

## DEVELOPMENT OF A LOW-DENSITY POLYETHYLENE-CONTAINING PASSIVE SAMPLER FOR MEASURING DISSOLVED HYDROPHOBIC ORGANIC COMPOUNDS IN OPEN WATERS

LIAN-JUN BAO,<sup>†‡</sup> SHI-PING XU,<sup>†</sup> YAN LIANG,<sup>§</sup> and EDDY Y. ZENG<sup>\*†</sup><sup>†</sup>State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China<sup>‡</sup>Graduate School, Chinese Academy of Sciences, Beijing, China<sup>§</sup>Department of Biology, Hong Kong Baptist University, Hong Kong, China

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**Abstract**—A passive water sampler with low-density polyethylene (LDPE) as the sorbent phase was built and field-tested for sensing freely dissolved concentrations of hydrophobic organic compounds (HOCs) in fresh and coastal water. Based on the measured LDPE–water partition coefficients ( $K_{\text{pew}}$ ) of 12 polycyclic aromatic hydrocarbons (PAHs) and dichlorodiphenyltrichloroethane (DDT) and its seven metabolites, the detection limits with the passive sampler containing 10-g LDPE ranged from 0.04 to 56.9 pg/L in the equilibrium sampling mode. Furthermore, the utility of the passive sampler in measuring dissolved HOC concentrations in open waters was examined through a comparison with solid-phase extraction combined with liquid–liquid extraction (SPE-LLE) and poly(dimethyl)siloxane (PDMS) coated fiber samplers. The total concentrations of PAHs (3.8–16 ng/L) obtained by the passive sampler were lower than those (87.7–115.5 ng/L) obtained through SPE-LLE. This large difference was probably attributable to slower water exchange in and out of the passive sampler as time progressed because of blockage by algae in eutrophia reservoirs and high dissolved organic carbon contents resulting in higher-than-expected PAH concentrations by SPE-LLE. Furthermore, the concentrations and compositional profiles of DDXs (sum of *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, *o,p'*-DDT, *o,p'*-DDD, *o,p'*-DDE, and *p,p'*-DDMU) at site A obtained by the passive sampler agreed with the results obtained with the PDMS-coated fibers, suggesting that the passive sampler was able to reasonably quantify dissolved HOCs in seawater. Environ. Toxicol. Chem. 2012;31:1012–1018. © 2012 SETAC

**Keywords**—Low-density polyethylene    Passive sampling    Hydrophobic organic compound    Open water    Field validation

## INTRODUCTION

Freely dissolved concentrations of hydrophobic organic compounds (HOCs), such as polycyclic aromatic hydrocarbons (PAHs), dichlorodiphenyltrichloroethane (DDT) and its metabolites (the sum is designated as DDTs), and polychlorinated biphenyls (PCBs) in open waters have received much attention. This is the case because they largely dictate the geochemical processes of HOC in aquatic systems, such as riverine transport, sedimentation, resuspension from sediment, and volatilization [1]. Dissolved concentration is also a critical parameter for characterizing biotransformation and bioconcentration of HOCs in organisms [2,3]. Consequently, monitoring HOCs in open waters can provide important information for examining the environmental fate of HOCs, as well as the magnitude of human exposure.

Active sampling techniques, such as liquid–liquid extraction (LLE) and solid-phase extraction (SPE) combined with LLE (SPE-LLE) have been used to measure HOC concentrations in open waters [4,5]. However, they are time-consuming and laborious, and they only respond to instantaneous water concentrations [6]. Passive sampling devices, such as semipermeable membrane devices [7,8], solid-phase microextraction fiber [9,10], polyethylene devices [11–14], and polyoxymethylene strips [15,16], have also been applied to sampling HOCs in open waters. In particular, polyethylene devices with low-density polyethylene (LDPE) as the sorbent phase have been used widely to measure dissolved PAHs, PCBs, pharmaceuticals,

and personal care products in aquatic environments [11–14], because they are biomimetic, inexpensive, and convenient for field deployment [17]. Conversely, polyethylene devices have been configured normally without physical protection and used mostly in rivers, harbors, and bays [11–13,18–20]. Because harbor and bay waters usually contain low levels of suspended solids and rusting materials, whether polyethylene devices can be effectively deployed in freshwater environments with eutrophia such as reservoirs and lakes to acquire acceptable results has remained unclear.

To address this issue, we developed and field-tested a passive sampler with LDPE as the sorbent phase. To proceed, the LDPE–water partition coefficients ( $K_{\text{pew}}$ ) of the target analytes were determined in laboratory calibration, and the salt effects on  $K_{\text{pews}}$  were examined for the sampler's field application in seawater. The present passive sampler was then deployed in four reservoirs (Supplemental Data, Fig. S1) and Hailing Bay (Supplemental Data, Fig. S2) of Guangdong Province, China, to quantify dissolved PAHs and DDTs in the equilibrium partitioning mode. Finally, the utility of the passive sampler was assessed and validated via a comparison of the field-measured concentrations of PAHs and DDTs by the passive sampler and other sampling techniques, that is, SPE-LLE and poly(dimethyl)siloxane (PDMS)-coated fibers.

## METHODS

*Preparation and sorption kinetic experiment*

Low-density polyethylene sheets (50- $\mu\text{m}$  film thicknesses) were purchased from TRM Manufacturing. Strips of LDPE ( $2 \pm 0.01$  mg for laboratory calibration and  $\sim 10$  g for field deployment) were precleaned (extracted) with dichloromethane, methanol, and high-purity water for 48, 24, and 24 h,

All Supplemental Data may be found in the online version of this article.

