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A Multisection Passive Sampler for Measuring Sediment Porewater Profile of Dichlorodiphenyltrichloroethane and Its Metabolites

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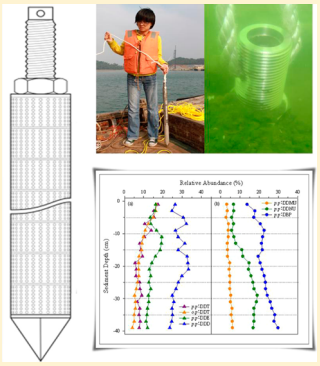
Supporting Information

ABSTRACT: In situ measurements of hydrophobic organic chemicals in sediment porewater, a central component in assessing the bioavailability and mobility of chemicals in sediment, have been scarce. Here, we introduce a multisection passive sampler with low-density polyethylene (LDPE) as the sorbent phase, which is appropriate for measuring vertical concentration profiles of chemicals in sediment porewater. This sampler is composed of a series of identical sampling cells insulated with seclusion rings. In each section, sorption of chemicals into LDPE is diffusion-controlled through the water layer separated from the sediment by a glass fiber filtration membrane and a porous stainless steel shield. Pilot laboratory testing indicated that the sampler can roughly determine the porewater concentrations of 1,1-dichloro-2,2-bis-(chlorophenyl)ethane (*p,p′*-DDD) and 1,1-dichloro-2,2-bis-(chlorophenyl)ethylene (*p,p′*-DDE), comparable to those yielded through centrifugation/liquid−liquid extraction, a conventional technique for sampling sediment porewater. Field deployment of the sampler was performed in an urbanized coastal region to measure the depth profiles of dichlorodiphenyltrichloroethane and its metabolites in sediment porewater. Sampling rate-calibrated and performance reference compound-calibrated concentrations were calculated, which were consistent with those obtained by the centrifugation/liquid−liquid extraction method. These results verified the utility of the sampler for measuring depth profiles of sediment porewater chemicals.



Sediment may act as both a reservoir and secondary source[1−3] of hydrophobic organic chemicals, such as polycyclic aromatic hydrocarbons, organic chlorinated pesticides, and polychlorinated biphenyls, in aquatic environments. Chemicals freely dissolved in contaminated sediment porewater are generally considered indicative of what is bioavailable for benthic organisms and, consequently, implicate possible human exposure through aquatic foodweb transfer.[4,5] In addition, the mobility of chemicals in sediment, typified by vertical movement and, subsequently, sediment-water flux caused by sediment erosion, molecular diffusion, bioturbation, and groundwater flow, is directly associated with chemical levels in sediment porewater.[6] Moreover, vertical profiles of sediment porewater concentrations can reflect chronological records of pollutant input histories, which is useful for calculating pollutant degradation rates and assessing the effectiveness of in situ remediation. As a result, reliable measurements of sediment porewater profiles of contaminants are desirable.[7]

Direct determination of porewater chemical concentrations is experimentally challenging because of mixing with the solid matrix. Over the past decades, passive probes have been employed for measurement of chemicals in surface sediment porewater, such as polymer-coated glass fibers,[8−12] polyoxymethylene films,[3,13] and polyethylene (PE) devices,[2,14−17] among others. Polymer-coated glass fibers are simple to use, efficient, and require little use of organic solvent but are fragile in field deployment.[18] Zeng et al.[19] utilized copper casing to prevent polymer-coated glass fibers from colliding with large suspended particles and minimize microbial growth. A similar but modified protective mechanism, with glass fiber membrane added to filter fine particles, was employed for measuring dissolved chemical concentrations in sediment porewater[12] and open water.[20] Polyoxymethylene films[3,13] and PE devices[2,14−17] with no protective shields were directly inserted into sediment to sense chemicals in porewater. These devices are inexpensive and robust and can easily be placed in sediment,[7,21,22] but measurements with such devices may be interfered with due to external impact (e.g., fine particles, algae, and benthos) on the polyoxymethylene or PE phase, especially in heavily polluted areas. Another important issue that was not addressed previously is the capability to synchronously measure depth profiles of chemicals in sediment porewater, which is vital for assessing the mobility of sediment chemicals, including sediment-water fluxes.[7]

