



# Significance of antifouling paint flakes to the distribution of dichlorodiphenyltrichloroethanes (DDTs) in estuarine sediment<sup>☆</sup>



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## ABSTRACT

Recently published literature indicated that dichlorodiphenyltrichloroethane (DDT)-containing antifouling paint flakes were heterogeneously distributed within estuarine sediments. However, the significance of antifouling paint flakes in the fate and transport of DDT compounds and other organic pollutants in estuarine sediment is yet to be adequately addressed. To fill this knowledge gap, estuarine sediment and paint flakes from cabin and boat surfaces were collected from a fishery base in Guangdong Province of South China and analyzed for DDT compounds. Coarse fractioned samples collected from the vicinity of boat maintenance facilities contained appreciable amounts of colorful particles, which were identified as paint flakes by Fourier transform infrared spectroscopy. The highest concentrations of DDXs (sum of DDTs and its metabolites) occurred in the heavy-density (>1.7 g cm<sup>-3</sup>) fraction of coarse-size (200–2000 μm) sediments from near the boat maintenance facilities, suggesting the importance of paint flakes in the distribution pattern of “hot spots” in estuarine sediment. Moreover, the desorption rates of DDT compounds from paint flakes and the heavy-density fraction of coarse-size sediment were both extremely slow. Apparently, unevenly distributed paint flakes in sediment can artificially inflate the sorption capacity of heavy-density sediment for DDT compounds, and therefore can substantially change the environmental fate and behavior of hydrophobic organic chemicals in estuarine sediment. Finally, commonly used source diagnostic indices of DDT compounds were mostly grain-size and density dependent in sediment, as a result of the occurrence of paint flakes, which may strongly compromise the outcome of any source diagnostics efforts.

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## 1. Introduction

Increased global concerns about the adverse effects of chemical products have prompted numerous investigations into their transport and fate in the environment (Dyer et al., 2006; Klaine et al., 2012; Law et al., 2010; Verhaegen et al., 2012; Zarfl et al., 2011). For example, many chemicals will eventually enter coastal oceans after use or disposal on land. Especially impacted are estuaries in populated or industrialized

areas. However, most previous studies have examined bulk environmental matrices (e.g., whole sediment) and the analysis of these provides average concentrations. In reality, the distribution of chemicals may be highly heterogeneous (Ghosh et al., 2003). Bioavailability may likewise vary. Hence, resultant risk assessments may be flawed.

Estuaries are often home to boat maintenance facilities that use large amounts of paints and coating materials, which are applied to surfaces of decks, cabins and hulls of boats to prevent colonization, as well as to provide UV resistance and corrosion and erosion protection. For example, approximately 150,000 small boats required annual maintenance in England, consuming up to 300 tons of Cu (Comber et al., 2002) and resulting in up to 2.1 kg Cu per boat per year (surface area below the waterline were

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assumed as  $30.7 \text{ m}^2$ ) leached into the surrounding estuaries (Boxall et al., 2000). Another commonly used biocide was dichlorodiphenyltrichloroethane (DDT), which was still detected in antifouling paints in previous studies (Yu et al., 2011a, 2011b). Paint particles generated during boat maintenance often range from a few microns to several centimeters in size (Champ, 2003; Harris et al., 1991; Singh and Turner, 2009). Because the majority of biocides discharged from boat maintenance is associated with paint particles (Thomas et al., 2002), the distribution of biocides in estuarine sediment may be dictated by the transport of size-fractionated paint particles and the interaction between biocides and paint particles or flakes.

The present study was conducted to examine the role of paint flakes in distributing boat maintenance-derived DDT in estuarine sediment. A fishery base in Hailing Bay, Guangdong Province of China (Figs. S1 and S2 of the Supplemental Material; "S" indicates texts, tables and figures in the Supplemental Material afterwards) was selected as the study region, where large amounts of DDT and its metabolites largely derived from antifouling paints were found (Yu et al., 2011a, 2011b). The occurrence of DDT compounds was examined in size and density fractionated sediments and paint flakes. In addition, the desorption and sorption kinetics of DDT compounds in size-fractionated sediments and paint flakes were determined to identify the affiliating capacity of paint flake for DDT compounds. Finally, the utility of DDT-related source diagnostic indices involving size-dependent sediment and paint flakes were assessed.

## 2. Materials and methods

### 2.1. Materials

Target analytes include *o,p'*- and *p,p'*- isomers of DDT and its metabolites, i.e., dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE), 1-chloro-2,2-bis(4'-chlorophenyl)ethylene (*p,p'*-DDMU) and 4,4'-dichlorobenzophenone (*p,p'*-DBP). The sum of *o,p'*- and *p,p'*-DDT, DDD and DDE is defined as DDTs, whereas the sum of DDTs, *p,p'*-DDMU and *p,p'*-DBP is defined as DDXs. All the target analytes, internal standard (PCB-82) and surrogate standards (PCB-67 and PCB-191) were purchased from AccuStandard (New Haven, CT, USA). *O,p'*-DDT- $d_8$  used as a surrogate standard and *p,p'*-DDT- $d_8$ , *p,p'*-DDD- $d_8$  and *p,p'*-DDE- $d_8$  used in sorption experiments were purchased from C/D/N Isotopes (Quebec, Canada). Sodium metatungstate monohydrate powers and XAD beads were purchased from Alfa Aesar and Supelco (Bellefonte, PA, USA), respectively.

### 2.2. Sample collection

Field sampling was conducted from August 2012 to November 2014. Sediment samples were collected with a stainless steel grab from three areas, i.e., in the vicinity of two boat maintenance facilities (labeled as A and B; Fig. S1), within the aquaculture zone and outside the aquaculture zone (Table S1). Paint flake samples from boat surfaces were collected from Boat Maintenance Facility B in 2012 and 2014. Overall, 22 sediments samples (Table S1) and two sets of antifouling paint flakes coded as A–I were obtained. All samples were cooled with ice during transport to the laboratory and were stored at  $-20 \text{ }^\circ\text{C}$  until analysis.

