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Review

Recent advances in the field measurement of the diffusion flux of hydrophobic organic chemicals at the sediment-water interface

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ABSTRACT

We describe and discuss recent advances in measurement of the diffusion flux of chemicals at the sediment-water interface. We analyze the key factors influencing diffusion flux (e.g., chemical-concentration gradient, mass-transfer resistance, sediment composition, hydrodynamics and temperature). We then discuss two main approaches to measure diffusion flux – two-point (i.e. chemical concentrations in sediment porewater and overlying water), and the traditional benthic chamber that can directly measure chemical-diffusion flux from sediment, but the measurement is done at the sorbent-water interface rather than the sediment-water interface. Finally, we present a recently-designed passive sampling device, which derives chemical-diffusion flux at the sediment-water interface from measured concentration profiles in overlying water and sediment porewater. Future work should be directed toward accurate determination of the chemical-diffusion coefficient in overlying water, which is still required for the new sampling device.

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1. Introduction

Sediment could be a gigantic reservoir of various hydrophobic organic chemicals (HOCs) [1,2] [e.g., polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs)], which may stem from a variety of routes (e.g., atmospheric dry/wet deposition, wastewater discharge, and solid-waste disposal) [3]. When exogenous inputs are effectively controlled, contaminated sediment may become a secondary source of contamination to adjacent aquatic eco-environments [4], releasing once-buried contaminants through molecular diffusion, colloidal transport, particle resuspension, gas ebullition, and bioirrigation/bioturbation [5–7]. Among these processes, molecular diffusion is generally the slowest, but it is active all year round, whereas other processes are sporadic and short lived. In addition, molecular diffusion is driven by the difference in freely-dissolved concentrations of a target chemical between sediment porewater and overlying water [8,9], which can be clearly defined and quantitatively characterized.

Measurement of sediment-water diffusion fluxes of chemicals is significant for assessing the environmental fate of chemicals and the quality of aquatic systems. First, the direction and the magnitude of sediment-water molecular diffusion, one of the most important processes in geochemical cycling of chemicals, can be used to discern whether sediment acts as a source or a sink of chemicals. With the help of source apportionment and constituent analysis, it can also be used to examine the spatial distribution of diffusion fluxes and the dominant factors governing regional environmental fate [7,10,11]. Second, measuring molecular diffusion fluxes is crucial for ecological risk assessment, because the freely-dissolved fraction of a chemical is considered mostly bioavailable so it may cause health hazards to wildlife and perhaps humans through aquatic food-web transfer [12]. Numerous studies have also found that the extent of bioaccumulation in aquatic organisms is proportional to the amount of chemicals releasing from sediment rather than the total amount in sediment [13,14]. Third, diffusion flux is a key reference index in the framework of remedial actions for contaminated sediment and can be used to evaluate the effectiveness of *in-situ* remediation. For example, it can be used to select suitable capping materials and layer thickness in capping-amendment programs, and to estimate the magnitudes of reduction in porewater concentrations and releasing fluxes [1]. Consequently, there is an increasing need to quantify diffusion fluxes and to recognize their implications for aquatic quality.

This article presents a short but critical overview of available techniques/methods for determining sediment-water diffusion fluxes of chemicals, focusing on the key factors influencing sediment-water fluxes, the availability of currently available technologies and their main drawbacks, and introduction of a new passive sampling device that we developed for diffusion-flux measurements. With increasing levels of environmental pollution throughout the globe, we expect this review to provide useful information for conducting *in-situ* sediment remediation and ecological risk assessment.

2. Key factors influencing diffusion flux at the sediment-water interface

2.1. Chemical-concentration gradient

By Fick's First Law of Diffusion, molecular diffusion flux is proportional to the chemical-concentration (or activity) gradient between sediment porewater and overlying water. In most cases, chemical concentrations are greater in sediment porewater than in overlying water. For example, Booij et al. [15] found a range of 1.2–44 times greater concentrations of PAHs in porewater than in overlying water in Harlingen Harbor, and Cornelissen et al. [16] observed up to 200 times greater concentrations of 2,3-ring PAHs in contaminated sediment in Oslo Harbor.

Sediment often acts as a significant source of chemicals, thereby exerting a release flux out of sediment (designated as "positive flux"). However, there are also exceptions {e.g., higher levels of PCB-52 and PCB-66 in overlying water than in sediment porewater in Dorchester Bay [17], and also PCB-153 and PCB-180 in Ijmuiden Harbor [9]}. In this case, sediment often acts as a sink of chemicals, thereby exerting a settlement flux into sediment (designated as "negative flux"). Also, there are cases where chemical concentrations were nearly identical in sediment porewater and overlying water {e.g., polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs) in the Baltic Sea [18] and hexachlorobenzene (HCB) in Delfzijl Harbor [15]}, so that no net diffusion flux was observed.