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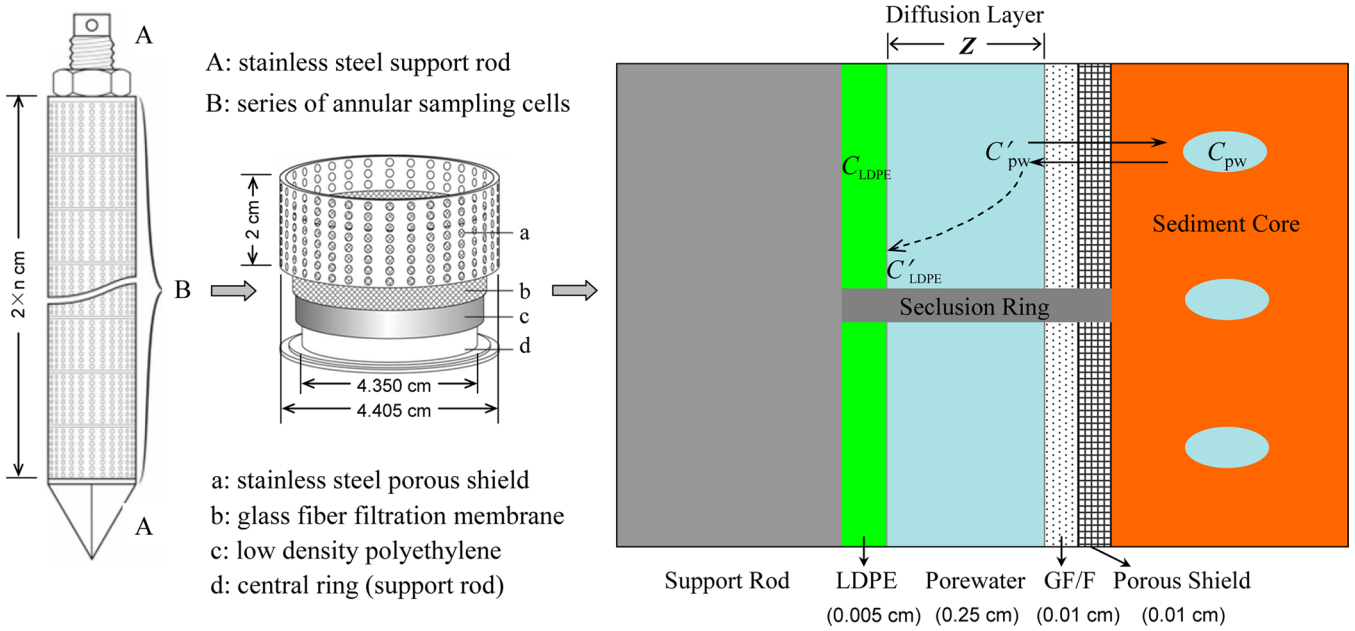

Figure 1. Schematic showing the configuration of the multisection passive sampler. LDPE = low density polyethylene, GF/F = glass fiber filtration membrane, C_{LDPE} = chemical concentration in LDPE, C'_{LDPE} = chemical concentration in water adjacent to LDPE, C_{pw} = chemical concentration in sediment porewater, and C'_{pw} = chemical concentration in sediment porewater just within the sampler cavity.

In response to the demand for more robust techniques for porewater chemical measurement, we developed a multisection passive sampler (application no. for patent cooperation treaty: PCT/CN2011/070789) for measuring depth profiles of chemicals in sediment porewater. Low-density PE (LDPE) was chosen as the sorbent phase and protective mechanisms were implemented to maximize the cost effectiveness with LDPE while minimizing any potential external impact mentioned above. A series of pilot laboratory tests were conducted to optimize the sampling parameters and verify the utility of the sampler for porewater chemical measurement. On that basis, the sampler was deployed in a coastal region for in situ measurement of porewater concentration profiles of dichlorodiphenyltrichloroethane (DDT) and its metabolites. Meanwhile, a conventional technique (i.e., centrifugation/liquid–liquid extraction) was used to test the robustness and capability of the sampler.

DESIGN AND CONFIGURATION OF THE MULTI-SECTION PASSIVE SAMPLER

The design of the multisection passive sampler (Figure 1) allows for the determination of sediment porewater profiles of chemicals using LDPE as the sorbent phase. The sampler consists of a series of annular sampling cells isolated with seclusion rings as individual sampling units (all parts were precleaned using a procedure described in Test S1 of the Supporting Information). The annular cells are interlinked to a stainless steel support rod with a diameter of 2.8 cm. Each annular cell consists of a LDPE strip wrapped by GF/F membrane and outfitted with a porous stainless steel shield. Target chemicals are allowed to freely penetrate through the porous shield and GF/F membrane and diffuse into the LDPE phase, while sediment particles are kept out of the sampler. On the other hand, water turbulence effects[23] on the mass transfer gradient from GF/F to LDPE (Figure 1) are deemed minimal as the apertures on the porous stainless steel shields and GF/F, with pore sizes of 1500 and 0.7 μm, respectively, are sufficiently small, and the system (sediment and porewater) is maintained in a static state. The water layer inside the sampler is essentially free of any chemical before sampling, and the sediment porewater chemical concentrations are presumably unaffected by sorption of the chemical to the LDPE phase (i.e., the extraction is nondepletive). In reality, the chemical concentration in porewater is no doubt disturbed; however, if the porewater concentration varies within 5% before and after extraction, the nondepletive condition is deemed satisfied.[24]

METHODS

Materials and Preparation. Standards of DDT and its metabolites (*p,p′*-DDT, *o,p′*-DDT, *p,p′*-DDD, *p,p′*-DDE, *o,p′*-DDE, *p,p′*-DDMU, *p,p′*-DDNU, and *p,p′*-DBP, sum of which is defined as DDXs), 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) used as performance reference compounds (PRCs) were purchased from C/D/N Isotopes (Quebec, Canada). Their physicochemical data are detailed in Table S1 of the Supporting Information, and other consumables are described in Text S1 of the Supporting Information.

