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ISOTOPIC EXCHANGE ON SOLID-PHASE MICRO EXTRACTION FIBER IN SEDIMENT UNDER STAGNANT CONDITIONS: IMPLICATIONS FOR FIELD APPLICATION OF PERFORMANCE REFERENCE COMPOUND CALIBRATION

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Abstract: An overlooked issue for field application of in situ performance reference compound (PRC) calibration methods is the validity of the assumption that both the sorption of a target compound and desorption of its corresponding PRC follow the first-order kinetics with the same rate constants under stagnant conditions. In the present study, disposable polydimethylsiloxane fibers of 2 sizes (7 and 35 μm) impregnated with 8 ^{13}C-labeled or deuterated PRCs were statically deployed into different marine sediments, from which the kinetics for sorption of the target compounds and desorption of the PRCs were characterized. Nonsymmetrical profiles were observed for exchange of the target analytes and their corresponding PRCs in sediment under stagnant conditions. The hysteretic desorption of PRCs in the kinetic regime may be ascribed to the low chemical potential between the fiber and sediment porewater, which reflects the inability of water molecules to rapidly diffuse through sediment to solvate the PRCs in the aqueous layer around the fiber surface. A moderate correlation ($r = 0.77$ and $r = 0.57$, $p < 0.05$ for both regressions) between the PRC-calibrated equilibrium concentrations of 1,1-dichloro-2,2-bis-(chlorophenyl) ethylene (p,p'-DDE) and polychlorinated biphenyl (PCB)-153 and the lipid normalized levels in worms (*Neanthes arenaceodentata*) was obtained in co-exposure tests under simulating field conditions, probably resulting from slightly overestimated bioavailability because of the hysteretic desorption of PRCs and toxic effects. *Environ Toxicol Chem* 2016;35:1978–1985.

Keywords: Passive sampling Performance reference compound calibration Hydrophobic organic compounds Nonsymmetrical relationship Stagnant sediment

INTRODUCTION

Passive sampling techniques, such as solid-phase microextraction (SPME) fiber [1] and polyethylene device [2], have often been used to measure the freely dissolved concentrations (C_{free}) of hydrophobic organic compounds (HOCs) in sediment porewater. Field measurement of freely dissolved HOCs or assessment of bioavailability is an important objective for the development of passive samplers [3]. However, the application of passive samplers in measuring C_{free} of HOCs in sediment porewater has been mostly limited to laboratory experiments, and only a few in situ field studies have been conducted [4–10].

Two calibration approaches, based on either equilibrium partitioning or diffusion kinetics, have been used to quantify C_{free} of HOCs in sediment. For equilibrium partitioning, C_{free} of HOCs is derived from the analyte concentration in the sampler's sorbent phase divided by the partition coefficient for the analyte between the sorbent and water [5]. However, previous studies showed that it may take several months for certain HOCs to reach equilibrium between the sorbent phase and water for highly HOCs under stagnant conditions [7,11]. To circumvent this limitation, a kinetically diffusion-controlled calibration method (i.e., calibration with the use of performance reference compounds [PRCs]), was introduced [12]. The PRC calibration was first applied in field sediment sampling with semipermeable membrane devices [13].

In a general application of PRC calibration, PRCs are preloaded onto the passive sampler's sorbent phase prior to deployment. When the PRCs are exposed to sediment, sorption of the target compounds from the matrix and desorption of their corresponding PRCs from the sorbent phase proceed concurrently; the rates of sorption (k_s) and desorption (k_{des}) are assumed to be identical. This assumption has been considered valid if the PRCs are isotope-labeled counterparts of the target analytes [14]. The PRC calibration approach was recently applied in SPME fibers and was able to estimate C_{free} of HOCs in sediments under mixed conditions [15]. One of the most beneficial uses of passive sampling techniques is field application, particularly in situ deployment in sediment, where stagnant conditions prevail. However, the assumption that k_s of a target analyte is equal to k_{des} of its PRC (even if it is isotope-labeled) has not been verified in sediment under stagnant conditions [16].

The objective of the present study was to examine the above-mentioned assumption by comparing the kinetic profiles of sorption of a target analyte and desorption of its isotope-labeled PRC in sediment under stagnant conditions. To accomplish this objective, disposable SPME fibers of 2 sizes (7 and 35 μm) were used with dichlorodiphenyltrichloroethanes (DDTs) and polychlorinated biphenyls (PCBs) as the model HOCs in a series of kinetics experiments. Co-exposure tests with preloaded SPME fibers and a marine worm (*Neanthes arenaceodentata*) in sediment were also conducted under simulated field conditions

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to further demonstrate the feasibility of the PRC calibration method for in situ applications.

METHODS AND MATERIALS

Materials

Disposable fibers in 2 sizes, including a 430-μm glass core coated with polydimethylsiloxane (PDMS) of 35-μm thickness and a 110-μm glass core coated with PDMS of 7-μm thickness, were purchased from Polymicro Technologies. All fibers were precleaned with ethyl acetate through Soxhlet extraction for 72 h. Each cleaned fiber was manually cut into 2-cm- or 5-cm-long pieces with a razor blade before use.

