Novel Passive Sampling Device for Measuring Sediment–Water Diffusion Fluxes of Hydrophobic Organic Chemicals

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Ⓢ Supporting Information

ABSTRACT: Molecular diffusion across the sediment–water interface, as one of the key geochemical processes, dictates whether a sediment is a source or sink of chemicals, providing useful data in designing remedial actions. Despite ample previous efforts in quantifying sediment–water diffusion fluxes, the resulting methods are largely unsatisfactory. Herein, we introduce a novel passive sampling device capable of measuring vertical profiles of chemical concentrations near the sediment–water interface, from which diffusion fluxes can be calculated based on a model that we developed. In laboratory testing, diffusion fluxes (0.032–310 ng m^{-2} d^{-1}) of dichlorodiphenyltrichloroethane and its metabolites obtained from the present sampling device were consistent with those (0.38–610 ng m^{-2} d^{-1}) determined by using a conventional active sampling

method, solid-phase extraction/liquid–liquid extraction. Field deployment of the sampling device yielded individual diffusion fluxes of p,p'-DDD, p,p'-DDE, p,p'-DDMU, o,p'-DDMU, p,p'-DDNU, and p,p'-DBP in the range of 5.9–150 ng m^{-2} d^{-1}, which were comparable to those (5.5–85 ng m^{-2} d^{-1}) obtained with a benthic chamber. Moreover, diffusion fluxes of p,p'-DDT and o,p'-DDT obtained with the sampling device were negative; i.e., the sediment is acting as a sink for these chemicals, while that could not be found using the benthic chamber. Thus, the passive sampling device can provide better information about the movement of chemicals through the sediment and overlying water for the choice of remedial strategies.
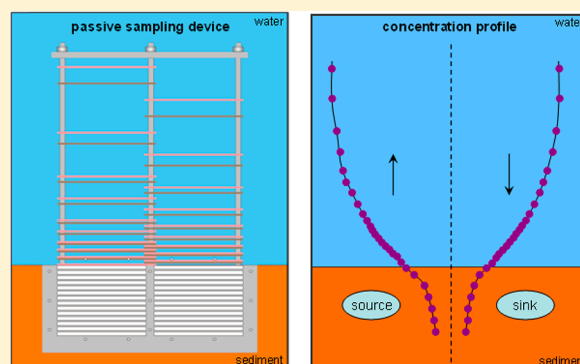
INTRODUCTION

Chemical residues of anthropogenic origin can be released into the environment through a variety of routes, such as atmospheric emission, wastewater discharge, and solid waste disposal.[1] Very often, these chemicals, especially hydrophobic organic chemicals (HOCs), find ways to enter aquatic environments and eventually sediments. Thus sediments have become a major reservoir of HOCs.[2,3] When exogenous inputs diminish, sequestered HOCs can be released from sediments via resuspension, molecular diffusion,[4] bioturbation,[5] gas ebullition,[6] tidal rush, etc., resulting in net fluxes from sediments to overlying water. Among these transport pathways, only molecular diffusion mainly involves the freely dissolved chemicals and is a direct reflection of the chemical fugacity difference between the two phases.[7,8] In this regard, the direction and magnitude of diffusion fluxes across the sediment–water interface are vital parameters for discerning whether a sediment acts as a source or sink of chemicals.

To date, two approaches have been used to determine sediment–water diffusion fluxes of HOCs.[7–9] The first approach is based on the assumption of a linear concentration gradient of HOCs between sediment porewater (C_{pw}) and

overlying water (C_w), and diffusion flux (F) can be calculated by $F = K_m(C_{pw} - C_w)$, with K_m being the sediment–water mass transfer coefficient.[7,8] The K_m values are currently available only for a selected group of chemicals,[4,10,11] and field-measured data are extremely limited.[12] In addition, chemical concentrations have often been determined at one single point or depth in the sediment and overlying water; such measurements are not representative of the actual concentration profiles through the sediment–water interface. The second approach involves deployment of a benthic chamber onto the surface sediment to directly measure sediment–water diffusion fluxes without disturbing the sampling system, where $F = M/(A \cdot t)$, with M being the chemical mass accumulated by a sorbent phase within the chamber, A the cross-section area of the sorbent phase, and t the sampling time.[9,13,14] The main deficit of this approach is that measurements are done at the sorbent phase–water interface rather than the sediment–water interface,[9] which may

