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Examination of factors dominating the sediment-water diffusion flux of DDT-related compounds measured by passive sampling in an urbanized estuarine bay☆

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The fate of hydrophobic organic compounds in aquatic environment are largely determined by their exchange at sediment-water interface, which is highly dynamic and subject to rapidly evolving environmental conditions. In turn, environmental conditions may be governed by both physicochemical parameters and anthropogenic events. To examine the importance of various impact factors, passive sampling devices were deployed at the seafloor of Hailing Bay, an urbanized estuarine bay in Guangdong Province of South China to measure the sediment-water diffusion fluxes of several metabolites of dichlorodiphenyltrichloroethane (DDT), *p,p′*-DDE, *p,p′*-DDD and *o,p′*-DDD. The physicochemical properties of water (temperature, pH, salinity and dissolved oxygen) and surface sediment (sediment organic matter, physical composition, pH, water content, colony forming unit and catalase activity) were also measured. The results showed that the diffusion fluxes of *o,p′*-DDD, *p,p′*-DDD and *p,p′*-DDE at sites A1 and A2 near a fishing boat maintenance facility ranged from 0.42 to 4.73 $\mathrm{ng\ m^{-2}\ d^{-1}}$ (from sediment to overlying water), whereas those at offshore sites varied between −0.03 and −3.02 $\mathrm{ng\ m^{-2}\ d^{-1}}$ (from overlying water to sediment), implicating A1 and A2 as the sources of the target compounds. The distribution patterns of the diffusion fluxes of the target compounds were different from those of water and sediment parameters (water temperature, salinity, sediment texture, pH, colony forming unit and catalase activity) at six sampling sites. This finding suggested that none of these parameters were critical in dictating the sediment-water diffusion fluxes. Besides, decreases in the contents of kerogen and black carbon by 6.7% and 11% would enhance the diffusion fluxes of the target compounds by 11–14% and 12–23%, respectively, at site A1, indicating that kerogen and black carbon were the key factors in mediating the sediment–water diffusion fluxes of DDT-related compounds in field environments.

1. Introduction

The sediment-water interface is an important junction dictating the biogeochemical cycling of many environmentally relevant chemicals. It not only serves as an essential component of aquatic ecosystems and benthic habitats, but also provides the mechanism to facilitate or prohibit any transformation processes between sediment and overlying water (Santschi et al., 1990). Sediment can be either a sink or a source of contamination under certain circumstances (Chalhoub et al., 2013; Couceiro et al., 2013), and information on related sediment-water diffusion flux of contaminants is critical for assessing the effectiveness of in-situ remediation (Eek et al., 2010; Rabiet et al., 2010). Contaminants in suspended particles may be consumed by fish and other aquatic organisms, resulting in food-chain transfer (Estoppey et al., 2014).

Sediment-water diffusion flux is affected by various natural and anthropogenic events. Natural factors include physicochemical properties of sediment and water and bioturbation caused by organisms, whereas anthropogenic influences are mainly derived from terrestrial waste discharge (Khalil et al., 2011). Prior attempts to measure sediment-water flux of organic compounds have been scarce, and even fewer have investigated the key factors

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dominating such process. Most previous studies have focused on two group of factors. The first group consists of parameters affecting the desorption of organic compounds from sediment, such as pH, sediment physical composition and sediment organic matter (SOM) (Huang et al., 2003, 2012; Kang, 1994). In particular, SOM constituents, such as organic carbon (OC), humic acid (HA), kerogen and black carbon (BC), are supposed to act as the sorbents of organic compounds in sediment. Changes in these SOM constituents would alter the concentrations of organic compounds in sediment porewater and thus the concentration gradient across the sediment-water interface. The second group contains variables related to concentrations of organic compounds in overlying water, including temperature, pH, salinity and other physicochemical parameters (Schwarzenbach et al., 2005). Although these studies did not directly examine governing factors on sediment-water flux, they nevertheless provide valuable baseline information for selecting appropriate parameters.

The present study was initiated to address the above-mentioned issue with a combined approach of field measurements and model calculations. The target compounds include *p,p′*-DDE, *p,p′*-DDD and *o,p′*-DDD, which were detected in abundant amounts in sediment and overlying water of the study region (Yu et al., 2011b), Hailing Bay of South China (Fig. 1). Sediment-water diffusion fluxes of the target compounds were measured using a passive sampling approach with low-density polyethylene (LDPE) as the sorbent phase and performance reference compounds (PRCs) for quantitation (Allan et al., 2009). To identify the dominant factors governing the sediment-water flux of the target compounds, water temperature, pH and salinity, dissolved oxygen, tidal currents, sediment physical composition, colony forming unit (CFU) and catalase activity were measured and used to correlate with sediment-water diffusion fluxes. In addition, the contents of OC, HA, kerogen and BC in sediments were also measured, and the potential impacts of these components on the changes of chemical gradients across the sediment-water interface, as well as the diffusion fluxes of the target compounds, were estimated using a modeling approach.

2. Materials and methods

2.1. Materials and passive sampler preparation

Among all target analytes initially screened, only *p,p′*-DDE, *p,p′*-DDD and *o,p′*-DDD were further investigated, because other analytes were not detected in the passive samplers deployed in Hailing Bay. Standard solutions of the target analytes, surrogate standards (PCB-67 and PCB-191) and internal standard (PCB-82) were purchased from AccuStandard (New Haven, CT, USA). Two deuterated compounds (p,p'-DDE-d_8 and p,p'-DDD-d_8) used as PRCs were purchased from C/D/N Isotopes (Quebec, Canada).