### 2.3. Separation of sediment sizes and densities

All sediment samples were wet sieved to remove large objects, and the residues were further fractionated into four sizes, i.e.,

200–2000  $\mu\text{m}$ , 63–200  $\mu\text{m}$ , 30–63  $\mu\text{m}$  and  $< 30 \mu\text{m}$ . Size-segregated samples from Sites 2 and 9 were further separated into two density fractions, i.e., light fraction (L) with  $\rho < 1.7 \text{ g cm}^{-3}$  and heavy fraction (H) with  $\rho > 1.7 \text{ g cm}^{-3}$ , by floating the samples in a sodium metatungstate solution. The density fractions were washed with purified water several times and centrifuged at 3500 g for 10 min to remove residual sodium metatungstate solution. Each of these size and density fractions was freeze-dried, weighed and stored at  $-20 \text{ }^\circ\text{C}$  until analysis.

### 2.4. Sample characterization

Size and density fractionated sediment samples from Sites 1, 2 and 9 and paint flakes coded C and J were imaged in high vacuum at  $1.03 \times 10^{-6}$  mbar with a Zeiss Ultra 55 scanning electron microscope (Oberkochen, Germany) equipped with an energy dispersive X-ray spectrometer. These samples were also analyzed with a Bruker Equinox 55 Fourier transform infrared spectrometer (Billerica, MA, USA), and the spectra were recorded by averaging 32 scans for every  $4 \text{ cm}^{-1}$  over the range of 4000–400  $\text{cm}^{-1}$ .

For total organic carbon (TOC) measurement, an aliquot of each sample was first acidified with 10% HCl overnight to remove carbonate, washed with purified water to remove chlorine ion and finally dried at  $60 \text{ }^\circ\text{C}$ . The contents of TOC were determined with an Element Analyzer Vario EL III (Elementar, Hanau, Germany).

### 2.5. Desorption and sorption kinetic studies

Desorption kinetics of DDT compounds on size and density fractionated samples were determined in duplicates with a modified version of the method described previously (Rockne et al., 2002; Shor et al., 2003). Briefly, 3 g of XAD beads (XAD-2:XAD-4 = 1:1 in mass) were wrapped with a stainless steel mesh (1500 mesh) and cleaned separately with methanol and water three times. An aliquot of heavy-density (10 g) or light-density (0.02 g) sediment sample from both Sites 2 and 9, or 0.7 g of paint flakes (coded C and J) was added to a 100-mL glass vial containing 80 mL of salt water (30‰ salinity) and XAD beads, and the vial was shaken ( $\sim 200$  rpm) in a mechanical shaker. Sodium azide (1 mg) was added to the aqueous phase to suppress microbial growth. At each of the preset timepoints (6, 24, 72 and 120 h), the stainless steel mesh containing XAD beads was taken out from the glass vial, rinsed with distilled water, dehydrated with oven-baked sodium sulfate and pre-cleaned filter papers and stored at  $-20 \text{ }^\circ\text{C}$  until analysis. Another set of fresh XAD beads was added to the vial to continue the desorption experiments.

In sorption experiments, 0.2 g of paint flakes A and J each were added to a 50-mL PTFE-vial containing 45-mL distilled water spiked with 500 ng of deuterated DDTs and 1 mg of sodium azide. All vials were mixed at 200 rpm on a horizon shaker. After 7 days, duplicate paint flake samples were taken out and pre-treated in the same manner as the XAD beads.

### 2.6. Sample extraction and instrumental analysis

Before extraction, all solid samples were impregnated with copper sheets for removal of sulfate and spiked with the surrogate standards. Sediment and paint flake samples were sonicated twice with 20 mL of hexane, dichloromethane and acetone mixture (2:2:1 in volume) each, whereas XAD bead samples were sonicated twice with 50 mL of hexane and acetone mixture (1:1 in volume) each. The remaining water samples from sorption experiments were liquid–liquid extracted three times each with

10 mL of hexane after addition of surrogate standards. Each extract was concentrated to 5–10 mL, solvent-exchanged to hexane and further concentrated to 1 mL with a Zymark Turbo-Vap 500 (Hopkinton, MA, USA). The concentrated extracts were purified on a neutral silica column with hexane and dichloromethane mixture (1:1 in volume) as the eluent. The extracts were further concentrated to 50  $\mu\text{L}$  and spiked with the internal standards before instrumental analysis.

Sample extracts were analyzed with a Shimadzu gas chromatograph coupled to a mass spectrometer (GCMS-2010 Plus) with an HP-5MS capillary column (30 m  $\times$  0.25 mm i.d. with 0.25  $\mu\text{m}$  film thickness). One microliter of each extract was automatically injected into the column. The column temperature was programmed from 60  $^{\circ}\text{C}$  (initial held for 1 min), ramped to 250  $^{\circ}\text{C}$  at 20  $^{\circ}\text{C min}^{-1}$  (held for 2 min), elevated to 280  $^{\circ}\text{C}$  at 5  $^{\circ}\text{C min}^{-1}$  (held for 15 min) and further increased to 300  $^{\circ}\text{C}$  at 20  $^{\circ}\text{C min}^{-1}$  (held for 15 min). The carrier gas was ultrahigh purity helium at a flow rate of 1 mL  $\text{min}^{-1}$ . The ion source temperature was set at 250  $^{\circ}\text{C}$ . Mass spectra were scanned from  $m/z$  100 to  $m/z$  320 in the electron ionization mode with an electron impact energy of 70 eV.