\* To whom correspondence may be addressed

(eddyzeng@gig.ac.cn).

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respectively, and were soaked again in high-purity water until used to protect from air contamination. Laboratory glassware was cleaned with a chromic acid mixture, washed with tap water after 4 h, then washed again with purified water for three times, and finally oven-dried at 450°C for 4 h before use. The passive sampler's components, such as Cu box, end cap, Cu screen, stainless steel sieve plate, and bracket, were wiped down of dirt and oil, then washed with water, dried in an oven at 120°C, sonicated three times in dichloromethane, and finally left to dry completely in a fume hood overnight. The glass fiber filtration membranes (GF/F; 0.7  $\mu\text{m}$  nominal pore size; Whatman International) were cut into strips (12.7  $\times$  20.3 cm) and baked at 450°C for 4 h before use. Seal rings made of LDPE were sonicated three times in dichloromethane.

The sorption kinetics of PAHs and DDTs were established for the 10 to 365 d, using the same procedures for polybrominated diphenyl ethers [21]. The spiked concentrations of individual PAH and DDT components were 0.2 and 0.25  $\mu\text{g/L}$  (Supplemental Data, Table S1), respectively. The salinity dependence of  $K_{\text{pew}}$  was assessed using high-purity water spiked with sodium chloride at mass contents of 1, 3.5, and 5%, respectively, and the sampling time was 150 d.

#### Field deployment

Information about the deployment sites (Supplemental Data, Figs. S1 and S2) is detailed in Supplemental Data, Table S2. The reservoirs (Supplemental Data, Fig. S1) for field deployment can be categorized as drinking water source (Liuxihe Reservoir), agricultural area (Zengtang Reservoir), and industrial area (Jinkeng Reservoir and Tongsha Reservoir) based on the extent of economic development. In each reservoir, three sites located along the same cross section were selected for field deployment. Each passive sampler was attached to an 8-mm twisted polypropylene rope at the depth of 1 m below the water surface. The entire sampling device was anchored by a brick and suspended in water with a float. In addition, grab water samples were collected into five 10-L brown glass containers, using a stainless steel submersible pump when the passive samplers were retrieved. For deployment at the coastal sites A, B-1, B-2, and C in Hailing Bay of Guangdong Province, China (Supplemental Data, Fig. S2), passive samplers were immersed at various water depths through an 8-mm twisted polypropylene rope anchored by two concrete bricks at each site.

Laboratory testing indicated that the equilibrium time for partitioning of PAHs and DDTs between LDPE and water was approximately 10 d at an agitation rate of 700 rpm, equivalent to a flow velocity of 1.5 m/s. Detailed procedures have been described by Bao et al. [21]. Because flow velocities in the field may deviate from those used in laboratory simulations, we chose a deployment time of 60 d to ensure that equilibrium sampling was achieved for all the target analytes. On completion of deployment, the passive sampler was detached carefully from the deployment device, placed into a polyethylene bag after water in the sampler's cavity was removed, and transported to the laboratory immediately in ice chests on a layer of ice at the bottom of a plastic box. The passive samplers deployed at site C in Hailing Bay were lost during the deployment time.

#### Extraction of polyethylene strips and water

The loaded LDPE stripes taken out of the passive sampler were rinsed with purity water to remove algae and then soaked consecutively in 150 ml dichloromethane for 24 h and in 150 ml

of hexane for another 24 h. The solutions from two extractions were combined and concentrated to 5 to 10 ml with a Zymark Turbo Vap II at 30°C. After dehydration with sodium sulfate and solvent-exchange to hexane, the extracts were reduced to 1 ml by the Zymark Turbo Vap II and purified with a 10-mm inner diameter glass column packed with a neutral alumina (6 cm, 3% deactivated) and a neutral silica gel (12 cm, 3% deactivated) from bottom to top. The effluents were concentrated by the Zymark Turbo Vap II to 0.5 ml. The internal standards, 2-fluoro-1,1-biphenyl, *p*-terhenyl- $\text{d}_{14}$ , dibenzo[*a,h*]anthracene- $\text{d}_{14}$ , and PCB-82, were added to the final extracts before instrumental analysis. The procedures for separation of water and suspending of particulates, extraction, purification, and chromatographic separation for water samples have been described in detail by Wang et al. [4] and Guan [5].

#### Instrumental analysis

A Shimadzu 2010 gas chromatograph coupled with a QP 2010 plus mass spectrometer (MS) were used for quantifying PAHs and DDTs. A 60 m  $\times$  0.25 mm inner diameter (with a 0.25- $\mu\text{m}$  film thickness) DB-5 column was used for chromatographic separation. The column oven temperature for PAHs were programmed from 60 to 200°C at a rate of 10°C/min, then raised to 214°C at a rate of 2°C/min, further ramped to 250°C at a rate of 5°C/min, and finally raised with 20°C/min to 290°C (held for 30 min). The temperature program for DDTs has been detailed by Bao et al. [22]. The injector temperature for PAH measurements was programmed from 100°C, and rapidly raised to 280°C at 200°C/min, where it was held for 30 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 qualitative analysis of the target analytes was determined in the full-scan mode.

