Short Communication

A case of anisotropic exchange of non-polar chemicals with absorption-based passive samplers in water

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Highlights

• Heavy fouling with SPM affects dissipation of PRCs from passive samplers exposed in water.
• An example of anisotropic exchange of chemicals with absorption-based passive samplers.
• Anisotropic exchange results in a bias of a factor of 3–4 in estimated contaminant concentrations in water.

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Abstract

Passive sampling is a powerful technique for the sampling hydrophobic organic contaminants present at trace level in water. A robust application of performance reference compounds (PRCs) for the estimation of in situ sampling rates, requires that dissipation of PRC and uptake of target compounds follow the same processes, i.e. the existence of isotropic exchange between the sampler and water. We report circumstantial evidence that in the presence of heavy fouling of samplers by suspended particulate matter (SPM) when deployed in a freshwater environment, SPM deposited on the surface of the sampler enhances the release of PRCs and reduces the uptake of target compounds. In this case, anisotropy of exchange resulted in on average a factor of 3.9 difference in estimate freely dissolved concentration in water.

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1. Introduction

Passive sampling is a technique that is increasingly being used for the monitoring of trace contaminants levels in water because it enables us to obtain time-integrated data, information on contaminant speciation and ultra-low limits of detection (Booij et al., 2015; Harman et al., 2012; Miège et al., 2015; Lohmann et al., 2017). For absorption-based passive sampling devices, performance reference compounds (PRCs) have long been used to estimate in-situ the kinetics of exchange of non-polar organic contaminants between water and sampler during deployment (Booij et al., 1998). The PRC technique has been applied with passive samplers such as semipermeable membrane devices (SPMDs), samplers made of low density polyethylene (LDPE), silicone rubber (SR; including polydimethylsiloxane), or solid phase micro extraction fibers (Rusina et al., 2009; Heringa and Hermens, 2003; Booij et al., 2003). During exposure in water, PRCs, non-naturally occurring analogues of chemicals of interest spiked into the sampler prior to deployment, dissipate from the sampler and enable us to estimate sampling rates, $R_s$, in-situ (Booij and Smedes, 2010). The fundamental principle behind the use of PRCs is that the uptake of target contaminants and release of PRCs follow the same exact same processes, i.e. that exchange is isotropic. For silicone rubber (SR) passive samplers, under most water exposure conditions, uptake is water boundary layer-controlled, meaning that transfer across the water boundary layer is the rate-limiting factor thereby simplifying the modelling required for estimating $R_s$ (Rusina et al., 2009; Booij and Smedes, 2010). Processes occurring at the surface of the
membrane such as diffusion across the water boundary layer or fouling are therefore likely to play a crucial role in contaminant uptake and PRC release.

The application of PRCs with absorption-based passive samplers is widely accepted nowadays however, it has not been tested under all possible environmental conditions. Field deployments of passive samplers in water can be done under large differences in temperature, salinity, pressure or type and amount of fouling. Literature on the effect of (bio)fouling on the uptake of contaminants into passive sampler so far is scarce and divergent with certain studies reporting effects on contaminant accumulation (Harman et al., 2009; Richardson et al., 2002) while others do not conclude on appreciable impacts (Booij et al., 2006). Until now however, there has been no evidence that the PRC technique is not able to provide accurate estimate of the in-situ uptake of target contaminants under specific environmental conditions in water. Here, we report evidence that the deposition and build-up of suspended particulate matter on the surface of silicone rubber passive samplers can be responsible for anisotropic exchange during riverine exposure of passive samplers. Our observations are based on data from routine SR passive sampler measurements conducted in three rivers in Norway over a four-year period. We compare the sampling rates \( R_i \) obtained for SR deployed in three rivers. The main noticeable difference between exposures in the different rivers is the level of fouling on samplers exposed in these rivers. On one occasion, additional measurements were conducted in this river with regular cleaning of the surface of the samplers to evaluate the impact of surface fouling. Levels of fouling were estimated by weighing the samplers upon retrieval.