Low density polyethylene sheets (50 μm film thickness) were purchased from TRM Manufacturing (Corona, CA). Strips of 50 μm LDPE (0.13 ± 0.006 g) (2 × 13.8 cm) were precleaned by extraction in DCM for 48 h, in methanol for 24 h, and in purified water (Text S1 of the Supporting Information) for 24 h, and were soaked again in purified water until use to minimize possible air contamination. When the PRCs-calibration technique was used for quantitation (Text S2 of the Supporting Information),[25,26] LDPE strips upon precleaning were immersed in a methanol:water (80:20 in volume) solution spiked with all PRCs each at 50 μg/L for 10 days. The loaded LDPE strips were rinsed with purified water, wrapped with cleaned aluminum foil, and frozen until deployment. In addition, three loaded LDPE strips were processed to

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determine the mass of PRCs initially loaded, whereas three other strips were used as field blanks to monitor any external interferences during deployment and recovery.

Measurement of Sampling Rate. In virtue of the unique configuration of the sampler, the porous stainless steel and glass fiber filtration membrane produce no resistance to the free flow of porewater, and thereby create no diffusive gradient of their own. The concentration gradient only occurs in the boundary porewater layer, under the premise of "zero sink" (Text S3 of the Supporting Information) for the LDPE phase. Use of Fick's first law of diffusion to describe the chemical transport process within the diffusion layer (Figure 1) leads to[27,28]

$$\bar{C}_{pw} = \frac{n_{LDPE}}{Rt} \quad (1)$$

where $\bar{C}_{pw}$ is the time-weighted average (TWA) concentration of a chemical in sediment porewater, which is valid only for the linear regime of the sorption kinetic profile,[29] n_{LDPE} is the chemical amount sorbed in the LDPE phase, R is defined as sampling rate (Text S4 of the Supporting Information), and t is the sampling time.

The sampling rate was determined by the mass of a chemical sorbed in LDPE and chemical concentration in water at various time points in the present study. Each 2 L glass container with 2 L of purified water was spiked with all target chemicals at 0.1, 0.2, and 0.5 μg/L and dosed with sodium azide at 0.2 g/L for prohibiting bacterial activity. Before use, the aqueous solutions were first agitated at 700 rpm (equivalent to a flow velocity of 1.5 m/s) for 2 h on a magnetic stirrer to achieve uniform distribution of the chemicals. Three annular sampling cells were placed into each container. All containers were sealed and shielded from light under static condition. Ambient temperature was maintained at 21 ± 2 °C. Sampling time points were 2, 3, 5, 7, 9, and 11 d. Similarly, sampling rates were also determined in three solutions prepared with 10 mg/L humic acid (HA), 3% sodium chloride (NaCl), and a mixture of 10 mg/L HA and 3% NaCl, respectively, each spiked with all target chemicals at 0.2 μg/L. It was noted that HA and target chemicals can form complexes, hence complexation equilibrium was allowed before the sampling cells were added (Text S5 of the Supporting Information). At each preset sampling time point, sampling cells were taken out, disassembled, and extracted, while the remaining water was transferred to a 2 L separatory funnel and liquid–liquid extracted three times with 100, 80, and 60 mL of DCM, respectively. In addition, sampling rates can also be derived theoretically, and detailed information is presented in Text S6 of the Supporting Information.

Pilot Laboratory Testing. The sampler is composed of a series of identical sampling cells. It is impractical to prepare large amounts of spiked sediment with sufficient depth in the laboratory; therefore, only three parallel sampling cells were used in the pilot testing. Presumably, if the three sampling cells can accurately determine chemical concentrations at one depth, the multisection sampler is deemed applicable for field deployment.

A sediment (1174 g), spiked with *p,p′*-DDD and *p,p′*-DDE and, subsequently, aged for two years (Text S7 of the Supporting Information), was used for laboratory testing. Concentrations of *p,p′*-DDD and *p,p′*-DDE in aged sediment porewater were determined using the sampling cells with laboratory-measured R values and compared to those obtained by centrifugation/liquid–liquid extraction (CEN/LLE) (Text S8 of the Supporting Information). In the CEN/LLE method, porewater was centrifuged from the sediment three times for 5 min each at 3500 rpm or RCF 1850g. The supernatants were combined and fine particles were removed through vacuum filtration with GF/F membranes (0.7 μm nominal pore size and 47 mm diameter). The filtrated porewater with a volume of 248 mL was liquid–liquid extracted. In addition, an aliquot of filtered porewater was adjusted to pH 2.0 ± 0.2 with 1 M hydrochloride acid for determination of dissolved organic carbon (DOC) with an Elementar Vario EL III (Shimadzu, Japan).

Field Deployment. Field validation of the sampler was conducted in Hailing Bay, located in Guangdong Province of South China (Figure S1 of the Supporting Information), on July 9–24, 2012. Four samplers, each with a length of 40 cm (20 cells × 2 cm), were vertically inserted into the sediment bed at two sites by a diver. At each site, one sampler with PRCs loaded and one without were deployed approximately 2 m apart from each other to avoid any possible interferences. All samplers were retrieved after 15 d and transported with ice to the laboratory where they were disassembled immediately and processed.

At the same time, four sediment cores were taken by a diver from each site (Figure S1 of the Supporting Information) with a cylindrical stainless steel pipe with a diameter of 15 cm and length of 60 cm. The sediment cores were placed on a self-designed extrusion machine and sliced in 2 cm increments from top to bottom. All sliced sediments were packed with aluminum foil into preservation boxes with ice and transported to the laboratory. To collect sufficient porewater volumes, corresponding slices of four sediment cores from each site were composited into one single sample. Porewater was centrifuged, purified, and liquid–liquid extracted, using the same procedures as in the pilot laboratory testing. Meanwhile, concentrations of DOC in porewater samples were measured in order to later correct dissolved concentrations for complexed contaminants (Text S8 of the Supporting Information).