A: Upper section for sampling overlying water
B: Connecting section
C: Lower section for sampling sediment porewater

a: Stainless steel porous shield
b: Glass fiber filtration membrane
c: Low-density polyethylene film
d: Stainless steel cross
e: Support pillar
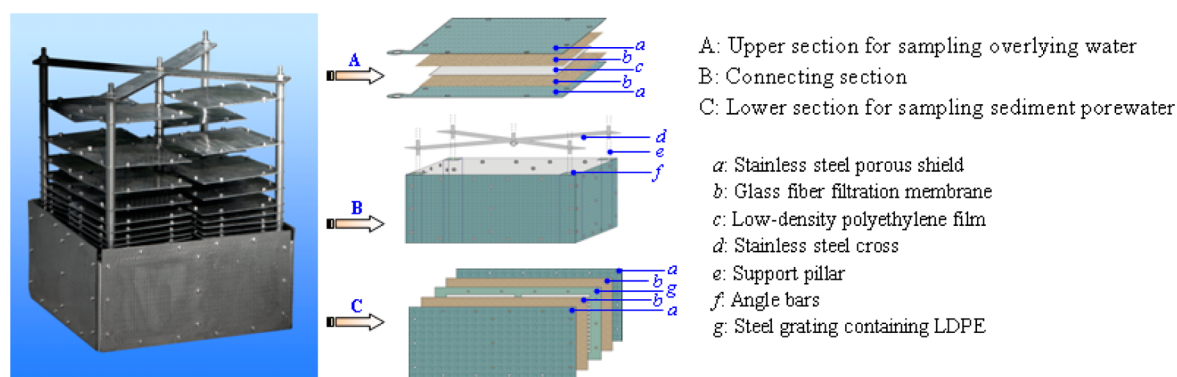f: Angle bars
g: Steel grating containing LDPE

Figure 1. Configuration of the passive sampling device. It consists of an upper section (horizontal sampling cells) for overlying water sampling and a lower sediment section (vertical sampling cells) for sediment porewater sampling; these two sections are connected by a stainless steel cross, angle bars, and some screw-nuts.

result in large uncertainty if the concentration gradients at the two interfaces are considerably different. In addition, the benthic chamber method determines only escaping fluxes from sediment; worse yet the sorbent phase can drive sequestered chemicals out of sediment in the enclosed space, inflating the measured fluxes.[9] It is noted that Lampert et al.[15] used individual polydimethylsiloxane-coated fibers to measure the vertical concentration profiles of HOCs in both sediment and overlying water, but their goal was to evaluate the contaminant migration rates through thin-layer sand caps with a simple flux model.

Herein we present a novel passive sampling device (Petition No. for Patent Cooperation Treaty: PCT/CN2013/070256) with low-density polyethylene (LDPE) as the sorbent phase, capable of measuring vertical concentration profiles of HOCs on both sides of the sediment−water interface. A mathematical model was developed to calculate diffusion fluxes from measured concentration profiles across the interface. This sampling device was subject to a series of tests to demonstrate its reliability and robustness, with comparison to two active sampling techniques, i.e., solid-phase extraction/liquid−liquid extraction (SPE-LLE) and benthic chamber, in laboratory verification and field validation, respectively. Target HOCs include p,p'-DDT, o,p'-DDT, p,p'-DDD, p,p'-DDE, p,p'-DDMU, o,p'-DDMU, p,p'-DDNU, and p,p'-DBP (Supporting Information Table S1), the sum of which is defined as DDXs.

SAMPLING DEVICE DESIGN AND CONFIGURATION

The sampling device (Figure 1) consists of two sections, intended for sampling overlying water and sediment porewater, respectively, and they are connected with a stainless steel cross and four pieces of stainless steel angle bars. Each section contains a series of sampling cells, and each sampling cell embraces a LDPE strip wrapped by glass fiber filtration (GF/F) membranes and outfitted with porous stainless steel shields. With this protective mechanism, target chemicals are allowed to freely penetrate through the porous shield and GF/F membrane and diffuse into the LDPE phase, while particles and benthos are kept out of the sampling device. Moreover the effect of water turbulence on chemical mass transfer is somewhat mitigated, as a result of the small apertures on porous stainless steel shields and GF/F membrane with pore sizes of 1000 and 0.7 μm, respectively.

In the upper section with a height of 20 cm, the sampling cells are horizontally in a spiral arrangement to facilitate water

flow and mounted on a central support pillar and four lateral support pillars isolated by stainless steel spacers of different thicknesses. The interval between two adjacent sampling cells decreases from top to bottom, i.e., 20.00, 15.04, 11.04, 8.04, 6.54, 5.04, 3.74, 3.04, 2.29, 1.87, 1.70, 1.53, 1.36, 1.19, 1.02, 0.85, 0.68, 0.51, 0.34, and 0.17 cm, and these intervals can be adjusted as needed using different-sized spacers.

In the lower section, the sampling cells are arranged vertically to minimize disturbance to sediment when deployed. This section is composed of four parts, interlinked by angle bars into a square hollow box with the bottom side uncovered. In each part, the sampling cells containing LDPE strips share the same GF/F membrane and stainless steel porous shield. The sandwiched LDPE strips (0.5 cm width) are isolated by stainless steel grating panels at an identical interval of 0.2 cm. In the present study, only seven sampling cells were used, with the midpoints representing distances at 0.25, 0.95, 1.65, 3.05, 5.15, 7.25, and 9.35 cm from the connection between the upper and lower sections.

Laboratory testing demonstrated that stainless steel shields and GF/F membranes used in the passive sampling device did not sorb significant amounts of the target chemicals.[16] Detailed cleaning and preparation procedures for assembly of the sampling device are presented in Supporting Information Text S1.

