at  $13 \text{ }^\circ\text{C}$  and a mean linear flow velocity of  $0.1 \text{ m s}^{-1}$  (as described above). The salinity of the water in the second exposure experiment ranged from 21.29 to 28.43 PSU NaCl. The initial start concentration of the test substances in the three Chemcatcher control samples were below limit of quantification. The uptake curves of test substances are presented in Fig. 3 (PCBs), Fig. 4 (PBDEs) and Fig. 5 (DDX).

The sampling rate  $R_s$  was calculated with eqn (7) and the standard derivation of the sampling rate with eqn (8), summarized in Table 3:

The sampling rate  $R_s$  varies between  $0.29 \text{ L d}^{-1}$  for PBDE 100 and  $0.89 \text{ L d}^{-1}$  for PCB 28 and PCB 101 in fresh water. The  $R_s$  value in salt water varies between  $0.15 \text{ L d}^{-1}$  for PBDE 100 and  $0.78 \text{ L d}^{-1}$  for PCB 28.

The comparison of both experiments shows only a small influence of salinity on the sampling rates for the highly hydrophobic organic test substances. Recently, Lohmann *et al.*<sup>34</sup> have estimated a similar trend with LDPE passive samplers by using the Setschenow equation. Booij *et al.*<sup>35</sup> predicted that the sampling rate is expected to decrease with increasing molecular mass. The experimental data in this work (highest sampling rate for the lowest molecular

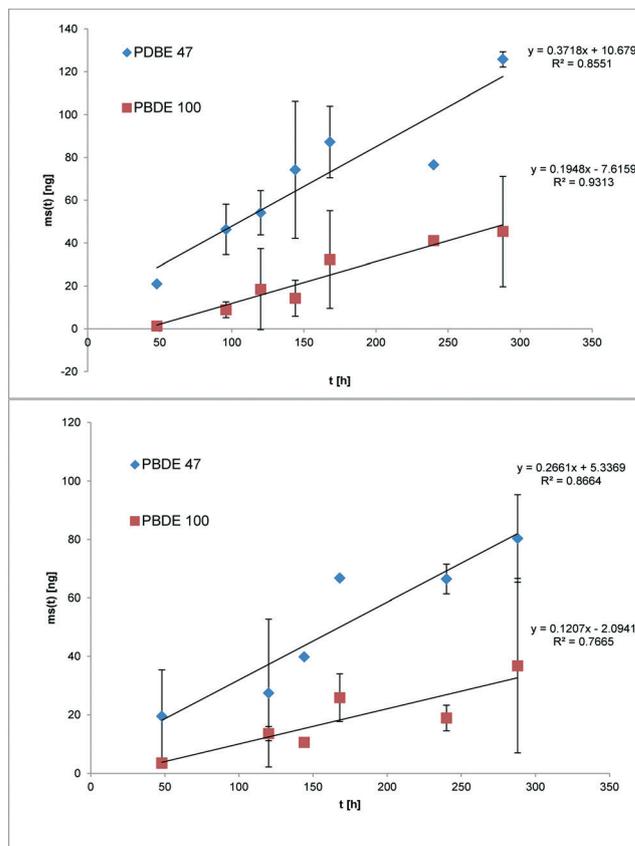


Fig. 4 Uptake curve of selected polybrominated diphenylether in fresh (up) and seawater (down) by effective velocity of  $0.1 \text{ m s}^{-1}$  and  $13 \text{ }^\circ\text{C}$ .