The passive sampler employed in the present study was identical to that used previously (Liu et al., 2013), and only a brief description is presented herein. The passive sampler contains two sections, with the upper section consisting of a series of horizontal sampling cells (LDPE strips compacted by filter paper and stainless steel shields) for sampling overlying water and the lower section comprising vertical sampling cells for sampling sediment porewater. The upper and lower sections are connected with a stainless steel cross, mounted by angle bars and screw nuts. Sheets of LDPE (50-μm thickness) were purchased from TRM Manufacturing (Corona, CA, USA), and was cut into appropriate sizes and extracted for 24 h with hexane and another 24 h in water before use. Each LDPE strip was incubated in a methanol and water solution (80:20 in volume) containing the PRCs at 20 μg L^{-1}. The PRCs-loaded LDPE strips were quickly washed with tap water and dried with filter paper, wrapped with cleaned aluminum foil and stored at −20 °C until use. In addition, three PRCs-loaded LDPE strips were used to determine the initial concentrations of PRCs prior to field deployment, whereas another three clean LDPE sheets were carried to the field when sampling was conducted in October 2014 and used as field travel blanks.

2.2. Field sampling

Field deployment was conducted at six sites (A1, A2, B, C, D and E) in Hailing Bay (Fig. 1) during October 30–November 26, 2014. The lower section of the passive sampler was inserted into the sediment at a depth of approximately 10 cm. Sites A1 and A2 are adjacent to a shipyard, one of the main sources of DDT and its metabolites. Each passive sampler was anchored by a concrete brick to maintain steady horizontally on the seafloor. At the end of deployment, all passive samplers recovered were disassembled immediately and LDPE strips were transported with ice to the laboratory for extraction. Surface sediments (0–5 cm) were grabbed at the same time when passive sampling devices were

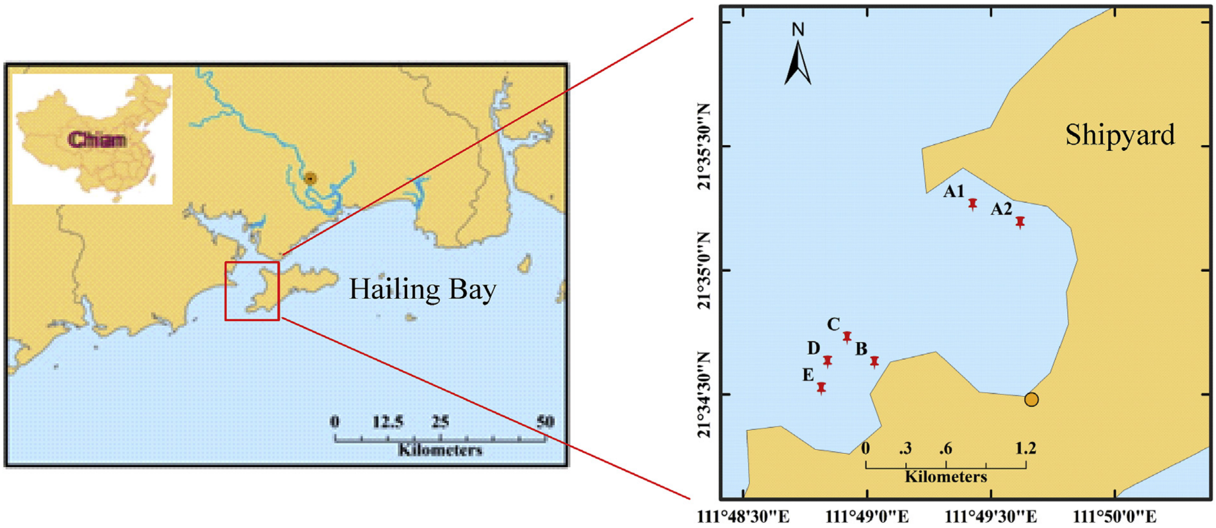

Fig. 1. Sampling sites in Hailing Bay, Guangdong Province, China.

deployed (October 30, 2014). At the same time samples of overlying water at 0.5 m underneath the air-water interface and 0.5 m above the sediment-water interface were also collected. Equal amounts of these two samples were mixed and used to measure pH, salinity, dissolved oxygen and total ammonia nitrogen to obtain average values. All sediment samples were wrapped with aluminum foil, sealed in polyethylene bags, and transported to the laboratory. Each sediment sample was divided into three portions, which were analyzed for DDT and its metabolites, SOM, and physicochemical properties, including physical composition, pH, water content, CFU and catalase activity. Furthermore, water temperature and depth, as well as flood tidal range, were also measured at the deployment sites.

2.3. Sample extraction, instrumental analysis and quality assurance/quality control

Procedures for sample extraction and instrumental analysis have been used frequently in our previous studies (Liu et al., 2013; Wu et al., 2016), and are detailed in the Supplementary Data.

For each batch of 20 field-deployed LDPE samples, a field blank, a procedural blank, and a spiked blank were also analyzed. The recoveries of the surrogate standards PCB-67 and PCB-191 were 83 ± 7% and 109 ± 29% in field blank, 98 ± 12% and 109 ± 4% in procedural blank, 83 ± 5% and 108 ± 12% in spiked blank samples, and 82 ± 25% and 102 ± 35% in field samples. In addition, a standard solution of *p,p′*-DDT was analyzed once for every batch of 12 samples prior to instrumental analysis to ensure the degradation rate of *p,p′*-DDT was less than 15%. The detection limits of *p,p′*-DDE, *p,p′*-DDD and *o,p′*-DDD were 0.01, 0.14 and 0.09 ng L^{-1} in overlying water and 0.01, 0.13 and 0.08 ng L^{-1} in sediment porewater.