THEORETICAL CONSIDERATIONS

Quantitation of Chemical Concentrations. Two quantitation methods were employed with the sampling device to determine chemical concentrations. The first method is based on the concept of "zero sink" (Supporting Information Text S2), which assumes that the chemical diffusing to the surface of the sorbent phase is immediately dragged into the interior so that its concentration at the sorbent surface can be regarded as zero.[17,18] This is an essential prerequisite for the derivation of time-weighted average concentration from Fick's First Law of Diffusion (Supporting Information Text S3). For the LDPE phase in the sampling device, use of Fick's First Law of Diffusion to describe the transport of a chemical diffusing into LDPE leads to

$$\overline{C_w} = \frac{n_{LDPE}}{R_s t} \tag{1}$$

where $\overline{C_w}$ is the time-weighted average (TWA) chemical concentration, n_{LDPE} is the chemical mass sorbed onto the

LDPE phase, R_S is defined as sampling rate, and t is the sampling time. The key to the successful application of this method is to accurately determine R_s,[19,20] which can be obtained experimentally and from theoretical derivation (Supporting Information Texts S4 and S5).

The second quantitation method is based on the use of performance reference compounds (PRCs; Supporting Information Text S6).[21] This method assumes that dissipation of PRCs, preloaded onto LDPE prior to sampling, is synchronous with uptake of the target chemicals. A first-order diffusion model is used to describe the exchange of a chemical between LDPE and water.[22] In this case, the chemical concentration C_w in water is expressed as

$$C_w = \frac{C_{\text{LDPE}}}{f_{\text{lost}} K_{\text{pw}}} \qquad (2)$$

where C_{LDPE} is the chemical concentration in LDPE after exposure time t, K_{pw} is the partition coefficient of the chemical between LDPE and water, and f_{lost} is the fraction of PRCs lost upon exposure, which represents the extent of equilibrium reached for the target chemical. Considering a typical instrumental analytical uncertainty of approximately 20%, the fraction of PRCs lost is normally maintained within 20−80%. It should be noted that if PRC-calibrated concentrations are obtained within the linear kinetic regime,[23,24] the concentrations are also time-weighted average values; otherwise, it is a time-integrated concentration rather than a TWA one.

Development of Flux Model. The key step in a successful application of the passive sampling device is to derive sediment−water diffusion fluxes from measured concentrations obtained with R_s-calculation or PRC-calibration methods. If the concentration of a target chemical at the depth of Z_w in overlying water is designated as C_w, this depth-dependent concentration can be expressed as a Taylor series, i.e.,

$$C_w = C_0(1 + a_1 Z_w + a_2 Z_w{}^2 + ... + a_n Z_w{}^n) \qquad (3)$$

where C_0 is the chemical concentration at the sediment−water interface ($Z_w = 0$) where the overlying water and sediment porewater concentrations converge and a_i ($i = 1, 2, ..., n$) is a fitting parameter. Hence, the diffusion flux (F_s) at the sediment−water interface is calculated by

$$F_s = -D_w \frac{dC_w}{dZ_w} = -D_w C_0 a_1 \qquad (4)$$

Apparently, F_s is an instantaneous flux. In reality, chemical concentrations are determined for a given time period with the passive sampling device. To be consistent with the above-described methods for quantifying chemical concentrations, time-weighted average is applied to both sides of eq 4, i.e.,

$$\overline{F_s} = -D_w C_0 \overline{a_1} \qquad (5)$$

In deriving eq 5, C_0 is assumed to be independent of time, which is reasonable as sediment is effectively an infinite reservoir of the target chemical. In this case, the chemical concentration in sediment porewater remains constant for the sampling period.

On the other hand, the depth profile of TWA chemical concentrations ($\overline{C_w}$) obtained with the passive sampling device can also be expressed as a Taylor series:

$$\overline{C_w} = \overline{C_0}(1 + a_1' Z_w + a_2' Z_w^2 + ... + a_n' Z_w^n) \qquad (6)$$

where $\overline{C_0} = C_0$ by definition and a_1' ($i = 1, 2, ..., n$) is a fitting parameter. Consequently, TWA sediment−water diffusion flux ($\overline{F_s}$) can be derived as

$$\overline{F_s} = -D_w C_0 a_1' \qquad (7)$$

In eq 5, $\overline{a_1}$ is the TWA value of all a_1 fitted from a depth profile of instantaneous concentrations and can be explained as

$$\overline{a_1} = \frac{1}{Z_w t} \int \ln \frac{C_w}{C_0}\, dt = \frac{1}{Z_w}\left(\frac{1}{t} \int \ln C_w\, dt - \frac{1}{t} \ln C_0 \right) \qquad (8)$$

On the other hand, a_1' in eq 7 is the fitting value from a depth profile of TWA concentrations and can be explained as

$$a_1' = \frac{1}{Z_w} \ln \frac{\frac{1}{t} \int C_w\, dt}{C_0} = \frac{1}{Z_w}\left(\ln \frac{1}{t} \int C_w\, dt - \frac{1}{t} \ln C_0 \right) \qquad (9)$$