2. Material and methods

2.1. Solvent and standards

Ultra-pure water was from an Elgast Maxima HPLC Deionization option 3 system. HPLC-grade dichloromethane and pentane were from Rathburn. HPLC grade cyclohexane was from J.T. Baker. Standards for polycyclic aromatic hydrocarbons (PAHs) and their deuterated homologues from Chiron were of analytical-grade with purities of >99% for PAHs and >99.5% for deuterated PAHs. Standards for fluorinated polychlorinated biphenyls (F-PCBs) were of similar analytical grade and purchased from Chiron. Analytical-grade standards and internal standards for PCBs and organochlorine compounds (OCs) were from LGC/Promochem.

2.2. Silicone membrane preparation

AlteSil™ silicone strips (2.5 cm wide, 100 cm long and 0.5 mm thick) from Altec Products Ltd were initially Soxhlet extracted to remove oligomers. Samplers were further soaked in methanol before spiking with performance reference compounds (deuterated PAHs and F-PCBs). Spiking of PRCs was performed according to procedures previously published using a methanol:water solution (Booij et al., 2002; Allan et al., 2010, 2013). PRCs used were ace-naphthene-d10, fluorene-d10, phenanthrene-d10, fluoranthene-d10, chrysene-d12 and benzo[a]pyrene-d12, and F-PCB 3, 28, 52, 105, and 156. Once spiked with PRCs, samplers dried with a wipe and stored in clean metal containers at \(-20\ ^\circ \text{C}\) until use. Generally, the variability in PRC spiked level was well below 10–15% (relative standard deviation based on measurements in blanks with \( n = 6 \) per batch of analysis).

2.3. Passive sampler exposures

Routine monitoring of three rivers, namely rivers Alna, Drammen and Glomma was conducted from 2013 to 2016 with SR passive samplers. Sampling location were at the lowest possible sampling point before the rivers joined the sea. Coordinates for the sampling sites on the Alna, Drammen and Glomma rivers were 59°54’16.70”N 10°47’30.35”E, 59°45’10.83”N 10°00’24.83”E, and 59°18’23.07”N 11°8’9.24”E, respectively. The Drammen and Glomma are large rivers fed by two large lakes with discharges in the period 2013–2016 in the range of 323–434 and 729–1049 \( \text{m}^3\text{s}^{-1} \), respectively. The Alna is, on the other hand, a much small river with a discharge of 0.9–1.8 \( \text{m}^3\text{s}^{-1} \) for the same period. With cross sectional areas of approximately 2.4, 630 and 2000 \( \text{m}^2 \) for the rivers Alna, Drammen and Glomma, respectively, water velocities in the range of 0.3–0.7, 0.5–0.7 and 0.3–0.5 \( \text{m} \text{s}^{-1} \) can be expected at the three sites, respectively.

Average suspended particulate matter (SPM) levels measured monthly for the period 2013–2016 were 12.7, 3.6 and 11.5 mg L\(^{-1}\) for the rivers Alna, Drammen and Glomma, respectively. The temperature of the three rivers varied relatively similarly over the year between values close to 0 °C in the winter to values close to 20 °C in the summer.

Sample deployments were undertaken four times a year to achieve continuous monitoring of the rivers. Average exposure times were 90 (range of 70–113 days), 91 (45–122 days) and 77 (42–122 days) days for the Rivers Alna, Drammen and Glomma. When samplers were retrieved, new samplers were deployed for approximately 3 months. For each exposure, duplicate SR passive samplers were deployed in each river. Each sampler was composed of two SR strips to obtain samplers with nominal mass of 30 g and surface area of 1000 cm\(^2\). Four SR strips were mounted onto spider holders and placed in a SPMD canister for exposure. One field blank/control sampler was used per river per exposure time, resulting in the use of 12 blank/control samplers per year. Field controls were opened to the air and manipulated in the same way as exposed samplers during deployment and retrieval operations.

