Passive sampling techniques for sensing freely dissolved hydrophobic organic chemicals in sediment porewater

Lian-Jun Bao, Eddy Y. Zeng

With compiled and analyzed information about recent advances in passive sampling techniques for sediment porewater, we discuss common quantitation methods (equilibrium and kinetic diffusion-controlled sampling), effects of temperature and salinity on passive sampling, and benefits and drawbacks of currently available passive samplers based on the principles of solid-phase microextraction.

The results show that the in-fiber standardization technique, which is kinetic diffusion-controlled, could shorten sampling time and obtain accurate results using isotopically-labeled reference compounds. Another quantitative method, time-weighted average sampling, may be viable for simultaneously measuring all analytes in sediment porewater, as it is more effective with respect to cost and time. In addition, the effects of temperature and salinity on passive sampling should be quantified in field applications.

Currently available passive samplers (e.g., employing polymer-coated fibers and low-density polyethylene sheets) can sense hydrophobic organic chemicals (HOCs) in sediment porewater, but the small capacity and the inflexibility of polymer-coated fibers need to be further improved, while better physical protection of polyethylene devices, particularly when they are deployed under rough conditions, should be carefully considered.

In conclusion, passive samplers for *in-situ* measurement of dissolved HOCs in sediment porewater should be combined with a suitable quantitative method and calibration for the effects of temperature and salinity.

Keywords: Equilibrium sampling; Hydrophobic organic chemical; In-fiber standardization; Kinetic diffusion-controlled sampling; Low density polyethylene; Passive sampler; Sediment porewater; Solid-phase microextraction; Time-weighted average sampling

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1. Introduction

Hydrophobic organic chemicals (HOCs) [e.g., polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs)], freely dissolved in sediment porewater, are actively involved in the processes of erosion, molecular diffusion, bioturbation and groundwater flow that occur in sediments [1]. As a consequence of these processes, contaminated sediment may become a secondary input source of HOCs in aquatic systems [2,3]. Sediment-bound HOCs desorb into sediment porewater, and then make their way to the overlying water. HOCs in sediment porewater can also be bioaccumulated in benthic organisms, posing potential hazards to wildlife and perhaps humans by transfer through the aquatic foodweb [4]. Clearly, assessment of the mobility and ecological risk of HOCs in aquatic environments largely hinges on accurate determination of dissolved HOC concentrations in sediment porewater.

Traditional active sampling protocols for measuring dissolved HOC levels in sediment porewater, which are generally costly and time consuming, include two steps:

(1) sediment is collected in field and transported to the laboratory; and,
(2) porewater is separated from sediment through centrifugation and filtration, and subsequently processed with liquid-liquid extraction or other procedures, and finally subject to instrument analysis.

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The limits of detection (LODs) of active sampling methods are usually high, because a large volume of porewater is difficult to obtain. Furthermore, possible mixing of overlying water into sediment during field sampling would underestimate the HOC levels in porewater. However, a modeling approach has also been employed for estimating dissolved HOC concentrations in sediment porewater, based on equilibrium partitioning of HOCs among the three interacting compartments of organic carbon matter in sediment, lipids in benthic organism, and porewater [5]. Essentially, the concentrations of freely dissolved HOCs in sediment porewater can be estimated from the organic carbon (or lipid) normalized concentrations in sediment (or organism) divided by the relevant partition coefficients. However, possible sequestration of HOCs in black carbon embedded in sediment and uncertainty in partition coefficients may affect the accuracy of such estimates [6–8]. Besides, although benthic species can often sense the bioavailability of HOCs in sediment [9], freely dissolved concentrations of HOCs estimated from organism lipid loading could be overestimated as both bound and freely dissolved HOCs in porewater may be accumulated by benthic species. Furthermore, benthic species have natural biological variability (e.g., lipid content and composition), and there is no single species that can be used to monitor freely dissolved HOCs in sediment porewater around the world. Obviously, it is highly desirable to develop a fast, inexpensive, reliable sampling technique for filling this technological gap.