A comparison of $\overline{a_1}$ and a_1' (Supporting Information Text S7) yields

$$\lim_{Z_w \to 0}\left(\frac{\overline{a_1}}{a_1'} \right) = \lim_{Z_w \to 0}\left(\frac{\frac{1}{Z_w}\left(\frac{1}{t} \int \ln C_w\, dt - \frac{1}{t} \ln C_0 \right)}{\frac{1}{Z_w}\left(\ln \frac{1}{t} \int C_w\, dt - \frac{1}{t} \ln C_0 \right)} \right)$$

$$= \lim_{z \to 0}\left(\frac{\lim_{n \to \infty}\left(\frac{1}{n} \sum_{j=1}^{n} \ln C_j \right) - \frac{1}{t} \ln C_0}{\ln\left(\lim_{n \to \infty} \frac{1}{n} \sum_{i=1}^{n} C_i \right) - \frac{1}{t} \ln C_0} \right)$$

$$\approx 1 \qquad (10)$$

Therefore, measured a_1' by the passive sampling device is equivalent to theoretically derived $\overline{a_1}$; i.e., eqs 5 and 7 can be interchangeably used in determination of sediment−water diffusion fluxes in field applications of the passive sampling device.

■ MATERIALS AND METHODS

Materials. Individual target analytes, surrogate standards (PCB-67 and PCB-191), and internal standard (PCB-82) were purchased from AccuStandard (New Haven, CT). Three deuterated compounds (p,p'-DDT-d$_8$, p,p'-DDE-d$_8$, and p,p'-DDD-d$_8$) were used as PRCs and were purchased from C/D/N Isotopes (Quebec, Canada). Other consumables are described in Supporting Information Text S1.

Low-density polyethylene sheets (50-μm film thickness) were purchased from TRM Manufacturing (Corona, CA). Before use, LDPE sheets were cut into appropriate slices (80 mm ×80 mm) or strips (5 mm × 90 mm), precleaned by extraction in dichloromethane (DCM) for 48 h, in methanol for 24 h, and in purified water for 24 h, and soaked again in purified water immediately prior to use in order to minimize possible air contamination. When PRCs were used for quantitation, precleaned LDPE slices/strips were immersed in a methanol:water (80:20 in volume) solution spiked with the PRCs at 20 μg L^{-1} for 10 d. The PRCs-loaded LDPE were rinsed with purified water, wrapped with cleaned aluminum foil, and frozen until use. In addition, three pieces of loaded LDPE were processed to determine the initial PRCs concentrations, whereas three other slices/strips were used as field blanks to monitor any external interference during deployment.

Laboratory Verification. Laboratory verification of the sampling device was conducted with a sediment−water

Table 1. Sediment−Water Diffusion Fluxes (F; ng m^{-2} d^{-1}) of DDXs Acquired with the Present Passive Sampling Device and by Active Sampling Methods

chemical	laboratory verification		field validation at Site A				field validation at Site B			
	$\overline{F_s}^a$	F_L^b	$\overline{F_s}^a$	$\overline{F_p}^c$	F_c^d	F'^e	$\overline{F_s}^a$	$\overline{F_p}^c$	F_c^d	F'^e
p,p'-DDT	150 ± 6.1	310 ± 21	−140	−80	75	1.1	−75	−45	51	0.82
o,p'-DDT	27 ± 3.2	45 ± 2.6	−23	−18	11	−1.5	−14	−9.8	10	−0.47
p,p'-DDD	310 ± 25	610 ± 20	150	110	85	336	85	89	64	171
p,p'-DDE	97 ± 3.8	110 ± 5.1	93	72	63	93	75	65	46	68
p,p'-DDMU	25 ± 2.0	21 ± 0.8	10	9.3	8.4	16	5.9	6.9	5.5	6.5
p,p'-DDNU	200 ± 9.3	490 ± 22	49		22	41	28		16	15
p,p'-DBP	240 ± 17	560 ± 17	59		31	36	31		25	28
o,p'-DDMU	0.032 ± 0.0091	0.38 ± 0.012								

^{a}Obtained with the passive sampling device (Figure 1) from sampling rate-calibrated concentration profiles. ^{b}Obtained with a solid-phase extraction/liquid−liquid extraction method using $F_L = m_L/(A \cdot t)$, where m_L is the total chemical amount released into overlying water during exposure time of t. ^{c}Obtained with the passive sampling device from performance reference compounds−calibrated concentration profiles. ^{d}Obtained with a benthic chamber (Supporting Information Figure S3). ^{e}Calculated with the activity model, $F' = (D_w/\delta) \cdot (C_{pw} - C_w)$.

