Science of the Total Environment 647 (2019) 1222–1229

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Deposition flux and mass inventory of polychlorinated biphenyls in sediments of the Yangtze River Estuary and inner shelf, East China Sea: Implications for contributions of large-river input and e-waste dismantling

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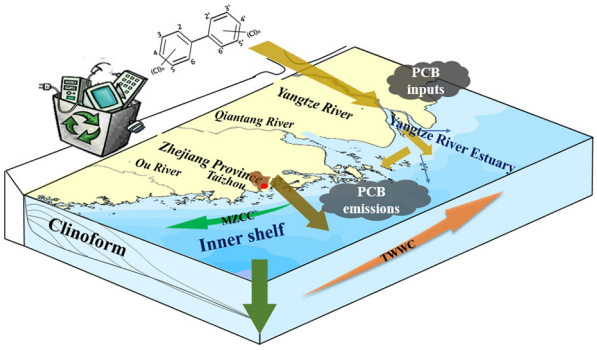
HIGHLIGHTS

- PCBs exhibited a spatial inconsistence with TOC or grain size in the two mud areas.
- Yangtze River input plays a considerable role in controlling the distribution of PCBs.
- The mass inventory of determined PCBs was estimated to be 50 tons in the sediment.
- Emission from e-waste dismantling is a significant source of PCBs in the coastal ECS.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 June 2018
Received in revised form 4 August 2018
Accepted 5 August 2018
Available online 06 August 2018

Editor: Thomas Kevin V

Keywords:
Coastal East China Sea
Deposition flux

ABSTRACT

Surface sediment samples were collected from the Yangtze River Estuary (YRE) to the inner-shelf mud area of the East China Sea (ECS) for a comprehensive study of the sources and fates of polychlorinated biphenyls (PCBs) based on their spatial distribution, deposition flux, and mass inventory. The total concentrations of 32 PCBs (Σ_{32}PCBs) varied from 0.3 to 11.9 ng/g dry weight. Under strong hydrodynamic conditions, the weak correlations between TOC or MD and Σ_{32}PCB concentrations were observed in the YRE. In contrast, there were relatively well relationships of PCBs with TOC content and sediment grain size in the inner shelf of the ECS due to the influence of hydrological sorting from the YRE to the inner shelf of the ECS. This suggests that the Yangtze River input plays a considerable role in controlling the distribution of PCBs in the coastal ECS. Compared with the annual discharge of Σ_{32}PCBs from the Yangtze River to the sea (3.21 t/yr), the deposition flux was estimated to be ~2.63 t/yr. Furthermore, a total mass inventory of 50 tons in the sediments suggests that the YRE and inner shelf mud of the ECS represents an important global sink of PCBs. Estimated 21–39% of sedimentary PCBs were derived from local

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https://doi.org/10.1016/j.scitotenv.2018.08.076

Mass inventory
PCBs

emissions (mainly dismantling of electronic waste) aside from Yangtze River input. Higher proportions of penta-CBs were also observed near the central Zhejiang Coast, providing further evidence that the local emission from e-waste dismantling near the coast is a significant contributor to sedimentary PCBs in the coastal ECS.

1. Introduction

Polychlorinated biphenyls (PCBs) are one of the 12 major persistent organic pollutants (POPs) targeted by the Stockholm Convention (UNEP, 2001). Although large-scale production and application of PCBs have long been prohibited globally, the decrease in PCB residues in the abiotic environment of China was not significant (Gao et al., 2013; Wu et al., 2011; Zhang et al., 2011). This is especially true in the southeastern coastal areas of China, such as Guangdong and Zhejiang provinces, where are characterized by intensive industrial activities and have received a large amount of imported electronic waste (e-waste) (Cui et al., 2013). Unintentional byproducts of industrial processes and primitive dismantling of outdated PCB-containing equipment have been reported as significant sources of PCBs to the environment in China (Wang et al., 2011).