#### Quality assurance and quality control

Procedural blanks (high purity water and water), LDPE blanks, and reprocessed LDPE samples were analyzed along with field samples. No DDTs were detected in these quality control samples, whereas low levels of PAHs (mean: 17.8 ng/g for naphthalene, 0.95 ng/g for acenapheylene, 1.8 ng/g for acenaphthene, 9.5 ng/g for fluorene, 76.2 ng/g for phenanthrene, 12.1 ng/g for anthracene, 3.6 ng/g for fluoranthene, and 1.6 ng/g for pyrene) were found in 10-g LDPE blanks, and high levels of PAHs (mean, 1,134 ng/L; the levels of low molecular PAHs including naphthalene, acenaphthylene, acenaphthene, fluorene, and phenanthrene accounted for 88% of the total concentration) were found in water blanks. Therefore, the concentrations of PAHs in blank samples were subtracted from the measured concentrations in water and LDPE samples to derive reported concentration values. The recoveries of the surrogate standards were 92  $\pm$  11% (PCB-67), 106  $\pm$  17% (PCB-191), 86  $\pm$  22% (C13-labeled *p,p'*-DDT), 83  $\pm$  12% (naphthalene- $\text{d}_8$ ), 82  $\pm$  16% (acenaphthene- $\text{d}_{10}$ ), 89  $\pm$  23% (phenanthrene- $\text{d}_{10}$ ), and 88  $\pm$  22% (chrysene- $\text{d}_{12}$ ) for the samples from the sorption kinetics experiments. The recoveries of perylene- $\text{d}_{12}$  were extremely high for blank samples because of chromatographic peak interferences that were not observed with other surrogate standards; therefore, the data were not reported. The recoveries of the same surrogate compounds for the passive samplers deployed in the reservoirs were 82  $\pm$  17%, 105  $\pm$  25%, 93  $\pm$  25%, 59  $\pm$  23%, 89  $\pm$  24%, 116  $\pm$  16%, and 74  $\pm$  17%, respectively. In addition, the recoveries of PCB-67 and PCB-191 for the passive samples deployed in the coastal locations were 95  $\pm$  10% and 107  $\pm$  7%, respec-

tively. Before instrumental analysis, the extent for breakdown of *p,p'*-DDT should be less than 20% [23] through the analysis of a standard solution of *p,p'*-DDT.

#### Data analysis

The dissolved concentration ( $C_w$ ) of a target analyte in water sensed with the passive sampler was estimated from the concentration in LDPE ( $C_{pe}$ ) divided by the LDPE–water partition coefficient ( $K_{pew}$ )

$$C_w = \frac{C_{pe}}{K_{pew}} \quad (1)$$

In the present study,  $K_{pew}$  of PAHs and DDTs were determined through kinetic sorption experiments. On the other hand, the salt effects on  $K_{pews}$  were examined for the sampler's field application in seawater. The concentrations of the target analytes measured by the present passive sampler in bays were calculated by Equation 1 with  $K_{pew,salt}$  (polyethylene–water partition coefficients corrected for salt effect; Supplemental Data, Table S3) instead of  $K_{pews}$ .

## RESULTS AND DISCUSSION

#### Assembly of passive water sampler

The passive sampler with LDPE as the sorbent phase (Fig. 1 and Supplemental Data, Fig. S3) is composed of a rectangular copper box capped with two open frames. The frames are filled with two 80-mesh copper meshes, two stainless steel sieve plates and GF/F. The copper meshes and stainless steel sieve plates are used to filter coarse particles and protect GF/F. The use of copper can also slow the growth of microbes on the

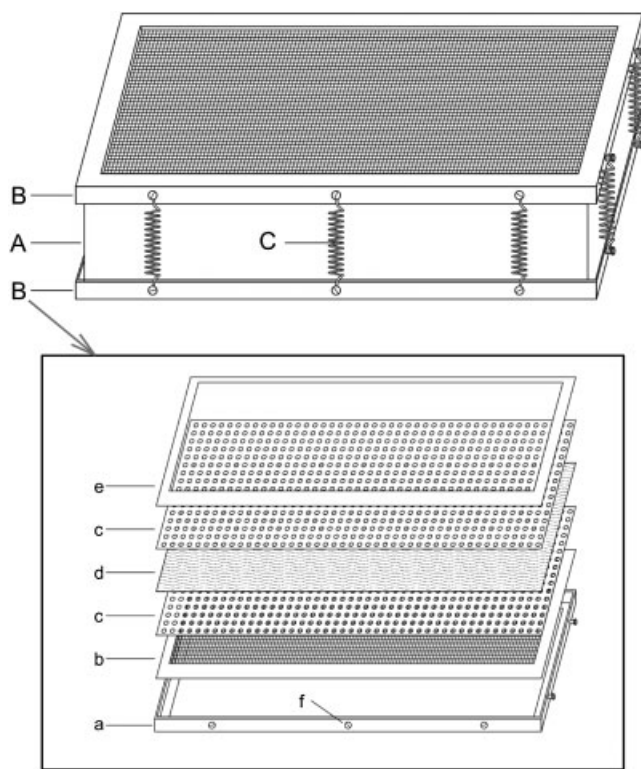


Fig. 1. Configuration of the low-density polyethylene passive sampler (China patent application number: 201110040648.8). A = copper box; B = end cap; C = spring; a = copper cap; b = copper screen; c = stainless steel sieve plate; d = glass fiber filtration membrane; e = polyethylene seal ring; f = hat peg for spring.

sampler's surfaces. The GF/F layer allows chemicals to freely penetrate to the sampler's cavity, but block particles ( $>0.7 \mu\text{m}$ ) from entering the sampler. In addition, a bracket of comb-like structure are used to ensure no crossing of the LDPE stripes and to facilitate water flow to speed up sampling rate. Three assembled samplers (Supplemental Data, Fig. S3) were deployed for 60 d. Despite severe eutrophication in these fresh-water systems, the loaded LDPE stripes remained quite clear on retrieval.