microcosm in a 42-L glass jar (W 30 × L 40 × H 35 cm), containing a 12-cm layer of marine sediment and a 23-cm layer of self-prepared solution (Supporting Information Figure S1). The sediment was collected from a DDXs heavily polluted area and sieved with a 20-mesh screen to remove large particles and shells, and the solution was prepared with 10 mg/L humic acid and 3% sodium chloride. Before a sampling device was placed into each jar, the system was allowed to sit for 3 d until particles in overlying water completely settled. Then the jars were sealed and shielded from light under static condition at 21 ± 2 °C. All sediment−water microcosms with sampling devices were performed in triplicate, and the sampling time was 20 d. Meanwhile, SPE-LLE was also used to measure diffusion fluxes in another three identical microcosms with no sampling devices present (detailed in Supporting Information Text S8). Thus the flux values were presented as average ± standard deviation. It should be noted that the PRC-calibration method was not appropriate in laboratory verification, because water flow in the microcosm was insufficient to drive significant amounts of PRCs out of LDPE, and a reuptake may have even occurred;[3] therefore only the R_s-calculation method was used for quantitation.

Field Validation. Field validation of the sampling device was conducted at two sites in Hailing Bay, an urbanized coastal region of South China (Supporting Information Figure S2), on July 24−August 8, 2012. Our previous studies have found abundant levels of DDXs in both sediment and water in this region, with p,p'-DDD, an anaerobic reductive product of p,p'-DDT, as the predominant constituent.[25−28] At each site, two sampling devices were placed onto the seafloor and kept steady horizontally, in which one sampling device with PRCs loaded and one without were deployed approximately 2 m apart. A benthic chamber (W 21 × L 26 × H 20 cm; Supporting Information Figure S3), containing a large sampling cell (LDPE slice in 203 mm × 254 mm; 2.47 g) mounted to an interior roof, was also deployed at each site to directly determine the fluxes of DDXs from sediment. The flux (F_c) of a chemical measured by a benthic chamber can be calculated by $F_c = m_c/A_s t$, with m_c being the chemical mass sorbed onto LDPE and A_s the area of sediment covered by the chamber.

One sampling device and one benthic chamber attached to a mooring were anchored by two concrete bricks at each site. All sampling devices and chambers were retrieved after 15 d and transported with ice to the laboratory where they were

disassembled immediately and loaded LDPE slices/strips were extracted.

Extraction of Low Density Polyethylene and Water/Porewater Samples. At each sampling time point, loaded LDPE slices/strips were rinsed with purified water and extracted consecutively with 100 mL of DCM for 24 h and 100 mL of hexane for 24 h. For determination of sampling rate in water, the solution after exposure experiments was transferred to a 2-L separatory funnel and liquid−liquid extracted three times with 100, 80, and 60 mL of DCM, respectively. For determination of sampling rate in sediment, the sediment was centrifuged three times for 5 min each at 3500 rpm or RCF 1848g, and the supernatants were combined and filtrated to remove fine particles. The filtrated porewater was liquid−liquid extracted three times with 50, 30, and 20 mL DCM, respectively. Surrogate standards PCB-67 and PCB-191 were added to all samples prior to extraction. Each extract was concentrated to 100 μL with the procedures detailed in Supporting Information Text S8.

Instrumental Analysis. Analyte concentrations were determined with a Shimadzu 2010 gas chromatograph coupled with a QP 2010 plus mass spectrometer, using electron ionization in the selected ion monitoring mode. Detailed instrumental procedures and quality assurance and quality control results are presented in Supporting Information Texts S9 and S10, respectively.

■ RESULTS AND DISCUSSION

Measured Sampling Rate. Sampling rate R_s was determined in laboratory experiments using a NaCl/HA mixed solution and marine sediment as the water and sediment calibration systems, respectively. Within 25 d of exposure, n_{LDPE}/C_w increased linearly with increasing exposure time t (Supporting Information Figure S4) with excellent correlations for all target chemicals ($r^2 = 0.99$; Supporting Information Table S2), indicating that 25-day exposure was valid for sampling during the linear kinetic regime[24] for all target chemicals. Thus, all concentrations calculated with R_s were TWA values.