Standards of 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl) ethane (*p,p′*-DDT), 1,1,1-trichloro-2,4-bis-(*o*-chlorophenyl) ethane (*o,p′*-DDT), 1,1-dichloro-2,2-bis-(chlorophenyl) ethane (*p,p′*-DDD), 1,1-dichloro-2,2-bis-(chlorophenyl) ethylene (*p,p′*-DDE), 1,1-dichloro-2,4-bis-(chlorophenyl) ethylene (*o,p′*-DDE), 1,1-dichloro-2,4-bis-(chlorophenyl) ethane (*o,p′*-DDD), 2 PCB congeners (PCB-52 and PCB-153), surrogates (PCB-67 and PCB-191), and internal standards (PCB-30 and PCB-82) were all purchased from AccuStandard. Standards of isotope-labeled PRCs including ^{13}C-labeled (^{13}C-PCB-52, ^{13}C-PCB-153, ^{13}C-*o,p′*-DDD, and ^{13}C-*o,p′*-DDE) and deuterated compounds (*p,p′*-DDT-d_8, *o,p′*-DDT-d_8, *p,p′*-DDD-d_8, and *p,p′*-DDE-d_8) were purchased from Cambridge Isotope Laboratories or C/D/N Isotopes. Solvents (hexane, dichloromethane, and acetone; Honeywell Burdick & Jackson) and other chemicals were of analytical grade.

Sediment collection and preparation

A marine sediment was collected from New Fields in Port Gamble (WA, USA), sieved through a 2-mm mesh, and stored at 4 °C before use. The sediment was spiked with the target compounds following the US Environmental Protection Agency's guidelines [15]. Briefly, 10 g of sand was spiked with a mixture of all DDT and PCB compounds, and the residual solvent was removed by keeping the sample in a fume hood. The treated sand sample was then mixed with 1.0 kg (dry wt equivalent) of wet sediment by rotating at 120 rpm for 1 h every day at room temperature. After 1 mo of mixing, activated carbon (particle size < 0.15 mm) from Calgon Carbon was added to the spiked sediment at 1%, 2%, or 5% (w/w, dry wt) to obtain sediments with different organic carbon contents. The activated carbon-amended sediments were mixed for 1 mo more to achieve homogeneous distribution. The organic carbon contents in the native and activated carbon-amended sediments were determined to be 0.27%, 0.99%, 1.72%, and 4.93%, respectively. The concentrations of DDT and its metabolites, the sum of which is abbreviated as DDTs hereafter, and PCBs in the spiked sediments (Supplemental Data, Table S1) were analyzed with a method given elsewhere [15].

Isotropy validation experiments

To prepare preloaded fibers, 50 clean fibers in a batch were equilibrated with individual isotope-labeled PRCs (at 20 μg/L each) contained in a 50-mL acetone–water (4:1 in volume) solution agitated at 80 rpm for 24 h [14,15]. The preloaded fibers were rinsed with deionized water prior to use. In addition, the actual preloaded amounts of individual PRCs were determined in a subset of 10 randomly selected fibers. The initial preloaded concentrations of PRCs on the 7-μm and 35-μm fibers were in the ranges of 110 μg/mL to 230 μg/mL and 540 ng/mL to 1250 ng/mL, respectively.

All native and activated carbon-amended sediment samples were used for isotropy examination. A 4-g aliquot (wet wt; 50% of water content) of native, 1% or 2% activated carbon-amended sediments was placed in a 20-mL glass vial and dosed with 2.0 mL sodium azide (2 mg/L) to suppress microbial activity. For 5% activated carbon-amended sediment, a larger sample size and container were needed (i.e., 10 g of sediment and a 50-mL glass jar), to compensate for the increased sorption resulting from the higher carbon content. All sample containers were mixed for 2 min on a vortex and stored at 4 °C overnight. The 2-cm-long preloaded fibers (7- and 35-μm) were placed into the 2-g sediment samples. For 5% activated carbon-amended sediment, 5-cm-long fibers with a 7-μm PDMS coating were used to ensure sufficient detection sensitivity. All sample containers were sealed and maintained at room temperature (21 ± 1 °C) under stagnant conditions.

At each predetermined time point (Supplemental Data, Table S2; i.e., 6 d, 11 d, 30 d, 52 d, 73 d, 105 d, or 165 d), for 7-μm fiber in native sediment, 3 replicate fibers were retrieved from 3 sampling vials, respectively, rinsed with deionized water, and gently wiped with a paper tissue to remove particles from the fiber surface. Each fiber was transferred to a 350-μL glass insert housed in a 2-mL gas chromatography (GC) vial, and 200 μL of hexane was added to the insert. The GC vials with fibers were sonicated in a water bath (FS110H, Fisher Scientific) for 20 min, and PCB-30 and PCB-82 (in 2 μL hexane) were added as internal standards to each insert. All PRCs and target analytes were measured with an Agilent 6890N GC system coupled with a 5973 mass selective detector in the selective ion scanning mode. The oven temperature program and instrumental parameters have been detailed elsewhere [15].

Co-exposure tests

Co-exposure bioaccumulation tests were carried out to evaluate the ability of the PRC–SPME method in predicting the bioavailability of HOCs in sediment under stagnant conditions [15,17]. Six replicates were used for each sediment type. After 1 wk of acclimation, 15 marine polychaete worms (*N. arenaceodentata*) and 5-cm-long 35-μm PDMS fibers preloaded with PRCs were introduced into a 1-L beaker containing 30 g dry weight of sediment and 300 mL of 32‰ artificial seawater. Each test vessel was continuously aerated, and the water level was maintained through periodic addition of artificial seawater. Worms and fibers were recovered by sieving the sediment slurry through a 100-mesh sieve at the end of 12-d exposure. The exposure time was selected through preliminary bioaccumulation experiments for reaching steady-state chemical concentrations in the test organism. After collection, the worms were exposed to clean artificial seawater for 48 h for depuration, after which they were stored at –20 °C until chemical analysis.