#### Determination of $K_{pew}$

The sorption kinetics varied with target analytes (Figs. 2 and 3). The partitioning of 12 PAHs (Supplemental Data, List S2) excluding indeno[1,2,3-*cd*]pyrene, dibenzo[*a,h*]anthracene

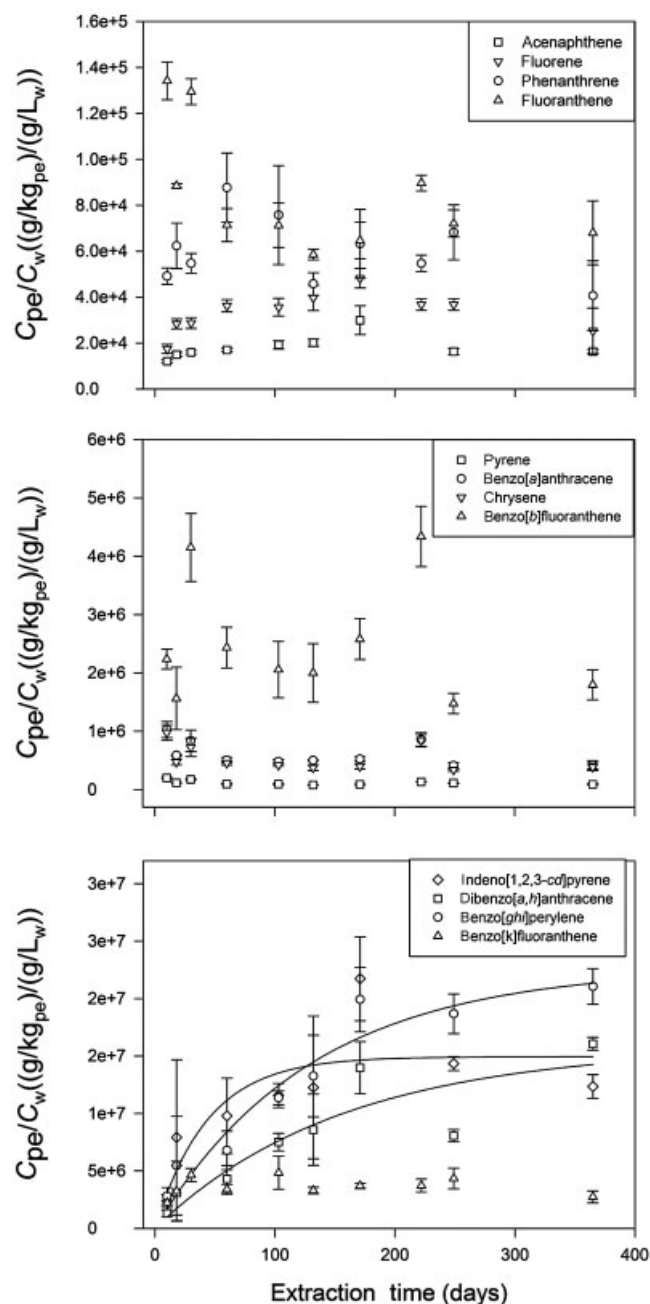


Fig. 2. Sorption kinetics of the target polycyclic aromatic hydrocarbons on 50- $\mu\text{m}$  low density polyethylene (LDPE) film expressed as  $C_{pe}/C_w$  versus time (days), where  $C_{pe}$  and  $C_w$  are the concentrations of an analyte in LDPE film and water, respectively.

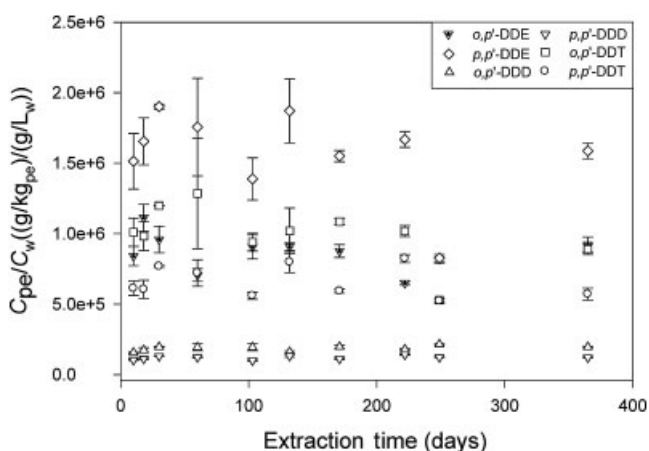


Fig. 3. Sorption kinetics of dichlorodiphenyltrichloroethane (DDT) and its metabolites on 50- $\mu\text{m}$  low density polyethylene (LDPE) film expressed as  $C_{pe}/C_w$  versus time (days), where  $C_{pe}$  and  $C_w$  are the concentrations of an analyte in LDPE film and water, respectively. DDE = dichlorodiphenyldichloroethylene; DDD = dichlorodiphenyldichloroethane.