In addition to laboratory calibration, R_s can also be estimated from empirical diffusion coefficients in water (D_w)[29,30] corrected for salinity at 20 °C (Supporting Information Text S5). With the NaCl/HA solution, experimentally determined sampling rates ($R_{experimental}^{water}$) of the target chemicals ranged from 0.064−0.11 L d^{-1}, similar to empirically derived ones ($R_{empirical}^{water}$;
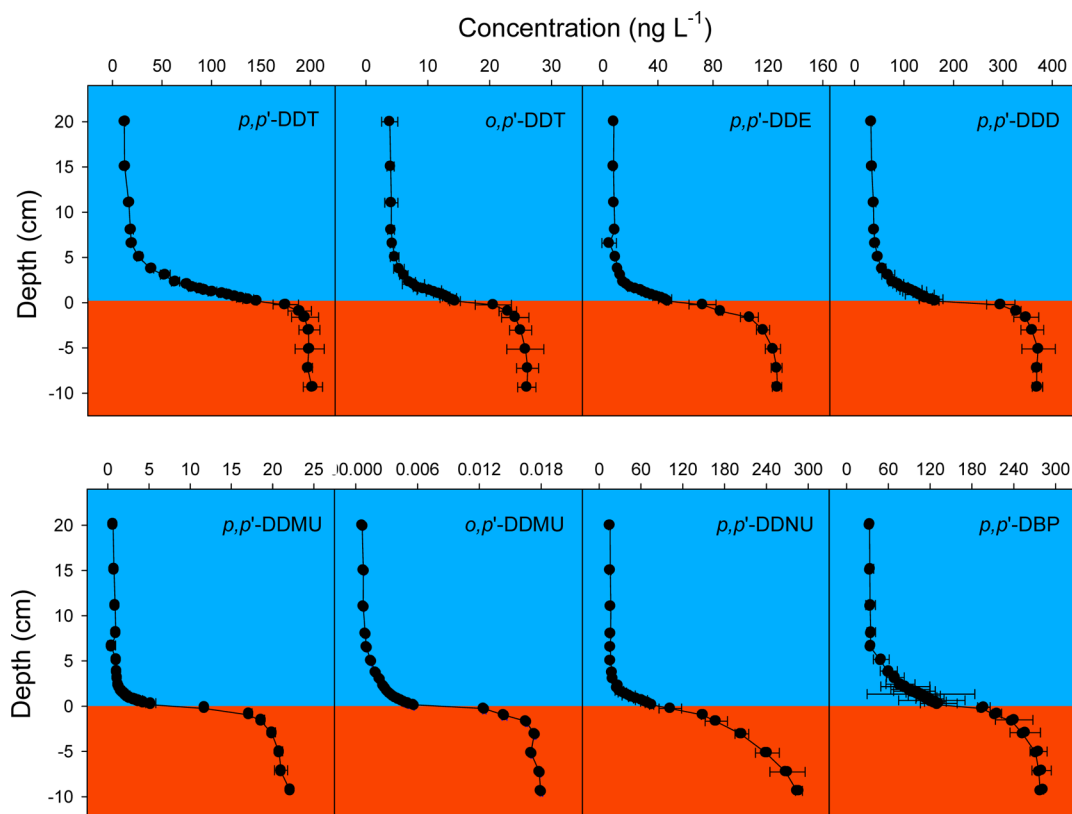
Figure 2. Vertical profiles of sampling rate (R_s)-calculated concentrations of DDXs obtained with the passive sampling device in laboratory sediment−water microcosms. Herein, DDXs include p,p'-DDT, o,p'-DDT, p,p'-DDD, p,p'-DDE, p,p'-DDMU, o,p'-DDMU, p,p'-DDNU, and p,p'-DBP. The sampling time was 20 days, and three parallel systems were set up at 21 ± 2 °C. The blue and brown portions represent overlying water and sediment, respectively.

0.089−0.12 L d^{-1}) (paired t-test; $p = 0.33$; Supporting Information Table S3). In addition, the experimentally determined sampling rates ($R_{experimental}^{sediment}$) with the sediment system ranged from 0.019−0.036 L d^{-1}, well within the minimum (0.018−0.025 L d^{-1}) and maximum (0.038−0.053 L d^{-1}) empirical values estimated with sediment porosities of 0.4 and 0.9,[31,32] respectively (Table 1). These experimentally determined sampling rates were used in subsequent tests.

Laboratory Verification Results. The R_s-calculated concentrations of all target chemicals in overlying water decreased exponentially with increasing distance from the sediment−water interface (Figure 2), documenting the diffusion of the target chemicals from sediment to overlying water. Moreover, concentrations of the target chemicals in sediment porewater showed a decreasing trend toward the sediment−water interface, consistent with the escaping tendency. The profiles in overlying water were fitted with eq 6, with the fitting parameters summarized in Supporting Information Table S4. Apparently, the good correlation coefficients ($r^2 = 0.95$−0.99) confirmed the dependability of the flux model. In addition, the a_1' values varied in a small range, i.e., from −0.72 to −0.16 cm^{-1} for all DDX components, suggesting similar diffusion kinetics for all the target chemicals. On the other hand, C_0 values varied widely from 0.043 to 200 ng L^{-1}, attributable to the significantly different levels of the target chemicals in the sediment. As a result, diffusion fluxes calculated with eq 7 were mainly dictated by chemical concentrations in sediment porewater.