In 2015, a single additional sampler exposure was conducted alongside the Alna deployment. Duplicate SR samplers (consisting of two SR strips each, as undertaken for the routine monitoring described above) were deployed in a second SPMD canister alongside the first one for the same period. On a biweekly basis, this cage was retrieved, and samplers gently wiped to remove the fouling. The samplers were placed back into the cage and placed in the water in the same position as the other cage. An additional field control sampler was used for this deployment. For the last two years of monitoring, a balance was brought in the field to weigh the samplers upon retrieval and prior to removing the fouling.

2.4. Silicone membrane extraction and analysis

SR were kept frozen at \(-20\ ^\circ \text{C}\) until extraction. While initial cleaning of the surface took place in the river during retrieval in the river, additional surface cleaning was undertaken in the laboratory by rinsing with ultra-pure water and then dried using a clean paper tissue. Samplers were soaked overnight in pentane. Recovery standards for PAHs (\( \text{d}_8\)-naphthalene, \( \text{d}_{10}\)-biphenyl, \( \text{d}_5\)-acenaphthylene, \( \text{d}_6\)-dibenzoanthracene, \( \text{d}_{12}\)-pyrene, \( \text{d}_2\)-benz[a]anthracene and \( \text{d}_2\)-perylene), PCBs/OCs (PCB 30, 53 and 204), were added. Soaking was repeated with fresh pentane. Extracts were combined as exposed samplers during deployment and retrieval operations. Extracts were combined and reduced under a gentle stream of nitrogen to about one mL. They were split into two fractions. The fraction intended for PAH, PRC and PCB analysis was analysed by GC/MS. Analysis for PAHs (and PRC), and for OCs (PCBs, pentachlorobenzene, hexachlorobenzene, \( \text{p},\text{p}’\)-DDE and \( \text{p},\text{p}’\)-DDT) was on an Agilent 7890 A gas chromatograph (GC) linked to an Agilent 5975c inert XL EI/Ci mass spectrometer (MS) operated in selected ion monitoring mode (SIM) with electron impact ionisation (70 keV). Separation was on a DB-
SR samplers: the silicone rubber passive sampler and Kpw the literature values of dian of optimised log(Rusina et al., 2009):

Temperature held constant for a further 5 min. Temperatures for the ion source, quadrupole and transfer line were set to 230, 150 and 280 °C, respectively. The relative response of surrogate internal standards and 7-point calibration curves were used for the quantification. Confirmation of compound identification was based on the relative response of the quantifier and qualifier ions.

2.5. Passive sampling data handling

We used the unweighted non-linear least-square method to estimate Rs from PRC dissipation data. This is done by assuming that the fraction of PRCs remaining in the sampler after exposure is a continuous function of the sampling rate (Booij and Smedes, 2010):

\[
f = \frac{N_f}{N_0} = \exp \left( -\frac{R_s t}{m K_{pw}} \right) \quad 1
\]

The sampling rate, Rs is itself related to the adjustable parameter \(\beta_{sil}\) according to a water boundary layer-controlled uptake model (Rusina et al., 2009):

\[
R_s = \beta_{sil} P_{pw}^{-0.08} \quad 2
\]

This parameter optimised based on PRC dissipation was then used to deduce Rs for chemicals with logKow > 3.5 with \(K_{pw}\) the polymer-water partition coefficient for AlteSil™ SR (Smedes et al., 2009). Freely dissolved contaminant concentrations in water, \(C_w\) are calculated from amounts accumulated during exposure (\(n_{acc}\)) in SR samplers:

\[
C_w = \frac{n_{acc}}{K_{pw} m \left( 1 - e^{-\frac{m}{\beta_{sil} P_{pw}}} \right)} \quad 3
\]

with \(C_w\) the freely dissolved concentration (ng L\(^{-1}\)), \(m\) the mass of the silicone rubber passive sampler and \(K_{pw}\) the literature values of AlteSil™-water partition coefficient (Smedes et al., 2009). No corrections for water temperature deviating from that at which \(K_{pw}\) were measured (for target compounds or PRCs) was applied to \(K_{pw}\) values.