and benzo[ghi]perylene, and DDTs between LDPE and water seemed to reach equilibrium within 10 d. The  $K_{pew}$  values for these target compounds were determined as the averages of the measured data ( $C_{pe}/C_w$ ) in each sampling timepoint, but any  $C_{pe}/C_w$  different from the average value by more than 100% was excluded in the calculation of  $K_{pew}$ . For example,  $C_{pe}/C_w$  for acenaphthene at 171 and 222 d were different from the average values by more than 100%; as a result, the  $\log K_{pew}$  of acenaphthene was revised to  $4.25 \pm 0.12$  from  $4.32 \pm 0.19$  after these two  $C_{pe}/C_w$  values were rejected. For indeno[1,2,3-*cd*]pyrene, dibenzo[*a,h*]anthracene and benzo[ghi]perylene, the kinetic profiles were regressed with an exponential equation, that is,  $C_{pe}/C_w = a(1 - e^{-bt})$ , where  $a$  and  $b$  are the fitting parameters. The  $K_{pew}$  of these three compounds are equal to the fitted  $a$  values when  $t$  approaches infinity, that is,  $\log K_{pew}$  were  $7.04 \pm 0.19$ ,  $7.20 \pm 0.07$ , and  $7.36 \pm 0.04$ , respectively (Table 1).

Because the concentrations of naphthalene and acenaphthylene in blank samples (LDPE and high purity water) were higher than those in the samples,  $K_{pew}$  for these two compounds could not be determined with confidence. Similarly,  $K_{pew}$  for anthracene and benzo[*a*]pyrene were also not determined because their concentrations in LDPE and water at each sampling timepoint were lower than the reporting limits (5 ng/mg and 6.7 ng/L, respectively).

#### Comparison with previously reported $K_{pew}$

Currently, few measured  $K_{pew}$  for HOCs are available in the literature. A compilation of existing data (Table 1) indicates that  $K_{pew}$  of 12 PAHs (Supplemental Data, List S2) and DDTs obtained in the present study generally agree well with the previously measured values from Adams et al. [11] and Hale et al. [24]. For example,  $\log K_{pew}$  of fluoranthene ( $4.93 \pm 0.14$ ), pyrene ( $5.07 \pm 0.14$ ), benzo[*a*]anthracene ( $5.79 \pm 0.15$ ), and chrysene ( $5.70 \pm 0.16$ ) are essentially identical to those ( $4.9 \pm 0.1$ ,  $5.0 \pm 0.1$ ,  $5.7 \pm 0.1$ , and  $5.7 \pm 0.1$ ) reported by Adams et al. [11], but  $\log K_{pew}$  of phenanthrene ( $4.78 \pm 0.12$ ) is 0.5 log units higher than the value ( $4.3 \pm 0.1$ ) obtained by the same authors. In addition,  $\log K_{pew}$  of *p,p'*-DDD and *p,p'*-DDT ( $5.08 \pm 0.05$  and  $5.82 \pm 0.07$ , respectively) are 0.2 log units less than those ( $5.32 \pm 0.03$  and  $6.08 \pm 0.08$ ) measured by Hale et al. [24]. These results suggest that the LDPE stripes used in the present study were comparable to those previously used

by other researchers. Furthermore,  $\log K_{pew}$  of phenanthrene ( $4.78 \pm 0.12$  and  $4.3 \pm 0.1$ ), fluoranthene ( $4.93 \pm 0.14$  and  $4.9 \pm 0.1$ ), pyrene ( $5.07 \pm 0.14$  and  $5.0 \pm 0.1$ ), and chrysene ( $5.70 \pm 0.16$  and  $5.7 \pm 0.1$ ) obtained from the present study and by Adams et al. [11] at  $21 \pm 2^\circ\text{C}$  and  $24 \pm 1^\circ\text{C}$ , respectively, are both higher than those ( $4.16 \pm 0.02$ ,  $4.71 \pm 0.02$ ,  $4.9 \pm 0.1$ , and  $5.0 \pm 0.1$ , respectively) measured by Booi et al. [25] at  $30^\circ\text{C}$ , reflecting a slight temperature effect on  $K_{pew}$ .

#### Determination of detection limits

Apparently, the detection limit of a specific analyte with the passive sampler depends on the amount of LDPE stripes used, the analyte's  $K_{pew}$  in the equilibrium extraction mode, and the minimum detectable amount of the target analyte with the specific detection method. In the present study, the minimum detectable amount of individual PAH and DDT compounds with the gas chromatography/mass spectrometry system used was 10 ng. In addition, 10 g of LDPE stripes were used in each passive sampler. From this information and Equation 1, the detection limits for individual target analytes in water using the passive sampler can be calculated. The detection limits range from  $0.4 \times 10^{-4}$  to  $0.6 \times 10^{-1}$  ng/L for individual PAHs and from  $0.6 \times 10^{-3}$  to  $8.3 \times 10^{-3}$  ng/L for DDT components (Table 1).