### 2.7. Quality assurance and quality control

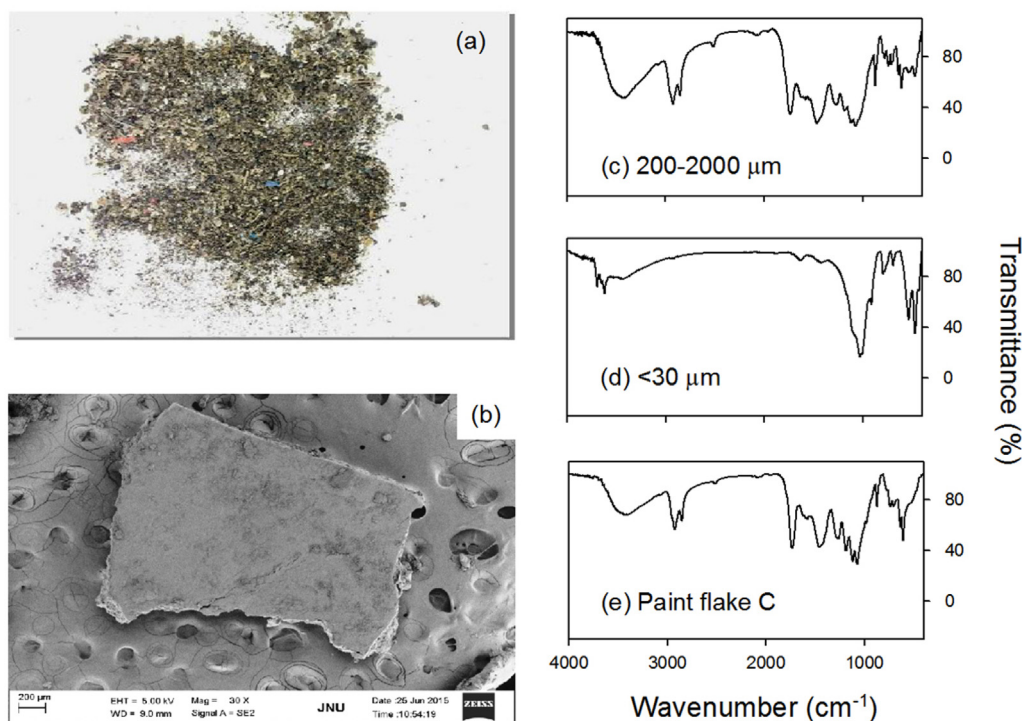
A standard solution of *p,p'*-DDT, a procedural blank sample, a matrix spiked sample and a sample duplicate were analyzed for every batch of 20 samples. The extent of breakdown of *p,p'*-DDT was maintained less than 15% before instrumental analysis was conducted. The recoveries of the surrogate standards, PCB-67, PCB-191 and *o,p'*-DDT- $d_8$  were  $75 \pm 36\%$ ,  $84 \pm 15\%$  and  $51 \pm 26\%$  in blank samples,  $83 \pm 23\%$ ,  $82 \pm 17\%$  and  $75 \pm 16\%$  in field samples and  $78 \pm 33\%$ ,  $78 \pm 17\%$  and  $79 \pm 18\%$  in matrix

spiked samples. The sum of the masses of DDT compounds in XAD beads at each sampling timepoint and in residual sediment was  $80 \pm 36\%$  of the initial masses. The lowest calibration concentrations divided by the actual sample weights (dry weight) were defined as the reporting limits (RL) for the target compounds, i.e., 0.5 ng  $\text{g}^{-1}$  for a 5-g sediment sample and 10 ng  $\text{g}^{-1}$  for a 0.25-g paint flake sample.

## 3. Results and discussion

### 3.1. Characterization of fractioned sediment and paint flake samples

The particle sizes and chemical elements in different size and density fractioned sediment and paint flake samples were heterogeneous (Figs. S3–S4). The coarse (200–2000  $\mu\text{m}$ ) fractioned samples contained appreciable amounts of colorful particles (Fig. 1), and the infrared spectra of coarse fractioned samples were different from those of other size fractioned sediments (Figs. S5 (a)–(h)). For example, there were a strong carbonyl C=O peak at 1736  $\text{cm}^{-1}$  and vibrational peaks between 1300 and 1000  $\text{cm}^{-1}$  derived from C–O–C stretching of aliphatic ester in the infrared spectra of coarse fractioned sample from Site 1 (Fig. S5 (a)), while only a strong peak at 1000  $\text{cm}^{-1}$  was visible in the infrared spectra of other size fractioned sediment samples (Figs. S5 (c)–(h)). Furthermore, the infrared spectra of the coarse size sample at Site 1 and the heavy-density fraction of the coarse-size sediment at Site 2 near the Boat Maintenance Facility A were similar to those of paint flakes (Figs. 1 and S5 (i) and (k)–(l)), which contained alkyd polymers acting as resins/binders. All these results indicated that paint flakes were unevenly distributed and mostly affiliated with coarse-size sediment, typically found near boat



**Fig. 1.** Characterization of fractioned sediment and paint flakes by scanning electron microscopy (SEM) and infrared spectroscopy: (a) appreciable amounts of paint flakes in coarse sediment; (b) SEM image of paint flakes; (c) infrared spectrum of coarse sediment from Site 1; (d) infrared spectrum of fine sediment from Site 1 and (e) infrared spectrum of paint flake C.

**Table 1**  
Concentrations of DDT and its metabolites (DDXs, range (average; median) ng g<sup>-1</sup> dry weight) in the grain-size (μm) and whole size sediments and paint flakes collected from Hailing Bay.

	All sites	Vicinity of boat maintenance facility A	Aquaculture zone	Outside the aquaculture zone
<i>Sediment</i>				
<i>Bulk sediment</i>				
	65–5600 (1400; 450)	450–5600 (800; 1370)	200–4100 (100; 820)	65–400 (187; 130)
<i>Grain-size fractioned</i>				
200–2000	<RL <sup>a</sup> –30000 (3700; 230)	13–33000 (10,000; 6200)	<RL–6200 (1000; 130)	<RL–290 (100; 20)
63–200	1–3400 (300; 30)	42–3000 (740; 400)	<RL–1200 (160; 20)	<RL–80 (20; 6)
30–63	1–1500 (300; 70)	180–1000 (740; 500)	<RL–1500 (260; 60)	<RL–180 (40; 20)
<30	10–1800 (200; 70)	100–600 (600; 400)	10–1800 (230; 40)	10–150 (40; 20)
<i>Density fractions</i>				
Heavy density (ρ > 1.7 g cm <sup>-3</sup> )	–	86–95000 <sup>b</sup>	30–5200 <sup>c</sup>	–
Light density (ρ < 1.7 g cm <sup>-3</sup> )	–	10,000–28000 <sup>b</sup>	2100–5500 <sup>c</sup>	–
<i>Paint flakes</i>				
Vessel	42,000–300,000 (150,000; 81,000)			
Cabin	<RL–1500 (450; <RL)			

<sup>a</sup> RL is the abbreviation of the reporting limit at 0.5 ng g<sup>-1</sup> dry weight for a 5-g sediment sample and 10 ng g<sup>-1</sup> dry weight for a 0.25 g paint flake samples.