2.2. Mass-transfer resistance

Although chemical-concentration gradient is the driving force for molecular diffusion, the magnitude of diffusion flux is dictated by the mass-transfer coefficient (K_m), the reciprocal of which is defined as total transfer resistance. In a sediment-water system, mass-transfer pathways include in-bed diffusion and overlying water transport [9,13]. Therein, overlying water transport is associated with the chemical-diffusion coefficient in water (D_w) [19]:

$$D_w = 0.01326/(\eta^{1.4} v^{0.589})$$

with η and v being the water viscosity and molar volume of the target chemical, respectively.

Similarly, in-bed diffusion is related to the chemical diffusion coefficient in porewater (D_s) [20,21]:

$$D_s = D_w/[1+3(1-\varphi)] \text{ or}$$

$$D_s = D_w/\theta^2$$

with φ and θ being the sediment porosity and tortuosity, respectively. K_m is therefore a comprehensive parameter integrating various physicochemical properties of the sediment-water system, and it can be obtained with laser-Doppler velocimeter, dissolved oxygen microprobe [22,23], alabaster-determined DBL-thickness [24,25] and other empirical formulas [10,13].

2.3. Sediment composition

Chemical concentrations in sediment porewater are largely governed by the distribution of chemicals between solid and aqueous phases, so sediment composition has been recognized as a main factor for phase-distribution patterns [26,27]. In particular, black carbon (BC), with stronger affinity to HOCs than amorphous organic carbon by a factor of 10–100 [28,29], is the most dominant sorbing substance in sediment. Sequestration of chemicals by BC limits chemical desorption from sediment, decreasing porewater chemical concentration or increasing in-bed resistance to diffusion. Thus, a generic organic carbon-water distribution coefficient is inappropriate for predicting porewater-chemical concentrations; in some cases, up to two orders of magnitude higher concentrations than measured values were predicted [14,25]. Although BC generally takes up only a small fraction of sediment composition {e.g., 0.6% in Boston Harbor [30], 0.3% in New York Harbor [30], 0.25–0.4% in Oslo Harbor [16], and 0.09–0.27% in Baltic Sea [18]}, it may sequester up to 90% of chemical constituents in sediment [18]. Apparently, BC content is an essential factor controlling chemical-diffusion fluxes.

2.4. Hydrodynamics

A key factor affecting the occurrence of chemicals in a water column is the hydrodynamic conditions. Generally, tidal currents can disperse chemicals, effectively diluting chemical concentration and propelling chemicals out of the sediment.

On the one hand, turbulent flows attenuate the thickness of the diffusion boundary layer (DBL) and enhance mass transport of chemicals across the sediment-water interface, hence molecular diffusion flux. Tengberg et al. [31] proposed an empirical formula to correlate flow shear velocity u with DBL thickness, i.e.:

$$\mathrm{DBL} = 76.18/(u^{0.933})$$

to describe the influence of hydrodynamics on the fluxes of inorganic substances (e.g., oxygen and mercury) in benthic flux chambers.

On the other hand, fierce current turbulence may destroy stratification in a water column [13], reduce the transport resistance of chemicals in the diffusion pathway, and facilitate chemical release from the sediment. This may be why Morgan et al. [8] did not detect higher than normal concentrations of PCBs in bottom water after two spring-tide events, which presumably would have caused the release of large amounts of PCBs from sediment to overlying water.

2.5. Temperature

The effects of temperature on sediment-water diffusion flux are mainly implicated in the temperature dependency of the mass-transfer coefficient. A graphical summary by Thibodeaux [7] indicated that field-observed K_m values of PCBs in several rivers displayed apparent seasonality, with K_m being lower during colder months and higher during warmer months.

Erickson et al. [32] and Connolly et al. [33] reported exchange coefficients of PCBs in Hudson River in the ranges 2.6-18.8 cm d^{-1} and 3–14 cm d^{-1}, respectively. These results all showed strong seasonality peaking from mid-May to early-July.

Morgan et al. [8] observed a higher concentration ratio for PCBs between bottom and surface water of Narragansett Bay in July and August, while the gradient gradually decreased or even reversed after August, suggesting more outflows of PCBs from sediment in the warmer season. Also, diffusion coefficients that may depend on temperature can be corrected by

$$D_{T_2} = D_{T_1} + 0.048\Delta T$$

where

$$\Delta T = T_2 - T_1$$

with T_1 and T_2 being two specific temperature points [34].