Extraction of Low Density Polyethylene Strips and Porewater. Loaded LDPE strips were rinsed with purified water and consecutively extracted with 100 mL of DCM for 24 h and 100 mL of hexane for 24 h. Centrifuged porewater samples were extracted three times with 50, 30, and 20 mL DCM, respectively, and the extracts were composited. Surrogate standards PCB-67 and PCB-191 at 0.013 μg/L and 0.15 μg/g, respectively, were spiked into all water and LDPE samples prior to extraction. Each extract was concentrated to approximately 5–10 mL with a Zymark TurboVap II (Hopkinton, MA) at 30 °C, dried using sodium sulfate, solvent-exchanged to hexane, and further volume-reduced to 1 mL. The final volume of each extract was reduced to 0.1 mL under a gentle stream of purified N_2. Internal standard PCB-82 was added to final extracts before instrumental analysis.

Instrumental Analysis. Chemical concentrations were quantified by a Shimadzu 2010 gas chromatograph coupled with a QP 2010 plus mass spectrometer, using electron ionization in the selected ion monitoring mode. A 60 m × 0.25 mm i.d. (with a 0.25 μm film thickness) DB-5 column was used for chromatographic separation. The column oven temperature was programmed from 50 °C (held for 1 min) to 210 °C at a rate of 20 °C/min, further raised to 260 °C with a rate of 2 °C/min, and finally ramped with a rate of 20 °C/min to 290 °C (held for 20 min). The injector temperature was programmed from 100 °C and rapidly raised to 280 °C at 200 °C/min where it was held for 30 min. Extract injection was conducted in the

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Table 1. Experimentally Determined and Theoretically Derived Sampling Rates (R; cm^3/s) of DDXs[a]

chemical	purified water	HA	NaCl	NaCl/HA	theoretical (T = 20 °C)
p,p'-DBP	0.00023 ± 0.00010	0.00037 ± 0.0000	–	0.00041 ± 0.00011	0.00061
p,p'-DDNU	0.00056 ± 0.00021	0.00027 ± 0.00014	0.00042 ± 0.00009	0.00095 ± 0.00042	0.00058
p,p'-DDMU	0.00032 ± 0.00011	0.00028 ± 0.00006	0.00050 ± 0.00014	0.00050 ± 0.00021	0.00057
o,p'-DDE	0.00027 ± 0.00010	0.00028 ± 0.00006	0.00046 ± 0.00013	0.00054 ± 0.00025	0.00046
p,p'-DDE	0.00027 ± 0.00011	0.00039 ± 0.00010	0.00040 ± 0.00013	0.00072 ± 0.00040	0.00046
p,p'-DDD	0.00028 ± 0.00011	0.00038 ± 0.00007	0.00041 ± 0.00010	0.00048 ± 0.00018	0.00045
o,p'-DDT	0.00023 ± 0.00009	0.00039 ± 0.00008	0.00035 ± 0.00011	0.00045 ± 0.00017	0.00044
p,p'-DDT	0.00022 ± 0.00010	0.00052 ± 0.00011	0.00032 ± 0.00012	0.00087 ± 0.00066	0.00044

[a]Standard solutions prepared with purified water, 10 mg/L humic acid (HA), 3% sodium chloride (NaCl), and NaCl/HA mixture were used in experiments.

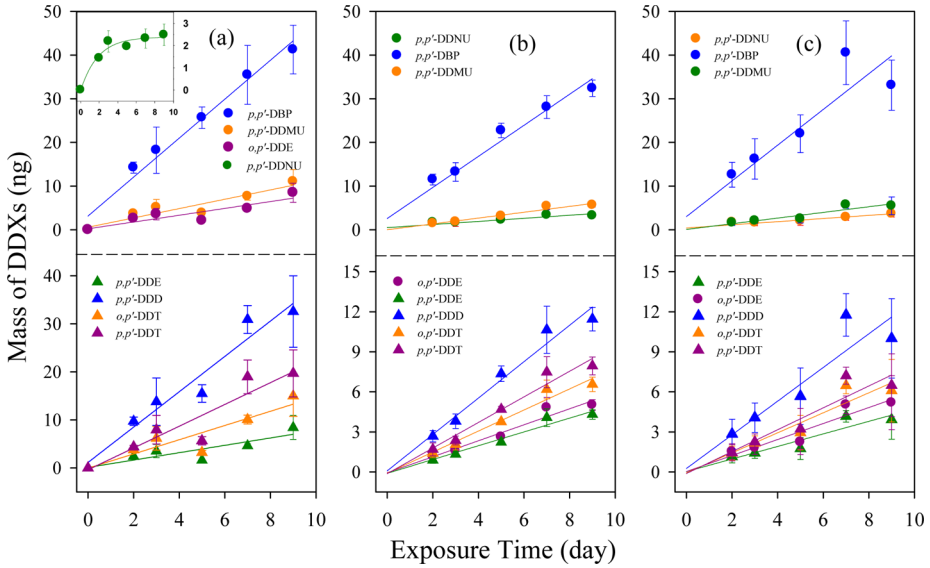

Figure 2. Correlations between the masses of DDXs sorbed in 50 μm low-density polyethylene (LDPE; 0.13 g) and exposure time in (a) 3% sodium chloride solution, (b) 10 mg/L humic acid solution, and (c) NaCl/HA mixed solution. Each solution was spiked with 0.2 μg/L DDXs under static condition at 21 ± 2 °C. One set of three identical annular sampling cells containing LDPE was used for each time point.