<sup>b</sup> Density fractions from Site 2 only.

<sup>c</sup> Density fractions from Site 9 only.

maintenance facilities.

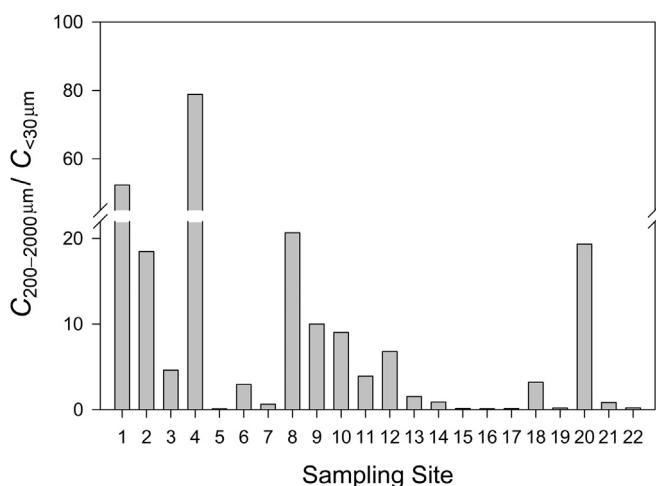
### 3.2. Occurrence of DDT compounds in sediments and paint flakes

Concentrations of DDXs in surface (bulk) sediment samples varied from 1.1 to 1100 ng g<sup>-1</sup> with a median of 16 ng g<sup>-1</sup>. As expected, the highest concentrations of DDXs occurred near the vicinity of the boat maintenance facilities, whereas the lowest concentrations occurred outside the aquaculture zone (Table 1). In addition, concentrations of DDXs in paint flakes from boat surfaces (42,000–290,000 ng g<sup>-1</sup>) were significantly higher than those from cabin surfaces (<RL–1500 ng g<sup>-1</sup>) and in bulk sediment (Table 1). These findings were consistent with our previous suggestion that DDTs (at 0.15–40,000 μg g<sup>-1</sup> wet wt) may have been blended into antifouling paints used locally in Hailing Bay (Yu et al., 2011c). Furthermore, the concentrations of DDTs (0.11–235 μg g<sup>-1</sup>) in dock road sediments (Guo et al., 2013), collected within approximately 1–80 m from Boat Maintenance Facility A (Fig. S1), were much greater (0.1–210 times) than those in the sediment samples collected in the present study. Apparently, paint flakes off abandoned and/or mooring

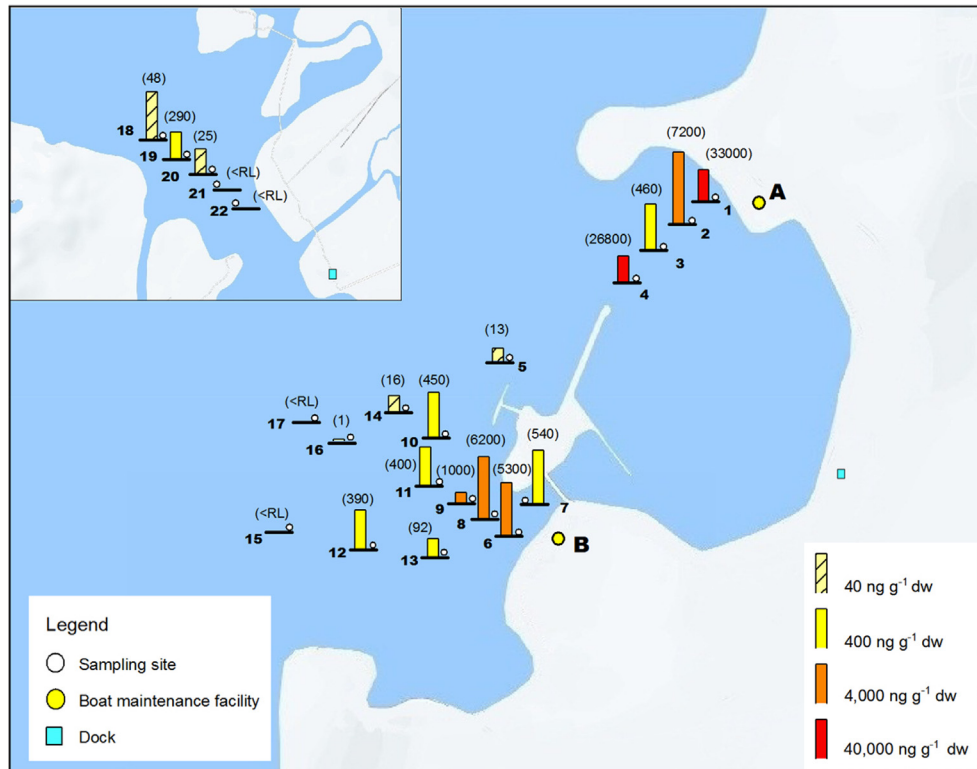
vessels or generated during boat maintenance may have been responsible for the distribution pattern of “hot spots” in estuarine sediment.