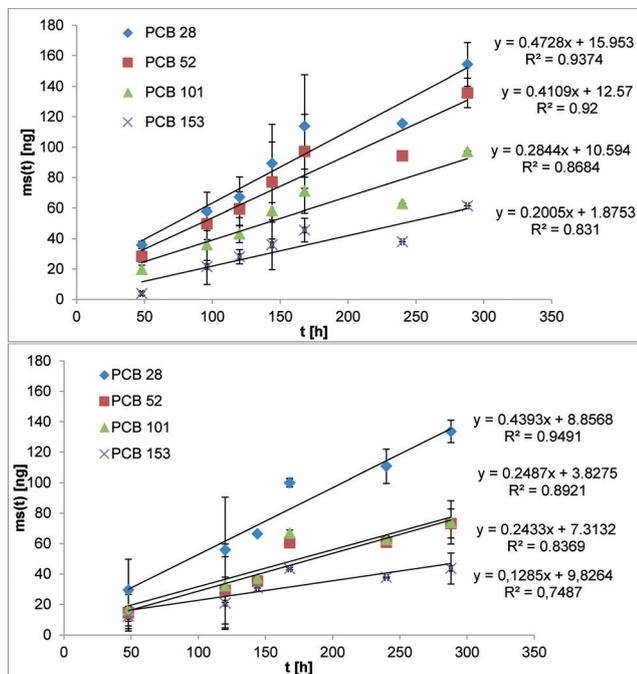


Fig. 3 Uptake curve of selected polychlorinated biphenyls in fresh (up) and seawater (down) by effective velocity of  $0.1 \text{ m s}^{-1}$  and  $13 \text{ }^\circ\text{C}$ .

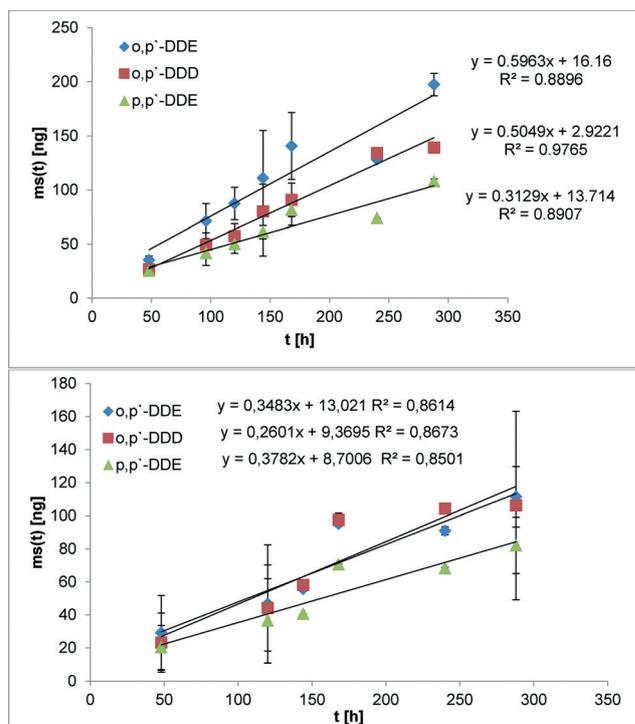


Fig. 5 Uptake curve of organochlorine pesticides in fresh (up) and seawater (down) by effective velocity of  $0.1 \text{ m s}^{-1}$  and  $13 \text{ }^\circ\text{C}$ .

**Table 3** Uptake rates  $R_s$  [ $L d^{-1}$ ] estimated in this study,  $c_w$  measured during the experiments and value of slopes  $b$  and  $p$ -values of the linear regression curves of the test substances (the standard deviations are given in the respective  $\pm$  columns)