2.6. Other factors

Apart from the factors discussed above, some substances [e.g., inorganic salt ions and dissolved organic carbon (DOC) in water/porewater] and biological indices (e.g., bioactivity and biomass in sediment) also affect the sediment-water fluxes of chemicals. For example, salinity affects chemical solubility due to salting-out effects [35], which in turn impact on the concentrations of freely-dissolved chemicals and the concentration gradient between sediment and water, and subsequently the magnitude and the direction of diffusion fluxes. On the one hand, the occurrence of DOC can promote desorption of chemicals from sediment, thereby increasing the chemical concentrations in water. On the other hand, DOC can bind chemicals through complexation, thereby decreasing the concentrations of freely-dissolved chemicals in water [36]. It is therefore difficult to evaluate quantitatively the effect of DOC on chemical diffusion flux. We should note that DOC may act as a carrier to facilitate the mass transfer of chemicals out of sediment. Organisms in sediment may also increase the chemical-diffusion flux through bioturbation, but the flux will decrease or even reverse direction if the organisms degrade or feed on these chemicals. Bioactivity and biomass in sediment are therefore important factors influencing chemical-diffusion fluxes across the sediment-water interface [5,7]. Also, chemical-diffusion fluxes depend on the physicochemical properties of chemicals (i.e. hydrophobicity, molecular volume and molecular weight).

3. Currently available techniques and their main drawbacks

3.1. Two-point measurement

As described above, chemical-concentration gradient is the driving force for molecular diffusion across the sediment-water interface (Fig. 1a and Table 1). In earlier studies, chemical concentrations were determined in core sediment and overlying water samples to derive the chemical-concentration gradient between the two phases, so we designate this technique a two-point measurement approach in the present review. The key parameter in this approach is the sediment-water distribution coefficient (K_d), and the diffusion flux can be estimated through Fick's First Law of Diffusion [37,38]:

$$F = \frac{D_w}{Z_w}\left(\frac{C_s}{K_d} - C_w\right) \tag{1}$$

where Z_w is the thickness of DBL, and C_s and C_w are chemical concentrations in sediment and overlying water, respectively. Here, D_w and Z_w can be obtained using empirical formulas [39], but K_d is commonly laboratory-calibrated, which is often inappropriate in field applications, as it is usually site-specific and chemical-dependent, resulting in several orders of magnitude difference in field-measured K_d values among different sediments [25,40]. In addition, measurements of C_s and C_w have often been conducted with active sampling, which has to collect large amounts of core sediment and water to achieve sufficient detection sensitivity. Subsequent extraction procedures are thereby laborious, time consuming and costly, thereby causing large uncertainties in quantitation [41,42]. Furthermore, active sampling often takes discrete grabs of spot samples, resulting in only snapshots of chemical concentrations at specific sampling-time points.

With the latest development of passive sampling techniques, direct determination of freely-dissolved chemical concentrations in sediment porewater and overlying water has greatly simplified the sampling procedures. This approach can obtain more reliable diffusion fluxes than the sediment-coring method, because the use of site-specific K_d and laborious active sampling procedures are no longer needed. In this approach, diffusion flux can be estimated by:

$$F = K_m(C_{pw} - C_w) \tag{2}$$

where C_{pw} is the freely-dissolved chemical concentrations in sediment porewater. Apparently, this approach is simple and easy to implement in field applications.

Passive sampling devices equipped with membrane materials are most widely used in the measurement of concentration-gradient-based diffusion fluxes (Table 2). For example, Cornelissen et al. [16] used several passive sampling materials [i.e., polyoxymethylene (POM) and polydimethylsiloxane (PDMS)] to measure PAH concentrations in sediment porewater and overlying water in Oslo Harbor, and the chemical-concentration ratio greater than 1 suggested that sediment might have been a source of PAHs. They also employed 17-μm POM as the sorbent material to measure fluxes of