Worm tissues were freeze-dried at –45 °C and extracted with 40 mL of acetone–dichloromethane (1:1 in volume) by sonication for 30 min. After 3 extractions, the combined extract was concentrated, and one-fifth of the extract was removed for analysis of lipid content. The remaining extract was purified through a solid-phase cartridge packed with 1-cm acidic silica, and the extract was eluted with 20 mL of hexane–dichloromethane (1:1 in volume). The eluent was concentrated to 0.1 mL under a nitrogen stream and spiked with the internal standards (PCB-30 and PCB-82 in 10 μL) prior to instrumental analysis.

Quality assurance and quality control

Laboratory blanks, prepared with clean fibers and anhydrous sodium sulfates used to dry sediments, were processed in parallel with preloaded fibers and sediments. No target analyte was detected in the blank samples. The recoveries of 2 surrogate standards (PCB-67 and PCB-191) were $101 \pm 12\%$ and $109 \pm 11\%$ for sediment and $102 \pm 4\%$ and $77 \pm 7\%$ for worm tissue samples. During instrumental analysis, a standard was injected after analysis of every 10 samples for evaluation of the standard calibration curves used to quantify the target analytes in all samples. The standard calibration curves were considered acceptable if the standard deviations between the relative response factors of all target analytes in the standard sample and initial calibration values were less than 20%.

RESULTS AND DISCUSSION

Sorption and desorption kinetics

The exponential uptake model can be used only as the mass transfer from sediment to polymer sampler is taken as a 2-compartment system, with only 1 rate-limiting step in the aqueous or sampler layer [5]. As Witt et al. [5] suggested, this requirement can be easily satisfied with well-mixed sediments in the laboratory. In stagnant sediment, the mass-transfer resistance contributed by the stagnant porous media should be included in profiling the sorption kinetics of target compounds when the sampler imposes local depletion of the target compounds in sediment in its vicinity. Alternatively, if a nondepletive extraction (i.e., the extracted amount of a target analyte in the sampler is less than 5% of that in sediment porewater) is conducted, the mass-transfer resistance from sediment may be neglected. This situation can probably be achieved for small samplers, such as PDMS fibers with 5×10^{-5} to 0.01 mL in volume. On the other hand, the accessible analyte in sediment was considered to be available for the water phase. The study of Smedes et al. [18] indicated that depletion (D') at equilibrium can be calculated by the following equation:

$$D' = \frac{K_f V_f}{K_{asw} M + K_f V_f} = \frac{K_f V_f}{0.63\, f_{oc} K_{ow} M + K_f V_f} \quad (1)$$

where K_f is the fiber–water partition coefficient of the analyte; V_f is the volume (mL) of fiber; K_{asw} is the sediment–water partition coefficient of the accessible pool (L/kg); M is the mass (g) of sediment; f_{oc} is the total organic carbon (TOC) content in sediment; and K_{OW} is the octanol–water partition coefficient. In the present study, the volumes of 7-μm and 35-μm fibers are 5×10^{-5} and 0.01 mL, respectively. The depletions of all target compounds except for PCB-52 and PCB-153 at equilibrium were less than 5% (Supplemental Data, Table S3). Therefore, the mass-transfer resistance could be neglected in the present study.

The uptake of a target HOC by the PDMS fiber can be described by a 1-compartment first-order kinetic model:

$$n = n_e\left(1 - e^{-k_s t}\right) \quad (2)$$

where n and n_e are the amounts of an HOC sorbed on the PDMS fiber at the sampling time t and at equilibrium, respectively. In the native sediment, the k_s values of DDTs for 7-μm and 35-μm PDMS fibers were in the ranges of $0.058\ d^{-1}$ to $0.097\ d^{-1}$ and $0.098\ d^{-1}$ to $0.12\ d^{-1}$, respectively, whereas the k_s values of PCB-52 were $0.033\ d^{-1}$ for the 7-μm fiber and $0.051\ d^{-1}$ for the 35-μm fiber (Table 1). It should be noted that the uptake amounts of *o,p′*-DDE and *p,p′*-DDE on the 7-μm fiber at 165 d were excluded, because the differences in the uptake amounts of *o,p′*-DDE and *p,p′*-DDE between 73 d and 105 d were not significant, but those between 105 d and 165 d were significantly different.

A 1-phase kinetic desorption model was used to fit desorption kinetics by using the remaining amounts of the preloaded PRCs (q) on the fiber at different sampling intervals:

$$q = q_0\, e^{-k_{des} t} \quad (3)$$

where q_0 is the impregnated amounts of PRCs before deployment ($t = 0$). The fit was excellent for all target compounds except ^{13}C-PCB-153, with r^2 ranging from 0.92 to 0.99 (Supplemental Data, Table S4). Under stagnant conditions, the k_{des} values of all PRCs (except ^{13}C-PCB-153) from the 7-μm and 35-μm PDMS fibers ranged from $0.0077\ d^{-1}$ to $0.23\ d^{-1}$ in the native and activated carbon-amended sediments, whereas the k_{des} values of ^{13}C-PCB-153 were $0.015 \pm 0.004\ d^{-1}$ and $0.032 \pm 0.004\ d^{-1}$ in the 5% activated carbon-amended sediment. Desorption of ^{13}C-PCB-153 from fibers was slow in the other sediments, and approximately 40% of the initially loaded PRCs remained on the fibers even after 107 d or 168 d. The slow desorption also resulted in larger