Concentrations of DDT compounds varied greatly among different sediment grain sizes (Table 1). The relative abundances of DDXs in the coarse (200–2000 μm) and fine (<30 μm) fractions ranged from 0.1 to 79 (Fig. 2). In particular, the concentrations of DDXs in 62% of coarse fraction samples at Sites 1–4 and 4–17 from the vicinity of the Boat Maintenance Facilities A and B were higher than those of fine fractions. For instance, the coarse and fine fractions from the vicinity of the Boat Maintenance Facility B (Fig. S1) contained DDXs at 460–33000 and 100–1800 ng g<sup>-1</sup>, respectively. The concentrations of DDXs in the coarse fractions were 0.15–63 times (with a median of 9.2) those in the whole sediment samples. In addition, the concentrations of DDT compounds in size-fractioned sediment samples declined sharply from Site 1 to Site 3 (Figs. 3 and S6), suggesting a dilution effect by ocean currents. The trend dramatically turned upward at Site 4, particularly in the coarse fraction (Fig. 3), which is located within a main vessel channel with frequent shipping activities. As a result, DDTs-containing paint flakes liberated from boat surfaces may have caused high concentrations of DDT compounds in sediment, further solidifying the importance of paint flakes in formation of “hot spots” in estuarine sediment.

Sediment organic carbon and grain size are important factors dictating the environmental distribution of hydrophobic organic compounds (HOCs) (Ghosh et al., 2003; Krauss and Wilcke, 2002). There is a positive (negative) correlation between the concentrations of HOCs and sediment TOC contents (grain sizes) in sediment. However, the present study obtained no significant ( $p > 0.05$ ) correlations between the concentrations of *p,p'*-DDT, *p,p'*-DDD and DDXs in the bulk sediment and size-fractioned samples and TOC or grain size (Figs. S7–S8). These findings were probably resulted from deposition of DDTs-containing paint flakes in coarse-size sediment, which can be further demonstrated by the elevated levels of DDTs in heavy-density fractions of coarse-sized sediment. For instance, the heavy-density (> 1.7 g cm<sup>-3</sup>) fraction of the coarse-size (200–2000 μm) sediment samples with low TOC contents (0.15% and 0.32%) contained large amounts of DDT compounds, i.e., 95,000 and 5200 ng g<sup>-1</sup> from Sites 2 and 9, respectively (Fig. 4 and Table 1). In general, light-density sediment fractions are mainly composed of coal/coke, wood and biodebris from algae and fish, and heavy-



**Fig. 2.** Ratio of DDXs concentrations in 200–2000 μm (C<sub>200–2000 μm</sub>) and <30 μm (C<sub><30 μm</sub>) size fractioned sediments.

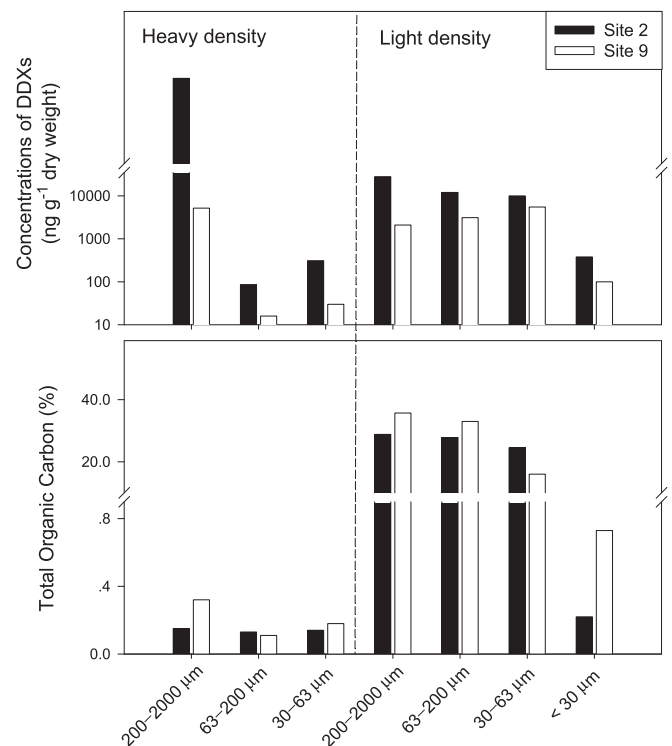


**Fig. 3.** Spatial distribution of DDT and its metabolites in 200–2000  $\mu\text{m}$  size fraction of surface sediments collected from Hailing Bay in Guangdong Province, South China. The numbers in parentheses are the concentrations of DDXs in  $\text{ng g}^{-1}$  dw.

density sediment fractions are composed primarily of sand, silt and clay. The heavy-density sediment fractions often contain low organic carbon contents and therefore possess weak sorption capacity for HOCs (Xiao et al., 2004). These results indicated that the paint flakes peeled off from boat surfaces may have artificially inflated the sorption capacity of heavy-density sediment particles for DDT compounds.

### 3.3. Desorption and sorption kinetics of DDT compounds

The desorption rates of individual DDT compounds from different size and density fractioned sediment samples varied widely but were site-specific (Fig. 5). The available fraction, defined as the mass which can be desorbed in 120 h with an infinite-sink desorption apparatus, varied from 0.1% to as high as 96%. For example, approximately 100% desorption of *p,p'*-DDE was achieved in 120 h for the 30–63  $\mu\text{m}$  size fraction of heavy-density sediment from Site 2, but less than 50% desorption was achieved for the same fraction from Site 9. This was consistent with previous findings that the structure and density of organic matter can affect the behavior of HOCs (Shor et al., 2003; Wang et al., 2001). Only 1–10% of DDT compounds desorbed from paint flakes after 120 h of desorption, probably because DDT compounds were strongly bound to the paint matrix. Similarly, the desorption rates of DDT compounds from the heavy-density fraction of coarse-size sediment were extreme slow. This result was different from the previous observation that HOCs generally desorb faster from heavy-density and coarse size sediment than those from light-density and fine size sediment, because of generally lower TOC content and/or specific surface area for heavy-density and coarse size sediment (Shor et al., 2003). These findings suggested that the amounts of DDT compounds discharged from paint flakes to surface water are expected to be low.



**Fig. 4.** Concentrations of DDXs and total organic carbon contents in each size- and density-fractioned sediment samples from Sites 2 and 9.