#### Field deployment in freshwater

In the present study, only 14 PAHs (designated as  $\Sigma_{14}\text{PAH}$ ; Supplemental Data, List S3) in four reservoirs (Supplemental Data, Fig. S2) were detected by the passive sampler and SPE-LLE method, and the concentrations of  $\Sigma_{14}\text{PAH}$  in the aqueous phase detected with the SPE-LLE method in four reservoirs ranged from 87.7 to 115.5 ng/L (Table 2). In addition, the concentrations of  $\Sigma_5\text{PAH}$  (sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene and dibenzo[*a,h*]anthracene; Supplemental Data, List S4) accounted for 14 to 29% of total PAH concentrations as measured by the SPE-LLE method. Similarly, the passive sampler also obtained a low proportion (<1%) of  $\Sigma_5\text{PAH}$  relative to the total amount of PAHs. The dissolved concentrations of  $\Sigma_{12}\text{PAH}$  (Supplemental Data, List S2) obtained by the passive sampler were 3.8 to 16 ng/L, an order of magnitude lower than those (73.2–93.9 ng/L) obtained with the SPE-LLE method (Table 2). The difference between the two sampling approaches may be attributed to two causes. First, water exchange in and out of the passive sampler became less efficient as time progressed because of blockage by algae in eutrophia reservoirs; therefore, the concentrations of PAHs within the sampler's interior were severely depleted, resulting in lower-than-expected PAH concentrations. Second, the aqueous PAH concentrations obtained through SPE-LLE were likely to be overestimated, because PAHs affiliated with dissolved organic carbon also may have been extracted; such an overestimate was especially magnified because the dissolved organic carbon contents were quite high in the waters of the four reservoirs (3.5–11.2 mg/L; Supplemental Data, Table S2), which is detailed in Supplemental Data. Furthermore, the analyte concentrations obtained by SPE-LLE were snapshots of the environmental values, whereas those from the passive samplers were time-integrated. Therefore, the utility of the passive sampler in freshwater deployment may be enhanced through the use of the kinetic diffusion-based sampling mode [26], and the results obtained by the passive sampler could be verified with other passive sampling techniques, such as solid-phase microextraction fiber.

Table 1. Comparison of polyethylene-water partitioning coefficients ( $K_{\text{pew}}$ , (g/kg<sub>pe</sub>)/(g/L<sub>w</sub>)) and detection limits (pg/L) for target polycyclic aromatic hydrocarbons and DDT and its metabolites on the 50- $\mu\text{m}$  low density polyethylene

	Log $K_{\text{OW}}^{\text{a}}$	Log $K_{\text{pew}}^{\text{b}}$	Log $K_{\text{pew}}^{\text{c}}$	Log $K_{\text{pew}}^{\text{d}}$	Detection limits in water
		T = 21 $\pm$ 2°C	T = 24 $\pm$ 1°C	T = 30°C	
Acenaphthene	4.03	4.25 $\pm$ 0.12			56.9
Fluorene	4.18	4.51 $\pm$ 0.12			30.9
Phenanthrene	4.63	4.78 $\pm$ 0.12	4.3 $\pm$ 0.1	4.16 $\pm$ 0.02	16.6
Fluoranthene	5.22	4.93 $\pm$ 0.14	4.9 $\pm$ 0.1	4.71 $\pm$ 0.02	11.8
Pyrene	5.22	5.07 $\pm$ 0.14	5.0 $\pm$ 0.1	4.9 $\pm$ 0.1	8.45
Benzo[a]anthracene	5.79	5.79 $\pm$ 0.15	5.7 $\pm$ 0.1		1.63
Chrysene	5.91	5.70 $\pm$ 0.16	5.7 $\pm$ 0.1	5.0 $\pm$ 0.1	1.99
Benzo[b]fluoranthene	5.78	6.33 $\pm$ 0.13			0.47
Benzo[k]fluoranthene	6.11	6.56 $\pm$ 0.13			0.28
Indeno[1,2,3-cd]pyrene	6.72	7.04 $\pm$ 0.19			0.09
Dibenzo[a,h]anthracene	7.19	7.20 $\pm$ 0.07			0.06
Benzo[ghi]perylene	7.10	7.36 $\pm$ 0.04			0.04
<i>o,p'</i> -DDE	6.00	5.94 $\pm$ 0.07		6.11 $\pm$ 0.14	1.15
<i>p,p'</i> -DDE	6.96	6.20 $\pm$ 0.10		6.27 $\pm$ 0.09	0.63
<i>o,p'</i> -DDD	6.23	5.27 $\pm$ 0.05		5.37 $\pm$ 0.03	5.37
<i>p,p'</i> -DDD	6.22	5.08 $\pm$ 0.05		5.32 $\pm$ 0.03	8.32
<i>o,p'</i> -DDT	6.79	6.00 $\pm$ 0.10		6.26 $\pm$ 0.16	1.00
<i>p,p'</i> -DDT	6.92	5.82 $\pm$ 0.07		6.08 $\pm$ 0.08	1.51

<sup>a</sup> The log  $K_{\text{OW}}$  of 16 PAHs and six DDTs were adopted from Mackay et al. [30] and De Bruijn et al. [31], respectively.

<sup>b</sup> From the present study.

<sup>c</sup> Acquired from Adams et al. [11].

<sup>d</sup> The log  $K_{\text{pew}}$  were acquired from Booij et al. [25] and converted to (g/kg<sub>pe</sub>)/(g/L<sub>w</sub>) when  $\rho_{\text{pe}} = 0.92 \text{ g/cm}^3$ .

<sup>e</sup> The log  $K_{\text{pew}}$  were acquired from Hale et al. [24] and converted to (g/kg<sub>pe</sub>)/(g/L<sub>w</sub>) when  $\rho_{\text{pe}} = 0.92 \text{ g/cm}^3$ .