2.4. Measurement of sediment organic matter

Separation of kerogen, HA, and BC was conducted in three steps (Song et al., 2002). The first step was to separate the HA + kerogen + BC (HKB) fraction from sediment with a hot HCl + HF acid mixture, followed by Soxhlet extraction with a mixture of methanol, acetone, and benzene at (2:3:5 in volume) to remove organic components. The second step was to fractionate HKB into kerogen and HA. A weighed amount of HKB was processed with 0.1 M NaOH solution for 12 h, and the residue was kerogen and BC. The extract was acidified to pH ~1 with 6 M HCl and the HA fraction was separated out. The last step was to isolate kerogen and BC from the mixed fraction. A weighed amount of kerogen and BC was oxidized using a dichromate (0.1 M) and sulfuric acid (2 M) mixed solution, and the remainder was BC (Song et al., 2002; Yu et al., 2006).

Organic carbon contents were measured with a high-temperature combustion method. Samples were treated with l M HCl for removal of inorganic carbonates (Hawthorne et al., 2007), and analyzed by an OC analyzer (Elementar Vario EL III, Hanau, Germany). Each sample was analyzed in duplicate, and the average relative difference was less than ±0.3%. For each batch of 20 field samples, three standards were analyzed.

2.5. Data analysis

Freely dissolved analyte concentrations in overlying water (C_w) and PE (C_{pe}) at exposure time t can be related to each other by

$$C_w = \frac{C_{pe}}{(1 - e^{-k_e t}) \times K_{pew}} \tag{1}$$

where K_{pew} is the PE-water partition coefficient of a target analyte and k_e is the release rate constant of a PRC, which is given by

$$k_e = -\frac{\ln(C_{PRC}/C_{0,PRC})}{t} \tag{2}$$

where C_{PRC} and $C_{0,PRC}$ are the amounts of the PRC remaining on the LDPE strips at t and the beginning of the exposure, respectively. The dissipation fractions of PRCs are presented in Table S1 of the Supplementary data ("S" indicates text, tables and figures in the Supplementary data afterwards). In the present study, the k_e of *p,p′*-DDE-d_8 was used to determine the sorption rate of *p,p*'-DDE and the k_e of *p,p′*-DDD-d_8 was used for *p,p′*-DDD and *o,p′*-DDD. Combining Equations (1) and (2) leads to

$$C_w = \frac{C_{pe}}{(1 - C_{PRC}/C_{0,PRC}) \times K_{pew}} \tag{3}$$

In estimating the sediment-water diffusion fluxes of the target compounds, C_w was designated as the analyte concentration in overlying water. The sediment-water diffusion flux (F) of a chemical is calculated with the field-measured data and Fick's First Law of Diffusion (Liu et al., 2013):

$$F = -D_w \frac{dC_w}{dZ_w} \tag{4}$$

where D_w is the diffusion coefficient; C_w is the time-weighted average concentration at Z_w, which is the distance from the sediment-water interface. The field-measured concentration profile in overlying water can be fitted to an exponential equation, i.e.,

$$C_w = C_{w,0} e^{a_0 Z_w} \tag{5}$$

where $C_{w,0}$ is the overlying water chemical concentration at the sediment–water interface, constrained by the analyte concentration in sediment porewater ($C_{w,pore}$), and a_0 is the fitting parameter, reflecting the concentration gradients across the sediment-water interface. Because sediment can be considered as an infinite reservoir, it is reasonable to assume $C_{w,0}$ as a constant during field sampling. Herein, $C_{w,0}$ was supposed to be the average concentration in sediment porewater (Tables 1 and S4). Therefore, the diffusion flux (F) of a chemical at the sediment-water interface ($Z_w = 0$) can be obtained by combining Equations (4) and (5):

Table 1
Average concentrations (ng L^{-1}) of DDT-related compounds in overlying water (all measured data at upper section), porewater (all measured data at lower section) and concentrations (ng g^{-1} dry weight) of DDT-related compounds in sediment at six sampling sites.

	A1	A2	B	C	D	E
Overlying water						
p,p'-DDE	0.09	0.13	<RL	0.03	<RL	0.01
p,p'-DDD	3.46	4.22	1.18	2.76	0.18	0.39
o,p'-DDD	1.58	1.79	0.85	1.30	0.17	0.30
o,p'-DDD/*p,p*'-DDD	0.46	0.42	0.72	0.47	0.95	0.76
Powerwater						
p,p'-DDE	0.18	0.43	<RL	0.08	<RL	0.01
p,p'-DDD	4.37	5.78	0.44	2.97	0.41	0.16
o,p'-DDD	2.27	3.61	0.22	1.35	0.31	0.13
o,p'-DDD/*p,p*'-DDD	0.52	0.62	0.50	0.45	0.76	0.81
Sediment						
p,p'-DDE	320	236	83	102	90	87
p,p'-DDD	410	286	91	107	130	97
o,p'-DDD	137	96	26	22	42	31
o,p'-DDD/*p,p*'-DDD	0.33	0.34	0.29	0.21	0.32	0.32

<RL: less than report limits.

$$F = -D_{\mathrm{w}} C_{\mathrm{w},0} a_0 \tag{6}$$

A positive flux value by definition indicates the diffusion of target analytes from sediment to overlying water, and vice versa.

To assess the impacts of the changes of SOM on $C_{\mathrm{w},0}$, as well as a_0 and F, the relationship between $C_{\mathrm{w},0}$ and sediment concentration (C_s) needs to be examined with the Freundlich isotherm models (Huang et al., 1997), i.e.,

$$\begin{aligned} C_s = {} & f_{\mathrm{OC}} K_{\mathrm{OC}} C_{\mathrm{w},0} + f_{\mathrm{HA}} K_{\mathrm{HA}} C_{\mathrm{w},0}^{n_1} + f_{\mathrm{kerogen}} K_{\mathrm{kerogen}} C_{\mathrm{w},0}^{n_2} \\ & + f_{\mathrm{BC}} K_{\mathrm{BC}} C_{\mathrm{w},0}^{n_3} \end{aligned} \tag{7}$$

where f_{OC}, f_{HA}, f_{kerogen} and f_{BC} are the fractions of OC, HA, kerogen and BC in sediment; K_{OC}, K_{HA}, K_{kerogen} and K_{BC} are the equilibrium partition coefficients of a target compound between OC-water, HA-water, kerogen-water and BC-water, respectively and n_1, n_2 and n_3 are the Freundlich isotherm nonlinearity indices.