splitless mode, but the split mode was turned on after 0.75 min. Helium was used as the carrier gas at a constant flow of 1.3 mL/min. The transfer line and ion source temperatures were both 250 °C. The quantifier and qualifier ions of p,p'-DDT, o,p'-DDT, p,p'-DDD, p,p'-DDE, o,p'-DDE, p,p'-DDMU, p,p'-DDNU, and p,p'-DBP were detailed elsewhere.[30]

Quality Assurance and Quality Control. Procedure blanks including purified water and LDPE and method blanks were analyzed along with actual water and LDPE samples. No target chemicals were detected in any blank samples. The recoveries of the surrogate standards for extraction of LDPE and purified water in laboratory testing were 90 ± 19% for PCB-67 and 113 ± 15% for PCB-191, whereas those for extracted LDPE and sediment porewater in field applications were 84 ± 14% for PCB-67 and 109 ± 14% for PCB-191. The recoveries of all target chemicals ranged from 83−135%, with an average relative standard deviation of 16% in spiked blank samples for laboratory validation using centrifugation/LLE. Three field blanks of PE strips analyzed as control samplers contained no detectable DDXs. Before instrumental analysis, the extent for breakdown of p,p'-DDT was less than 20% through the analysis of a standard solution of p,p'-DDT.[31]

RESULTS AND DISCUSSION

Measurement of Sampling Rate (R). The sampling rate (R) can be expressed as (Text S4 of the Supporting Information)

$$R = \frac{D_w A}{Z} \quad (2)$$

Theoretically, the surface area (A) of the sorbent phase and the length (Z) of the water diffusion layer for a given sampling cell are presumably constants, which are 27.6 cm^2 and 0.25 cm, respectively, for the multisection passive sampler. The diffusion coefficient (D_w) can be estimated by the Othmer−Thakar equation (Text S6 of the Supporting Information). In this case, the theoretically derived R values ranged from 0.00044 to 0.00061 cm^3/s based on the empirical formula for deriving diffusion coefficients in water (D_w)[32,33] calibrated for water salinity at 20 °C (Text S6 of the Supporting Information).

Alternatively, sampling rates were also obtained experimentally. With purified water as the sample matrix, the amounts of DDXs sorbed in LDPE increased linearly with increasing extraction time (Figure S2 of the Supporting Information), highlighted by good linear correlation (r^2 = 0.77−0.99; Table S2 of the Supporting Information), which indicated that the exposure was performed within the kinetically linear regime.[34] It should be noted that the amounts of DDXs sorbed in LDPE

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increased with increasing spiking concentrations (i.e., 0.1, 0.2, and 0.5 μg/L) highlighted by the increasing slope (Table S2 of the Supporting Information), but R values (the quotient of slope divided by C_{pw}) were not significantly different at distinct spiking concentrations (t test; $p < 0.05$). Apparently, sampling rate is mainly related to the sampler's configuration rather than chemical concentrations. As a result, all measured sampling rates are reported as average ± standard deviation (Table 1). The substantial difference between the experimentally determined R values in purified water (0.00022−0.00056 cm^3/s) and those derived theoretically (0.00044−0.00061 cm^3/s) (Table 1) may have resulted from matrix interferences, which was further examined in the present study.

Sampling rates determined in solutions of NaCl (Figure 2a), HA (Figure 2b), and NaCl/HA mixture (Figure 2c) were all greater than those obtained in purified water (Table 1). The presence of NaCl increased the solutions' ion strength, and thus decreased the chemicals' solubility due to a salting-out effect.[35] In addition, HA, which binds chemicals through complexation, can act as a mass transfer carrier to enhance the diffusion of chemicals into LDPE phase and to reduce the amounts of chemicals sorbed onto other phases (e.g., glassware wall and stirring bar surface[36]). The sampling rates acquired with the mixed solution of NaCl and HA were further elevated compared to those in purified water (t test; $p = 0.0018$) due to the combined effect of salting-out and complexation, and were close to the theoretically derived values (t test; $p = 0.16$) (Table 1). Indeed, the sampling rates (R) determined in 3% NaCl solution were much closer to those salt-considered theoretical values (Text S6 of the Supporting Information) than those in 10 mg/L HA solution. However, considering the ubiquity of organic matter in natural water (even so in sediment porewater), the measured R values (0.00041−0.00095 cm^3/s) with the mixed solution of 10 mg/L HA and 3% NaCl were employed in subsequent tests. Meanwhile, the sampling rates were also measured in a sediment spiked with p,p'-DDD and p,p'-DDE (Text S7 of the Supporting Information). The time series data (Figure S3 of the Supporting Information) indicated that the measured R values of p,p'-DDD and p,p'-DDE (0.00067 and 0.00056 cm^3/s, respectively) were similar to those measured in water bath experiments. Therefore, although the present sampler is designed for deployment in sediment, it is actually intended to measure chemicals in porewater, which is why the sampling rates were determined in saline and DOC-rich solutions instead of sediment.