Table 1. Rate constants (d^{-1}) for sorption (k_s) and desorption(k_{des}) of dichlorodiphenyltrichloroethanes and polychlorinated biphenyls and the corresponding performance reference compounds on polydimethylsiloxane-coated fibers of 7-μm and 35-μm thicknesses in native New Fields (Port Gamble, WA) sediment under stagnant conditions (mean ± standard deviation; $n = 3$)

	k_s			k_{des}	
Compound	7-μm	35-μm	PRCs	7-μm	35-μm
PCB-52	0.033 ± 0.010	0.051 ± 0.016	^{13}C-PCB-52	0.020 ± 0.002	0.014 ± 0.003
PCB-153		0.051 ± 0.013	^{13}C-PCB-153	0.011 ± 0.006[a]	0.011 ± 0.007[a]
o,p′-DDD	0.087 ± 0.012	0.11 ± 0.021	^{13}C-*o,p′*-DDD	0.024 ± 0.003	0.013 ± 0.003
o,p′-DDE	0.058 ± 0.010	0.098 ± 0.036	^{13}C-*o,p′*-DDE	0.014 ± 0.001	0.0098 ± 0.0018
p,p′-DDD	0.097 ± 0.014	0.12 ± 0.018	*p,p′*-DDD-d_8	0.032 ± 0.003	0.020 ± 0.003
p,p′-DDE	0.061 ± 0.010	0.098 ± 0.036	*p,p′*-DDE-d_8	0.013 ± 0.001	0.0087 ± 0.0015
o,p′-DDT	0.097 ± 0.016		*o,p′*-DDT-d_8	0.011 ± 0.002	0.0098 ± 0.0018
p,p′-DDT	0.031 ± 0.0060		*p,p′*-DDT-d_8	0.012 ± 0.001	0.0077 ± 0.0010

[a]Average value of k_{des} calculated by fitting retained fractions of ^{13}C-PCB-153 with Equation 3 at all sampling timepoints.

PCB = polychlorinated biphenyls; PRCs = performance reference compounds; *o,p′*-DDD = 1,1-dichloro-2,4-bis-(chlorophenyl) ethane; *o,p′*-DDE = 1,1-dichloro-2,4-bis-(chlorophenyl) ethylene; *p,p′*-DDD = 1,1-dichloro-2,2-bis-(chlorophenyl) ethane; *p,p′*-DDE = 1,1-dichloro-2,2-bis-(chlorophenyl) ethylene; *o,p′*-DDT = 1,1,1-trichloro-2,4-bis-(*o*-chlorophenyl) ethane; *p,p′*-DDT = 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl) ethane.

deviations in the estimated k_{des} values (Table 1). Therefore, k_{des} values of ^{13}C-PCB-153 in the native and 1% or 2% activated carbon-amended sediments were excluded in the following discussion.

The k_{des} values of PRCs consistently increased with increasing activated carbon contents in sediments (Figure 1 and Supplemental Data, Figure S1). The dependence of k_{des} on the sediment organic carbon content may be attributed to increased driving force as a result of enhanced HOC partitioning into the sediment. For field measurement of dissolved HOCs in sediment by passive samplers, a previous study conducted with polyethylene (PE)-containing samplers and the PRC calibration method suggested that samplers should be retrieved when the lost fractions of PRCs were within 20% to 80%, so as to minimize analytical uncertainties [19]. Moreover, the nonlinear least-squares regression method, which correlates the lost fractions of PRCs with log-based octanol–water coefficients (log K_{OW}) to estimate sampling rates, was able to use the full loss range of PRCs (i.e., between 0% and 100%) [20]. On the other hand, native sediment often contains various amounts of organic materials such as peat, lignite, charcoal, and lignite coke [21,22]; therefore, sediment TOC contents should be considered in the selection of optimized field sampling time to achieve optimal lost fractions of PRCs for quantification.