3. Results and discussion

3.1. Comparison of sampling rates in the three rivers

The dissipation of performance reference compounds from silicone rubber samplers was used to estimate in situ contaminant exchange rates between samplers and the water they were exposed to using Equations (1) and (2). Duplicate samplers were treated independently. For all concomitant exposures in the three rivers, concentrations were obtained by averaging all field blanks from a same batch and GC run. As shown on Fig. 1, Rs values for SR samplers deployed in the Alna river are significantly higher than for those exposed in the Drammen or Glomma. For the Alna, the median of optimised \(\log_{10} R_s\) was 2.05 ± 0.08 (range of 1.5–2.4). This is much higher those obtained for the rivers Drammen (median of 0.68 with a range of −0.045 to 1.9) and Glomma (median of 1.07 with a range of 0.31–1.66). These \(\log_{10} R_s\) translate into a median \(R_s\) (at \(\log_{10} K_{pw} = 5\)) values of 43 (range of 13–103), 1.9 (range of 0.36–34) and 4.7 (range of 0.8–18) L d\(^{-1}\) for samplers exposed in the Alna, Drammen and Glomma rivers, respectively over the four-year period. For each exposure and sampler, the standard error (SE) on \(\log_{10} R_s\) was estimated from the deviation between the modelled PRC dissipation data from Equation (2) and observed PRC dissipation. These values were back-transformed to a SE for \(R_s\) at logKpw = 5. On average, relative standard errors in Rs at logKpw = 5 for all individual sampler exposures were 20, 25 and 24% for the Rivers Alna, Drammen and Glomma, respectively.

For deployments in winter the water temperature was very low and close to freezing and this can partly explain the low sampling rates observed for exposures in the Drammen and Glomma. These \(R_s\) are close to or equivalent to exposure conditions of nearly stagnant water. As mentioned before, no corrections were applied to \(K_{pw}\) values for water temperature deviating from that at which \(K_{pw}\) were measured (20 °C). Polymer-water partition coefficients will increase with decreasing water temperature (Jonker et al., 2015; Reitsma et al., 2013) as a result of the stronger drop in solubility in water than that in silicone rubber. An increase in \(K_{pw}\) for PRCs would result in an increase in estimated sampling rates. As an example, a correction of \(K_{pw}\) values of PRCs for a water temperature of 1 °C instead of 20 °C according to equations given in Jonker et al. (2015) resulted in an increase in \(R_s\) by 40%. This, however, would impact \(R_s\) for SR deployed in all rivers and does not explain the large difference between the \(R_s\) for deployments in the Alna and in the two other rivers. Although not measured, it unlikely that the water turbulences at these sampling sites were significantly different, particularly since the use of SPMD canisters and spider holders tend to strongly reduce the water flow around the samplers. High \(R_s\) were obtained for SR samplers exposed to the Danube river water with help of the dynamic passive sampling unit that allowed the sampler exposure under higher water velocity (Vrana et al., 2018). In that study, sampling rates \(R_s\) were in the range of 54–108 L d\(^{-1}\) for 392 cm\(^2\)-SR samplers, corresponding to \(R_s\) values in the range 140–276 L d\(^{-1}\) for 1000 cm\(^2\) samplers. For coastal deployments of AlteSil™ SR samplers in Belgium, surface area corrected \(R_s\) values were 4.2–75 L d\(^{-1}\) (Monteyne et al., 2013).