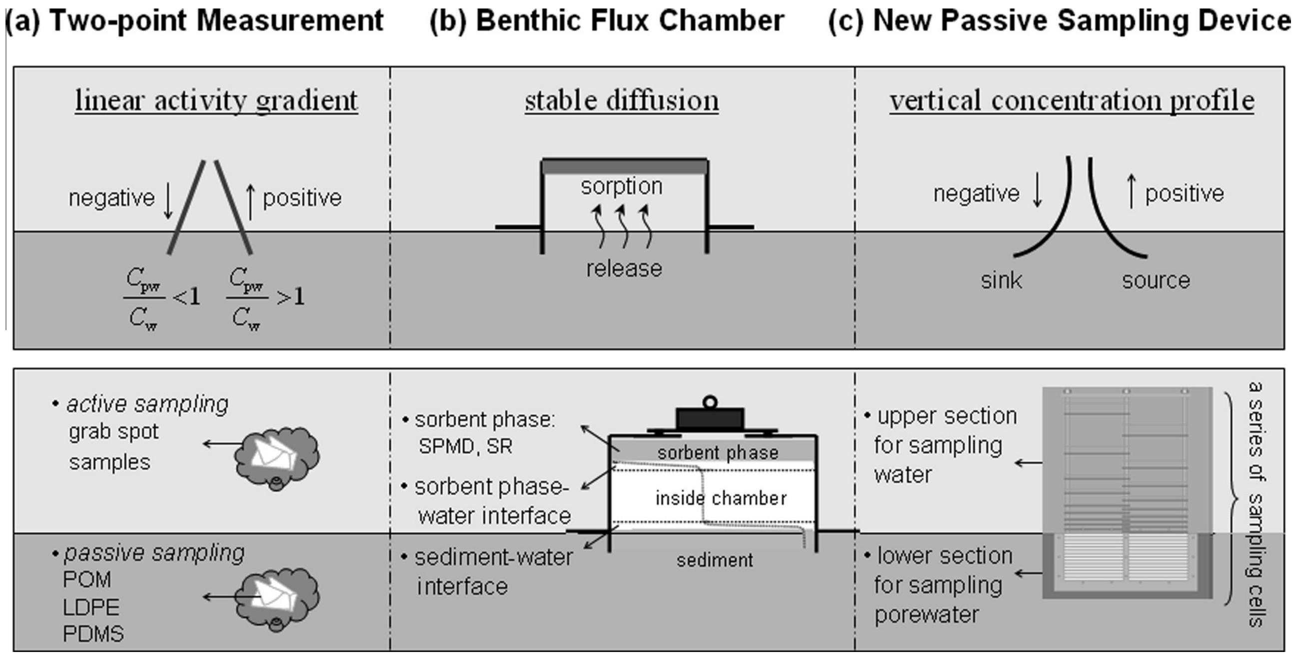

Fig. 1. Different techniques for measuring diffusion fluxes of chemicals across the sediment-water interface. The upper sections depict the underlying assumptions for the sampling techniques, whereas the lower sections display the schemes for applying the sampling techniques. POM, Polyoxymethylene; PDMS, Polydimethylsiloxane; LDPE, Low-density polyethylene; SPMD, Semi-permeable membrane device; SR, Silicon rubber.

Table 1
Comparison of three available techniques for measuring chemical-diffusion fluxes across the sediment-water interface

Item	Two-point measurement	Benthic flux chamber	New passive sampling device
Crucial assumption	Linear activity gradient	Constant and stable diffusion	Vertical concentration profile
Configuration	No needed with active sampling, membrane materials with passive sampling	A box-like box with infinite-sink sorbent being mounted onto the inside roof of the chamber	A integrated device with the upper and lower sections, and each section contains a series of sampling cells
Sorbent phase	No needed with active sampling, POM, LDPE or PDMS[a]	Semipermeable membrane devices, silicon rubber	Low-density polyethylene, other membrane materials
Conc. quantitation[b]	Taking discrete grabs of spot samples, or equilibrium sampling	——[c]	Kinetic sampling: sampling rate-calculation and PRC-calibration[d]
What measured	Concentrations of chemicals in overlying water and porewater	Amount of chemicals accumulated onto sorbent phase in chamber	Concentration profile of chemicals across the sediment-water interface
Key parameter	Distribution coefficient (K_d), or mass transfer coefficient (K_m)	Cross-section area of sediment (A_s), sampling time (t)	Profile-fitting parameter (a_1), diffusion coefficient (D_w)
Quantitative model	$F = \frac{D_w}{Z_w}\left(\frac{C_s}{K_d} - C_w\right)$ or $F = K_m(C_{pw} - C_w)$	$F = \frac{M_s}{A_s t}$	$F_s = -D_w C_0 a_1$
Advantage	Easy to implement, Easy to understand, Simplified with passive sampler	Simple, little interferences, Little disturbance to environment	Actual concentration profile, Little disturbance to environment Discern positive or negative flux
Disadvantage	Snapshot of concentration in spot sample, A linear concentration gradient, Site/Chemical-specific K_d (K_m)	Not suitable with sediment as a sink, Flux measurements at the sorbent phase-water interface rather than the sediment-water interface	Theoretical diffusion coefficient, Difficult to understand

[a] POM, Polyoxymethylene; LDPE, Low-density; PDMS, Polydimethylsiloxane.
[b] Conc., Concentration.
[c] Assuming the sorbent material is an infinite sink, the sorption rate is constant and the flux is calculated directly with the amount of chemicals accumulated onto the sorbent material.
[d] PRC, Performance reference compound.