The measured TWA diffusion fluxes ranged from 0.032 to 310 ng m^{-2} d^{-1}, with p,p'-DDD and o,p'-DDMU being the

most and least released components, respectively (Table 1). These values were consistently (except for p,p'-DDMU) smaller than those obtained with the SPE-LLE method (0.38−610 ng m^{-2} d^{-1}; Table 1), probably because the microcosm did not satisfy the nondepletive condition during the sorption process. An assessment of the depletion conditions using the actual experimental parameters (Supporting Information Text S11) showed that ratios of the masses sorbed by LDPE and released from the sediment for all the target analytes were in the range of 0.18−0.73 (Supporting Information Table S5), exceeding the widely accepted threshold of 0.05 (or 5%) for the nondepletion criterion.[33,34] Another source of difference could be the large variability in dissolved organic carbon (DOC)−water partition coefficient (K_{DOC}) used in the SPE-LLE method (Supporting Information Text S8). Generally, K_{DOC} varies greatly with the compositions and sources of DOC and may result in up to an uncertainty range of a factor of 2.5 in chemical concentrations.[35,36] In addition, it should be noted that only freely dissolved chemicals can be sensed by LDPE. Because of possible losses of target chemicals due to complexation with dissolved organic matter, sorption to glass wall and other unknown mechanisms, diffusion fluxes of the target chemicals may have been underestimated by the sampling device. Nevertheless, the diffusion fluxes obtained with the sampling device and SPE-LLE method were within the same order of magnitude, validating the ability of the sampling device to measure sediment−water diffusion fluxes of target chemicals in laboratory experiments.

Field Validation Results. The chemical concentrations from field validation were quantified by the R_s-calculation (eq
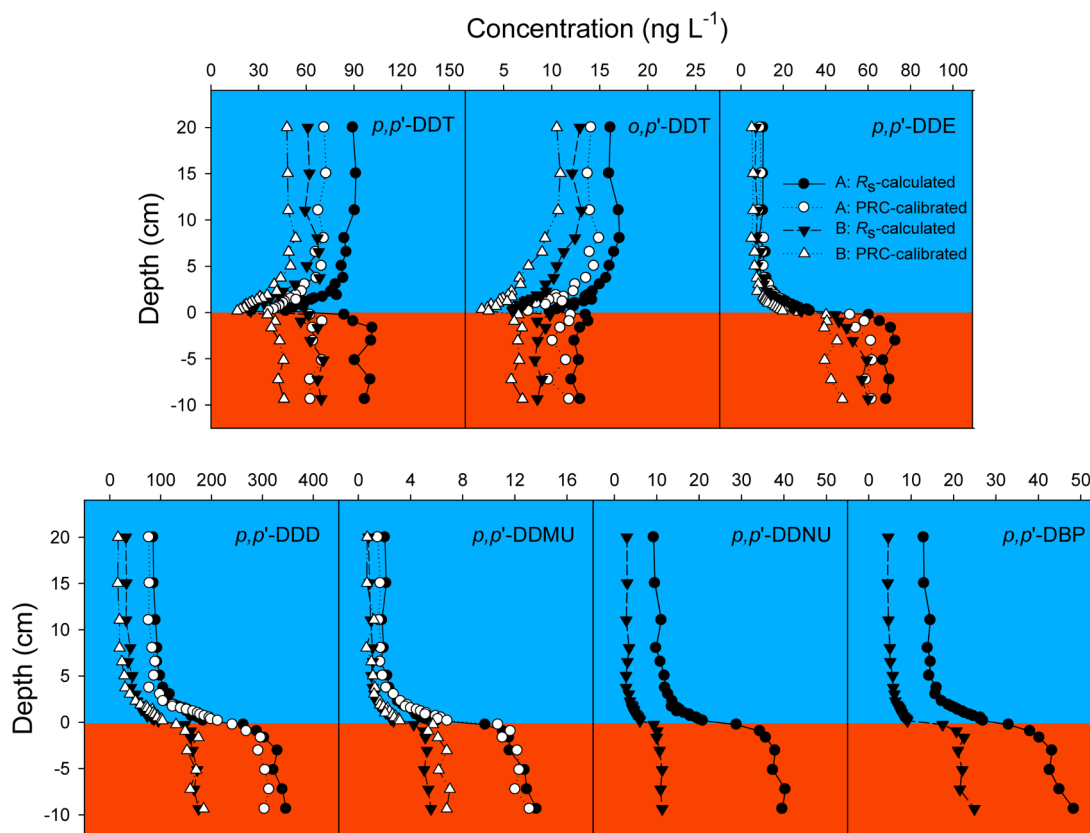
Figure 3. Field-measured vertical concentration profiles of DDXs by the passive sampling device; quantitation was performed with the sampling rate (R_s)-calculation and performance reference compounds (PRC)-calibration methods. Herein, DDXs include p,p'-DDT, o,p'-DDT, p,p'-DDD, p,p'-DDE, p,p'-DDMU, p,p'-DDNU, and p,p'-DBP. Field deployment of the passive sampling device was conducted at two sites (A and B) in Hailing Bay of South China (Supporting Information Figure S2). The blue and brown portions represent overlying water and sediment, respectively.

1) and PRC-calibration (eq 2) methods. As shown in Figure 3, PRC-calibrated concentrations were slightly lower (ca. 0−30 ng L⁻¹) than those R_s-calculated. Because K_{pw} may vary by a factor of 2, resulting in an uncertainty range of a factor of 2 for C_w,[37,38] the field measured concentrations by these two methods were deemed comparable with each other.

