Mediated distribution pattern of organic compounds in estuarine sediment by anthropogenic debris

Chen-Chou Wu [a,d], Lian-Jun Bao [b], Shu Tao [c], Eddy Y. Zeng [b,*]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[b] School of Environment and Guangzhou Key laboratory of Environmental Exposure and Health, and Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou 510632, China
[c] Laboratory of Earth Surface Processes, College of Urban and Environmental Science, Peking University, Beijing 100871, China
[d] University of Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- Concentrations of OPFRs, OTs and PAEs are elevated in coarse fractions.
- Removal of debris from carbon-rich sediments can lower organics concentrations.
- Debris is responsible for the formation of "hot spots" in estuarine sediment.

GRAPHICAL ABSTRACT
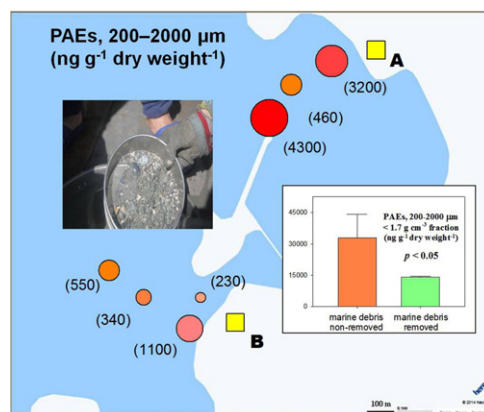
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ABSTRACT

Natural organic matter and grain size are considered as important parameters dictating the transport and fate of organic compounds in sediment. However, increasing evidence suggested that manufactured debris may alter the underlying mechanisms for biogeochemical cycling of organic compounds. To examine this assumption, estuarine sediment and embedded debris were collected from a fishery base in Guangdong Province of South China and analyzed for organophosphorus flame retardants (OPFRs), phthalates (PAEs), organotin compounds (OTs) and dichlorodiphenyltrichloroethanes (DDTs). Coarse-size debris ($>200\ \mu m$) were heterogeneously distributed in sediment, and most abundant near the boat maintenance facilities, aquaculture zone and shipping channel. The median concentrations of OPFRs, OTs, PAEs and DDTs in debris were 11, 0.2, 11 and 3.9 $\mu g\ g^{-1}$ dry sample weight^{-1}, respectively, 1 to 3 orders of magnitude greater than those in bulk sediment (19, 60, 240 and 570 $ng\ g^{-1}$ dry sample weight^{-1}, respectively). Furthermore, OPFRs, OTs and PAEs were mostly ($>99\%$) enriched in coarse-size (63–$2000\ \mu m$) sediment, and there was no significant correlation ($p > 0.05$) between the concentrations of OPFRs, OTs and PAEs in bulk and size-fractioned sediment samples and total organic carbon or grain size, similar to the distribution pattern of DDTs reported previously. When distinct debris were removed from the light-density ($<1.7\ g\ cm^{-3}$) fraction of coarse-size (200–$2000\ \mu m$) sediment, the concentration levels of

* Corresponding author.
  E-mail address: eddyzeng@jnu.edu.cn (E.Y. Zeng).

OPFRs, OTs, PAEs and DDTs declined by 84%, 59%, 55% and 7%, respectively. Obviously, debris irregularly distributed in sediment can alter the sediment sorption capacity for OPFRs, OTs and PAEs, and thus may undermine the significance of organic matter and grain size to the distribution of organic chemicals in sediment. Finally, commonly used procedures for preparing sediment samples and screening of debris may disturb the grain size distribution or underestimate the abundance of heavy-density debris, resulting in flawed sediment quality assessment.

1. Introduction

Natural organic matter and carbonaceous materials of different origins were shown to impact the distribution of organic compounds in sediment (Hung et al., 2007; Jonker and Koelmans, 2002). Particle grain size also exerts significant influences on the biogeochemical cycling of organic compounds in general (Pierard et al., 1996). Because small-sized particles have large specific surface areas, they have high adsorption capacity for organic compounds (Jonker and Koelmans, 2002; Weiler and Mills, 1965). Therefore, total organic carbon (TOC) and sediment grain size are expected to be positively and negatively, respectively, correlated with sediment organic compounds, especially if the adsorbents and adsorbates are of the same source (Ali et al., 2014; Hung et al., 2007; Koh et al., 2006). Previous studies also showed that there was no or weak significant correlation between the concentrations of organic compounds and TOC or particle grain size in heavy anthropogenically impacted regions, such as in the vicinity of industries, coasts and harbors (Casado-Martinez et al., 2009; Edgar et al., 2003; Environment Agency, 2007; Khim et al., 1999; Khim et al., 2001; Thompson et al., 1996). For instance, Edgar et al. (2003) did not find any significant correlation between the concentrations of polychlorinated biphenyls and TOC or sediment grain size in intertidal sediment of the Clyde Estuary, United Kingdom.

Anthropogenic debris are a group of manufactured or processed solid waste materials that enter into the environment either directly or indirectly after use or disposal and eventually occur in lands or oceans (Jambeck et al., 2015). The amount of debris was found to be proportional to the extent of anthropogenic impacts in regions within 200 km of the coastline (van Sebille et al., 2015). Debris encompass metals (e.g., derelict vehicles and beverage containers), glass (e.g., light bulbs and bottles), plastics and other materials (e.g., lumber, rubber and textile) (The United States Environmental Protection Agency's (US EPA) Office of Water). Additives are often used to enhance product durability (Hansen et al., 2013), which may subsequently increase the persistency of obsolete merchandises in the environment. An example is the addition of organophosphorus flame retardants (OPFRs), phthalates (PAEs) and organotin compounds (OTs) to a variety of industrial and consumer products to lessen the effects of heat and light on plastics. Debris can also act as sorbents to accumulate organic compounds from the environment, e.g., the amount of phenanthrene accumulated from seawater by plastics was 2 orders of magnitude greater than that in sediment (Teuten et al., 2007). Clearly, the distribution of organic compounds in sediment may be mediated by the occurrence of debris. For example, our previous study reported that paint flakes unevenly distributed in estuarine sediment could artificially inflate the sorption capacity of heavy-density (>1.7 g cm^{-3}) sediment for DDT compounds (Wu et al., 2016).