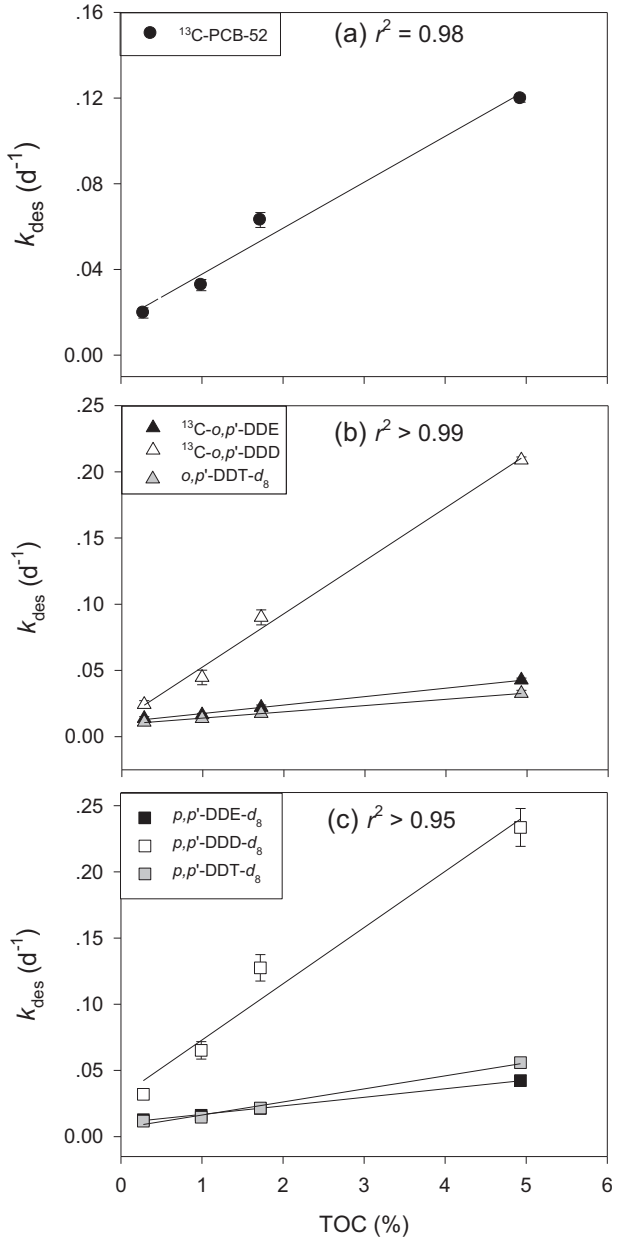

Figure 1. Correlations between the desorption rates (k_{des}; d^{-1}) of isotope-labeled analogs from 7-μm polydimethylsiloxane fiber under stagnant conditions and contents of total organic carbon (TOC; %) in New Fields (Port Gamble, WA, USA) sediments amended without and with activated carbon. ^{13}C-*o*,*p*′-DDE = ^{13}C-1,1-dichloro-2,4-bis-(chlorophenyl) ethylene; ^{13}C-*o*,*p*′-DDD = ^{13}C-1,1-dichloro-2,4-bis-(chlorophenyl) ethane; *o*,*p*′-DDT-d_8 = 1,1,1-trichloro-2,4-bis-(*o*-chlorophenyl) ethane-d_8; *p*,*p*′-DDT-d_8 = 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane-d_8; *p*,*p*′-DDD-d_8 = 1,1-dichloro-2,2-bis-(chlorophenyl)ethane-d_8; *p*,*p*′-DDE-d_8 = 1,1-dichloro-2,2-bis-(chlorophenyl)ethylene-d_8.

Isotropy validation

To make PRC calibration work, the sorption rate of a target compound should be identical to the desorption rate of the corresponding isotope-labeled counterpart (PRC) with SPME fiber, that is,

$$\frac{n}{n_e} + \frac{q}{q_0} = 1 \quad (4)$$

Our previous study demonstrated that the sorption kinetics of DDTs were symmetrical with the desorption kinetics of the PRCs under mixed conditions [15]. However, the present study showed that the sorption kinetics of PCBs and DDTs and the desorption kinetics of their PRCs were not symmetrical on the 7-μm and 35-μm fibers under stagnant conditions (Figures 2 and 3, and Supplemental Data, Figure S2). These nonsymmetrical profiles were also observed for uptake of PCBs and depletion of their PRCs (PCB-29, PCB-69, PCB-103, PCB-155, and PCB-192) in field sampling with polyoxymethylene-based samplers [4].

As shown in Figures 2 and 3, the sum of n/n_e for 4 nonlabeled DDT metabolites and q/q_0 for the labeled PRCs was mostly greater than 1.2 throughout the exposure time under stagnant conditions, that is, for a test value of 1.2, $p < 0.05$ for *o*,*p*′-DDE and *p*,*p*′-DDE and their labeled PRCs and $p > 0.05$ for *p*,*p*′-DDD and *p*,*p*′-DDD-d_8 by 1-sample *t*-test. Apparently, DDTs and PCBs equilibrated between the PMDS-coated fibers and porewater faster than the corresponding labeled PRCs. Previous studies have demonstrated that dissolved organic matter (DOM), colloids, and surfactants could enhance the diffusive mass transport of an HOC between the aqueous phase and sorbents of passive samplers [23–26]. For example, the rate constant of fluoranthene from a 600-μm PDMS-coated fiber (source) to another 600-μm PDMS-coated fiber (sink) in humic acid solution was enhanced by a factor of 9 at a humic acid concentration of 10 g/L compared with pure water [24]. Ter Laak et al. [26] also found that humic acid could facilitate the transport of PCBs and PBDEs from a PDMS polymer to an aqueous medium. Therefore, DOM, or colloidal materials, in native and activated carbon-amended sediments may better facilitate the sorption mass transport of DDTs and PCBs from porewater to a PDMS polymer than the desorption transfer of labeled PRCs from a PDMS polymer to porewater under stagnant conditions. These results suggested that the prerequisite for accurately measuring analyte concentrations through PRC calibration (i.e., the presence of a symmetrical relationship between the sorption kinetics of target analytes and desorption kinetics of their corresponding PRCs) was not satisfied in native sediment under stagnant conditions.