One noticeable difference between these exposures was the amount of fouling on the surface of the samplers after exposure. For the last seven exposures of the monitoring programme, SR were weighed on site prior to removing the fouling and placing them into bins for transport back to the laboratory. On average, the total wet weights of fouling on the samplers (in grams) were 35.0 (sd = 29), 5.0 (sd = 3) and 6.3 (sd = 3) for the rivers Alna, Drammen and Glomma, respectively. This is less than the maximum fouling observed of 75 g wet weight for 42 cm-long SPMDs for a 34 d exposure in the sea (Booij et al., 2006). Clearly, amounts of fouling were higher on the samplers deployed in the Alna. This is perhaps not surprising since the river is very silt and with a relatively high SPM load. The SPMD canister and spider holders may contribute to reduce the flow and promote deposition of SPM on the samplers.

3.2. Effect of regular removal of fouling deposited on aina-deployed SRs

For a 113-d deployment, the fouling found on the co-deployed set of samplers exposed under identical conditions (and from the same batch of samplers) in the river Alna was removed on a regular basis (every two weeks). The fouling was composed mostly of sediment particles and was only loosely bound to the samplers which made it easy to remove. Wet weights of the samplers were measured prior to removing the fouling. On average the wet weight of fouling accumulated over two weeks of exposure was 14 g (sd = 9). Based on this value, the fouling layer was estimated to be
no more than a couple of hundred micrometres in thickness. It was not possible to complete the final scheduled fouling removal operations and about 50 g wet weight of fouling was found on the samplers when retrieving them for analysis. These masses of fouling are similar to those measured for the samplers for which no cleaning was undertaken. This means that when we compare non-cleaned with cleaned samplers, the latter were not total free of fouling either. In Fig. 2, we plotted PRC dissipation curves and NLS model output for the two sets of duplicate samplers as a function of log\(K_{pw}\). A significant decrease in PRC dissipation can be observed for samplers that were cleaned of fouling on a biweekly basis. This lower PRC dissipation is equivalent to a factor of three decrease in \(R_s\) for cleaned samplers when compared with non-cleaned samplers for non-temperature corrected \(K_{pw}\) values. \(R_s\) optimisations with the NLS method were performed without the F-PCB PRC data (although these are shown as triangles on Fig. 2) since \(K_{pw}\) values for these compounds have not been measured. However, the clear differences in PRC dissipation rates for the two sets of SR observed for deuterated PAH PRCs could also be seen for F-PCBs. Removing the fouling apparently contributed to lowering the sampling rates for samplers indicates that fouling with suspended particulate matter promotes the release of PRCs from the passive samplers. The organic carbon content of SPM in the Alna river comprises a significant proportion of black carbon-type particles (e.g. from storm water road and urban run-off) that will provide a highly sorptive phase for PRCs when brought into contact with the samplers (Allan et al., 2016). The presence of particles in the vicinity of the sampler surface during exposures in mixed sediment slurries has been shown to increase sampling rates significantly (Booij et al., 2003). However, static exposures in sediments result in lower uptake kinetics as time goes by since, as the contaminant level becomes depleted in the vicinity of the sampler, compounds have to travel increasing distances to reach the sampler.

With the apparent decrease in \(R_s\) upon sampler cleaning, we could expect lower masses of target chemicals accumulated under linear uptake kinetics, by a factor of three or so. Surprisingly, when we compare masses accumulated in samplers, \(n_{acc}\) (Fig. 3), we observe higher masses of PAHs and PCBs in samplers that were cleaned routinely. For certain PAHs, masses are a factor of up to 27 higher than in non-cleaned samplers. This is the case specifically for phenanthrene, anthracene and fluoranthene. For the more hydrophobic PAHs and OCs, differences remain important but lower, with less than a factor of two in \(n_{acc}\) between cleaned and non-cleaned samplers (Fig. 3). There is a slight trend in decrease of the \(n_{acc}\) (surface cleaning)/\(n_{acc}\) (no cleaning) ratio with increasing target compound hydrophobicity.