The present study was conducted to examine the hypothesis that anthropogenically derived debris is vital to the patchy distribution of organic compounds in estuarine sediment. Target analytes include OPFRs, PAEs, OTs and dichlorodiphenyltrichloroethanes (DDTs), which are commonly used plastic additives in synthetic materials and biocides in antifouling paint (Diez et al., 2002; Yu et al., 2011). A fishing harbor in Hailing Bay, Guangdong Province of China was selected as the study region, one of the top 10 fishing harbors in China and also serves as an important aquaculture zone (Yangjiang Municipal People's Government). The objectives of the present study were to (1) determine the size and density occurrence of the target compounds in sediment (except for DDTs) and anthropogenic debris; (2) examine how debris mediated the distribution patterns of the target compounds in estuarine sediment and (3) assess the procedures for preparing sediment samples and sorting out debris.

2. Materials and methods

2.1. Materials

Standards of the selected target analytes were supplied by Chiron AS, Trondheim, Norway (TIBP), AccuStandard, New Haven, CT, USA (TnBP, TPhP and TDCPP), Dr. Ehrenstorfer GmbH, Augsburg, Germany (TCEP, TCIPP, TBOEP, EHDPP, TCPs and TEHP) and Adamas Reagent, Shanghai, China (DCPs mixtures). The standards of OTs were purchased from J&K Scientific, Beijing, China (n-butyltin-trichloride) and ChemService, West Chester, PA, USA (Tetraphenyltin). The standards of PAEs, i.e., DMP, DEP, DIBP, DBP, DMPP, DMEP, DEEP, DPP, DHxP, BBP, DBEP, DCHP, DEHP, DNOP, DPhP and DNP, were acquired from O2si Smart Solutions, Charleston, SC, USA. The abbreviations of individual OPFRs, PAEs and OTs and related information about DDTs are presented in the Supplementary Data ("S" indicates tables and figures in the Supplementary Data afterwards) Table S2. DEHP-d_4, PCB-67, PCB-191, o,p'-DDT-d_8, TnBP-d_{27} and TPhP-d_{15} were used as surrogate standards, and p-terphenyl-d_{14}, PCB-82 and benzyl benzoate were used as internal standards. Among them, TnBP-d_{27} and TPhP-d_{15} were purchased from Cambridge Isotope Laboratories, o,p'-DDT-d_8 from C/D/N Isotopes Quebec, Canada, DEHP-d_4 form Dr. Ehrenstorfer GmbH and other standards from AccuStandard. Sodium metatungstate monohydrate powers were purchased from Alfa Aesar (Bellefonte, PA, USA).

2.2. Sample collection

The first set of surface sediment samples, used to quantify the target compounds, was collected from a fishery base in Hailing Bay, Guangdong Province of China (Fig. S1) from August 2012 to November 2014, in proximity to two boat maintenance facilities (labeled as A and B in Fig. S1). Detailed procedures for sample collection were described elsewhere (Wu et al., 2016). To further examine the role of anthropogenic debris, another set of nine surface sediment samples (labeled as MD1 to MD9; Fig. S1) were taken in the same study region in November 2015 and only used to sort out anthropogenic debris.

2.3. Separation of sediment particles and debris

The first set of sediment samples were wet-fractionated into four sizes, i.e., 200–2000 µm, 63–200 µm, 30–63 µm and <30 µm. The size-segregated sediment samples from an aquaculture zone (Site 9) and shipping channel (Site 2) were further separated into two density fractions by floating them in a sodium metatungstate solution ($\rho = 1.7$ g cm^{-3}) (Wu et al., 2016). The procedure described in Wu et al. (2016) was slightly modified to separate anthropogenic debris from sediment. Briefly, sediment samples were wet sieved onboard with seawater, and the fractions remaining on 10- and 80-mesh sieves were collected, resulting in two size fractions, i.e., > 2000 µm and between 200 and 2000 µm. Such fractionation was based on the fact that paint flakes were mostly affiliated with coarse-size sediment (Wu et al., 2016) and

debris of <100 μm were difficult to identify by microscopy if they had no distinct shapes or colors (Song et al., 2014). Anthropogenic debris were sorted out with naked eyes from the selected size fractions, and weighed and stored at −20 °C until analysis. All anthropogenic debris were further divided into 9 individual categories for measurement of the target compounds, i.e., clothing, fiber or texture, rope, plastic line, plastic bag, food package, paint flake or particle, crust of cable or wire and wall paper (Fig. S2).

2.4. Sample extraction and instrumental analysis

All dry samples were spiked with the surrogate standards and impregnated with copper sheets for removal of sulfate before extraction. Both sediment and debris samples were sonicated twice with 20 mL of a mixture of hexane, dichloromethane and acetone (2:2:1 in volume) each. Each extract was concentrated, and the solvent was exchanged to hexane and further concentrated to 1 mL with a Zymark TurboVap 500 (Hopkinton, MA, USA). The concentrated extract was subsequently purified on a neutral silica column and eluted with a dichloromethane:acetone mixture (1:1 in volume). The eluates were collected, concentrated and solvent exchanged to hexane, further concentrated to 100 μL for sediment samples and 500 μL for debris samples and spiked with the internal standards prior to instrumental analysis.

Sample extracts were analyzed with a Shimadzu gas chromatograph coupled to a mass spectrometer (GCMS-2010 Plus) with a CD-5MS capillary column (30 m × 0.25 mm i.d. with 0.25 μm film thickness). One microliter of each extract was automatically injected into the column. The oven program was started from 60 °C (initially held for 1 min), ramped to 250 °C at 20 °C min^{-1} (held for 2 min), elevated to 280 °C at 5 °C min^{-1} and further increased to 300 °C at 20 °C min^{-1} (held for 20 min). Ultrahigh purity helium was used as the carrier gas at a constant flow rate of 1 mL min^{-1}. The ion source temperature was set at 250 °C. Mass spectra were scanned from m/z 63 to m/z 400 in the electron ionization mode with an electron impact energy of 70 eV. Because no standards were available for all cresyl phosphate and cresyl diphenyl phosphate, their concentrations were estimated based on the response factors of their homologues.