PCBs enter the marine environment mainly through riverine runoff and atmospheric deposition (Hiller et al., 2011). Due to their hydrophobic property, PCBs tend to readily associate with particulate fractions (e.g., colloids, dissolved organic/suspended particulate matters) in water, and are ultimately deposited on surface sediments through vertical settling. Resistance of PCBs to chemical and biological transformations can lead to their accumulations in sediments where anaerobic condition prevails. Therefore, estuarine and shelf sediments act as vital ultimate sinks for PCBs in the ecosystem (Savinov et al., 2003).

The Yangtze River flows through the most urbanized and industrialized region of eastern China, supporting the livelihood of 400 million inhabitants and contributing approximately 42% of China's gross domestic product (Yang et al., 2006). Our previous studies have revealed that the direct riverine input from the Yangtze River was the dominant source of several POPs to the offshore East China Sea (ECS), with 232, 5.8, and 3.75 tons of polycyclic aromatic hydrocarbon (PAH), dichlorodiphenyltrichloroethane (DDT), and hexachlorocyclohexane (HCH), respectively, released annually (Hu et al., 2011; Lin et al., 2013; Lin et al., 2016). Most of these pollutants are trapped in the mud areas both the Yangtze River Estuary (YRE) and the inner shelf of the ECS. The spatial distributions of these organic compounds are related to key physicochemical factors in sediments, especially total organic carbon (TOC) and grain size (Hu et al., 2011; Lin et al., 2013). Additionally, nearby local release of pollutants may drive their spatial heterogeneities as well. Li et al. (2016) found that local emissions from e-waste dismantling/recycling centers were an important source of polybrominated diphenyl ethers (PBDEs), differing from the riverine input of pesticide HCHs and DDTs in this area. PCBs are known to be released during e-waste dismantling operations (Wang et al., 2011). Although several researchers have investigated the occurrence and distribution of PCBs in the sediments of the coastal ECS (Duan et al., 2013; Gao et al., 2013; Wang et al., 2016; Liu et al., 2017), to our knowledge the contribution of land-based emissions to PCB contamination in this area has not been definitely quantified.

The objectives of this study were 1) to clarify the roles of Yangtze River input and depositional feature on the fate of PCBs in the YRE and the inner shelf of the ECS, and 2) to estimate the PCB deposition flux and mass inventory in this region, and then quantitatively assess the significance of Yangtze River input and other potential sources. The data reported here can provide a better understanding of the role of Yangtze River input in contributing to PCB pollution within this heterogeneous environmental system.

2. Materials and methods

2.1. Study area and sampling

Fig. 1 presents the sampling sites, which covered an area of approximately 85,000 km^2 within the YRE to the inner shelf of the ECS (120.83°E to 123.84°E and 26.40°N to 32.26°N). The coastal ECS, which is an important sink at a regional scale, receives Yangtze River-derived sediments and associated pollutants released into the sea (Liu et al., 2006). Meanwhile, the central coast of Zhejiang province (e.g., Taizhou) is characterized as a booming center for e-waste recycling in China. A total of 88 surface sediment samples from the YRE and the inner shelf of the ECS were strategically collected during two campaigns, including A1–A13 in March 2014 onboard the R/V "Runjiang 1" and DH3–DH7 in September 2016 onboard the R/V "Kexue 3." Surface sediment samples were obtained using a stainless steel box corer. All top layer surface (0–3 cm) sediments were packed in aluminum foil and stored at −20 °C until organic matter analysis.

2.2. Measurement of sediment properties

Freeze-dried sediments were treated with 4 M hydrochloric acid (HCl) to remove inorganic carbon, and then oven-dried overnight at 60 °C. TOC of the carbonate-free samples was then analyzed with a Vario EL-III Elemental Analyzer. Grain size composition of the surface sediments was determined directly using a laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., UK). The grain size was divided into four components based on median diameters $\Phi = -\log 2\varphi$ (where φ is the diameter, mm): $\Phi > 8$ was categorized as clay, $4 < \Phi < 8$ as silt, $2 < \Phi < 4$ as gravel, and $\Phi < 2$ as sand (Hong et al., 2012). Detailed information on the sediment properties datasets of TOC and sediment grain size (MD) of the samples is provided in the Supporting Information (Table S1).