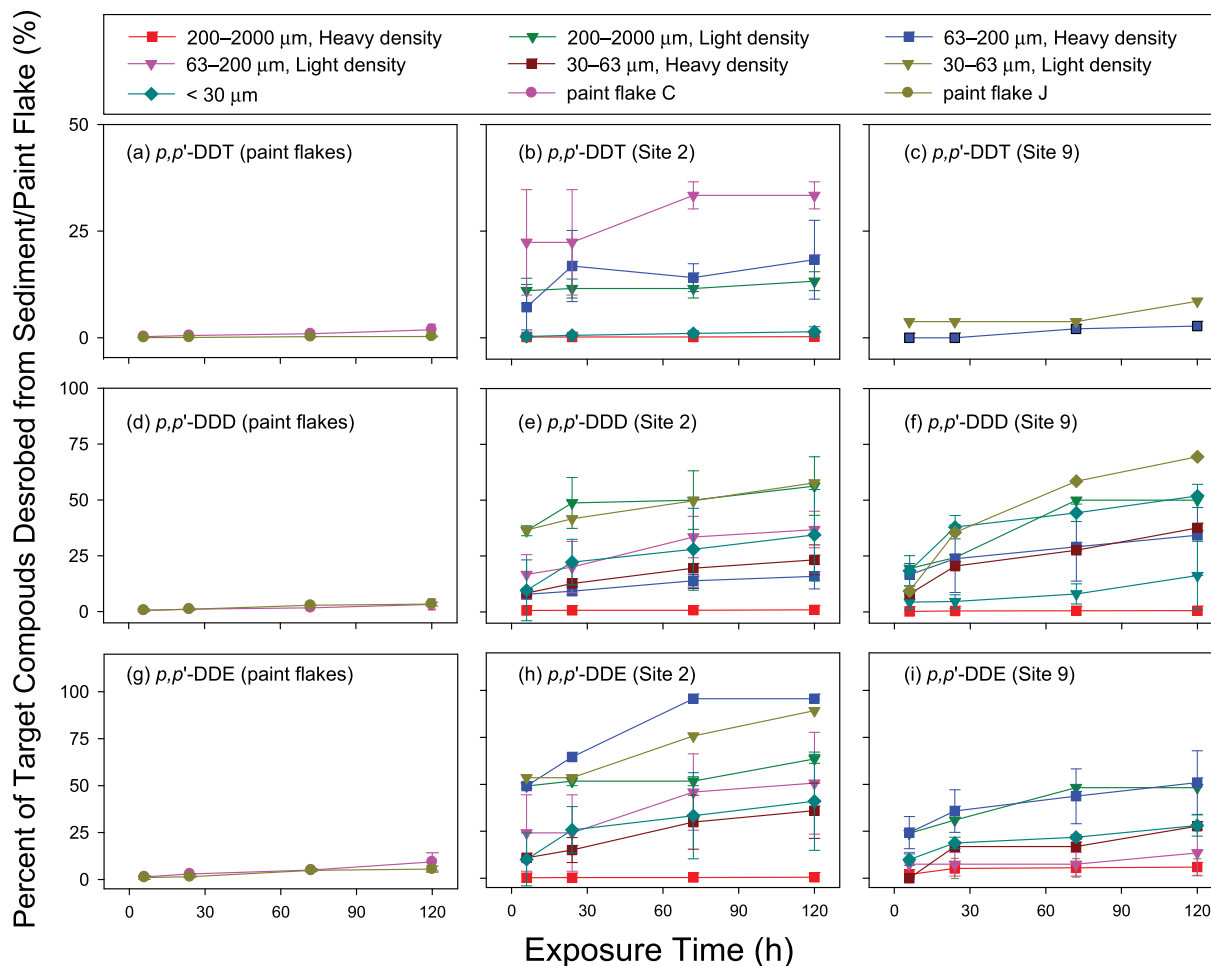


Fig. 5. Desorption kinetics of  $p,p'$ -DDT,  $p,p'$ -DDD and  $p,p'$ -DDE from paint flakes (C and J) or size fractionated sediments collected at Sites 2 and 9.

Furthermore, approximately 90–100% of  $p,p'$ -DDE- $d_8$ ,  $p,p'$ -DDD- $d_8$  and  $p,p'$ -DDT- $d_8$  were sorbed by paint flakes C and J after 7-d sorption (Table S2), an indication of strong sorption for DDT compounds by paint flakes. On the other hand, two higher-order metabolites of DDT, i.e.,  $p,p'$ -DDMU and  $p,p'$ -DBP, were also detected in the paint flake samples collected from boat surfaces in 2012 and 2014 (Table S3). These results suggested that boat surface paints and/or paint flakes can act as the sorbents to accumulate pollutants from surrounding water. As is well known, binders/resins constituting approximately 14–30% of the contents in paints (Wanninkhof, 1992; Zappa et al., 2001) can also sorb organic pollutants (Dominguez et al., 2011; Wu et al., 2010). Apparently, unevenly distributed paint flakes can substantially change the environmental fate and behavior of HOCs in estuarine sediment.