Passive sampling techniques [e.g., based on the principles of solid-phase microextraction (SPME) and employing low density polyethylene (LDPE) and other polymer materials as the sorbent phases] have commonly been used for sensing HOCs in sediment porewater [2,9]. In the non-equilibrium sampling mode, the molecular diffusion of the freely dissolved analytes onto the sorbent phase, a critical step in the process, can be rapid and used to determine time-weighted average (TWA) concentrations of HOCs. Passive sampling is mostly simpler to use and more cost effective than active sampling. In addition, non-depletive extraction, characteristic of typical passive samplers, does not disturb the partitioning equilibrium, thus the concentrations of freely dissolved HOCs in sediment porewater can be determined [10].

This review presents a brief, but critical, overview of the available passive sampling methods for sensing freely dissolved HOCs in sediment porewater, focusing on the quantitative procedures, controlling environmental factors, and the benefits and the drawbacks of currently available passive samplers.

2. Quantitative methods in passive sampling

Currently, quantification of dissolved HOC concentrations in sediment porewater through passive sampling is largely based on equilibrium partitioning or a kinetic diffusion-controlled process. When equilibrium partitioning of HOCs between sorbent phase and porewater is established, the dissolved concentration (C_{pw}) of an HOC in porewater is constant and can be calculated by:

$$C_{pw} = \frac{C_s}{K_{sorbent-porewater}} \quad (1)$$

and at any sampling time t, C_{pw} is given by:

$$C_{pw} = \frac{C_{s(t)}}{(1 - e^{-k_e t}) \times K_{sorbent-porewater}} \quad (2)$$

where:
C_s is the HOC concentration in the sorbent phase at equilibrium ($t \to \infty$);
$K_{sorbent\text{-}porewater}$ is the equilibrium partition coefficient of the HOC between the sorbent phase and porewater, which may be dependent on certain environmental factors (e.g., temperature and dissolved salts) [11]; and,
k_e is the exchange-rate coefficient.

Equilibrium extraction is capable of acquiring relatively accurate results, but has to endure long sampling time. For example, the equilibrium time for sampling PAHs in the field with 100-μm LDPE and 500-μm polyoxymethylene was more than 119 days [2]. Because loss or damage of samplers in field deployment is inevitable, prolonged sampling time would restrict the utility of passive samplers in field applications. To mitigate this problem, particularly for passive sampling of HOCs in sediment porewater, k_e can be estimated by the desorption of pre-loaded performance reference compounds (PRCs) in the sorbent phase, which is first applied in SPME fiber and then is referred to as an in-fiber standardization technique [12]. So, combined with Equation (2), the dissolved HOC concentration in sediment porewater can be estimated by:

$$C_{pw} = \frac{C_{s(t)}}{\left(1 - \frac{C_{s,PRC(t)}}{C_{s,PRC(0)}}\right) \times K_{sorbent-porewater}} \quad (3)$$

where $C_{s,PRC(t)}$ and $C_{s,PRC(0)}$ are the PRC concentrations in the sorbent phase at deployment time $t = t$ and $t = 0$, respectively. Equation (3) indicates that the difference between the concentrations of a PRC in the spiked sorbent phase before ($t = 0$) and after sampling ($t = t$) must be sufficiently large (i.e. desorption rate should be fast enough) so that a meaningful C_{pw} can be obtained. In addition, a PRC should have physico-chemical properties nearly identical to those of the analyte under consideration. Apparently, isotopically-labeled counterparts are perfect candidates of PRCs.

However, isotopically-labeled compounds are expensive and not readily available for all target analytes of interest. Alternative compounds, which are similar in physico-chemical properties to the target analytes and rarely found in the environment, have been used to replace isotopically-labeled PRCs. The k_e of an alternative

PRC can be adjusted for the target analyte through calibration (e.g., a molar volume adjustment) [13]. However, such calibration still cannot completely eliminate the variability in k_e resulting from the difference in physico-chemical properties between the alternative PRC and the target analyte in general.