2.3. Sample extraction and instrumental analysis

In the laboratory, sediment samples were freeze dried for 36 h, pulverized, and passed through 80-mesh stainless steel sieves. About 10 g of sample was spiked with recovery standards, consisting of a mixture of 2,4,5,6 tetrachloro m xylene (TCmX), PCB30, PCB198, and PCB209, and each sample was then extracted with dichloromethane (DCM) in a Soxhlet apparatus for 48 h. Activated copper granules were added to remove elemental sulfur. The extracts were concentrated using a rotary evaporator, solvent-exchanged to n hexane, and reduced under a stream of highly purified N_2. Concentrated extracts were purified and fractionated on a packed alumina/silica column (8 mm internal diameter) containing neutral alumina (3 cm, 3% deactivated), neutral silica gel (3 cm, 3% deactivated), 50% (by weight) sulfuric acid silica (2 cm), and anhydrous sodium sulfate (1 cm) from the bottom to the top. The PCB fraction was subsequently eluted with 50 mL of DCM/n hexane (1:1 v/v), solvent-exchanged to n hexane, and then further concentrated to 0.2 mL under a gentle steam of nitrogen gas. A known quantity of pentachloronitrobenzene (PCNB) was added as an internal standard for quantification of PCBs prior to instrumental analysis.

PCBs were measured with an HP-5890 Series II gas chromatograph (GC) coupled to a Ni electron capture detector, and chromatographic separation was achieved through an HP-5 capillary column (50 m ×