2.5. 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 10 samples. The extent of breakdown of p,p'-DDT was maintained <15% before instrumental analysis was initiated. The recoveries of the surrogate standards, TnBP-d_{27}, TPhP-d_{15}, PCB-67, PCB-191, o,p'-DDT-d_8 and DEHP-d_4, were 87 ± 12%, 96 ± 16%, 87 ± 16%, 94 ± 15%, 93 ± 16%

and 97 ± 10% in blank samples, 67 ± 12%, 95 ± 17%, 83 ± 23%, 82 ± 17%, 75 ± 16% and 77 ± 10% in field samples and 88 ± 13%, 98 ± 13%, 78 ± 31%, 78 ± 17% and 79 ± 18%, 75 ± 12% in matrix spiked samples. All reported concentrations were obtained by normalizing instrumentally measured concentrations to sample dry weight. Furthermore, the reporting limit (RL) was 0.25 ng g^{-1} for OPFRs and DDTs, 1.25 ng g^{-1} for n-butyltin-trichloride, 5 ng g^{-1} for tetraphenyltin and 2 ng g^{-1} for PAEs in a 0.1-g debris sample. For a 5-g sediment sample, the RLs for all target analytes were four times those for debris.

3. Results and discussion

3.1. Characterization of anthropogenic debris in surface sediment

The distribution patterns of paint flakes or particles were variable in the estuary sediment under investigation (Fig. 1 and Table S3). For instance, the relative abundance of paint flakes in coarse-sized sediment (>200 μm) declined sharply with increasing distance from the boat maintenance facilities (Fig. 1). However, the mass abundance of paint flakes in both the >2000 μm and 200–2000 μm size fractions turned upward at site MD5 (Fig. 1), which is located at a main shipping channel. Plastic rope, feed package and plastic bag, wall paper flakes and crust of cable or wire, which are mostly related to aquaculture farming and/ or aquaculture installation, were also found to unevenly distribute in surface sediment (Table S3). Overall, the distribution pattern of large debris suggested that these coarse size items were either directly or accidentally discharged from anthropogenic activities.

3.2. Occurrence of organic compounds in anthropogenic debris and sediment

The concentrations of OPFRs, OTs, PAEs and DDTs in anthropogenic debris ranged from <RL to 36, <RL to 740, 0.3 to 37,000 and 0.02 to 473 μg g^{-1}, with median values of 11, 0.2, 11 and 3.9 μg g^{-1}, respectively (Tables 1 and S4). Relatively great concentrations (37 and 34 mg g^{-1}) of PAEs occurred in wall paper flakes and crust of cable or wire, whereas antifouling paint flakes/particles contained the greatest concentrations of OPFRs, OTs and DDTs (36, 0.7 and 430 μg g^{-1}, respectively). By comparison, the concentrations of OPFRs, OTs and PAEs in surface (bulk) sediment samples ranged from <RL to 300, <RL to 160 and 28 to 520 ng g^{-1} with median values of 19, 60 and 240 ng g^{-1} (Table 1). The concentrations of OPFRs, OTs and PAEs also declined sharply with increasing distance from the boat maintenance facilities (Fig. S3), which was consistent with the occurrence of DDTs in the same study region (Wu et al., 2016).
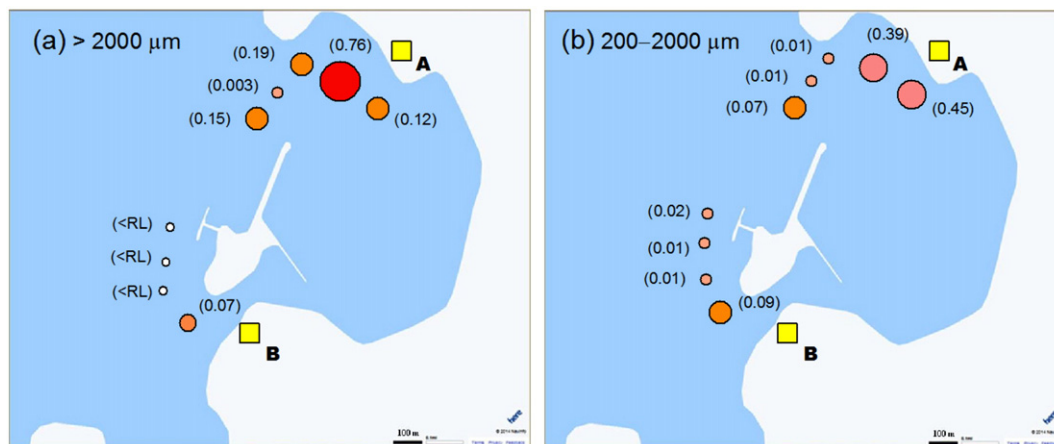

Fig. 1. Spatial distribution of paint flakes (mass abundance; g kg^{-1} dry weight^{-1}) in coarse size fractioned sediment (>200 μm) in Hailing Bay, 200–2000 μm (a), 63–200 μm (b) size fraction of surface sediments.

Table 1
Concentrations of OPFRs, OTs, PAEs and DDTs (range (mean; median) ng g^{-1} dry weight^{-1}) in the grain-size (μm) and whole size sediment and anthropogenic debris collected from Hailing Bay.