Tomaszewsky and Luthy [14] compared two approaches (molar volume adjustment and exposure adjustment factor [15]) with two alternative PRCs (PCB-29 (log K_{ow} = 5.6) and PCB-69 (log K_{ow} = 6.04) for calibrating the k_e values of a series of PCBs (63 congeners plus 26 coeluting groups) on PE samplers. The results matched field-measured k_e within a factor of 2 for most PCB congeners. Both calibration methods tended to overestimate and to underestimate the k_e for small (log K_{ow} < 6.3) and large compounds (log K_{ow} > 6.7), respectively.

Fernandez et al. [8] also reported that pyrene and chrysene concentrations in sediment porewater calibrated by phenanthrene-d_{10} through molar volume adjustment were 40% and 60% of those calibrated by pyrene-d_{10} and chrysene-d_{12}, respectively. Furthermore Fernandez et al. [16] presented a passive sampler-sediment bed mass-transfer theory for rectifying this problem. When the concentrations of 11 PAHs (phenanthrene, anthracene, 1-methylphenanthrene, 1-methylanthracene, fluoranthene, pyrene, 3,6-dimethylphenanthrene, 9,10-dimethylanthracene, 2-methylfluoranthene, benzo[*a*]anthracene, and chrysene) in sediment porewater were calibrated by phenanthrene-d_{10}, pyrene-d_{10} and chrysene-d_{12}, this theory matched well with those corrected by total organic carbon content and K_{OC}. The concentrations of the large chemicals (benzo[*b*]fluoranthene and benzo[*k*]fluoranthene (measured together), indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene, and dibenz[*a,h*]anthracene) were lower than those corrected by total organic carbon content and K_{OC}.

Kinetic diffusion-controlled sampling methods, such as the in-fiber standardization technique [12] and TWA sampling [17], are time efficient, requiring sampling time varying from days to weeks. As mentioned above, the in-fiber standardization technique has been widely applied for sensing dissolved HOCs in sediment porewater [14,16,8], but requires the use of PRCs, which limits the number of analytes that can be quantified. However, the TWA sampling approach can basically quantify all analytes, as it does not use any PRCs. Based on the Fick's first law of diffusion, the TWA concentration (C_{TWA}) of an analyte in an environmental medium (e.g., air or sediment porewater) can be estimated by:

$$C_{TWA} = \frac{m}{Rt} = \frac{zm}{ADt} \quad (4)$$

where:

m is the mass of the analyte in the sorbent phase;
R (=AD/z) is the sampling rate;
t is the sampling time;
z is the diffusion path length;
A is the area of the diffusion cross-section; and,
D is the diffusion coefficient of the analyte in the environmental medium.

The TWA approach has been used to measure analyte concentrations in air and water [17,18], but not in sediment porewater. One of the requirements for TWA sampling is a carefully-configured structure that satisfies specific TWA conditions [19] {e.g., those applied in the fiber-retracted devices [18]}. In addition, because trace constituents (e.g., humic substances) in sediment porewater are likely to impact the mass transfer of HOCs from porewater to the sorbent phase under static condition [20], the diffusion coefficient (D) used to calibrate the sampling rate ($R = AD/z$) is difficult to determine. Nevertheless, TWA sampling appears to be a viable alternative for measuring HOC concentrations in sediment porewater.

3. Effects of temperature and salinity on passive sampling

3.1. Temperature

As $K_{sorbent\text{-}porewater}$ is temperature-dependent by definition, the effect of temperature on $K_{sorbent\text{-}porewater}$ may not be ignored, especially if the ambient temperature is significantly different from that used to determine $K_{sorbent\text{-}porewater}$ in the laboratory. For example, the partition coefficients of PCB-28 and PCB-52 between LDPE and water were l.5 times higher at 2°C than at 30°C, while those of acenaphthene, phenanthrene, fluoranthene, pyrene and benzo[*a*]anthracene were also several times higher at 2°C than at 30°C [21]. However, the effects of temperature on the partition coefficients of benzene, toluene, ethylbenzene and *o*-xylene between poly(dimethyl)siloxane (PDMS) and water were insignificant (i.e., only a 4% difference between 12°C and 25°C) [22].

DiFilippo and Eganhouse [11] also noted that the temperature dependence of partition coefficients between PDMS and water was greater for larger compounds with increasing molecular size.