Determination of Sampling Time and Detection Limit. The best field sampling time is a range of time points within which the chemical amount sorbed in LDPE exceeds the chemical's minimum detectable amount but remains in the linear sorption regime. The minimum sampling time (t_{mini}) can thus be calculated by

$$t_{mini} = \frac{n_{mini}}{C_{pw}R} \tag{3}$$

where n_{mini} is the minimum detectable amount with the GC−MS system employed in the present study. Using R values determined in the NaCl/HA mixed solution, t_{mini} values ranged from 0.01 to 2.06 days (Table S3 of the Supporting Information), suggesting that a 2 day exposure can result in sufficient masses of DDXs in LDPE for instrumental analysis (Figure S4 of the Supporting Information). Given the wide linear sorption regime (Figure 1 and Figure S2 of the Supporting Information), a sampling time as long as 15 days can be used to achieve optimal detection sensitivity. It should be noted that the best sampling time for a specific chemical may vary, depending on the physicochemical properties and actual concentrations of the chemical, and adjustments may be needed in field applications.

The detection limits of the sampler depend on the mass of LDPE used and the physicochemical properties of the chemical under investigation. In the present study, approximately 0.13 g LDPE was used, the minimum detectable amount of the target chemical (n_{mini}) was approximately 1 ng, and the final extract volume was 100 μL. Thus, the detection limit of a target chemical in sediment porewater ($C_{detected}$) can be calculated by

$$C_{detected} = \frac{n_{mini}}{Rt} \tag{4}$$

where t is 15 days in the present study. Detection limits of DDXs calculated with eq 4 ranged from 0.81 to 1.88 ng/L at 20 °C (Table S3 of the Supporting Information), which are deemed sufficient for many field applications as organic chemicals are often concentrated in sediment porewater.

Time for Target Chemicals to Equilibrate between Sampler Cavity (Seawater) and Sediment Porewater. When a multisection sampler is deployed into a sediment bed, its cavity would be initially filled with seawater presumably containing nondetectable target chemicals. The time (t_{eq}) for chemicals to diffuse from sediment porewater into the sampler's cavity and reach equilibrium is a key factor for determining whether the true porewater chemical concentration is sensed by the sampler. Ideally, t_{eq} should be insignificant compared to the actual sampling time so that any depletion in chemical concentration due to seawater dilution can be rapidly compensated. When such a diffusion process does occur, the concentration gradient within the diffusion layer is assumed to take the form of a universal exponential function; in other words,

$$C'_{pw} = C_{pw}(1 - e^{-k_e t}) \tag{5}$$

where C'_{pw} is the chemical concentration in the sampler cavity, C_{pw} is the chemical concentration in ambient sediment porewater, and k_e is the exchange rate. Similarly, the Fick's first law of diffusion can be used to describe the chemical transport process within the diffusion layer; in other words,

$$F = -D_w\frac{dC}{dZ} = \frac{1}{A}\frac{dm}{dt} \tag{6}$$

where m ($=C'_{pw}ZA$) is the chemical mass transporting from sediment porewater to the sampler cavity, and other parameters are identical to those mentioned above. Substituting eq 5 into eq 6 with further simplification yields

$$k_e = \frac{D_w}{Z^2} \tag{7}$$

From eqs 5 and 7, t_{eq} can be expressed as

$$t_{eq} = -\frac{Z^2}{D_w}\ln(1 - x) \tag{8}$$

where x is the extent of equilibrium {$=[(C'_{pw})/(C_{pw})]$}. In eq 8, D_w can be calculated empirically (Text S6 of the Supporting Information) and Z can be derived from eq 2, in which A is 27.6 cm^2 and R is predetermined experimentally. In general, an equilibrium extent of 95% is assumed to represent the equilibrium state (i.e., $x = 0.95$). The t_{eq} values thus calculated