In general, chemical concentrations in both sediment porewater and overlying water of site A were greater than those of site B, probably because site A is closer to the fishing boat maintenance facility, which has been suggested to be an important source of sediment DDXs.[27,39] The concentration profiles of the target chemicals (Figure 3) were consistent with the presence of new input sources in the area and the biodegradation pathways of DDT.[16,25,27] Briefly, the concentrations of p,p'-DDD, p,p'-DDE, p,p'-DDMU, o,p'-DDMU, p,p'-DDNU, and p,p'-DBP, metabolites of p,p'-DDT or o,p'-DDT, in overlying water all sharply decreased outward the sediment−water interface, indicating the sediment as a source of these chemicals. On the other hand, the profiles of overlying water p,p'-DDT and o,p'-DDT, initially present in input sources (i.e., antifouling paint residues), exhibited apparent decreasing trends toward the sediment−water interface. The average ratio of o,p'-DDT versus p,p'-DDT was 0.19 and 0.18 at Site A and Site B, respectively, comparable to those (0.20−0.32) in antifouling paint products, values that we previously acquired in the same region.[25,27] These results showed a strong signal of new inputs of DDTs to the sampling area, despite the official ban on their agriculture use in China since 1983.[40]

The R_s-calculated and PRC-calibrated concentration profiles were used to demonstrate the utility of the sampling device in measuring diffusion fluxes using eq 7, in comparison with the results acquired with the benthic chamber (Supporting Information Figure S3). The values of a_1' ranged from −3.3 to 0.85 cm⁻¹ and C_0 from 3.5 to 230 ng L⁻¹ for all target chemicals (Supporting Information Table S4). The resulting diffusion fluxes (−140 to 150 ng m⁻² d⁻¹) by R_s-calculation were slightly greater than those (−80 to 110 ng m⁻² d⁻¹) by PRC-calibration, but paired t-test indicated that the two data sets were not significantly different ($p = 0.90$; Table 1). In addition, benthic chamber measurements obtained diffusion fluxes of 8.4−85 ng m⁻² d⁻¹ at site A and 5.5−64 ng m⁻² d⁻¹ at site B for the target chemicals. These benthic chamber measured fluxes were all positive, inconsistent with the negative values (from −140 to −9.8 ng m⁻² d⁻¹) for o,p'-DDT and p,p'-DDT obtained by the sampling device (Table 1). Clearly, the benthic chamber failed to capture the chemicals from current input sources. For other target chemicals, diffusion fluxes (5.5−85 ng m⁻² d⁻¹) acquired with the benthic chamber were slightly lower than those (5.9−150 ng m⁻² d⁻¹) obtained with the sampling device but were well correlated with each other ($y = 0.61x$; $r^2 = 0.94$ and $p < 0.01$; Supporting Information Figure S5). Lower flux values by the benthic chamber may have resulted from the thicker diffusion boundary layer inside the chamber than outside, because of retarded water flows inside the enclosed space.[9] Nevertheless, the flux values obtained by the two sampling methods were within the same order of magnitude, thus cross-validating each other.

Alternatively, flux values were also calculated with a traditional concentration activity model $F' = (D_w/\delta)(C_{pw}' - C_w')$,[7,8,41,42] where D_w values are summarized in Supporting Information Table S1; δ, length of the diffusion boundary layer, is designated as the distance between the sediment−water interface and a specific point in overlying water, where the change of diffusion flux with depth is the lowest; and C_{pw}' and C_w' are the chemical concentrations in sediment porewater just below the sediment−water interface and in overlying water just above the diffusion boundary layer (Supporting Information Table S6). The flux values thus calculated for the metabolites of DDT were generally in good agreement with those obtained with the passive sampling device and benthic chamber (Table 1). However, the flux values of p,p'-DDT and o,p'-DDT obtained by the activity model were substantially different from those by the sampling device (Table 1), which was probably attributed to the disconnection between the chemical concentrations in overlying water and sediment (Figure 3).

Overall, the field deployment results demonstrated that the passive sampling device is able to obtain sediment−water diffusion fluxes of HOCs through synchronously measured vertical concentrations of HOCs at various depths of overlying water column and at the sediment−water interface. This is an advantage over the activity gradient methods, which only use chemical concentrations at single depth in sediment and overlying water. In addition, the passive sampling device measured chemical diffusion fluxes in open systems rather than an enclosed microcosm in the benthic chamber and demonstrated clear superiority over the benthic chamber when the sediment acted as a sink for p,p'-DDT and o,p'-DDT. Consequently, the passive sampling device can be deployed to obtain information about the movement of HOCs through the sediment and overlying water, thus determining whether the sediment acts as a source or sink. It can also be used to evaluate conditions before, during, or after sediment remedial activities so that effective remediation strategies may be adopted. Furthermore, with appropriate sorbent phases and configurations, this passive sampling device can in principle be applied to other chemical types (e.g., inorganic species and hydrophilic organic chemicals) and other interfaces (e.g., water−air and soil−air).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional text, tables, and figures containing information about the laboratory procedures, sampling sites, and selected results from data analyses not presented in the main text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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