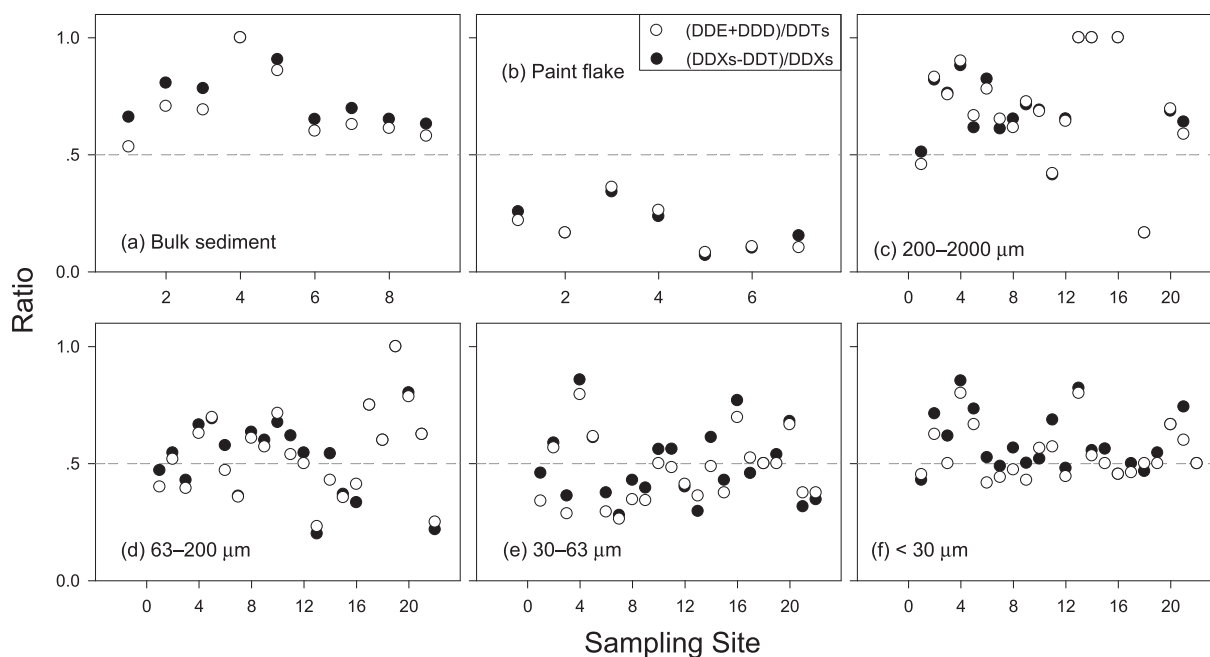
### 3.4. Utility of source diagnostic indices

The size- and density-dependent concentration data acquired in the present study allowed us to assess the utility of DDT-related source diagnostic indices. As is well known, a value of  $(\text{DDD} + \text{DDE})/\text{DDTs}$  (Qiu et al., 2005), or  $(\text{DDXs-}\text{DDT})/\text{DDXs}$  if higher-order metabolites of DDTs are considered (Yu et al., 2011a), greater than 0.5 indicates that DDT is derived from weathered residues. The value of  $\text{DDD}/\text{DDE}$  has been used to indicate whether DDT is mainly dehydrochlorinated to DDE under aerobic conditions

(smaller than 1) or largely dechlorinated to DDD under anaerobic conditions (greater than 1) (Lin et al., 2009).

In the present study, the  $(\text{DDD} + \text{DDE})/\text{DDTs}$  or  $(\text{DDXs-}\text{DDT})/\text{DDXs}$  were greater than 0.5 in bulk sediment. However, this does not necessarily implicate historical residues as the main sources of DDTs, as paint flakes had values of  $(\text{DDD} + \text{DDE})/\text{DDTs}$  or  $(\text{DDXs-}\text{DDT})/\text{DDXs}$  below 0.5. Interestingly, the percent of the samples with the values of  $(\text{DDD} + \text{DDE})/\text{DDTs}$  or  $(\text{DDXs-}\text{DDT})/\text{DDXs}$  below 0.5 was 11% (9–14%), 36% (32–41%), 57% (55–59%) and 30% (23–36%), respectively, for the 200–2000, 63–200, 30–63 and < 30  $\mu\text{m}$  size fractions (Fig. 6). Thus, the coarse-size fractions (200–2000  $\mu\text{m}$ ) contained DDT compounds derived mainly from historical residues, whilst the < 200  $\mu\text{m}$  size fractions contained fair amounts of DDT compounds from fresh inputs.

The values of  $\text{DDD}/\text{DDE}$  ranged from 1 to 105 in the sediment samples (Fig. S9), suggesting prevailing anaerobic conditions in the sampling sites. Meanwhile, the  $\text{DDD}/\text{DDE}$  values in paint flakes were in the range of 1–13, which was contradictory to the fact that paint flake samples collected from boat surfaces and cabin were supposedly subject to aerobic conditions. As aforementioned, boat surface paints can serve as sorbents, and therefore may uptake organics from the surrounding water. Because the concentrations of DDD in sediment and water were greater than those of DDE in Hailing Bay (Yu et al., 2011a, 2011b), paint flakes may directly sorb DDD and DDE from the water



**Fig. 6.** Values of  $(\text{DDD} + \text{DDE})/\text{DDTs}$  and  $(\text{DDXs} - \text{DDT})/\text{DDXs}$  in bulk sediments, paint flakes and size fractionated sediments. DDD = sum of  $p,p'$ -DDD and  $o,p'$ -DDD; DDE = sum of  $p,p'$ -DDE and  $o,p'$ -DDE; DDTs = sum of  $p,p'$ -DDT,  $o,p'$ -DDT,  $p,p'$ -DDD,  $o,p'$ -DDD,  $p,p'$ -DDE and  $o,p'$ -DDE; DDXs = sum of DDTs,  $p,p'$ -DDMU and  $p,p'$ -DBP; DDT = sum of  $p,p'$ -DDT and  $o,p'$ -DDT.

column, and thereby contain high DDD/DDE values. Apparently, source diagnostic indices for DDTs in sediment are mostly grain-size and density dependent, and paint flakes present in environmental matrices can strongly affect the outcome of source diagnostics.

#### 4. Conclusions

Unevenly distributed paint flakes were responsible for the distribution pattern of “hot spots” (characterized by the occurrence of DDT compounds) within estuarine sediment. In addition, the higher-order metabolites of DDT were detected in paint flakes from boat surfaces, suggesting that paint flakes also served as sorbents of HOCs in surrounding water. On the other hand, the desorption kinetics of DDT compounds from paint flakes and the heavy-density fraction of coarse-size sediment were both quite slow. Overall, the role of paint flakes needs to be adequately considered in any assessment of the environmental fate and transport of DDT compounds in estuarine sediment.

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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.2015.12.012>.