DDT = dichlorodiphenyltrichloroethane; DDE = dichlorodiphenyldichloroethylene; DDD = dichlorodiphenyldichloroethane.

#### Field deployment in seawater

With a sampling time of 60 d, six DDTs (Supplemental Data, List S5) and *p,p'*-DDMU, *p,p'*-DDNU, and *p,p'*-DBP, the tertiary and final degradation products of *p,p'*-DDT [22,27–28], were assessed by the passive sampler in Hailing Bay (Supplemental Data, Fig. S2). The dissolved concentrations of *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, *o,p'*-DDT, *o,p'*-DDD, *o,p'*-DDE, and *p,p'*-DDMU at sites A, B-1, and B-2 (Supplemental Data, Fig. S2) were obtained. Because  $K_{\text{pew}}$  of *p,p'*-

DDNU and *p,p'*-DBP are not available in the literature, the field dissolved concentrations could not be quantified. Instead, the concentrations of *p,p'*-DDNU and *p,p'*-DBP in LDPE are reported (Supplemental Data, Table S4). The concentrations of DDXs (sum of *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, *o,p'*-DDT, *o,p'*-DDD, *o,p'*-DDE, and *p,p'*-DDMU; Supplemental Data, List S6) at site A (with a water depth of 13 m) were 0.165, 0.55, 1.27, and 1.74 ng/L at the depths of 12.5, 12, 6.5, and 1 m, respectively, from the air-water interface. At site B-1, the concentrations of DDXs were 0.293, 1.69, 0.578, and 6.01 ng/L at the

Table 2. Comparison of dissolved concentrations (ng/L) of polycyclic aromatic hydrocarbons obtained by a solid-phase extraction combined with liquid-liquid extraction method and the newly developed passive sampler with approximately 10 g low-density polyethylene in four reservoirs of Guangdong Province, China<sup>a</sup>

	TS <sup>a</sup>		JK <sup>a</sup>		ZT <sup>a</sup>		LXH <sup>a</sup>	
	SPE-LLE	LDPE	SPE-LLE	LDPE	SPE-LLE	LDPE	SPE-LLE	LDPE
Acenaphthene	15.3	0.86 $\pm$ 0.6	19.3	0.19 $\pm$ 0.2	26.0	0.51 $\pm$ 0.72	13.7	0.21 $\pm$ 0.06
Fluorene	7.55	1.4 $\pm$ 1.4	18.1	0.80 $\pm$ 0.67	7.28	1.1 $\pm$ 0.07	nd	0.76 $\pm$ 0.35
Phenanthrene	22.2	5.4 $\pm$ 3.3	29.7	4.82 $\pm$ 3.52	24.8	4.83 $\pm$ 3.2	35.4	1.79 $\pm$ 0.58
Anthracene	3.72	na	4.55	na	1.67	na	3.74	na
Fluoranthene	1.63	2.5 $\pm$ 1.0	2.85	1.1 $\pm$ 0.55	2.86	1.81 $\pm$ 0.05	0.51	1.16 $\pm$ 1.26
Pyrene	13.4	1.9 $\pm$ 0.6	15.7	0.39 $\pm$ 0.20	10.8	1.21 $\pm$ 0.15	11.6	0.71 $\pm$ 0.89
Benzo[a]anthracene	0.51	nd	nd	nd	nd	0.015 $\pm$ 0.02	nd	nd
Chrysene	8.81	0.2 $\pm$ 0.1	7.80	0.064 $\pm$ 0.09	nd	0.123 $\pm$ 0.11	5.57	0.04 $\pm$ 0.050
Benzo[b]fluoranthene	nd	0.04 $\pm$ 0.05	nd	nd	nd	0.008 $\pm$ 0.008	3.12	0.002 $\pm$ 0.003
Benzo[k]fluoranthene	2.20	0.015 $\pm$ 0.03	nd	nd	nd	0.008 $\pm$ 0.008	21.3	0.0035 $\pm$ 0.005
Benzo[a]pyrene	14.8	na	17.1	na	14.5	na	4.83	na
Indeno[1,2,3-cd]pyrene	nd	nd	0.41	nd	nd	nd	nd	nd
Dibenzo[a,h]anthracene	nd	nd	nd	nd	nd	nd	nd	nd
Benzo[ghi]perylene	1.76	nd	nd	nd	nd	nd	nd	nd
PAHs	91.6	12.2 $\pm$ 5.1	116	7.4 $\pm$ 3.9	87.7	9.6 $\pm$ 2.3	99.8	4.7 $\pm$ 3.2

<sup>a</sup> Supplemental Data, Fig. S2.

TS = Tongsha Reservoir; JK = Jinkeng Reservoir; ZT = Zengtang Reservoir; LXH = Luixihe Reservoir; PAHs = polycyclic aromatic hydrocarbons; SPE-LLE = solid-phase extraction combined with liquid-liquid extraction; LDPE = low-density polyethylene; nd = not detected; na = not applicable.