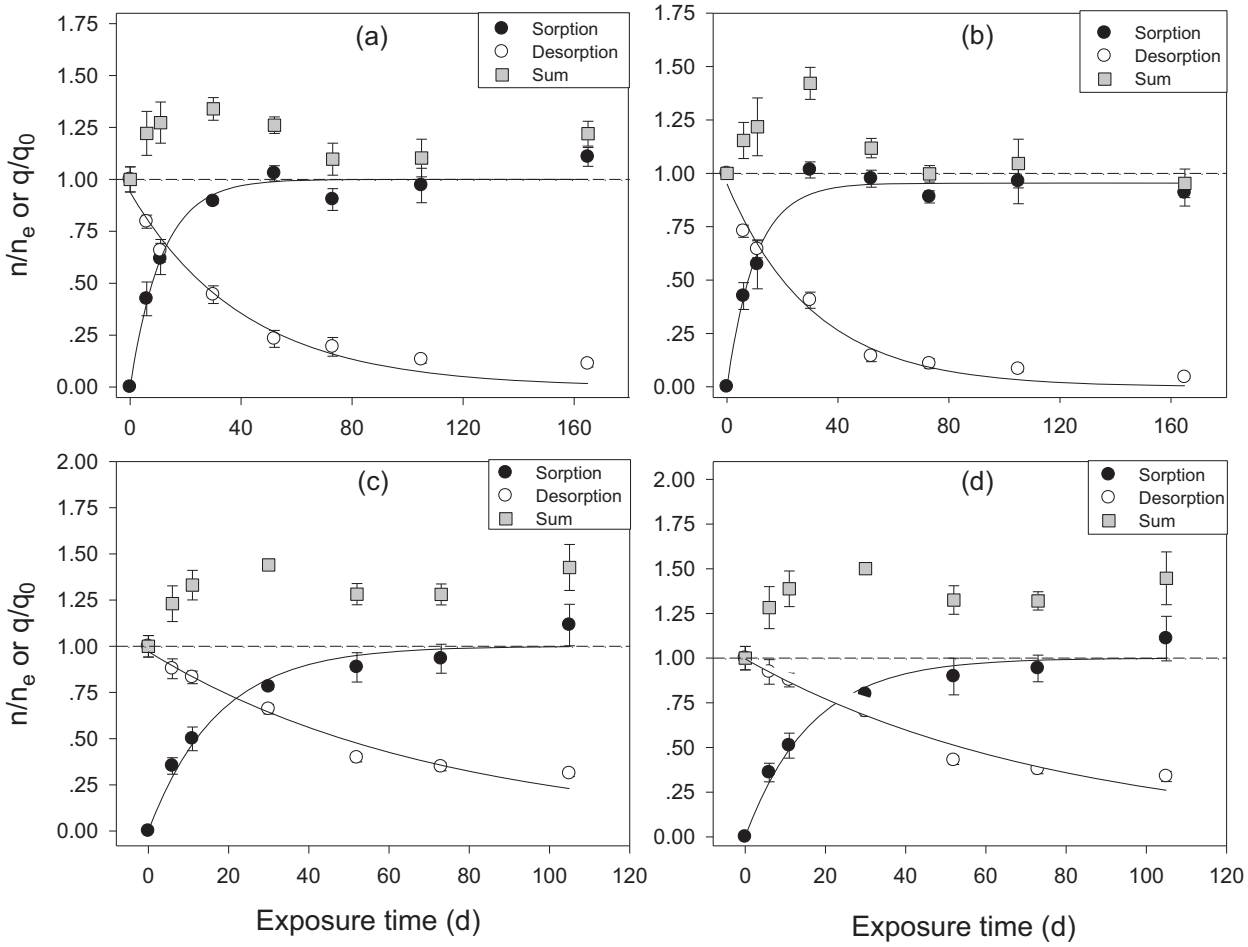

Figure 2. Sorption kinetics of target compounds and desorption kinetics of corresponding isotope-labeled analogs (as performance reference compounds [PRCs]) on 7-μm polydimethylsiloxane fiber in native New Fields (Port Gamble, WA, USA) sediment under stagnant conditions. (**a**) 1,1-dichloro-2,4-bis-(chlorophenyl) ethane (*o,p′*-DDD) and ^{13}C-1,1-dichloro-2,4-bis-(chlorophenyl) ethane (^{13}C-*o,p′*-DDD); (**b**) 1,1-dichloro-2,2-bis-(chlorophenyl) ethane (*p,p′*-DDD) and 1,1-dichloro-2,2-bis-(chlorophenyl) ethane-d_8 (*p,p′*-DDD-d_8). (**c**) 1,1-dichloro-2,4-bis-(chlorophenyl) ethylene (*o,p′*-DDE) and ^{13}C-1,1-dichloro-2,4-bis-(chlorophenyl) ethylene (^{13}C-*o,p′*-DDE). (**d**) 1,1-dichloro-2,2-bis-(chlorophenyl) ethylene (*p,p′*-DDE) and 1,1-dichloro-2,2-bis-(chlorophenyl) ethylene-d_8 (*p,p′*-DDE-d_8). q_0 is the initial amount of PRC on the fiber; q is the amount of PRC remaining on the fiber at time t; n and n_e are the amounts of target compound on the fiber at time t and at equilibrium; sum $= q/q_0 + n/n_e$.

Proposed mechanism for nonsymmetrical relationship

In principle, sorption of target compounds and desorption of PRCs between SPME fiber and sediment porewater may be governed by thermodynamic and/or kinetic mechanisms. Sorption of target compounds and desorption of isotope-labeled PRCs would eventually reach thermodynamic equilibrium between the fiber and porewater. The hysteretic desorption of PRCs in the kinetic regime may be the result of the low chemical potential between the fiber and sediment porewater, which reflects the inability of water molecules to rapidly diffuse through sediment to solvate PRCs in the aqueous layer around the fiber surface [4]. These nonsymmetric kinetics for sorption and desorption of 2 compounds with the same physiochemical properties were also observed for chlorpyrifos between sediment and water even under mixed conditions [27]. Previous studies suggested that prolonged desorption of HOCs from contaminated soil or sediment may be ascribed to the formation and deformation of internal pores within organic matter, leading to sequestration of sorbed target compounds [27–29]. However, PDMS polymer acts like a viscous liquid that distinguishes it from sediment organic matter. Consequently, the nonsymmetric relationship such as that observed in the present study (Figures 2 and 3) may vary with increasing water diffusive rate induced by external forces, such as bioturbation in field sediments.

Implications for field passive sampling

The nonsymmetric kinetic profiles (Figures 2 and 3) for sorption of DDTs and PCBs and desorption of their corresponding PRCs were obtained at high sediment concentrations of DDTs and PCBs under stagnant conditions. However, field passive sampling of HOCs with PRC calibration may be subject to bioturbation induced by benthic organisms, resulting in a situation somewhere between the mixed and stagnant conditions. To obtain a robust assessment, the experimental conditions for co-exposure tests with preloaded fibers and *N. arenaceodentata* in spiked sediments were similar to those in field sediment. The results (Figure 4) demonstrated that there were moderate correlations between the concentrations of *p,p′*-DDE and PCB-153 in the worms and the equilibrium fiber concentrations estimated from the lost fractions of PRCs (Equation 4) dividing the fiber volume. The slopes of 1.8 ± 0.3 and 1.6 ± 0.5 in Figure 4 suggested that the bioavailability of *p,p′*-DDE and PCB-153 in sediment was slightly overestimated, which was probably the result of nonsymmetry in the sorption kinetics of native target