#### References

- Boxall, A.B.A., Comber, S.D., Conrad, A.U., Howcroft, J., Zaman, N., 2000. Inputs, monitoring and fate modelling of antifouling biocides in UK estuaries. *Mar. Pollut. Bull.* 40, 898–905.
- Champ, M.A., 2003. Economic and environmental impacts on ports and harbors from the convention to ban harmful marine anti-fouling systems. *Mar. Pollut. Bull.* 46, 935–940.
- Comber, S.D.W., Franklin, G., Gardner, M.J., Watts, C.D., Boxall, A.B.A., Howcroft, J., 2002. Partitioning of marine antifoulants in the marine environment. *Sci. Total Environ.* 286, 61–71.
- Dominguez, J.R., Gonzalez, T., Palo, P., Cuerda-Correa, E.M., 2011. Removal of common pharmaceuticals present in surface waters by Amberlite XAD-7 acrylic-ester-resin: influence of pH and presence of other drugs. *Desalination* 269, 231–238.
- Dyer, R.A., Tolhurst, L.E., Hilton, M.J., Thomas, K.V., 2006. Bioaccumulation of the antifouling paint booster biocide Irgarol 1051 by the green alga *Tetraselmis suecica*. *Bull. Environ. Contam. Toxicol.* 77, 524–532.
- Ghosh, U., Zimmerman, J.R., Luthy, R.G., 2003. PCB and PAH speciation among particle types in contaminated harbor sediments and effects on PAH Bioavailability. *Environ. Sci. Technol.* 37, 2209–2217.
- Guo, G., Zhang, C., Wu, G., Ding, Q., Wang, S., Li, F., 2013. Health and ecological risk-based characterization of soil and sediment contamination in shipyard with long-term use of DDT-containing antifouling paint. *Sci. Total Environ.* 450, 223–229.
- Harris, J.R.W., Hamlin, C.C., Stebbing, A.R.D., 1991. A simulation study of the effectiveness of legislation and improved dockyard practice in reducing TBT concentrations in the Tamar estuary. *Mar. Environ. Res.* 32, 279–292.
- Klaine, S.J., Koelmans, A.A., Horne, N., Carley, S., Handy, R.D., Kapustka, L., Nowack, B., von der Kammer, F., 2012. Paradigms to assess the environmental impact of manufactured nanomaterials. *Environ. Toxicol. Chem.* 31, 3–14.
- Krauss, M., Wilcke, W., 2002. Sorption strength of persistent organic pollutants in particle-size fractions of urban soils. *Soil Sci. Soc. Am. J.* 66, 430–437.
- Law, K.L., Moret-Ferguson, S., Maximenko, N.A., Proskurowski, G., Peacock, E.E., Hafner, J., Reddy, C.M., 2010. Plastic accumulation in the north Atlantic subtropical gyre. *Science* 329, 1185–1188.
- Lin, T., Hu, Z., Zhang, G., Li, X., Xu, W., Tang, J., Li, J., 2009. Levels and mass burden of DDTs in sediments from fishing harbors: the importance of DDT-containing antifouling paint to the coastal environment of China. *Environ. Sci. Technol.* 43, 8033–8038.
- Qiu, X.H., Zhu, T., Yao, B., Hu, J.X., Hu, S.W., 2005. Contribution of dicofol to the current DDT pollution in China. *Environ. Sci. Technol.* 39, 4385–4390.
- Rockne, K.J., Shor, L.M., Young, L.Y., Taghon, G.L., Kosson, D.S., 2002. Distributed sequestration and release of PAHs in weathered sediment: the role of sediment structure and organic carbon properties. *Environ. Sci. Technol.* 36, 2636–2644.
- Shor, L.M., Rockne, K.J., Taghon, G.L., Young, L.Y., Kosson, D.S., 2003. Desorption kinetics for field-aged polycyclic aromatic hydrocarbons from sediments.

- Environ. Sci. Technol. 37, 1535–1544.
- Singh, N., Turner, A., 2009. Trace metals in antifouling paint particles and their heterogeneous contamination of coastal sediments. *Mar. Pollut. Bull.* 58, 559–564.
- Thomas, K.V., McHugh, M., Waldock, M., 2002. Antifouling paint booster biocides in UK coastal waters: inputs, occurrence and environmental fate. *Sci. Total Environ.* 293, 117–127.
- Verhaegen, Y., Monteyne, E., Neudecker, T., Tulp, I., Smagghe, G., Cooreman, K., Roose, P., Parmentier, K., 2012. Organotins in north sea brown shrimp (*Crangon crangon* L.) after implementation of the TBT ban. *Chemosphere* 86, 979–984.
- Wang, X.C., Zhang, Y.X., Chen, R.F., 2001. Distribution and partitioning of polycyclic aromatic hydrocarbons (PAHs) in different size fractions in sediments from Boston Harbor, United States. *Mar. Pollut. Bull.* 42, 1139–1149.
- Wanninkhof, R., 1992. Relationship between wind–speed and gas–exchange over the ocean. *J. Geophys. Res.–Ocean* 97, 7373–7382.
- Wu, J., Xu, Z., Zhang, W., Lv, L., Pan, B., Nie, G., Li, M., Du, Q., 2010. Application of heterogeneous adsorbents in removal of dimethyl phthalate: equilibrium and heat. *Aiche J.* 56, 2699–2705.
- Xiao, B.H., Yu, Z.Q., Huang, W.L., Song, J.Z., 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.
- Yu, H.-Y., Bao, L.-J., Liang, Y., Zeng, E.Y., 2011a. Field validation of anaerobic degradation pathways for dichlorodiphenyltrichloroethane (DDT) and 13 metabolites in marine sediment cores from China. *Environ. Sci. Technol.* 45, 5245–5252.
- Yu, H.-Y., Guo, Y., Bao, L.-J., Qiu, Y.-W., Zeng, E.Y., 2011b. 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., 2011c. Inputs of antifouling paint-derived dichlorodiphenyltrichloroethanes (DDTs) to a typical mariculture zone (South China): potential impact on aquafarming environment. *Environ. Pollut.* 159, 3700–3705.
- Zappa, C.J., Asher, W.E., Jessup, A.T., 2001. Microscale wave breaking and air–water gas transfer. *J. Geophys. Res. Ocean* 106, 9385–9391.
- Zarfl, C., Fleet, D., Fries, E., Galgani, F., Gerdtts, G., Hanke, G., Matthies, M., 2011. Microplastics in oceans. *Mar. Pollut. Bull.* 62, 1589–1591.