The K_{OC} value can be empirically related to the octanol-water partition coefficient (K_{ow}) by $K_{\mathrm{OC}} = 0.63\ K_{\mathrm{ow}}$ (Kang, 1994). Because K_{BC} values are available mostly for PAHs, the K_{BC} model of PAHs was used to calculate K_{BC} values for the target DDT compounds, i.e. $\log K_{\mathrm{BC}} \approx 0.83\gamma_{\mathrm{W}}^{\mathrm{sat}} - 1.58$ (Lohmann et al., 2005), where $\gamma_{\mathrm{W}}^{\mathrm{sat}}$ is the aqueous activity coefficient at saturation. Contributions of kerogen to overall sorption by sediment have rarely been investigated and only a few publications reported the K_{kerogen} values of organic compounds. Cornelissen et al. (2005) indicated that kerogen and BC possessed similar C-normalized sorption coefficients for phenanthrene. As a result, the values $\log K_{\mathrm{BC}}$ were also set as those of $\log K_{\mathrm{kerogen}}$ for the target DDT-related compounds in the present study. Values of n_1, n_2 and n_3 were obtained through numerical simulation of sediment concentrations with porewater concentrations of the target compounds approaching the field-measured concentrations in sediments at six sites (Table S9).

In addition, diffusion coefficient D_{w} can be estimated by $D_{\mathrm{w}} = (13.26 \times 10^{-5})/(\eta^{1.4} V_{\mathrm{m}}^{0.589})$ (Hayduk and Laudie, 1974), with η as the viscosity of saline water at a salinity of 30‰ and V_{m} as the molar volume of target analyte. All $\log K_{\mathrm{ow}}$, $\log K_{\mathrm{pew}}$, V_{m} and D_{w} values are listed in Table S2. Finally, all concentrations are normalized to sample dry weight unless otherwise specified.

3. Results and discussion

3.1. Analyte concentrations in overlying water, sediment porewater and sediment

The numerical freely dissolved concentrations in overlying water (C_{w}) and sediment porewater ($C_{\mathrm{w,pore}}$) are presented in Table S3 and profiled in Fig. 2. At all sites, C_{w} and $C_{\mathrm{w,pore}}$ of *p,p′*-DDD and *o,p′*-DDD ranged from 0.1 to 15 ng L^{-1}, whereas those of *p,p′*-DDE were all below 1 ng L^{-1}. The samples from sites A1 and A2, situated near the main fishing boat maintenance facility in the region, contained the highest concentrations of DDT compounds, followed by sites B and C, and the lowest concentrations were found at sites D and E. Sediment concentrations of individual DDT-related compounds varied over a large range of 22–410 ng g^{-1} (Table 1), similar to the value (3.7–180 ng g^{-1}) obtained by our previous study conducted in 2007 in the same general area (Yu et al., 2011a). The ratio of

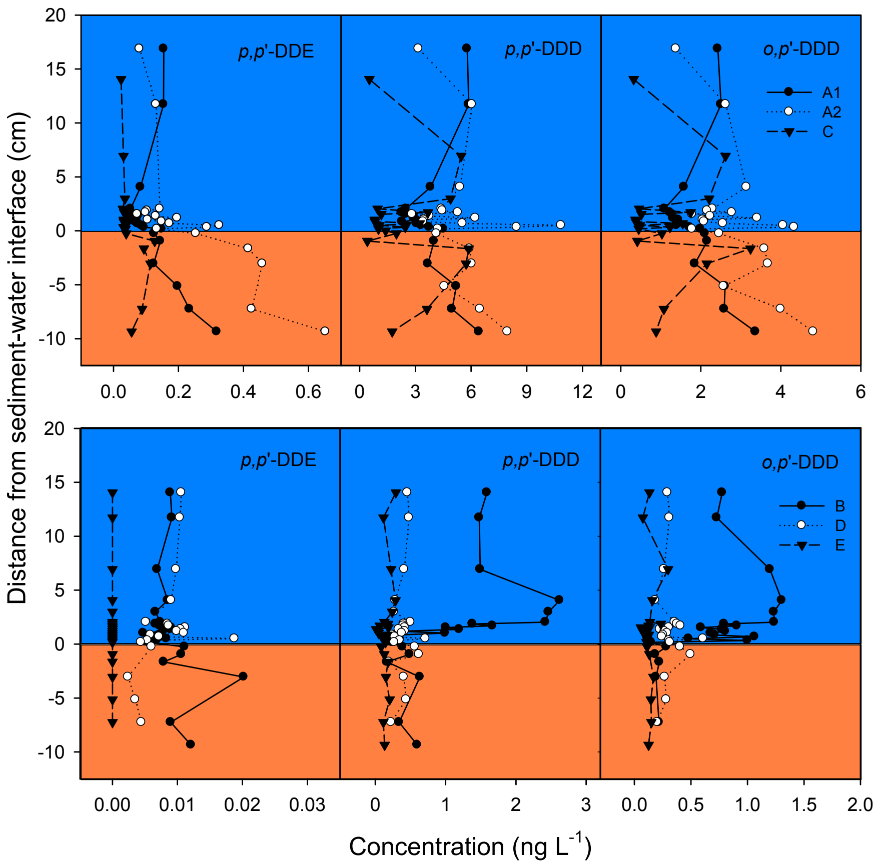

Fig. 2. Concentration profiles with depth of *p,p′*-DDE, *p,p′*-DDD and *o,p′*-DDD in overlying water and sediment porewater in Hailing Bay, South China (Fig. 1). Blue and beige colors indicate overlying water and sediment, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