	OPFRs	OTs	PAEs	DDTs
Sediment				
Bulk sediment				
	<RL[a]–300 (81; 19)	<RL–160 (70; 60)	28–520 (250; 240)	16–1100 (570; 690)[b]
Grain-size fraction				
200–2000	<RL–2400 (560; 260)	<RL–280 (60; 20)	230–4300 (1400; 550)	460–31,000 (7200; 4900)[b]
63–200	1–320 (120; 100)	<RL–50 (10; 10)	37–2000 (630; 190)	10–3200 (790; 350)[b]
30–63	<RL–460 (120; 21)	100–10 (40; 20)	61–2900 (910; 180)	100–1500 (670; 450)[b]
<30	<RL–94 (31; 18)	<RL–470 (120; 20)	83–500 (210; 140)	90–1600 (540; 320)[b]
Density fractions				
Heavy density (ρ > 1.7 g cm^{-3})				
Vicinity of boat maintenance facility A[c]	2–46	10–400	16–120	86–95,000[b]
Aquaculture zone[d]	1–3	<RL–50	15–310	10,000–28,000[b]
Light density (ρ < 1.7 g cm^{-3})				
Vicinity of boat maintenance facility A	0–3100	110–3500	2700–32,000	30–5200[b]
Aquaculture zone	160–1600	<RL–50	1100–21,000	2100–5500[b]
Anthropogenic debris				
	<RL–36,000 (14,700; 11,000)	<RL–740,000 (150,000; 200)	0.3–37,000,000 (8,000,000; 11,000)	0.02–473,000 (62,000; 3900)

[a] RL = reporting limit.
[b] Data cited from Wu et al.(Wu et al., 2016).
[c] Density fractions from site 2 only.
[d] Density fractions from site 9 only.

Grain-sized distributions of OPFRs, OTs and PAEs were highly variable (Table 1), which was similar to that of DDTs (Wu et al., 2016). The concentrations of OPFRs, OTs and PAEs were greater in all coarse fractions (200–2000 μm) than in fine fractions (<30 μm) from all but sites 6 and 7, probably because these sites are located at a semi-closure bay (Fig. S1), ideal for sedimentation of fine suspended materials. The concentration ratios of OPFRs, OTs and PAEs in the coarse and fine fractions were in the ranges of <0.4–710, <0.01–4.1 and 0.7–43, respectively (Fig. 2). The concentrations of OPFRs, OTs and PAEs in the coarse fractions were 0.1–130, <0.01–5.2 and 0.9–48 times (with median values of 3.4, 1.4 and 8.3) than those in bulk sediment. Spatially, the concentrations of size-fractioned sediment OPFRs, OTs and PAEs declined steeply both from site 1 to site 3 and from site 6 to site 9 (Figs. 3 and S4–S5). However, the spatial trends of OPFRs and PAEs in coarse fraction samples markedly turned upward at site 3, and they also peaked at sites 8 and 9, respectively (Figs. 3 and S5), which are located within the aquaculture zone and a main shipping channel.

The concentrations of OPFRs, OTs and PAEs and TOC in size- and density-fractioned sediment samples are displayed in Fig. 4. Except for the fine grain fraction (<30 μm), the light-density fractions (<1.7 g cm^{-3}) contributed to the majority of OPFRs, OTs and PAEs in sediment. For instance, light-density fractioned sediment, representing only 0.15% of total sediment, contains approximately 98–99%, 85–90% and 98–99% of the concentrations of OPFRs, OTs and PAEs, respectively. In addition, OPFRs, OTs and PAEs were mostly enriched in the coarse size fraction (63–2000 μm) from sites 2 and 9, i.e., 89–92%, 58–88% and 92%.

3.3. Association of organic compounds with sediment grain sizes and debris

In general, small particles with large specific surface area and organic carbon-rich particles can possess strong surface adsorption capacity for hydrophobic organic compounds (Khalil et al., 2006). However, there was no significant correlation ($p > 0.05$) between the concentrations of OPFRs, OTs and PAEs in bulk sediment and size-fractioned samples and TOC or grain size in the present study (Figs. S6–S7). This may suggest that the majority of the target compounds were not sorbed on the external surface of sediment particles, and other controlling factors should be considered.

On the other hand, anthropogenic debris in sediment contained abundant organic compounds; e.g., the level of PAEs in crust of cable/wire (34 mg g^{-1}) was 5 to 6 orders of magnitude greater than those in bulk sediment (28 to 520 ng g^{-1}). After anthropogenic debris, i.e., distinct tiny colorful pieces, films or particles, were carefully
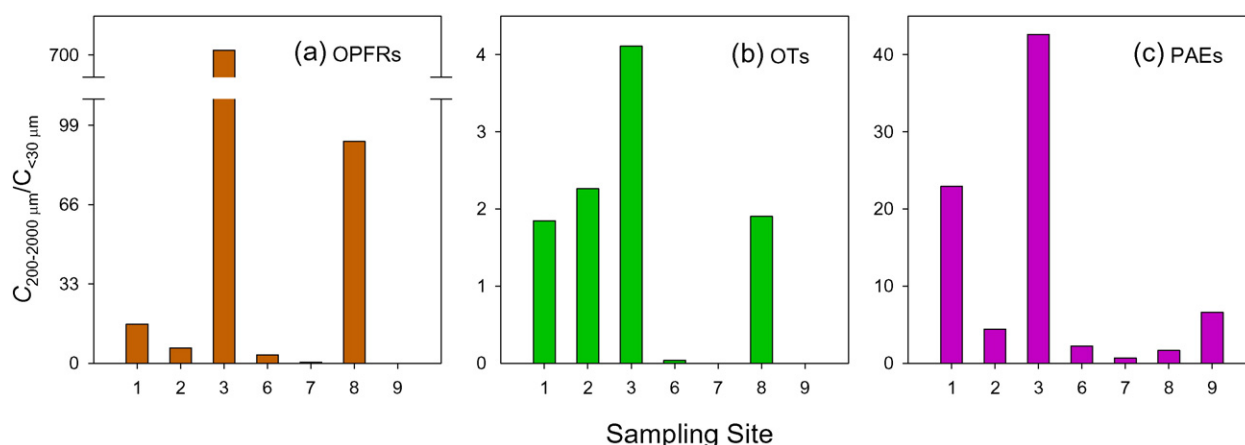