Overall, the combination of differences in \(R_s\) and \(n_{acc}\) between samplers that were cleaned regularly or not resulted in differences in estimated concentration from a factor of 1.4 for acenaphthylene to 27 for fluoranthene. For most compounds still in the linear phase of uptake (with log\(K_{pw}\) > 5–5.2), the difference in \(C_w\) was a factor of
Considering the generally expected accuracy and uncertainties (e.g., uncertainties in $K_{pw}$ values) of absorption-based passive sampling, such a bias in estimated $C_w$ is significant (Allan et al., 2009; Booij et al., 2017). The presence of an increasingly large fouling layer on the samplers apparently induced a higher rate of PRC dissipation that was not mimicked by the amounts accumulated in the samplers. The exchange of chemicals between the SR and water, in these conditions of fouling build-up with SPM, appears anisotropic. Our supposition is that the deposited SPM, containing a significant fraction of organic carbon with a strong sorption capacity for our PRCs, was able to enhance the release of PRCs from the SR. Past analyses of SPM from the river Alna showed the total organic carbon content can vary from 5 to 12%. Rock-Eval analysis of the SPM from the River Alna indicated that over 60% of the organic carbon was refractory carbon, i.e., black carbon which can provide strong sorption capacity for our deuterated PAHs and F-PCB PRCs (Allan et al., 2016). In that study, the evaluation of the accessible fraction of PAHs showed that only 5–60% of PAHs present in the Alna SPM could be released from the SPM during 6-week long non-exhaustive extractions. In the present study, it is likely that because of slow desorption kinetics, the transfer of SPM-sorbed PAHs and PCBs to the SR was not as efficient as the transfer of PRCs from the SR to the SPM layer. This is supported by the results of a recent study of PCB exchange to and from polyethylene passive samplers exposed statically in sediments that also showed potential for anisotropy (Choi et al., 2016). The authors also postulated that PCB aging in the sediment and a sorption-desorption hysteresis may be responsible for anisotropy. Another possibility in our case is that biodegradation of PRCs takes place at the SPM-SR interface or in the SPM layer, contributing to increased dissipation of PRCs. This phenomenon would also impact the uptake of native PAHs. Since we observe that the SPM removal also resulted differences in the release of the more degradation-recalcitrant F-PCB PRCs, in line with that of deuterated PAHs, biodegradation is unlikely to be playing major role.

4. Conclusions

Our data indicate that it is possible that under specific circumstances of fouling, in our case heavy fouling with suspended particulate matter with a high proportion of refractory carbon, the exchange of chemicals between absorption-based passive samplers and the aquatic environment the sampler is exposed to may be anisotropic. Here, sorption-desorption hysteresis for PRCs and native compounds is likely responsible for the discrepancy between the $C_w$ estimated from passive samplers whose fouling was regularly removed and those left in place in water for the entire exposure duration. SPM settling on the samplers resulted in an underestimation of $C_w$ by a factor of 3.9 on average. While this may not be viewed as particularly high, when considering all other uncertainties of passive sampling, this error or bias in the data in these special cases of fouling is significant. This issue would not be observed from the PRC data only since, it did not affect shape of the PRC dissipation profile shown in Fig. 2. While these environmental conditions may not necessarily be encountered very often, this is likely the case in relatively small urban freshwater environments.
that are prone to contamination from urban storm waters and run-off. The narrow openings of SPMD canisters tend to strongly reduce the water flow around the samplers and this may have favoured the deposition of suspended particles onto the membranes in our study. Although, there is no evidence of its occurrence here, biodegradation of relatively labile chemicals used as PRCs, i.e. deuterated PAHs, may be possible in the fouling layer (Belles et al., 2016; Tcacu et al., 2018). More work is needed to gain an overview of conditions under which these phenomena can occur. This will help define the window of operating conditions for the use of passive samplers in regulatory settings. Some solutions may include shorter deployments to minimise fouling albeit limitations in the integrative sampling strength of passive samplers, the use of the dynamic passive sampling unit or more “open” types of deployment cages than SPMD canisters to minimise potential for SPM deposition, or regular removal of the fouling layer.

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