sediment *o,p′*-DDD/*p,p′*-DDD was 0.21–0.33 (Table 1), well overlapped with that (0.2–0.33) of *o,p′*-DDT/*p,p′*-DDT reported in antifouling paints purchased from a local store (Yu et al., 2011b). Because *o,p′*-DDD/*p,p′*-DDD was expected to approximate *o,p′*-DDT/*p,p′*-DDT in sediment, the above-mentioned result suggested that antifouling paints may have been a main source of DDT-related compounds in Hailing Bay (Yu et al., 2011b). In addition, *o,p′*-DDD/*p,p′*-DDD in overlying water and sediment porewater ranged from 0.42 to 0.95 (Table 1), probably implicating that *p,p′*-DDD is more easily degraded than *o,p′*-DDD. A previous study found that the removal rate of *p,p′*-DDD (0.848 μM d^{-1}) in sediment slurries collected from the Keelung River (Taipei, Taiwan) was faster than that of *o,p′*-DDD (0.416 μM d^{-1}) (Huang et al., 2001).

3.2. Sediment-water diffusion fluxes of the target compounds

Time-weighted average sediment-water diffusion fluxes, estimated from Equations (5) and (6) (with fitting parameters presenting in Table S4), varied widely (−0.03–4.73 ng m^{-2} d^{-1}) with locations and individual target compounds (Table 2). Site A2 contained the largest fluxes of *p,p′*-DDE and *o,p′*-DDD, i.e., 1.22 and 3.80 ng m^{-2} d^{-1}, respectively. Site A1 also contained positive fluxes for these target compounds, i.e., 4.73, 2.39 and 0.40 ng m^{-2} d^{-1} for *p,p′*-DDD, *o,p′*-DDD and *p,p′*-DDE, respectively. In contrast, the sediment-water diffusion fluxes at sites B, C, D and E were all negative and comparable for all the target DDT-related compounds (−0.03 to −3.02 ng m^{-2} d^{-1}; Table 2). The fluxes of *p,p′*-DDE at sites B, C, D and E and *o,p′*-DDD at site D were difficult to calculate because the analyte concentrations were statistically indistinguishable ($p > 0.05$) in overlying water and sediment porewater. At sites B, D and E, *p,p′*-DDE concentrations were all close to the detection limits, so no fluxes of *o,p′*-DDD at site D and *p,p′*-DDE at sites B, C, D and E were obtained for following discussions.

The above-mentioned findings suggested that the target compounds, primary metabolites of *o,p′*-DDT and *p,p′*-DDT at sites A1 and A2, may be released from contaminated sediment to overlying water, i.e., sediment is the source of contamination. On the other hand, sediment at sites B, C, D and E largely acted as sinks for these chemicals. In general, sediment acts as a sink for DDT and its metabolites initially. As DDT continues to accumulate in sediment, the fugacity of DDT and its metabolites in sediment would eventually surpass that in surrounding overlying water if analyte concentrations in overlying water decline due to the control on the use of DDT-containing antifouling paint; sediment would become a source of DDT-related compounds. The amount of DDT and its metabolites, used as constituents in antifouling paint, emitted to Hailing Bay was estimated at 0.7 tons yr^{-1}, resulting in abundant accumulation of DDT and its metabolites from the 1950s to 2011 (Yu et al., 2011b).

The sampling sites A1 and A2 are located at the inner fishing harbor adjacent to a shipyard (Fig. 1). The sediment-water diffusion fluxes of *p,p′*-DDE, *p,p′*-DDD and *o,p′*-DDD were large and positive, thus sediment acted as a source of these target analytes. On the other hand, sites B, C, D and E are located near the outer harbor (Fig. 1), and therefore are subject to strong tidal currents. Consequently, desorbing chemicals from sediment may have been removed effectively; therefore, the sediment-water diffusion fluxes of the target compounds at sites B, C, D and E were small and negative, implicating sediment as a sink of *p,p′*-DDD (site D) and *p,p′*-DDD and *o,p′*-DDD (sites B, C and E). These results further confirmed the commonly accepted notion that sediment at “hot spots” (such as sites A1 and A2) are likely to be the sources of organic contaminants, whereas those at offshore sites tend to become a sink (Koelmans et al., 2010).

Table 2
Time-weighted average sediment-water diffusion fluxes (ng m^{-2} d^{-1}) of target DDT-related compounds.

Target analyte	A1	A2	B	C	D	E
p,p′-DDE	0.42	1.22	na	na	na	na
p,p′-DDD	4.73	na	−0.92	−3.02	−0.24	−0.08
o,p′-DDD	2.39	3.80	−0.24	−1.37	na	−0.03

na: not available because the fitting correlation coefficients for concentration profiles of target analytes were less than <0.01 (Table S4), and there were insignificant differences in concentrations of these two target compounds between overlying water and sediment porewater. Positive fluxes indicate prevailing transport of target compounds from sediment to overlying water, and vice versa.