Fig. 2. Concentration ratios of OPFRs, OTs and PAEs in 200–2000 μm ($C_{200-2000\ \mu m}$) and <30 μm ($C_{<30\ \mu m}$) size fractioned sediments.
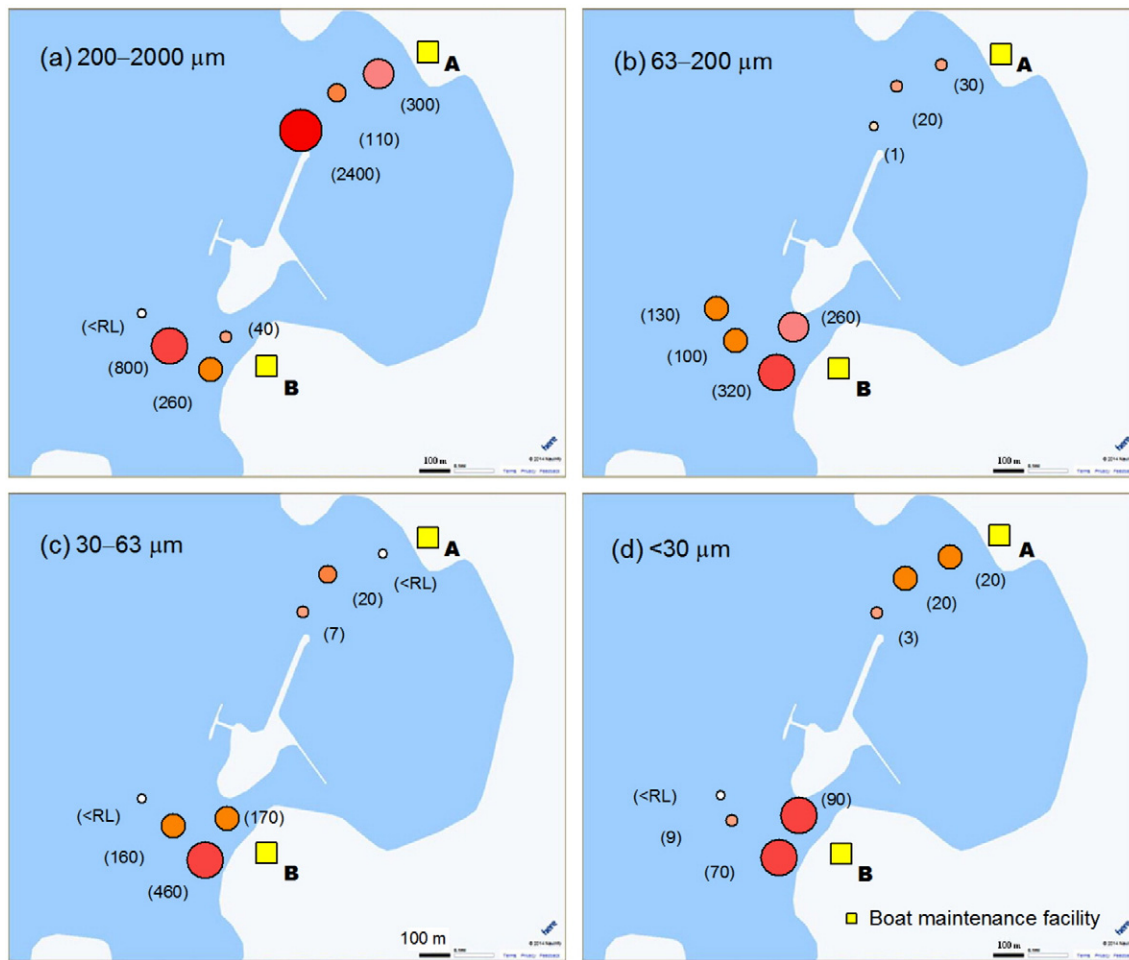
Fig. 3. Spatial distribution of OPFRs in the 200–2000 μm (a), 63–200 μm (b), 30–60 μm (c) and <30 μm (d) size fraction of surface sediments collected from Hailing Bay in Guangdong Province, South China. The numbers in parentheses are the concentrations of OPFRs in ng g^{-1} dry weight^{-1}.

removed from the light-density fraction (<1.7 g cm^{-3}) of coarse-size (200–2000 μm) sediment, the concentrations of OPFRs, OTs and PAEs declined sharply (Fig. 5). This finding further solidified that anthropogenic debris unevenly distributed in sediment were responsible for the distribution pattern of "hot spots" within estuarine sediment (Wu et al., 2016).

Previous studies showed that weathered coal tar pitch associated with coarse size fractions (>63 μm) in light-density sediment (<1.8 g cm^{-3}) was mainly responsible for the high PAH concentrations in the vicinity of a manufactured gas plant with a history of heavy shipping and industrial activities (Ghosh et al., 2000; Khalil et al., 2006). Our previous results also indicated that DDTs-containing paint flakes artificially inflated the concentrations of DDTs in the heavy-density fraction (>1.7 g cm^{-3}) of coarse-size sediment (200–2000 μm) with low TOC contents (0.15–0.3%) in the vicinity of boat maintenance facilities (Wu et al., 2016).

The present study suggested that the distribution of organic compounds in estuarine sediment can be substantially influenced by the distribution and chemistry of anthropogenic debris. Although this result was derived from coarse-size sediment, similar conclusions are expected with small-size sediment. In some situations, sediment with high organic carbon contents and/or large specific surface area may not dictate the transport and therefore distribution of organic compounds. This finding may implicate significant consequences for risk assessment under certain circumstances. For example, application of sewage biosolids in agricultural fields for crop growth may result in abundant organic matter and nutrients in soil, but at the same time may also

bring in large amounts of synthetic fibers and organic or inorganic compounds (X. Li et al., 2014; Y. Li et al., 2014; Passuello et al., 2010; Zubris and Richards, 2005). Risk assessment results may be erroneous if the effects of debris on the sorption capacity of soil are not adequately accounted for.