PCDD/Fs and PCBs in the open Baltic Sea; in this case, the chemical-concentration ratios were around 1, suggesting the target chemicals nearly equilibrated between sediment and overlying water [18].

Koelmans et al. [9] obtained negative diffusion fluxes of PCBs in Ijmuiden Harbor, The Netherlands, using POM and silicone-rubber samplers, suggesting sediment as a sink of PCBs. Also, low-density polyethylene (LDPE) is a superior passive sampling material for determination of freely-dissolved chemical concentrations. It was employed in measurement of PCBs, PAHs, and HCB in sediment porewater and overlying water in Delfzijl Harbor [15] and PCBs in Narragansett Bay [8].

Table 2
Summary of available passive samplers and their field applications for measuring diffusion fluxes across the sediment-water interface

Passive sampler	Field exposure	Chemical	Applications
SPMD[a]	None	PCDD/Fs[e]	Evaluation of the effect of various capping materials on the sediment-to-water flux and bioaccumulation of chemicals [1]
SPMD and LDPE	South Basin	PCBs[f]	Investigation of active carbon-amendment effectiveness and possible adverse effects at a field scale [58]
SPMD	None	PCBs, PAHs, DDTs[g]	Investigation of the reduction of chemicals fluxes and bioaccumulation in a gastropod under the capping of sandy materials [59]
SPMD	None	PAHs, PCBs	Physicochemical tests for the reduction of chemicals fluxes under the capping of active carbon and coke [60]
SPMD-Chamber	Oslo Harbor	PAHs, PCBs	Determination of chemical fluxes and diffusion mass transfer coefficient across the sediment-water interface in filed [25]
PDMS-Chamber	Trondheim Harbor	PAHs[h]	A marine underwater field pilot study with different thin-layer capping materials for PAHs flux [44]
POM[b] and PDMS[c]	None	PCBs, PAHs, PBDEs[i]	Measurement of chemicals concentration in porewater and overlying water, and calculation of diffusion flux by Empore disks [9]
LDPE membrane	Delfzijl Harbor	PCBs, PAHs, HCB	Measurement of chemicals in porewater and overlying water by equilibration and kinetic passive sampling techniques [15]
POM and LDPE[d]	None	PAHs	Field testing of freely dissolved PAHs and their concentration ratios in porewater and overlying water by equilibrium passive samplers [16]
POM membrane	Baltic Sea	PCDD/Fs, PCBs	Determination of chemical concentrations and sediment-water concentration ratios for discerning the direction of diffusion flux [18]

[a] SPMD, Semi-permeable membrane device.
[b] POM, Polyoxymethylene.
[c] PDMS, Polydimethylsiloxane.
[d] LDPE, Low-density polyethylene.
[e] PCDD/Fs, Polychlorinated dibenzo-*p*-dioxins and -furans.
[f] PCBs, Polychlorinated biphenyls.
[g] DDTs, Dichlorodiphenyltrichloroethane and its metabolites.
[h] PAHs, Polycyclic aromatic hydrocarbons.
[i] PBDEs, Polybrominated diphenyl ethers.

3.2. Benthic flux chamber

The benthic flux chamber is a box-like device, designed to isolate a limited area of the sea-floor (sediment) together with a volume of overlying water (Fig. 1b and Table 1). In this approach, diffusion flux (F) is calculated from chemical mass (M_s) accumulated in an infinite-sink sorbent mounted on the inside roof of the chamber, i.e.:

$$F = \frac{M_s}{A_s t} \tag{3}$$

where A_s is the cross-section area of sediment covered by the chamber and t is the sampling time. This is a simple method, because it can directly measure chemical-diffusion fluxes without disturbing the sediment-water system and the use of site-specific K_d and variable K_m. Moreover, the closed space inside a chamber is not subject to interferences from hydrodynamic conditions and human activities, allowing chemicals to flow out of the sediment steadily.

This technique was once widely used in measuring fluxes of inorganic substances [31,43], and was gradually adopted in measurement of HOCs (Table 2). For example, Eek et al. [25] used SPMD and silicone-rubber sheet as sorbent materials in a chamber for deployment in Oslo Harbor's clayed-capped seabed and obtained fluxes of 0.3–1.6 $\mu g\ m^{-2}\ d^{-1}$ and 2–8 $\mu g\ m^{-2}\ d^{-1}$ for pyrene and PCB-52, respectively, which were consistent with results calculated from the concentration gradient between sediment porewater and overlying water.