3.3. Factors impacting sediment-water diffusion flux: physicochemical properties of sediment and water

The diffusion flux of organic compounds across the sediment-water interface may occur through two main mechanisms: (1) sediment resuspension followed by desorption from suspended particles to overlying water and (2) desorption from sediments to porewater and then diffusion from sediment porewater to overlying water (Sherwood et al., 2002). The first process is influenced mainly by tidal turbulence and bioturbation (Lick, 2006), which can be assessed through measurements of water velocity, CFU and catalase activity (Albrechtsen and Winding, 1992; Thibodeaux and Bierman, 2003). The second process may be impacted by various factors, with the most important one being the concentration gradient of a target compound between overlying water (C_W) and sediment porewater ($C_{W,pore}$). The values of C_W and $C_{W,pore}$ vary with exposure conditions such as water temperature, salinity, tidal currents, pH, sediment texture and SOM. Rising temperature increases target compounds' diffusion coefficients at the sediment-water interface. Salinity can exert ‘salting out’ effects by lowering the solubility of target compounds (Xie et al., 1997). Obviously, tidal currents can cause turbulence within water and sediment, mobilizing target compounds from sediment. The pH values affect the residual levels of target compounds by changing the number of interaction sites of HA (Gong et al., 2004). The silt and clay portions of sediment were found to have a higher capacity to sorb target compounds than whole sediment because they possess their higher OC contents and larger specific surface areas (Khim et al., 2001). Therefore, SOM plays a leading role in sorption of target compounds by sediment (Sun et al., 2008; Xiao et al., 2004; Yu et al., 2006).

During the deployment period in the present study, tidal turbulence occurred episodically, thereby its effect on diffusion fluxes of the target compounds is unpredictable. Water temperature consistently varied between 26 and 28 °C at all sites, and thus the effect of temperature on diffusion of the target compounds was expected to be weak. It is interesting to note that the sediment-water diffusion fluxes of *p,p′*-DDE and *o,p′*-DDD were greater at site A2 than at site A1 (Table 2). However, various physicochemical properties of overlying water (i.e., temperature, salinity, pH, DO and tidal currents) were similar at these two sites (Table S5). Among several targeted sediment characteristics, i.e., physical composition, pH, water content, CFU and catalase activity (Tables S6 and S7), only CFU was substantially different (3.2×10^{-5} cells g^{-1} at A1 and 1.5×10^{-5} cells g^{-1} at A2). Lou et al. (2012) found no significant difference in the release of sediment pentachlorophenol to water within the ranges of 5–9 for pH, 0–5% for salinity and 1:1–1:10 for solid/liquid ratio. It can be speculated that the influences of physical composition, pH and water content on diffusion fluxes of the target analytes were neglected at sites A1 and A2, because pentachlorophenol is a polar compound, which is more sensitive to these

Table 3
Effect of change in concentration at sediment-water interface ($C_{w,0}$, ng L^{-1}), fitting parameter (a_0, cm^{-1}) and diffusion flux (F, ng m^{-2} d^{-1}) with the contents of organic carbon, humic acid, kerogen and black carbon (f_{oc}, f_{HA}, $f_{kerogen}$ and f_{BC}) in sediments at site A1.

		p,p'-DDE				*p,p*'-DDD				*o,p*'-DDD			
		$C_{w,0}$	a_0	F	ΔF	$C_{w,0}$	a_0	F	ΔF	$C_{w,0}$	a_0	F	ΔF
f_{oc}	1.2%	0.175	−0.76	0.416		4.37	−0.35	4.73		2.27	−0.34	2.39	
	1.5%	0.171	−0.74	0.397	−4.6%	4.00	−0.32	3.96	−16%	2.10	−0.31	2.03	−15%
	1.0%	0.178	−0.77	0.429	3.2%	4.67	−0.37	5.34	13%	2.38	−0.36	2.52	5.7%
f_{HA}	0.0003%	0.175	−0.76	0.416		4.37	−0.35	4.73		2.27	−0.34	2.39	
	0.0006%	0.175	−0.76	0.416		4.37	−0.35	4.73		2.25	−0.34	2.34	−1.7%
	0.0001%	0.175	−0.76	0.416		4.37	−0.35	4.73		2.26	−0.34	2.35	−1.5%
$f_{kerogen}$	0.075%	0.175	−0.76	0.416		4.37	−0.35	4.73		2.27	−0.34	2.39	
	0.080%	0.164	−0.71	0.366	−12%	4.15	−0.33	4.24	−10%	2.13	−0.32	2.09	−13%
	0.070%	0.187	−0.81	0.473	14%	4.6	−0.37	5.26	11%	2.39	−0.36	2.67	12%
f_{BC}	0.027%	0.175	−0.76	0.416		4.37	−0.35	4.73		2.27	−0.34	2.39	
	0.030%	0.158	−0.69	0.341	−18%	4.12	−0.33	4.21	−11%	2.11	−0.31	2.05	−14%
	0.024%	0.194	−0.84	0.510	23%	4.62	−0.37	5.3	12%	2.41	−0.36	2.72	14%

factors than DDT-related compounds. On the other hand, higher CFU indicated the presence of a more active benthic macrofaunal community at site A1 than A2. As known, benthic organisms can mix sediment particles and porewater in the upper sediment layer, resulting in resuspension of buried chemicals from sediment (Josefsson et al., 2010). As an example, Granberg et al. (2008) reported that bioturbation enhanced the release of particles enriched with organic compounds from hypoxic sediment in Baltic Sea. All these analyses implicated bioturbation as an important factor dictating the sediment-water diffusion flux of organic compounds with positive impact. In the present study, the different distribution patterns of the fluxes of *p,p*′-DDE and *o,p*′-DDD and CFU at sites A1 and A2 may suggest that another factor such as microorganism density should be included in the assessment of bioturbation in sediment. Nevertheless, future work should further quantify the correlation between the physicochemical properties of overlying water or sediment and sediment-water diffusion fluxes of chemicals.

3.4. Factors impacting sediment-water diffusion flux: sediment organic matter

Besides the physicochemical properties of sediment and water discussed above, sediment organic matter was expected to be another significant factor for mediating the sediment-water diffusion flux. In the present study, the ranges of OC, kerogen and BC were 0.65–1.26%, 0.05–0.07% and 0.01–0.02%, respectively, whereas humic acid constituted a negligible portion (<0.0016%) of organic matter in surface sediment samples (Table S7). To examine the importance of facilitated diffusion by SOM, we used site A1 as an example and simulated diffusion fluxes with varying SOM contents. The concentrations of the target compounds in sediment and overlying water were assumed to be constant, and changes in the analyte concentrations in porewater and concentration gradients across the sediment-water interface with varying SOM contents were determined.