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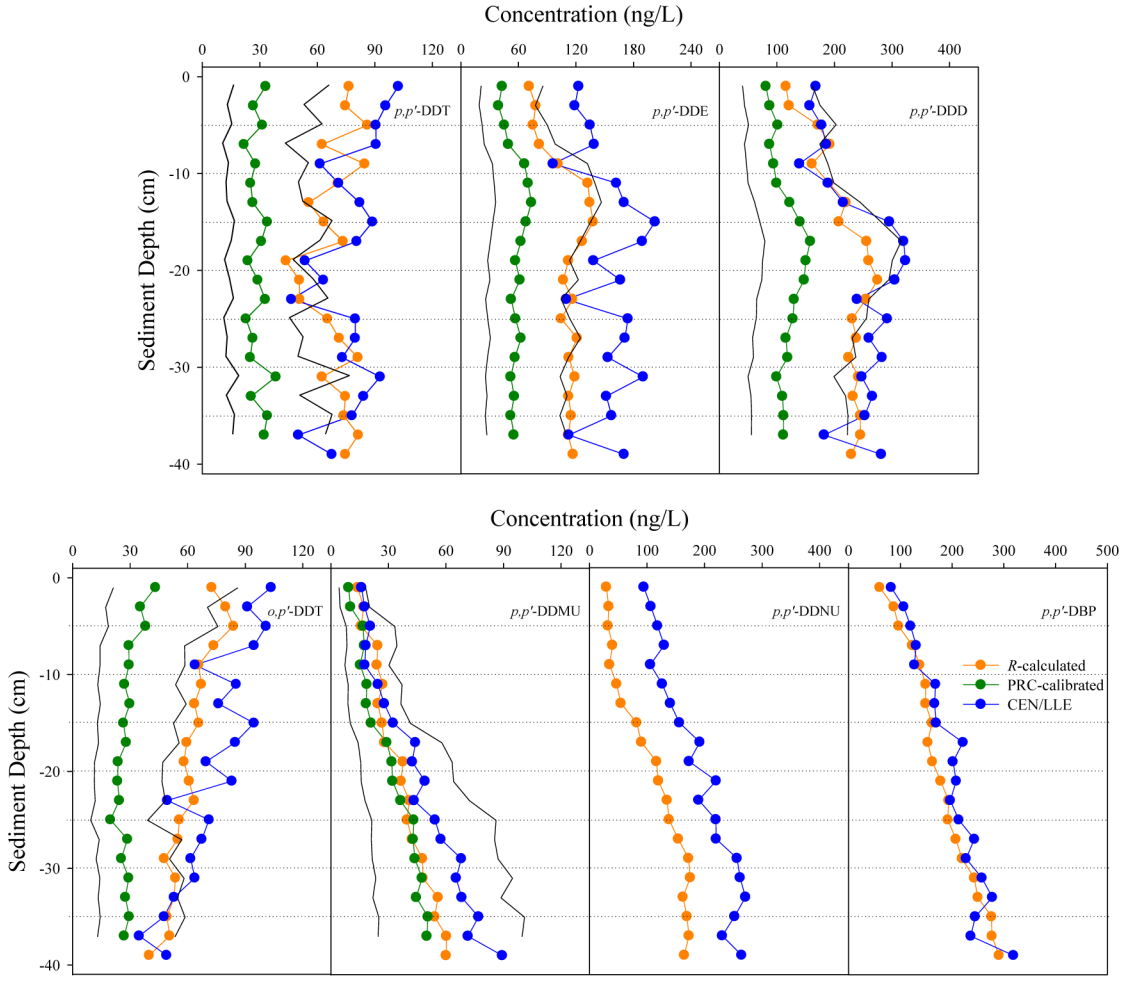

Figure 3. Vertical profiles of the sampling rate (R)-calculated, performance reference compound (PRC)-calibrated and centrifugation/liquid–liquid extracted (CEN/LLE) concentrations of DDXs in sediment porewater at site A (Figure S1 of the Supporting Information) in an urbanized coastal region of South China. The dark solid line is the range of PRC-calibrated concentrations if the partition coefficient (K_{LDPE}) varies by a factor of 2.

(Table S4 of the Supporting Information) ranged from 3.36 to 20.9 h for the target chemicals. Apparently, the sampling time of 15 days selected in the present study was adequate for achieving reliable measurement authenticity.

Laboratory Validation Results. Laboratory validation of the multisection sampler was conducted through parallel measurements with CEN/LLE, as described above. The concentrations of *p,p′*-DDE and *p,p′*-DDD in spiked sediment porewater derived from the sampling cells were 32 ± 7.5 ng/L and 194 ± 35 ng/L, respectively, as compared to 34 and 54 ng/L obtained by CEN/LLE.

It should be noted that imperfect centrifugation sampling procedures, such as insufficient centrifugal rate (3500 rpm or RCF 1850*g*) and small porewater volume (248 mL) may have resulted in large uncertainties for the sediment porewater measurements.[37,38] In addition, K_{DOC}, used for concentration correction in centrifuged porewater (Text S8 of the Supporting Information) can vary by a factor of 2,[39,40] which may cause an uncertainty range of 2 for the measured porewater concentrations. Overall, the results obtained with the sampling cells were roughly consistent with those from CEN/LLE, thereby somewhat demonstrating the utility of the multisection passive sampler for sensing chemicals in sediment porewater on a laboratory scale. The reasonable results allowed further validation of the utility of the sampler from laboratory-scale testing to field deployment.

In addition to the above calibration exercises, we also examined whether other mechanical parts of the sampler would retain target chemicals, thus depleting chemical concentrations in porewater. After sampling in laboratory tests, porous stainless steel shields and GF/F membranes disassembled from the sampling cells were processed along with the LDPE samples. No detectable target chemicals were found in GF/F membranes, whereas the amounts of *p,p′*-DDE and *p,p′*-DDD sorbed in the porous stainless steel shields accounted for only 9–14% and 4–6% of the total spiked amounts. With these small amounts of sorption to the porous stainless steel shield, the measured chemical concentrations were obviously not disturbed because the target chemicals in LDPE were directly quantified. Even if porewater chemicals in moderate amounts are sorbed onto steel shields, they can be compensated rapidly by the surrounding sediment because, based on our previous modeling results,[41] the minimum sediment volume required to maintain a nondepletive sampling environment for each sampling cell was only 3.1 mL, or 0.11 cm, of sediment layer.