In addition, Ouyang et al. [23] found that a temperature change from 14 ± 1°C to 24 ± 1°C had no apparent impact on the mass-uptake rates of naphthalene, acenaphthene and fluorene in TWA water sampling.

Apparently, effects of temperature may be more pronounced for larger-sized chemicals and equilibrium sampling than smaller-sized chemicals and kinetic

diffusion-controlled sampling. It is therefore desirable that experimental parameters {e.g., $K_{sorbent\text{-}porewater}$ and sampling rate R in TWA methods [19]} are calibrated at an appropriate temperature range similar to that possibly encountered in field deployment.

3.2. Salinity

Available information [2,3,9] shows that, so far, harbors have been selected most widely for sediment porewater sampling, so the partitioning of target analytes between sediment porewater and the sorbent phase could be impacted by dissolved salt. Adams et al. [24] found that the partition coefficients of phenanthrene and pyrene between LDPE and freshwater were approximately 94% of those obtained with 0.1 M NaCl solution instead of freshwater, but the deviation could be corrected with the Setschenow constant [25]. Generally, the aqueous solubility of HOCs would decrease with increasing dissolved salt content, similar to the salting-out effects in liquid-liquid extraction. Consequently, the partition coefficients of HOCs obtained with freshwater should be corrected for any salinity effects, if they are to be used in sampling HOCs in sediment porewater from harbors or tidal mudflats [8].

4. Benefits and shortfalls of available passive sampling techniques

The SPME-based analytical technique introduced by Arthur and Pawliszyn [26] and subsequent modified versions {e.g., negligible depletive SPME [27] and matrix-SPME [28]} have been the prevailing methods for sensing dissolved HOCs in sediment porewater [29,30]. Similar techniques were also used to estimate the porewater median effect concentration (EC50; 23 μg/L) of pyrene for the euedaphic springtail, *Folsomia candida* [27] and to determine the K_{DOC} of fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*+*k*] fluoranthene, benzo[*a*]pyrene, perylene, and benzo[*ghi*]perylene [31] (Table 1). Clearly, SPME-based passive samplers are useful tools for estimating HOC concentrations in sediment porewater. In addition, they are almost or fully solvent-free, and the samples thus acquired can be directly analyzed with gas chromatography (GC) without further purification.

Polymer-coated fibers have been widely used in SPME-based passive samplers {e.g., commercially available PDMS, polydimethylsiloxane–divinylbenzene (PDMS–DVB), polyacrylate (PA) and carboxen–polydimethylsiloxane (CAR–PDMS)}. However, these fibers are fragile in field deployment [32] and quite costly. Available polymer-coated fibers have not been used for *in-situ* measurement of dissolved HOCs in sediment porewater (Table 1). Furthermore, the capacity of polymer-coated fibers is proportional to the polymer-coating volume (or thickness), and the partition equilibrium time would increase with increasing coating thickness. For example, the LODs of matrix-SPME with 15-μm PDMS-coated fiber were 550 pg/L for fluoranthene (less hydrophobic) and 4 pg/L for PCB-180 (more hydrophobic) in sediment porewater [28]. Clearly, the generally small capacity and inflexibility of polymer-coated fibers limits their utility in passive sampling, particularly in the measurement of HOCs in field-sediment porewater, which often contains low levels of HOCs.

Low-density polyethylene was used in earlier days as permeable membrane bag in semi-permeable membrane devices [33]. It has been shown to be able to accumulate HOCs with high partition coefficients, and developed into the sorbent phase used in polyethylene devices (PEDs). These PEDs have been used to measure dissolved HOC levels in sediment porewater [3,8,9] and to assess the effects of sediment resuspension on the bioavailability of PCBs [9] (Table 1). Thin LDPE sheets are cheap (US$0.40/m^2) [34], firm, easily deployable in sediment, and scalable to various sensitivity needs, so they are ideal for monitoring dissolved HOC levels in sediment porewater. 30 mg of 25-μm LDPE were able to detect a PAH, such as benzo[*a*]pyrene, at 1 pg/L in sediment porewater using GC coupled with mass spectrometry (GC-MS) analysis of a 100-μl extract [8]. Because target analytes sorbed into the PE phase need to be extracted with organic solvent (e.g., hexane and dichloromethane), the blank levels of the target analytes in PEDs should be quantified, especially for determination of PAHs [3].