Substance	Molecular weight $g mol^{-1}$	$\log K_{ow}$	$R_s$ [ $L d^{-1}$ ]	$c_w$ [ $ng L^{-1}$ ]	$b$ [ $ng h^{-1}$ ]	$p$ -value
Tap water 14 days calibration experiment						
PCB 28	257.54	5.87	$0.89 \pm 0.18$	$12.94 \pm 2.09$	$0.48 \pm 0.06$	$3.40 \times 10^{-04}$
PCB 52	291.99	5.97	$0.76 \pm 0.14$	$13.32 \pm 1.90$	$0.42 \pm 0.05$	$6.34 \times 10^{-04}$
<i>o,p'</i> -DDE	318.03	5.43	$0.81 \pm 0.18$	$18.38 \pm 3.40$	$0.62 \pm 0.08$	$1.43 \times 10^{-03}$
<i>p,p'</i> -DDE	318.03	5.69	$0.57 \pm 0.15$	$12.70 \pm 2.59$	$0.30 \pm 0.05$	$1.40 \times 10^{-03}$
<i>o,p'</i> -DDD	320.04	6.42	$0.65 \pm 0.15$	$18.38 \pm 3.40$	$0.50 \pm 0.07$	$2.88 \times 10^{-05}$
PCB 101	326.43	6.38	$0.89 \pm 0.21$	$13.21 \pm 2.62$	$0.29 \pm 0.04$	$2.24 \times 10^{-03}$
PCB 153	360.88	6.58	$0.76 \pm 0.41$	$9.84 \pm 5.00$	$0.20 \pm 0.04$	$4.25 \times 10^{-03}$
PDBE 47	485.79	6.81	$0.58 \pm 0.15$	$15.90 \pm 3.25$	$0.39 \pm 0.06$	$2.87 \times 10^{-03}$
PBDE 100	564.68	7.24	$0.29 \pm 0.10$	$15.58 \pm 3.97$	$0.19 \pm 0.04$	$4.31 \times 10^{-04}$
25 PSU water 14 days calibration experiment						
PCB 28	257.54	5.87	$0.78 \pm 0.17$	$13.14 \pm 1.70$	$0.43 \pm 0.07$	$9.88 \times 10^{-04}$
PCB 52	291.99	5.97	$0.41 \pm 0.12$	$13.50 \pm 1.75$	$0.23 \pm 0.06$	$4.53 \times 10^{-03}$
<i>o,p'</i> -DDE	318.03	5.43	$0.57 \pm 0.17$	$13.59 \pm 1.13$	$0.32 \pm 0.09$	$7.57 \times 10^{-03}$
<i>p,p'</i> -DDE	318.03	5.69	$0.40 \pm 0.13$	$14.48 \pm 2.61$	$0.24 \pm 0.07$	$6.92 \times 10^{-03}$
<i>o,p'</i> -DDD	320.04	6.42	$0.44 \pm 0.14$	$19.49 \pm 2.24$	$0.35 \pm 0.11$	$8.89 \times 10^{-03}$
PCB 101	326.43	6.38	$0.39 \pm 0.13$	$13.74 \pm 2.04$	$0.23 \pm 0.07$	$1.06 \times 10^{-02}$
PCB 153	360.88	6.58	$0.19 \pm 0.08$	$14.93 \pm 3.33$	$0.12 \pm 0.04$	$2.60 \times 10^{-02}$
PDBE 47	485.79	6.81	$0.35 \pm 0.10$	$17.02 \pm 1.58$	$0.25 \pm 0.07$	$7.02 \times 10^{-03}$
PBDE 100	564.68	7.24	$0.15 \pm 0.06$	$17.39 \pm 4.14$	$0.11 \pm 0.04$	$2.23 \times 10^{-02}$

mass and *vice versa*) are in close agreement with this theoretical model.

The obtained uptake rates for several test substances can be compared with results reported by De la Cal *et al.*<sup>29</sup> In the present work much higher sampling rates for these substances (Table 4) were found. This may result from a different experimental setup used by De la Cal *et al.*<sup>29</sup> where no carousel device was used to ensure similar hydrodynamic conditions for all Chemcatchers. They placed the Chemcatchers at the bottom of the exposure tank and used a stirrer to mix the solution above. Furthermore, problems arose as a result of the extraction of the water from the tank because of the high uncertainty and the low recovery of the test substances, which influence the value of the sampling rate.

Some Chemcatcher sampling rates from our fresh water experiment can be compared with rates reported for the semipermeable membrane device (SPMD) Table 5 shows these data, for comparison normalized to  $1 cm^2$  for both sampler types. This was necessary due to the very different surface areas of SPMD ( $460 cm^2$ ) and Chemcatcher ( $17 cm^2$ ).<sup>35</sup> The uptake of highly hydrophobic substances is

flow-dependent, *i.e.* increases with water turbulences. As expected, the uptake rates in this study are higher than  $R_s$  values for the SPMD at  $0.004 cm s^{-1}$  but lower than  $R_s$  for SPMD at  $90 cm s^{-1}$ .

#### 4.5 Offload kinetics

The PRC concept presents a possibility to adjust the lab-derived uptake rates for the effects of biofouling, temperature or hydrodynamic conditions during field exposure.<sup>38</sup> Five compounds were tested in the present study as possible PRCs for highly hydrophobic organic compounds: PCB 202, PCB 54,  $D_{10}$ -Benz(a)anthracene,  $^{13}C_6$ -HCB and  $D_{10}$ -Fluoranthene.  $2 \mu g$  of each PRC were added to the receiving phase before exposure. The offload of the PRCs were observed during the 14 days experiments. The characteristic offload curves are presented in supplementary data (Fig. S2 and S3<sup>†</sup>). The offload rates were obtained by nonlinear regression analysis using eqn (4) and were between  $0.017 d^{-1}$  to  $0.027 d^{-1}$  in fresh water and  $0.034 d^{-1}$  to  $0.051 d^{-1}$  in 25 PSU NaCl water (see Table 6). In the presence of NaCl the elimination constant is higher than in fresh water. However, due to the high variation of the mass of PRC remaining in the Empore disk in fresh water, these elimination rates are relatively uncertain. These higher uncertainties may result from the fact that the PRCs were not loaded homogeneously to the receiving phases of Chemcatchers under investigation. Another explanation was given by Huckins *et al.*<sup>39</sup> who found out that the detecting of the elimination of PRCs with  $\log K_{ow}$  values higher than  $>5.5$  from SPMDs could be problematic unless they were deployed in warm and highly turbulent environment.

