

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.

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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.

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 bio-availability 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:

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

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

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

where:

C_s is the HOC concentration in the sorbent phase at equilibrium ($t \rightarrow \infty$);

$K_{\text{sorbent-porewater}}$ 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:

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

where $C_{s,\text{PRC}(t)}$ and $C_{s,\text{PRC}(0)}$ 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

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