3.4. Importance of debris to the distribution of organic compounds

As debris may contain a variety of organic compounds (Tables 1 and S4), e.g., the concentrations of PAEs and DDTs were 40–80 and 3.1–17 μg g^{-1}, respectively, in PE plastic bag and food package. This suggests that debris can act as sorbents to accumulate organic compounds from surrounding environments. A previous study demonstrated that the amounts of organic compounds accumulated in plastics could be up to 6 orders of magnitude greater than those in seawater (Mato et al., 2001). Debris may also contain a mixture of additives derived from original products, e.g., DDTs or OTs based antifouling paint (Yu et al., 2011) and wallpaper and building materials laden with phthalate plasticizers and flame retardants (Kajiwara et al., 2011). Additives, such as plasticizers (e.g., phthalates), flame retardants and inorganic pigment (i.e., cadmium, chromium and lead compounds), can constitute 10–70%, 12–18% and 0.01–10% of the contents in synthetic polymer materials (Hansen et al., 2013). In some cases, Cu and Zu in polymeric paint matrix may constitute up to 35% and 15%, respectively, of the total dry weight (Turner, 2010). Weathering of polymers can increase their sorption capacity for organic compounds due to an increase in the amount of fine cracks on the surface area and/or extended residence time in the
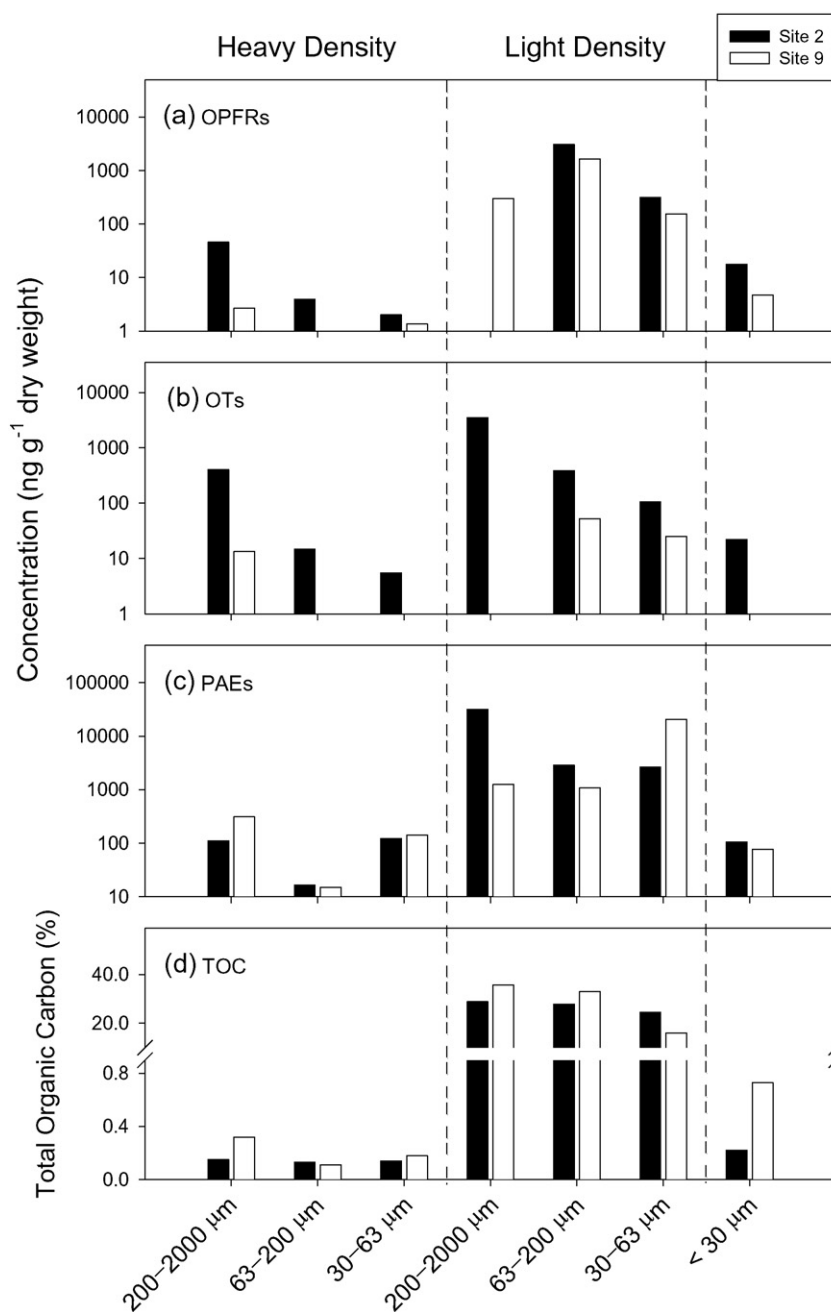
Fig. 4. Concentrations of OPFRs, OTs and PAEs and total organic carbon contents in each size- and density-fractioned sediment samples from sites 2 and 9.

environment (Endo et al., 2005). Abrasion of polymeric/organic matrices may artificially inflate the levels of organic compounds, because particles enriched with bromines do not occur freely in the dust; instead they may be embedded within the polymeric/organic matrix framework (Suzuki et al., 2009; Webster et al., 2009). On the other hand, the desorption rates of organic compounds were shown to differ between debris and the organic matrix, e.g., PAHs and DDTs desorbed more rapidly from sediment than from plastics and paint flakes (Teuten et al., 2007; Wu et al., 2016). As a result, debris may affect the bioavailability of organic compounds in sediment, as these compounds are accumulated in debris embedded in sediment and become unbioavailable. As a result, the presence of small amounts of contaminated debris may substantially increase the concentrations of organic compounds in sediment, which seems to be especially significant in highly populated and industrialized regions and in the vicinity of shipping channels. All the above analyses implicated debris as a key factor for the patchy distribution of organic compounds in sediment and should be considered as an important constituent in assessment of sediment quality.