Cornelissen et al. [44] also used a thick PDMS sheet as sorbent material to test the capping effectiveness of active carbon mixed with sand or clay in Trondheim Harbor. An active carbon-clay mixture was found to be the most effective capping material for sequestration of PAHs, with the flux reduction up to a factor of 10 compared to a reference field. Generally, the benthic flux chamber is suited to field measurement of diffusion fluxes with sediment as a source of chemicals, but unsuitable for measuring chemical fluxes from overlying water to sediment.

3.3. Main drawbacks

The two-point measurement approach is easy to implement, but also plagued with intrinsic drawbacks that may lead to large uncertainties in field-measured data, although the successful introduction of passive sampling techniques has significantly simplified sampling procedures. In the two-point measurement approach above [Equation (1)], the flux calculation requires the use of K_d for the target chemical under consideration. In addition, use of Equation (1) for flux measurement is based on the assumption of a linear concentration gradient for the diffusion zone, which is hardly satisfied in field applications [45,46]. The introduction of passive sampling techniques into the two-point measurement approach [Equation (2)] eliminates the use of K_d, but still assumes a linear chemical-concentration gradient between sediment porewater and overlying water.

However, the benthic chamber approach directly measures chemical-diffusion fluxes and is able to reduce interferences from hydrodynamic conditions and any short-term artificial disturbances. But, flux measurements with the benthic chamber approach are done at the sorbent-phase-water interface rather than the sediment-water interface [25]. As a result, large measurement errors are expected if the concentration gradients at these two interfaces are significantly different. Furthermore, the benthic chamber approach can determine only the magnitude of escaping fluxes from sediment under ideal conditions, but cannot discern the diffusion directions because the infinite-sink sorbent phase inside a chamber can uptake freely-dissolved chemicals from the enclosed space, driving sequestered chemicals out of sediment [25]. To obtain sufficient detection sensitivity, the cross-section area of a sorbent phase must be large enough to induce large amounts of chemicals to be released from sediment. In addition, although the benthic chamber approach has not been found to influence ebullition-facilitated flux [47], the vitality of benthic organisms inside the chamber may decrease after a few days under anaerobic conditions, thereby leading to a reduction in the bioturbation-driven release of chemicals [48].

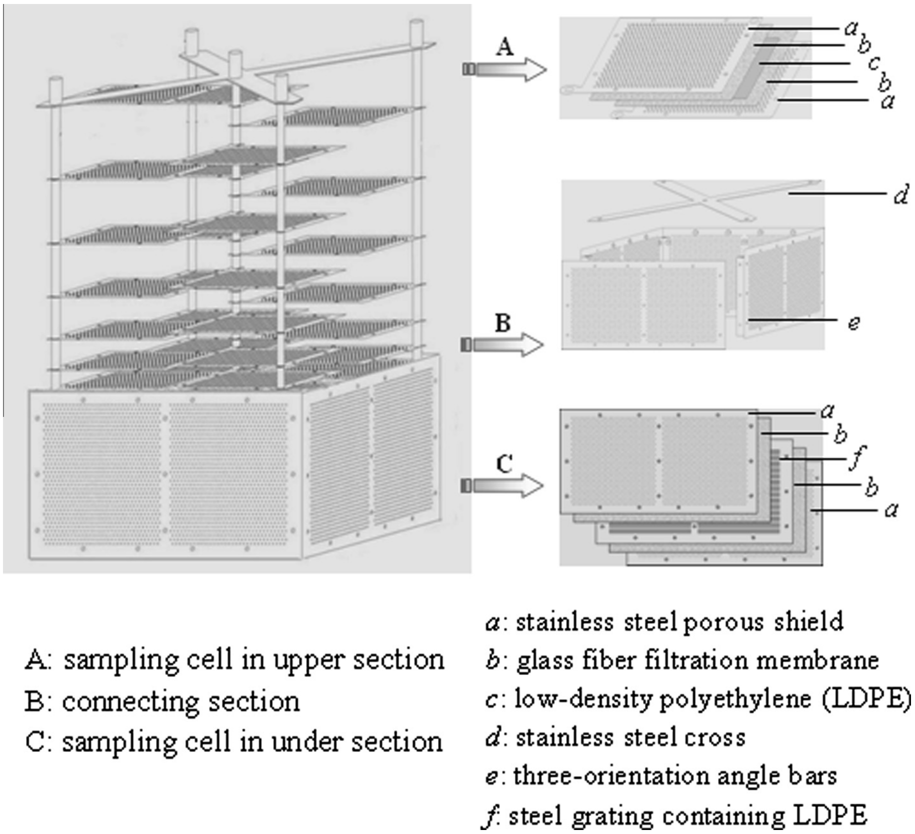

Fig. 2. Configuration of the new passive sampling device capable of measuring vertical concentration profiles of hydrophobic organic chemicals in sediment porewater and overlying water [49]. The left panel shows the sampling device, which includes two sections (i.e. the upper section for overlying water sampling and the lower section for sediment porewater sampling). The right panel shows the compositions (*a–f*) of the sampling cell (A and C) and the connecting section (B).