Just like polymer-coated fibers, LDPE strips may also be vulnerable to external forces when used in field deployment. So far, PEDs directly inserted into sediment comprise a thin LDPE strip punctured by stainless-steel wire or attached to triangular aluminum frames [2], and have no protection. Sorption of dissolved organic matter directly to PE strips would artificially increase the amounts of HOCs in PEDs, as demonstrated in the case of PDMS-coated fiber [10].

Table 2 compares the concentrations of PAHs and PCBs in sediment porewater obtained with PED and centrifugation [14], as well as from calibration with organic carbon content in porewater and K_{OC} [16] and lipid-water partition coefficient [9]. The concentration of PCBs (1129 ± 139 ng/L) in sediment porewater under the condition of no resuspension obtained from PEDs was twice that (534 ± 95 ng/L) estimated by lipid-water partitioning [9]. This might be attributed to a number of reasons (e.g., metabolism of low log K_{ow} PCBs in benthic organisms, exposure of benthic organisms to overlying water, and sorption of dissolved organic matter directly to PE strips). In addition, protective shields added in passive samplers may minimize sorption of large-sized particles into the sorbent phase; for example, Xing et al.

Table 1. A summary of available porewater passive samplers and related sorbent phases and field applications

Passive sampler	Sorbent phase	Field exposure	Analyte	Applications	Ref.
Polymer-coated fiber	28.5-μm PDMS[c]	N[e]	Pyrene	Estimation of the porewater median effect concentration (23 μg/L) of pyrene for euedaphic springtail, *Folsomia candida*	[27]
	7-μm PDMS	N	PAHs[g]	Determination of K_{DOC} for eight PAHs	[31]
	15-μm PDMS	N	PAHs, PCBs[h] and *p,p*′-DDE		[28]
	10-μm PDMS			Study of desorption of HOCs[i] from sediment.	[38]
PED[a]	25-um LDPE[d]	Y[f]	PAHs, PCBs		[8]
	70-μm LDPE	Y	PCBs, PAHs and HCB[j]	Determination of immobile portion of PAHs (95%) and PCBs (50%) in sediment, and sediment as a potential source of PAHs in Harlingen Harbor	[3]
	51-μm LDPE	Y	PCBs	Assessment of the effectiveness of activated carbon amendment of contaminate sediment	[14]
	74–84-μm LDPE	N	PAHs	Simulation of uptake of bioavailable PAHs in contaminated marine sediment	[39]
	51-μm LDPE	N	PCBs	Assessment of sediment resuspension effects on PCBs bioavailability for polychaete, *Nereis virens*	[9]
POM[b]	50 and 500-μm POM	N	PAHs	Examination of sediment as PAH diffusion source in Oslo Harbor	[2]

[a] PED = Polyethylene device.
[b] POM = Polyoxymethylene.
[c] PDMS = Poly(dimethyl)siloxane.
[d] LDPE = Low-density polyethylene.
[e] Denotes that passive sampler was not used for *in-situ* measurement of HOC concentrations in sediment porewater.
[f] Denotes that passive sampler was used for *in-situ* measurement of HOC concentrations in sediment porewater.
[g] PAHs = Polycyclic aromatic hydrocarbons.
[h] PCBs = Polychlorinated biphenyls.
[i] HOCs = Hydrophobic organic chemicals.
[j] HCB = Hexachlorobenzene.