3.5. Implications for sediment sample preparation and screening of debris

Large particles, such as stoves and shells, are often considered to contain low levels of organic compounds and thus understate bulk concentrations in sediment samples. They are usually removed from bulk sediment samples, particularly with a method of dry-sieving using specified mesh screens (Yu et al., 2011). However, analyses of the bulk and size- and density-fractioned sediment samples (Table 1) indicated that OPFRs, PAEs and OTs were affiliated mostly with coarse-size sediment (63–2000 μm) collected from the vicinity of boat maintenance facilities, while fine-size sediment (<30 μm) contained <1% of total OPFRs, PAEs and OTs. In addition, grounding and dry-sieving can artificially
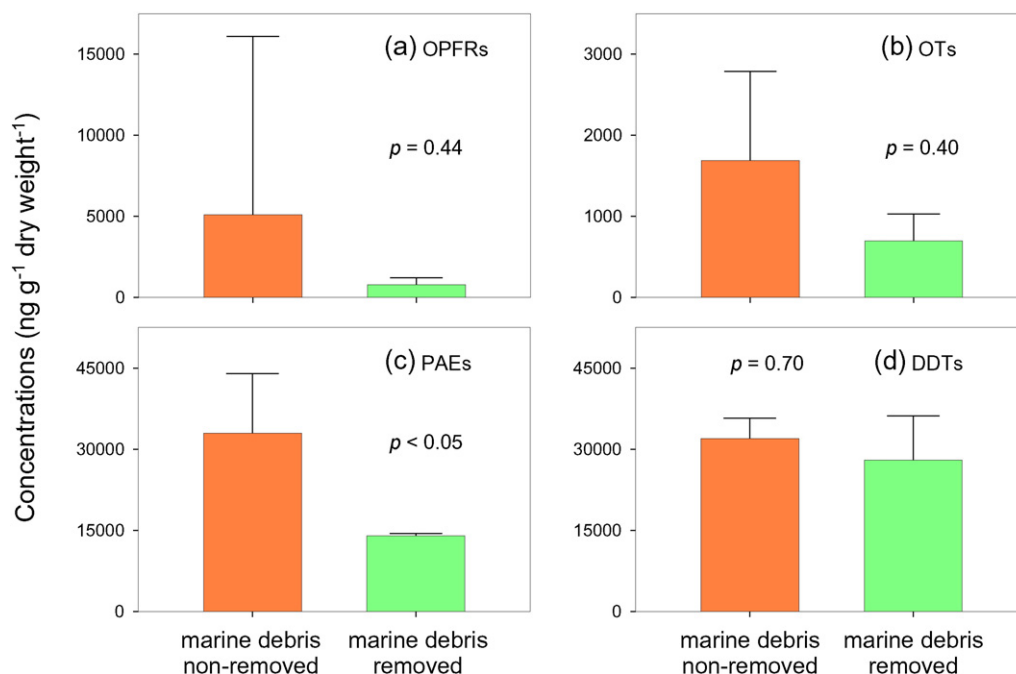
Fig. 5. Concentrations of OPFRs, OTs, PAEs and DDTs in light-density (<1.7 g cm^{-3}) fraction of the coarse-size (200–2000 μm) sediment from site 2 after removed/non-removed distinct tiny colorful pieces, films or particles.

break down embedded constituents and alter their grain-sized distribution in sediment, resulting in flawed risk assessment results.

On the other hand, collection and separation of debris from bulk sediment are generally assisted by density flotation, filtration, sieving and/or visual sorting, and there is generally lack of standardized protocols (Hidalgo-Ruz et al., 2012). However, density flotation may underestimate the abundance of heavy density particles, such as crust of cable or wire, wall paper and paint flakes, which was shown to contain abundant organic compounds in the present study. Thus, we recommend a procedure of wet-sieving for size and/or density separation of bulk sediment to screen debris, particularly for sediment samples collected near any contaminant sources.

4. Conclusions

Irregularly distributed anthropogenic debris were mainly responsible for the formation of "hot spots" (characterized by the occurrence of OPFRs, OTs and PAEs) in estuarine sediment. Furthermore, debris can alter the sorption capacity of sediment for organic chemicals and weaken the influences of organic matter and sediment grain size on the distribution of organic chemicals in estuarine sediment, particularly in the vicinity of shipping channels and aquaculture zones. Overall, the role of anthropogenic debris needs to be adequately considered in any assessment for biogeochemical cycling of organic compounds in estuarine environments.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.04.141.

References

Ali, U., Syed, J.H., Liu, J.W., Sanchez-Garcia, L., Malik, R.N., Chaudhry, M.J.I., Arshad, M., Li, J., Zhang, G., Jones, K.C., 2014. Assessing the relationship and influence of black carbon on distribution status of organochlorines in the coastal sediments from Pakistan. Environ. Pollut. 190, 82–90.

Casado-Martinez, M.C., Forja, J.M., DelValls, T.A., 2009. A multivariate assessment of sediment contamination in dredged materials from Spanish ports. J. Hazard. Mater. 163, 1353–1359.

Diez, S., Abalos, M., Bayona, J.M., 2002. Organotin contamination in sediments from the Western Mediterranean enclosures following 10 years of TBT regulation. Water Res. 36, 905–918.

Edgar, P.J., Hursthouse, A.S., Matthews, J.E., Davies, I.M., 2003. An investigation of geochemical factors controlling the distribution of PCBs in intertidal sediments at a contamination hot spot, the Clyde Estuary, UK. Appl. Geochem. 18, 327–338.

Endo, S., Takizawa, R., Okuda, K., Takada, H., Chiba, K., Kanehiro, H., Ogi, H., Yamashita, R., Date, T., 2005. Concentration of polychlorinated biphenyls (PCBs) in beached resin pellets: variability among individual particles and regional differences. Mar. Pollut. Bull. 50, 1103–1114.