The PRCs values determined in this laboratory study can be used together with offload rates of PRCs measured during

**Table 4** Comparison of experimental and literature  $R_s$  for nonpolar Chemcatcher® for PBDEs and DDT and its metabolites

Substance	$R_s$ experimental <sup>a</sup> [ $L d^{-1}$ ]	$R_s$ literature <sup>b</sup> [ $L d^{-1}$ ]
<i>o,p'</i> -DDE	$0.81 \pm 0.18$	0.002
<i>p,p'</i> -DDE	$0.57 \pm 0.15$	0.001
<i>o,p'</i> -DDD	$0.65 \pm 0.15$	0.003
PBDE 47	$0.58 \pm 0.15$	0.32

<sup>a</sup> Determined by  $13 ^\circ C$ .  $0.1 m s^{-1}$ . <sup>b</sup> Determined by  $11 ^\circ C$ . 20 rpm (no carousel device).<sup>29</sup>

**Table 5** Surface area normalized sampling rates ( $R_s$  [L d<sup>-1</sup>] per 1 cm<sup>2</sup>) of test substances determined with the Chemcatcher (present study) and the SPMD (literature data)

Compound	$R_s$ [L d <sup>-1</sup> ] per 1 cm <sup>2</sup>			
	Chemcatcher (present study)	SPMD <sup>35</sup>	SPMD <sup>36</sup>	SPMD <sup>37</sup>
	13 °C. 10 cm s <sup>-1</sup>	13 °C. 90 cm s <sup>-1</sup>	12 °C. 0.004 cm s <sup>-1</sup>	10 °C. 0.004 cm s <sup>-1</sup>
PCB 28	0.052		0.019	
PCB 52	0.045	0.254	0.014	
PCB 101	0.052		0.014	
PCB 153	0.045	0.212	0.008	
<i>o,p'</i> -DDE	0.048			0.005
<i>p,p'</i> -DDE	0.034			0.006
<i>o,p'</i> -DDD	0.038			0.005

**Table 6** Elimination constants of studied PRCs in tap water and 2.5% salt water

PRC	$k_{ex}$ fresh water [d <sup>-1</sup> ]	$k_{ex}$ salt water [d <sup>-1</sup> ]
D <sub>10</sub> -Fluoranthene	0.024	0.051
<sup>13</sup> C <sub>6</sub> -HCB	0.022	0.042
D <sub>10</sub> -Benz(a)anthracene	0.017	0.035
PCB 202	0.024	0.034
PCB 54	0.027	0.034

future field campaigns to obtain more realistic uptake rates for the target substances with the Chemcatcher by calculating field sampling rates  $R_{s-f}$  according to eqn (5).

## 5. Conclusion

This study demonstrates again the suitability of the nonpolar Chemcatcher® device for time-integrated monitoring of highly hydrophobic organic substances in different aqueous environments. Further laboratory studies and especially field campaigns are necessary to investigate more detailed the effect of dissolved salt(s) in the water matrix on both, the uptake of target analytes in the sampler and the elimination of preloaded performance reference compounds from the device. As the refined characterization of the water flow (pattern) along the Chemcatcher surface showed, it is very important to consider the design of the exposure tank used in laboratory studies. The authors used, for example, in subsequent studies a stainless steel tank with a square cross section instead of a round glass cylinder because this modification can prevent the dragging of the water phase by the rotating carousel (at least to a large extent). Also the exposure of inexpensive passive flow monitors (based on the determination of mass loss from a cast of calcium sulfate) alongside the Chemcatcher devices in tank experiments and field trials (as successfully demonstrated by O'Brien *et al.*<sup>40</sup>) can help to consider the influence of the hydrodynamic and thus to reduce the uncertainty of sampling rates and of final TWA concentrations. This approach we prefer in our ongoing application of the nonpolar Chemcatcher for time-integrated

monitoring of organic micropollutants in German coastal waters and selected rivers.

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