Field Deployment Results. In the field deployment, both the sampling rate (R)-calculated (Text S4 of the Supporting Information) and PRC-calibrated (Text S2 of the Supporting Information) concentrations were obtained. Given the wide

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linear sorption regime (Figure 1 and Figure S2 of the Supporting Information), PRC-calibrated concentrations were also TWA values, as those obtained by the *R*-calculated approach. But because no partition coefficients are available for *p,p′*-DDNU and *p,p′*-DBP, they were not quantified with the PRC-calibrated method (Text S2 of the Supporting Information). The vertical concentration profiles of DDXs from sites A and B (Figure S1 of the Supporting Information) are displayed in Figure 3 and Figure S5 of the Supporting Information, respectively. As shown, for the first five target chemicals (i.e., *p,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD, *o,p′*-DDT, and *p,p′*-DDNU), the sum concentrations by the *R*-calculated approach at site A ranged from 350 to 550 ng/L (eq 1), nearly overlapping with those (380−670 ng/L) by the CEN/LLE approach (Text S8 of the Supporting Information) but moderately greater than those (198−310 ng/L) by the PRC-calibrated method (Text S2 of the Supporting Information). Similar results were obtained in samples from site B (i.e., 340−470 ng/L by the *R*-calculated approach, 350−680 ng/L by CEN/LLE, and 194−250 ng/L by PRC-calibration). Apparently, the PRC-calibrated method underestimated chemical concentrations; however, as K_{LDPE} may vary by a factor of 2,[39,40] C_{pw} can carry an uncertainty range of 2 (shown by the black solid lines in Figure 3 and Figure S5 of the Supporting Information). In addition, the sum concentrations of *p,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD, *o,p′*-DDT, *p,p′*-DDNU, *p,p′*-DDNU, and *p,p′*-DBP by *R* calculation ranged from 439 to 999 ng/L and from 436 to 943 ng/L at Site A and B, respectively, comparable to those (611−1240 ng/L and 560−1162 ng/L) by the CEN/LLE approach. Overall, no significant difference between the three measurement methods for individual contaminant concentrations at each depth was found (paired *t* test; $p > 0.05$), which has somewhat provided a valuable cross-validation of the sampler for field measurement of chemicals in sediment porewater.

Relative abundances of *p,p′*-DDT and *o,p′*-DDT decreased with increasing sediment depth at both sites A (Figure 4a) and B (Figure S6a of the Supporting Information), indicating that they gradually degraded in sediment. The relative abundance of *p,p′*-DDE, an oxidative metabolite of *p,p′*-DDT, peaked at relatively shallow depths of 10−15 cm, whereas that of *p,p′*-DDD, a reductive metabolite of *p,p′*-DDT, peaked at deeper depths of 15−20 cm. The relative abundances of both metabolites, on the other hand, declined slowly downward (Figure 4a), as they may have further degraded to other high-order metabolites,[30] which indeed experienced rapid increases in relative abundance (Figure 4b). Among all target chemicals, *p,p′*-DDD and *p,p′*-DBP were the most detectable components with relative abundances of 23−33% and 14−30%, respectively, which was quite similar to the results of total concentrations in sediment cores[30] collected from the approximate area, as in the present study. The good agreement between the sediment porewater and sediment profiles of DDXs further validated the reliability of the sampler in field measurement of sediment porewater profiles of chemicals.

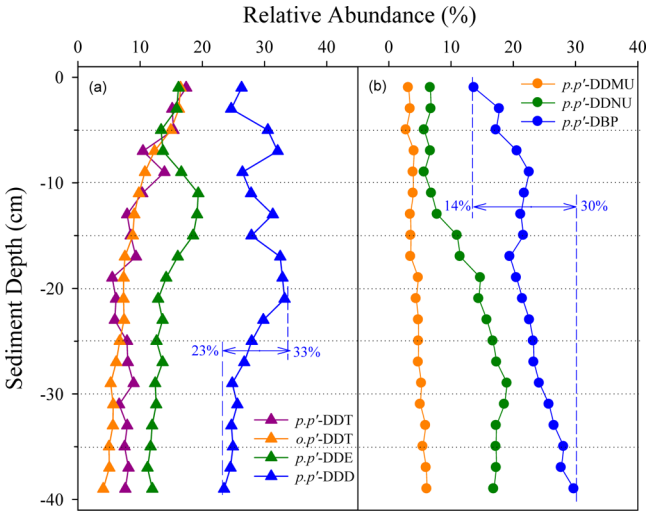

Figure 4. Relative abundances of the sampling rate (*R*)-calculated concentrations of individual components normalized to DDXs (sum of *p,p′*-DDT, *o,p′*-DDT, *p,p′*-DDD, *p,p′*-DDE, *p,p′*-DDMU, *p,p′*-DDNU, and *p,p′*-DBP) at site A (Figure S1 of the Supporting Information) in an urbanized coastal region of South China.

CONCLUSIONS

In the present study, we designed a novel multisection passive sampler with an optimal protective mechanism and flexible layer interval. The uniqueness of this passive sampler is characterized by its capability of obtaining high-resolution concentration profiles of sediment porewater hydrophobic organic chemicals at low cost, robustness in field deployment, and rapid sampling time that allows one to acquire time-weighted average analyte concentrations. With this sampler, our ability to assess the bioavailability and mobility of chemicals in sediment of various depths is greatly strengthened, which is helpful for the management community to gain information leading to the selection of appropriate strategies for environmental monitoring and contaminated site remediation. In addition, this sampler can, in principle, be applicable to measurements of trace inorganic and other chemicals in sediment porewater with the use of appropriate sorbent phases (and perhaps the sampler configuration) and adequate calibration.

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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