Table 3 presents the effects of the changes in $C_{w,0}$, a_0 and F of *p,p*′-DDE, *p,p*′-DDD and *o,p*′-DDD at site A1. Apparently, HA-induced changes in F of all target compounds (0–1.7%) were negligible. This was obviously because the HA contents were extremely low in sediments under investigation (Table S7), posing limited impact on the overall sorption capacity by sediment. Although OC in sediment was much more abundant than BC and kerogen (Table S7), it posed less effect on F than kerogen and BC. For example, a decrease in OC content by 17% enhanced F by 3.2–13%, while a 6.7% reduction of kerogen content could result in an increase of F by 11–14% (Table 3). As expected, kerogen and BC mediated similar changes in the F of all target compounds with the same $K_{kerogen}$ and K_{BC} (Table S8). The physicochemical property of the target compounds was also an important factor in inducing the changes of diffusion fluxes. The difference in the changes of F for *p,p*′-DDE exerted by OC and kerogen or BC was much greater than those of *p,p*′-DDD and *o,p*′-DDD, obviously because the difference (0.51) between K_{OC} and $K_{kerogen}$ or K_{BC} for *p,p*′-DDE was greater than those for *p,p*′-DDD (0.41) and *o,p*′-DDD (0.41) (Table S8). Overall, the impacts of SOM on diffusion fluxes were dependent on kerogen and BC contents and physicochemical characteristics of the target compounds. In addition, as kerogen ($n_2 = 0.53$) and BC ($n_3 = 0.42$) exhibited strong nonlinear sorption isotherms (Table S9), the nonlinear sorption index and its effects on diffusion fluxes warrant further investigations.

4. Conclusions

The results of the present study indicated that sediment at nearshore sites tends to be the source of the target DDT-related compounds in overlying water. Parameters such as water temperature, salinity, sediment texture, pH, water content, CFU and catalase activity appeared not to be the critical factors in dictating the sediment-water diffusion fluxes of the target compounds. Furthermore, kerogen and BC exhibited the strongest effects on the variability in the sediment-water diffusion fluxes of the target DDT-related compounds, i.e., decreases in the contents of kerogen and BC by 6.7% and 11% enhanced the diffusion fluxes of the target compounds at site A1 by 11–14% and 12–23%, respectively, whereas the impact of HA was negligible.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.08.046.

References

Albrechtsen, H.J., Winding, A., 1992. Microbial biomass and activity in subsurface sediments from Vejen, Denmark. Microb. Ecol. 23, 303–317.

Allan, I.J., Booij, K., Paschke, A., Vrana, B., Mills, G.A., Greenwood, R., 2009. Field performance of seven passive sampling devices for monitoring of hydrophobic substances. Environ. Sci. Technol. 43, 5383–5390.

Chalhoub, M., Amalric, L., Touze, S., Galle, P., Reiller, P.E., Doucet, N., Clozel, B., Bataillard, P., 2013. PCB partitioning during sediment remobilization-a 1D column experiment. J. Soils Sediments 13, 1284–1300.

Cornelissen, G., Gustafsson, O., Bucheli, T.D., Jonker, M.T.O., Koelmans, A.A., Van Noort, P.C.M., 2005. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. Environ. Sci. Technol. 39, 6881–6895.

Couceiro, F., Fones, G.R., Thompson, C.E.L., Statham, P.J., Sivyer, D.B., Parker, R., Kelly-Gerreyn, B.A., Amos, C.L., 2013. Impact of resuspension of cohesive sediments at the Oyster Grounds (North Sea) on nutrient exchange across the sediment-water interface. Biogeochemistry 113, 37–52.

Eek, E., Cornelissen, G., Breedveld, G.D., 2010. Field measurement of diffusional mass transfer of HOCs at the sediment-water interface. Environ. Sci. Technol. 44, 6752–6759.

Estoppey, N., Schopfer, A., Omlin, J., Esseiva, P., Vermeirssen, E.L., Delemont, O., De Alencastro, L.F., 2014. Effect of water velocity on the uptake of polychlorinated biphenyls (PCBs) by silicone rubber (SR) and low-density polyethylene (LDPE) passive samplers: an assessment of the efficiency of performance reference compounds (PRCs) in river-like flow conditions. Sci. Total Environ. 499, 319–326.

Gong, Z.M., Tao, S., Xu, F.L., Dawson, R., Liu, W.X., Cui, Y.H., Cao, J., Wang, X.J., Shen, W.R., Zhang, W.J., Qing, B.P., Sun, R., 2004. Level and distribution of DDT in surface soils from Tianjin, China. Chemosphere 54, 1247–1253.

Granberg, M.E., Gunnarsson, J.S., Hedman, J.E., Rosenberg, R., Jonsson, P., 2008. Bioturbation-driven release of organic contaminants from Baltic sea sediments mediated by the invading polychaete *Marenzelleria neglecta*. Environ. Sci. Technol. 42, 1058–1065.

Hawthorne, S.B., Grabanski, C.B., Miller, D.J., 2007. Measured partition coefficients for parent and alkyl polycyclic aromatic hydrocarbons in 114 historically contaminated sediments: part 2. Testing the $K_{OC}K_{BC}$ two carbon-type model. Environ. Toxicol. Chem. 26, 2505–2516.

Hayduk, W., Laudie, H., 1974. Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions. Chemosphere 20, 611–615.

Huang, H.J., Liu, S.M., Kuo, C.E., 2001. Anaerobic biodegradation of DDT residues (DDT, DDD, and DDE) in estuarine sediment. J. Environ. Sci. Health B 36, 273–288.