4. A new approach to passive sampling

4.1. Design and application

With the drawbacks of the currently available techniques, we recently designed a new passive sampling device capable of simultaneously measuring vertical concentration profiles of chemicals in overlying water and sediment porewater (Fig. 1c and Table 1), from which the magnitude and the direction of sediment-water diffusion fluxes can be determined using a mathematical model that we developed ourselves [49]. This sampling device employs LDPE as the sorbent phase, and glass-fiber filtration (GF/F) membranes and porous stainless-steel shields as the protective mechanism (Fig. 2). The mathematical model can be briefly described as follows. If C_w is the depth-dependent concentration of a target chemical at the depth of Z_w in overlying water, it can be expressed as a Taylor series, i.e.:

$$C_w = C_0(1 + a_1 Z_w + a_2 Z_w^2 + \ldots + a_n Z_w^n) \quad (4)$$

where C_0 is C_w or the porewater-chemical concentration at the sediment-water interface and a_i ($i = 1, 2, \ldots$, n) is a fitting parameter. Based on Fick's First Law of Diffusion, the diffusion flux (F_s) across the cross-section at Z_w is calculated by:

$$F_s = -D_w \frac{dC_w}{dZ} = -D_w C_0 (a_1 + 2a_2 Z_w + \ldots + n a_n Z_w^{n-1}) \quad (5)$$

At the sediment-water interface, $Z_w = 0$; hence, the diffusion flux in this case can be derived by setting $Z_w = 0$ in Equation (5):

$$F_s = -D_w C_0 a_1 \quad (6)$$

This passive sampling device has been successfully used to measure overlying water and sediment porewater concentration profiles of dichlorodiphenyltrichloroethane and its metabolites in a pilot laboratory testing and field application in an urbanized coastal region. The model-calculated fluxes were consistent with those acquired by solid-phase extraction/liquid-liquid extraction and a benthic chamber [49], suggesting that the sampling device is a powerful tool for measuring fluxes of HOCs across the sediment-water interface.

4.2. Quantitation method

Equilibrium sampling is the simplest, most widely-used approach, but equilibrium time is often too long for HOCs, thereby increasing the risk of biofouling and vandalism of deployed passive samplers, or degradation of sorbed chemicals. However, kinetically diffusion-controlled sampling methods are time saving and cost effective, with sampling time varying from days to weeks. Two kinetic calibration methods were therefore used with our passive sampling device to quantify chemical concentrations [i.e. sampling-rate (R_s) calculation and performance-reference-compound (PRC) calibration]. With the R_s-calculation method, the measured chemical concentration is a time-weighted average (TWA), i.e.:

$$C_w(\text{or } C_{pw}) = \frac{n_s}{R_s t} \quad (7)$$

where n_s is the chemical amount sorbed onto the sorbent phase (LDPE for the present device), and R_s is the sampling rate, which is a constant, if appropriate conditions are maintained. This can be done with a carefully-designed sampler configuration, such as a fiber-retracted device [50]. Alternatively, a diffusion layer can be manipulated so that the water-side boundary-layer diffusion is not the rate-limiting step, as for diffusive gradients in thin-film devices [51]. With our newly developed device, the experimental conditions for R_s measurement were prepared so as to simulate the field environment [i.e. the solution used for R_s measurement was spiked with humic acid (10 mg L^{-1}) and sodium chloride (30‰) and the testing temperature was maintained at 21 ± 2°C]. Although water flow was not controlled, the configuration of the passive sampling device was intended to mitigate the influences of water flow.

It should be noted that the R_s-calibration method is suitable for only the initial linear kinetic regime [52]. However, the PRC-calibration method introduced in 1991 [53] can be applied over a wider kinetic range. In this method, the passive sampler is preloaded with PRCs prior to deployment, and the chemical concentration can be determined by:

$$C_w = \frac{C_p}{(1 - e^{-k_e t})K_d} \tag{8}$$

where k_e is the exchange-rate coefficient obtained by desorption kinetics of PRCs and C_p is the chemical sorbed onto the sorbent phase. The main assumption with this approach is that the desorption rates of PRCs are identical to the uptake rates of the target chemicals. Hence, any variation in measured chemical concentrations under field conditions can be accounted for by the desorption kinetics of the PRCs [54,55]. Despite the initial success of the PRC-calibration technology, its intrinsic drawbacks have also been identified [56].