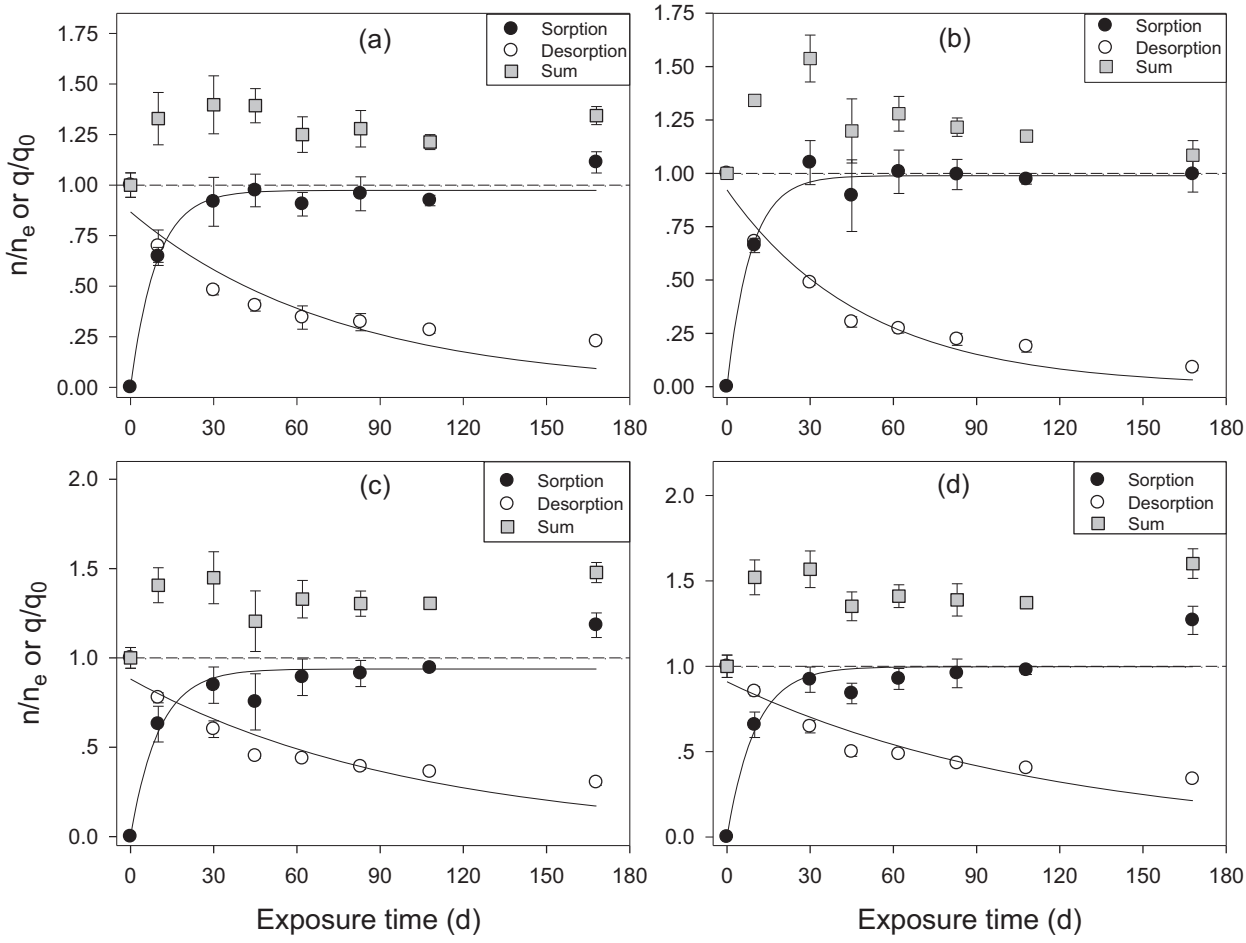

Figure 3. Sorption kinetics of target compounds and desorption kinetics of corresponding isotope-labeled analogs (as performance reference compounds (PRCs)) on 35-μm polydimethylsiloxane fiber in native New Fields (Port Gamble, WA, USA) sediment under stagnant conditions. (**a**) 1,1-dichloro-2,4-bis-(chlorophenyl) ethane (*o*,*p*′-DDD) and ^{13}C-1,1-dichloro-2,4-bis-(chlorophenyl) ethane (^{13}C-*o*,*p*′-DDD). (**b**) 1,1-dichloro-2,2-bis-(chlorophenyl) ethane (*p*,*p*′-DDD) and 1,1-dichloro-2,2-bis-(chlorophenyl) ethane-d_8 (*p*,*p*′-DDD-d_8). (**c**) 1,1-dichloro-2,4-bis-(chlorophenyl) ethylene (*o*,*p*′-DDE) and ^{13}C-1,1-dichloro-2,4-bis-(chlorophenyl) ethylene (^{13}C-*o*,*p*′-DDE). (**d**) 1,1-dichloro-2,2-bis-(chlorophenyl) ethylene (*p*,*p*′-DDE) and 1,1-dichloro-2,2-bis-(chlorophenyl) ethylene-d_8 (*p*,*p*′-DDE-d_8). q_0 is the initial amount of PRC on the fiber; q is the amount of PRC remaining on the fiber at time t; n and n_e are the amounts of target compound on the fiber at time t and at equilibrium; sum $= q/q_0 + n/n_e$.