Huang, W., Peng, P.a., Yu, Z., Fu, J., 2003. Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments. Appl. Geochem. 18, 955–972.

Huang, W.L., Young, T.M., Schlautman, M.A., Yu, H., Weber, W.J., 1997. A distributed reactivity model for sorption by soils and sediments. 9. General isotherm nonlinearity and applicability of the dual reactive domain model. Environ. Sci. Technol. 31, 1703–1710.

Huang, Y., Liu, Z., He, Y., Zeng, F., Wang, R., 2012. Quantifying effects of primary parameters on adsorption–desorption of atrazine in soils. J. Soils Sediments 13, 82–93.

Josefsson, S., Leonardsson, K., Gunnarsson, J.S., Wiberg, K., 2010. Bioturbation-driven release of ruried PCBs and PBDEs from different depths in contaminated sediments. Environ. Sci. Technol. 44, 7456–7464.

Kang, Y.J., 1994. Adsorption/desorption hysteresis in organic pollutant and soil/sedirnent interaction. Environ. Sci. Technol. 28, 859–867.

Khalil, B., Ouarda, T.B.M.J., St-Hilaire, A., 2011. Estimation of water quality characteristics at ungauged sites using artificial neural networks and canonical correlation analysis. J. Hydrol. 405, 277–287.

Khim, S., Lee, K.T., Kannan, K., Villeneuve, D.L., Giesy, J.P., Koh, C.H., 2001. Trace organic contaminants in sediment and water from Ulsan bay and its vicinity, Korea. Arch. Environ. Contam. Toxicol. 40, 141–150.

Koelmans, A.A., Poot, A., De Lange, H.J., Velzeboer, I., Harmsen, J., van Noort, P.C.M., 2010. Estimation of in situ sediment-to-water fluxes of polycyclic aromatic hydrocarbons, polychlorobiphenyls and polybrominated diphenylethers. Environ. Sci. Technol. 44, 3014–3020.

Lick, W., 2006. The sediment-water flux of HOCs due to “diffusion” or is there a well-mixed layer? if there is, does it matter? Environ. Sci. Technol. 40, 5610–5617.

Liu, H.H., Bao, L.J., Zhang, K., Xu, S.P., Wu, F.C., Zeng, E.Y., 2013. Novel passive sampling device for measuring sediment-water diffusion fluxes of hydrophobic organic chemicals. Environ. Sci. Technol. 47, 9866–9873.

Lohmann, R., MacFarlane, J., Gschwend, P., 2005. Importance of black carbon to sorption of native PAHs, PCBs, and PCDDs in Boston and New York harbor sediments. Environ. Sci. Technol. 39, 141–148.

Lou, L.P., Luo, L., Yang, Q., Cheng, G.H., Xun, B., Xu, X.H., Chen, Y.X., 2012. Release of pentachlorophenol from black carbon-inclusive sediments under different environmental conditions. Chemosphere 88, 598–604.

Rabiet, M., Margoum, C., Gouy, V., Carluer, N., Coquery, M., 2010. Assessing pesticide concentrations and fluxes in the stream of a small vineyard catchment-effect of sampling frequency. Environ. Pollut. 158, 737–748.

Santschi, P., Hohener, P., Benoit, G., Buchholtzenbrink, M., 1990. Chemical processes at the sediment water interface. Mar. Chem. 30, 269–315.

Schwarzenbach, R.P., Gschwend, P.W., Imboden, D.M., 2005. Environmental Organic Chemistry. John Wiley & Sons, Inc, Hoboken, New Jersey, United States.

Sherwood, C.R., Drake, D.E., Wiberg, P.L., Wheatcroft, R.A., 2002. Prediction of the fate of *p,p*'-DDE in sediment on the Palos Verdes shelf, California. USA. Cont. Shelf Res. 22, 1025–1058.

Song, J., Peng, P.a., Huang, W., 2002. Black carbon and kerogen in soils and sediments. 1. Quantification and characterization. Environ. Sci. Technol. 36, 3960–3967.

Sun, X., Peng, P.a., Song, J., Zhang, G., Hu, J., 2008. Sedimentary record of black carbon in the Pearl River estuary and adjacent northern South China Sea. Appl. Geochem. 23, 3464–3472.

Thibodeaux, L.J., Bierman, V.J., 2003. The bioturbation-driven chemical release process. Environ. Sci. Technol. 37, 252a–258a.

Wu, C.C., Bao, L.J., Guo, Y., Tao, S., Zeng, E.Y., 2016. Significance of antifouling paint flakes to the distribution of dichlorodiphenyltrichloroethanes (DDTs) in estuarine sediment. Environ. Pollut. 210, 253–260.

Xiao, B., Yu, Z., Huang, W., Song, J., Peng, P.a., 2004. Black carbon and kerogen in soils and sediments. 2. Their roles in equilibrium sorption of less-polar organic pollutants. Environ. Sci. Technol. 38, 5842–5852.

Xie, W.H., Shiu, W.Y., Mackay, D., 1997. A review of the effect of salts on the solubility of organic compounds in seawater. Chemosphere 44, 429–444.

Yu, H.Y., Guo, Y., Bao, L.J., Qiu, Y.W., Zeng, E.Y., 2011a. Persistent halogenated compounds in two typical marine aquaculture zones of South China. Mar. Pollut. Bull. 63, 572–577.

Yu, H.Y., Shen, R.L., Liang, Y., Cheng, H., Zeng, E.Y., 2011b. Inputs of antifouling paint-derived dichlorodiphenyltrichloroethanes (DDTs) to a typical mariculture zone (South China): potential impact on aquafarming environment. Environ. Pollut. 159, 3700–3705.

Yu, Z., Huang, W., Song, J., Qian, Y., Peng, P., 2006. Sorption of organic pollutants by marine sediments: implication for the role of particulate organic matter. Chemosphere 65, 2493–2501.