Table 3. Comparison of dissolved concentrations (ng/L) of DDT and its metabolites in overlying water obtained by open water passive sampler with 10 g low density polyethylene as sorbent phase and modified polydimethylsiloxane coated solid-phase microextraction fibers at sites A, B-1 and B-2 in Hailing Bay of Guangdong Province, China<sup>a</sup>

Compounds	LDPE		PDMS-coated fiber <sup>b</sup>	LDPE		PDMS-coated fiber		
	A		A	B-1		B-2		B
	$C_w^c$	$C_{w,salt}^d$	$C_w$	$C_w$	$C_{w,salt}$	$C_w$	$C_{w,salt}$	$C_w$
<i>p,p'</i> -DDMU	0.034 <sup>c</sup>	0.034 <sup>c</sup>	0.213	0.085 <sup>c</sup>	0.085 <sup>c</sup>	0.003 <sup>e</sup>	0.003 <sup>e</sup>	0.141
<i>o,p'</i> -DDE	0.0059	0.0035	0.036	0.019	0.011	u.r. <sup>f</sup>	u.r. <sup>f</sup>	0.030
<i>p,p'</i> -DDE	0.0262	0.0162	0.109	0.148	0.092	0.0025	0.0015	0.104
<i>o,p'</i> -DDD	0.672	0.377	0.616	2.0	1.13	0.078	0.044	0.468
<i>p,p'</i> -DDD	2.02	1.13	2.38	6.78	3.78	0.247	0.138	1.49
<i>o,p'</i> -DDT	0.031	0.0175	u.r. <sup>f</sup>	0.168	0.094	0.0034	0.0019	u.r. <sup>f</sup>
<i>p,p'</i> -DDT	0.267	0.16	0.152	1.37	0.819	0.028	0.017	0.096
DDXs <sup>g</sup>	3.06	1.74	3.51	10.6	6.01	0.361	0.205	2.33

<sup>a</sup> Supplemental Data, Fig. S2.

<sup>b</sup> Acquired from Xing et al. [29].

<sup>c</sup> The concentration of an analyte ( $C_w$ , pg/L) in water was calculated from  $C_w = \frac{C_{pe}}{K_{pew}}$ , where  $C_{pe}$  is the analyte concentration in LDPE,  $K_{pew}$  is polyethylene-water partitioning coefficients uncorrected for salt effect, which is presented in Table 1.

<sup>d</sup> The concentration of an analyte ( $C_{w,salt}$ , pg/L) in water was calculated from  $C_{w,salt} = \frac{C_{pe}}{K_{pew,salt}}$ , where the  $K_{pew,salt}$  is polyethylene-water partitioning coefficients with corrected for salt effect, which is presented in Supplemental Data, Table S3. The salinity of water at the sampling site is 29.8‰ and the log  $K_{pew,salt}$  for an analyte with 3.5% NaCl in water was used for calculation.

<sup>e</sup> Data were calculated from  $\log K_{pew} = 5.37 \pm 0.07$  (g/cm<sup>3</sup><sub>pe</sub>)/(g/cm<sup>3</sup><sub>water</sub>) as given Hale et al. when  $\rho_{pe} = 0.92$  g/cm<sup>3</sup>.

<sup>f</sup> The abbreviation for under limits of detection.

<sup>g</sup> Sum of *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, *o,p'*-DDT, *o,p'*-DDD, *o,p'*-DDE and *p,p'*-DDMU.

LDPE = low density polyethylene; PDMS = polydimethylsiloxane; DDMU = dichlorodiphenylmonochloroethylene; DDE = dichlorodiphenyldichloroethylene; DDD = dichlorodiphenyldichloroethane; DDT = dichlorodiphenyltrichloroethane.

depths of 3.5, 3, 2, and 1 m. In addition, the levels of DDXs at site B-2 were 0.265 and 0.204 ng/L (not significantly different) at the depths of 5 and 1 m.

To validate the utility of the passive sampler further, the concentrations of DDT components at sites A, B-1, and B-2 obtained with the passive sampler were compared to those measured with a modified PDMS-coated fiber sampler [29] in August 2007 (Table 3). Because the concentrations of DDXs measured by the PDMS-coated fiber sampler [29] were not corrected for salt effects, the concentrations acquired by the present passive sampler were also calculated without correcting the salt effect. Table 3 indicates that the concentration (3.06 ng/L) of DDXs measured with the present passive sampler was considerably similar to that (3.51 ng/L) obtained with the PDMS-coated fiber sampler [29] at sites A and A' (Supplemental Data, Fig. S2). In particular, the compositional profiles of DDXs obtained by the present passive sampler and the PDMS-coated fiber sampler were also similar, with *p,p'*-DDD dominating all detectable components (relative abundances of 66% and 68%, respectively), followed by *o,p'*-DDD and *p,p'*-DDT. In addition, the concentrations of DDXs (10.6 ng/L) obtained by the present passive sampler were 10.6 ng/L at site B-1 and 0.361 ng/L at site B-2, as compared to that (2.33 ng/L) acquired by the PDMS-coated fiber sampler [29] at site B' (Supplemental Data, Fig. S2). Given the substantial difference between the sampling times, the results obtained with the present passive sampler and the modified PDMS coated fiber sampler can be reasonably considered comparable, demonstrating that the present passive sampler is able to accurately assess HOC concentrations in seawater.

## CONCLUSIONS

A passive sampler with LDPE as the sorbent phase was developed and field-tested for determination of the dissolved concentrations of PAHs and DDTs in four reservoirs and one

coastal location. The results from the field applications demonstrated that the utility of the present passive sampler in freshwater with eutrophication could be improved in the kinetic diffusion-based sampling mode, and the sampler is able to accurately measure HOC concentrations in seawater.

## SUPPLEMENTAL DATA

Additional tables and figures including a photo of the passive sampler, field sampling sites and information, and the concentrations of DDXs determined with the passive sampler in Hailing Bay of Guangdong Province, China.

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