4.3. Rate-limiting steps in passive sampling

During the transfer of a chemical from an environment matrix to the sorbent phase, the rate-limiting step can occur at the sampler-water interface or at the sediment-porewater interface. With LDPE as the sorbent phase, our previous studies [49,57] demonstrated that LDPE is an ideal sorbent (i.e. uptake of a chemical by LDPE is so rapid that the chemical concentration can be maintained at nearly 0 at the sorbent surface). As a result, the concentration gradient between LDPE and the ambient environment is controlled by environmental concentration C_w or C_{pw}. Consequently, the rate-limiting step does not occur at the sampler-water interface.

Such a passive sampling device will deplete the target chemicals in field deployment. Subsequently, the chemicals must be rapidly compensated from the ambient environment, so the time (t_{eq}) for the chemicals to diffuse from the environmental matrix to the sampler to reach diffusion equilibrium is a crucial factor for discerning if the rate-limiting step occurs in bulk water or at the sediment-porewater interface. With sediment, the chemical concentration gradient within the diffusion layer is expressed as:

$$C'_{pw} = C_{pw}(1 - e^{-k'_e t}) \tag{9}$$

where C'_{pw} and C_{pw} are the chemical concentrations in the sampler cavity and ambient sediment porewater, which become C'_w and C_w for water sampling. k'_e is the exchange rate in the diffusion layer, where transport flux (F') can be calculated by Fick's First Law, i.e.:

$$F' = -D_w \frac{dC}{dZ} = \frac{1}{A}\frac{dm}{dt} \tag{10}$$

where Z is the diffusion layer length, A is the cross-section area of the sorbent phase, and m $(= C'_{pw}ZA)$ is the chemical amount being transported from sediment porewater to the sampler cavity. Combining Equation 9 and 10 yields:

$$k'_e = \frac{D_w}{Z^2} \tag{11}$$

From Equations 9 and 11, t_{eq} can be expressed as:

$$t_{eq} = -\frac{Z^2}{D_w}\ln(1 - x) \tag{12}$$

where x is the extent of equilibrium $(= \frac{C'_{pw}}{C_{pw}})$. In general, a value of x at 0.95 is assumed to represent the equilibrium state. Thus, chemical desorption from sediment would be a rate-limiting step within time t_{eq}, but it is not outside t_{eq}. With this sampling device and the analytes detected [49,57], t_{eq} was generally less than 24 h, much shorter than the sampling time (15 d), so the rate-limiting step should not occur at the sampler-water interface, and chemical-diffusion flux can be measured reliably.

4.4. Benefits and drawbacks

The uniqueness of this sampling device is characterized by its capability to obtain high-resolution concentration profiles, its robustness in field deployment, and its rapid sampling time {15 days, compared to 28 days with two-point measurement [9] and 28–44 days with the benthic chamber [25]}. The sampling device can also measure the mobility of HOCs in aquatic environments and examine if contaminated sediment acts as a source or a sink. In addition, this passive sampling device should also be applicable to the analysis of trace inorganic and hydrophilic organic compounds at the interfaces of air-water, air-soil and air-sediment, with minor modifications to the sorbent phase or configuration.

It should be recognized that D_w still needs to be laboratory-calibrated with the new sampling device [Equation (6)], which was only salinity-corrected in our study [49]. As described above, the transport of chemicals in overlying water is related to water viscosity and chemical molar volume, and related to sediment porosity and tortuosity in sediment porewater. D_w is therefore a comprehensive parameter integrating various physicochemical properties of the sediment-water system. Apparently, further improvements to diffusion-flux measurement may be made by incorporating a number of available techniques (e.g., Empore disks and laser Doppler anemometry) to obtain more accurate more robust D_w values.

5. Conclusions

The above discussions suggest that significant technological advances have been made in measurement of chemical diffusion flux, especially with the adoption of passive sampling techniques, although there is room for improvement. In the two point measurement approach, direct determination of freely-dissolved chemical concentrations in sediment porewater by passive sampling techniques has eliminated the use of K_d for calculating chemical concentrations in porewater concentrations from those in bulk sediment. The benthic chamber approach measures diffusion flux *in situ* without the assumption of the linear concentration gradient used in the two-point measurement approach, but it contains two main drawbacks (i.e. the diffusion flux is measured at the sorbent phase-water interface and its direction cannot be discerned). The new passive sampling device that we developed [49] measures diffusion flux at the sediment-water interface with no need to assume a linear concentration gradient, although the chemical-diffusion coefficient in overlying water still needs to be calibrated in the laboratory. After further improvements, this device could be a powerful tool for evaluating *in-situ* remediation efficiency and assessment of ecological risk.

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