Table 2. Comparison of concentrations (ng/L) of polycyclic aromatic hydrocarbons (PAHs) and polychlorobiphenyls (PCBs) in sediment porewater using polyethylene devices (PEDs), centrifugation, TOC corrected[a] and lipid-water partitioning[b]

Analyte	Centrifugation	TOC corrected	Lipid-water partitioning	PEDs	Ref.
PCBs[c]			534 ± 95[f]	1129 ± 139	[9]
PCBs[d]	12.6 ± 1.4 (n = 3)[g]			19.9 ± 3.3 (n = 4)	[14]
	50.8 ± 3.7 (n = 2)[h]			56.6 ± 1.7 (n = 3)	[14]
PAHs[e]		33889		28942	[16]

[a] The analyte concentration in sediment porewater was calculated from the values measured in unfiltered porewater corrected by total organic carbon content and K_{OC}.
[b] The analyte concentration in sediment porewater was calculated based on lipid concentration using the lipid-water partition coefficient.
[c] Sum of PCB-18, -28, -44, -52, -66, -99, -101, -110, -128, -138, -153 and -170.
[d] Sum of PCB-1, -3, -4 + -10, -7 + -9, -6, -8 + -5, -12 + -13, -18, -15 + -17, -24 + -27, -16 + -32, -26, -25, -31, -28, -21 + -33, -53, -51, -22, -45, -46, -52 + -49, -43, -47, -48, -44, -37 + -42, -41 + -71, -64, -40, -100, -63, -74, -70 + -76, -66, -95, -91, -56 + -60, -92 + -84 + -89, -101, -99, -119, -83, -97, -81 + -87, -85, -136, -77 + -110, -82, -151, -107, -123 + -149, -118, 134, -114 + -131, -146, -153, -105, -132, -141, -137 + -176 + -130, -163 + -138, -158, -178, -187 + -182, -183, -128, -185, -174, -177, -202 + -171 + -156, -157 + -200, -172,-197, -180, -193, -191, -199, -170 + -190, -198, -201, -203 + -196, -189, -208 + -195, -207, -194, -205, -206 and -209.
[e] Sum of phenanthrene, anthracene, 1-methylphenanthrene, 1-methylanthracene, fluoranthene, pyrene, 3,6-dimenthylphenanthrene, 9,10-dimethylanthracene, 2-methylfluoranthene, benzo[*a*]anthracene, chrysene, benzo[*b*]-plus benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, and benzo[*ghi*]perylene, dibenzo[*a,h*]anthracene.
[f] In sediment porewater, under condition of no resuspension.
[g] Field deployment (28 days) of PED.
[h] Laboratory deployment (28 days) of PED.

[35] used a glass-fiber filtration (GF/F) membrane and copper mesh to protect a PDMS-coated probe from contact with suspended particles in water.

5. Conclusions and future perspectives

Several points can be made from the above discussions.

First, the in-fiber standardization technique, a widely used quantitation method for porewater passive sampling, could shorten sampling time and obtain results just as accurate as equilibrium extraction. However, it requires the use of PRCs, which limit the number of analytes that can be quantified simultaneously. Another quantitative method (i.e. TWA sampling) may be a viable alternative for measuring all analytes in sediment porewater.

Second, the effect of temperature may be more pronounced for larger-sized chemicals and equilibrium sampling than smaller-sized chemicals and kinetic diffusion-controlled sampling. In addition, salinity can enhance the partitioning of a polar chemical between the sorbent phase and water in equilibrium sampling. Overall, the effects of temperature and salinity on passive sampling should be considered in field applications.

Third, passive sampling techniques employing LDPE as sorbent phase appear to have great potential for *in-situ* measurement of freely dissolved HOCs in sediment porewater, and have been proposed as the basic tool for monitoring sediment porewater HOCs globally [36].

In field deployment of PEDs, only sediment porewater at the depth of 10–15 cm below the sediment-water interface has been investigated so far and no vertical profiles obtained [3,14]. However, vertical profiles of HOCs in sediment porewater can provide indications of their mobility in sediment and whether the contaminated sediment is a source or a sink. To fill this technological gap, we recently developed a multi-sectional passive sampler employing LDPE as the sorbent phase and operating in the kinetic diffusion-controlled mode [37]. This sampler was successfully used to obtain vertical concentration profiles of dichlorodiphenyltrichloroethane and its metabolites in sediment porewater of an urbanized coastal region. In addition, with minor modifications, the new passive sampler can be used for synchronous measurements of HOCs within the sediment-water, air-water, and soil-water systems.

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