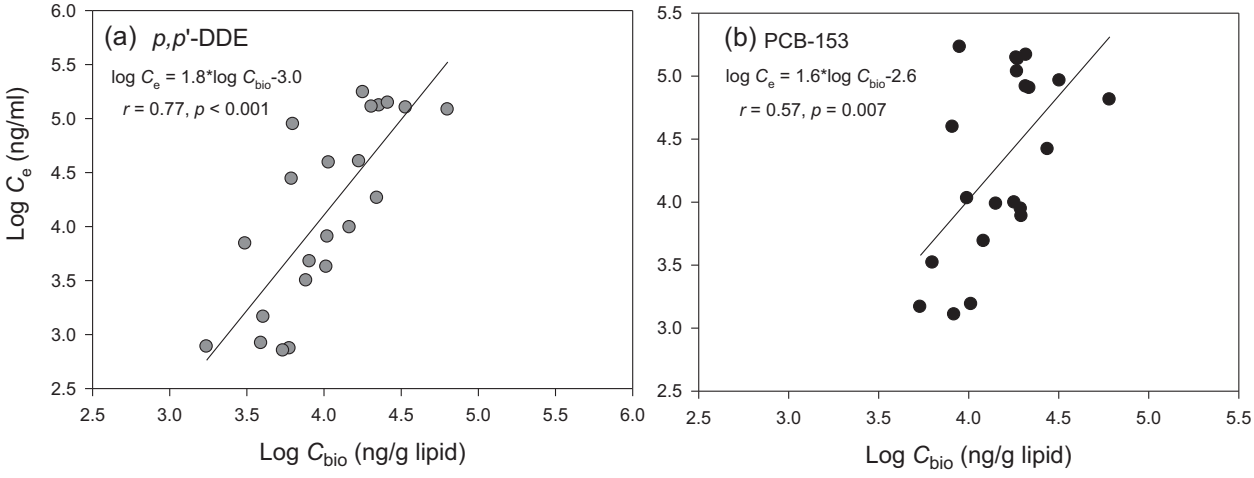

Figure 4. Correlations between the log-based tissue concentrations (C_{bio}) in the *Neanthes arenaceodentata* and equilibrium concentrations (C_e) of 1,1-dichloro-2,2-bis-(chlorophenyl) ethylene (*p*,*p*′-DDE), (**a**) and polychlorinated biphenyl (PCB)-153 (**b**) on 35-μm disposable polydimethylsiloxane fiber estimated by performance reference compound calibration. The preloaded fibers and worms were co-exposed to New Fields (Port Gamble, WA, USA) sediment amended without and with 1%, 2%, and 5% activated carbon for 12 d.

compounds and desorption kinetics of PRCs and toxic effects on the test organisms. Hysteretic desorption of PRCs would lead to smaller n/n_e for p,p'-DDE and PCB-153 (Equation 4) at the exposure time, and consequently overestimated equilibrium fiber concentrations. Moreover, the organic carbon normalized concentrations of DDTs at 1.0 mg/g_{oc} to 1.5 mg/g_{oc} in exposed sediment were within the range of lethal concentrations (10 d; 1.0−2.5 mg/g_{oc}) for marine amphipods [17,30]. Abnormal behaviors of worms (e.g., moving their heads out of sediment or toward the sediment surface) were observed during the co-exposure experiments.

On the other hand, Bayen et al. [31] suggested that organisms can agitate the aqueous phase by breathing through their gills, resulting in decreased aqueous diffusion layer thickness and enhanced mass transfers of target compounds between sediment and the deployed sampler. Furthermore, the k_{des} values of PCBs (0.0003−0.001 h^{-1}) for PE-based samplers in co-exposure systems [32] were within the range of field (stagnant) and laboratory (well-mixed) values [7]. Nevertheless, the average lost fractions (14−33%) of p,p'-DDE-d_8 after deployment in the co-exposure system for 12 d were essentially identical to those (15−37%) obtained in sediment under stagnant conditions for 10 d to 13 d in the present study. Such a small difference may have been the result of low worm weights (<0.5 g wet wt) used in the present study, as opposed to those (3−5 g wet wt) used in the previous study [32], in which the effects of bioturbation on k_{des} values of PCBs in sediment were significant. Apparently, benthic organisms may have measurable influences on the k_{des} values of PRCs. In addition, there are some natural dynamic processes of groundwater discharge and tidal pumping in the field environment, which probably play an important role in desorption of PRCs.

Because PRC calibration methods have the substantial benefits of shortened field sampling time and offsetting the effects of field exposure conditions on the uptake of target analytes in passive sampling, they have become the most preferable option for quantifying freely dissolved HOCs in sediment. To this end, the mechanisms for in situ calibration of the sorption of target compounds from the desorption of PRCs should be thoroughly understood [33,34]. Although the present study has demonstrated the nonsymmetry of sorption and desorption kinetics for quite a few compounds under stagnant conditions, additional efforts are still needed to investigate other HOCs and even polar organic chemicals [35], to facilitate the utility of passive sampling techniques in field applications.

CONCLUSIONS

In the present study, we have verified the nonsymmetrical relationship for the uptake of DDTs and release of their corresponding PRCs between PDMS fiber and sediment porewater under stagnant conditions. The low chemical potential between the fiber and sediment porewater may lead to the hysteretic desorption of PRCs in the kinetic regime, which reflects the inability of water molecules to rapidly diffuse through sediment to solvate the PRCs in the aqueous layer around the fiber surface. The nonsymmetric profiles reported in the present study provide an initial understanding of the mechanisms for in situ calibration with PRCs, and thus facilitate the utility of passive sampling techniques in field applications.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.3345.

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Data availability—Data, associated metadata, and calculation tools are available in the Supplemental Data and from the authors (baolj@gig.ac.cn).

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