Environment Agency, 2007. Report 8: environmental concentrations of polychlorinated biphenyls (PCBs) in UK soil and herbage. https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/291162/scho0607bmtb-e-e.pdf (accessed on March 1, 2016).

Ghosh, U., Gillette, J.S., Luthy, R.G., Zare, R.N., 2000. Microscale location, characterization, and association of polycyclic aromatic hydrocarbons on harbor sediment particles. Environ. Sci. Technol. 34, 1729–1736.

Hansen, E., Nilsson, N.H., Lithner, D., 2013. Hazardous substances in plastic materials. www.miljodirektoratet.no/old/klif/publikasjoner/3017/ta3017.pdf (accessed on January 25, 2016).

Hidalgo-Ruz, V., Gutow, L., Thompson, R.C., Thiel, M., 2012. Microplastics in the marine environment: a review of the methods used for identification and quantification. Environ. Sci. Technol. 46, 3060–3075.

Hung, C.-C., Gong, G.-C., Chen, H.-Y., Hsieh, H.-L., Santschi, P.H., Wade, T.L., Sericano, J.L., 2007. Relationships between pesticides and organic carbon fractions in sediments of the Danshui River estuary and adjacent coastal areas of Taiwan. Environ. Pollut. 148, 546–554.

Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. Science 347, 768–771.

Jonker, M.T.O., Koelmans, A.A., 2002. Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment mechanistic considerations. Environ. Sci. Technol. 36, 3725–3734.

Kajiwara, N., Noma, Y., Takigami, H., 2011. Brominated and organophosphate flame retardants in selected consumer products on the Japanese market in 2008. J. Hazard. Mater. 192, 1250–1259.

Khalil, M.F., Ghosh, U., Kreitinger, J.P., 2006. Role of weathered coal tar pitch in the partitioning of polycyclic aromatic hydrocarbons in manufactured gas plant site sediments. Environ. Sci. Technol. 40, 5681–5687.

Khim, J.S., Kannan, K., Villeneuve, D.L., Koh, C.H., Giesy, J.P., 1999. Characterization and distribution of trace organic contaminants in sediment from Masan Bay, Korea. 1. Instrumental analysis. Environ. Sci. Technol. 33, 4199–4205.

Khim, J.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.

Koh, C.H., Khim, J.S., Villeneuve, D.L., Kannan, K., Giesy, J.P., 2006. Characterization of trace organic contaminants in marine sediment from Yeongil Bay, Korea: 1. Instrumental analyses. Environ. Pollut. 142, 39–47.

Li, X., Luo, X., Mai, B., Liu, J., Chen, L., Lin, S., 2014a. Occurrence of quaternary ammonium compounds (QACs) and their application as a tracer for sewage derived pollution in urban estuarine sediments. Environ. Pollut. 185, 127–133.

Li, Y., Li, J., Deng, C., 2014b. Occurrence, characteristics and leakage of polybrominated diphenyl ethers in leachate from municipal solid waste landfills in China. Environ. Pollut. 184, 94–100.

Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., Kaminuma, T., 2001. Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. Environ. Sci. Technol. 35, 318–324.

Passuello, A., Mari, M., Nadal, M., Schuhmacher, M., Domingo, J.L., 2010. POP accumulation in the food chain: integrated risk model for sewage sludge application in agricultural soils. Environ. Int. 36, 577–583.

Pierard, C., Budzinski, H., Garrigues, P., 1996. Grain-size distribution of polychlorobiphenyls in coastal sediments. Environ. Sci. Technol. 30, 2776–2783.

Song, Y.K., Hong, S.H., Jang, M., Kang, J.-H., Kwon, O.Y., Han, G.M., Shim, W.J., 2014. Large accumulation of micro-sized synthetic polymer particles in the sea surface microlayer. Environ. Sci. Technol. 48, 9014–9021.

Suzuki, G., Kida, A., Sakai, S.I., Takigami, H., 2009. Existence state of bromine as an indicator of the source of brominated flame retardants in indoor dust. Environ. Sci. Technol. 43, 1437–1442.

Teuten, E.L., Rowland, S.J., Galloway, T.S., Thompson, R.C., 2007. Potential for plastics to transport hydrophobic contaminants. Environ. Sci. Technol. 41, 7759–7764.

The United States Environmental Protection Agency's (US EPA) Office of Water, A. Marine debrishttp://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P1008EDW.txt (accessed on January 24, 2016).

Thompson, A., Allen, J.R., Dodoo, D., Hunter, J., Hawkins, S.J., Wolff, G.A., 1996. Biphenyls in mussels and sediments from Great Britain and the Irish Sea coast. Mar. Pollut. Bull. 32, 232–237.

Turner, A., 2010. Marine pollution from antifouling paint particles. Mar. Pollut. Bull. 60, 159–171.

van Sebille, E., Wilcox, C., Lebreton, L., Maximenko, N., Hardesty, B.D., van Franeker, J.A., Eriksen, M., Siegel, D., Galgani, F., Law, K.L., 2015. A global inventory of small floating plastic debris. Environ. Res. Lett. 10, 124006.

Webster, T.F., Harrad, S., Millette, J.R., Holbrook, R.D., Davis, J.M., Stapleton, H.M., Allen, J.G., McClean, M.D., Ibarra, C., Abdallah, M.A.-E., Covaci, A., 2009. Identifying transfer mechanisms and sources of decabromodiphenyl ether (BDE 209) in indoor environments using environmental forensic microscopy. Environ. Sci. Technol. 43, 3067–3072.

Weiler, R.R., Mills, A.A., 1965. Surface properties and pore structure of marine sediments. Deep Sea Res. Oceanogr. Abstr. 12, 511–529.

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

Yangjiang Municipal People's Government, d. Marine fishery resourceshttp://www.yangjiang.gov.cn/english/Investment/Investment_Environment/Marine_Fishery/201203/t20120315_65843.html (accessed on January 24, 2016).

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

Zubris, K.A.V., Richards, B.K., 2005. Synthetic fibers as an indicator of land application of sludge. Environ. Pollut. 138, 201–211.