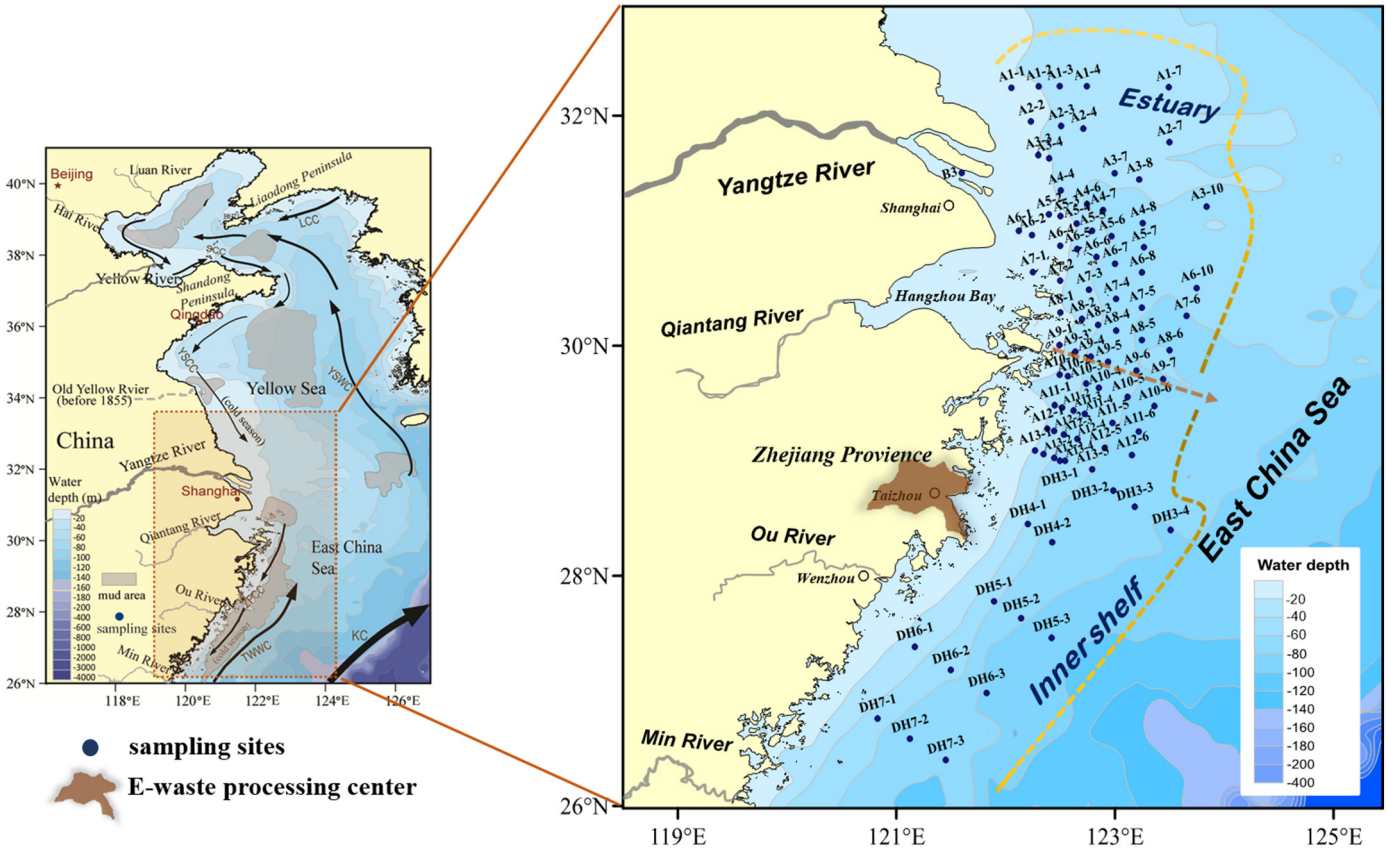

Fig. 1. Locations of sampling sites in the Yangtze estuarine-inner shelf of the ECS. KC: Kuroshio Current; TWWC: Taiwan Warm Current; ZFCC: Zhejiang-Fujian Coastal Current; YSCC: Yellow Sea Coastal Current; YSWC: Yellow Sea Warm Current; circulations and mud areas are modified from Hu et al. (2011).

0.25 mm × 0.25 μm; DB-5MS, Agilent, USA). The GC temperature program was as follows: oven temperature began at 110 °C, was increased to 170 °C at a rate of 1.8 °C min^{-1} (3 min hold time), then to 226 °C at 2.5 °C min^{-1}, and then was ramped to 280 at 40 °C min^{-1} and maintained for 10 min. Identification of compounds was based on retention time with corresponding standards. A total of 25 chromatographic PCB peaks, corresponding to 32 individual and co-eluting congeners (i.e., IUPAC PCBs 18/17, 31/28, 33, 52, 49, 44, 74, 70/95, 101, 99, 87, 110, 82/151, 118, 132/153, 138/158, 187, 183, 128, 156, 180, 208/195, 194, 205, and 206), were monitored and quantified in the sediments.

2.4. Estimation of PCB flux and mass inventory

The surface deposition flux and mass inventory of PCBs were estimated within the study area, which was divided into 88 compartments of different sizes. Each compartment contained one sampling site which was made to be near the center of one sector (Fig. 1). The PCB concentration within each compartment was assumed to be homogeneous. The surface deposition flux (F, t/yr) was estimated based on Eq. (1) (Lin et al., 2016):

$$F = \sum_{i=1}^{88} Ci \cdot Ai \cdot \rho \cdot pi \quad (1)$$

where Ci is the PCB concentration in the sediment at site i (ng/g); Ai is the area of the compartment represented by site i (km^2) (Table S2); ρ is the recommended sediment dry density of 1.2 g/cm^3 for this area, as referenced from Liu et al. (2007); and pi is the sedimentation rate at each sampling site, according to Liu et al. (2006).

The total mass inventory (I, in tons) was estimated as the product of the surface mass inventory (I_{3cm}, in tons) and a conversion factor k:

$$I = I_{3cm} \cdot k = \sum_{i=1}^{88} Ci \cdot Ai \cdot \rho \cdot d \cdot k \quad (2)$$

where d is the thickness of the sediment sample (3 cm); k is the ratio of the total mass inventory to the surface (0–3 cm) mass inventory in the individual sediment core (mean value, 6.67) according to our unpublished data in this study area.

2.5. Quality control and quality assurance

A procedural blank (solvent with filter paper identical to that used to wrap the sediment) and a spiked blank (32 PCB congeners spiked into solvent with filter paper) for Soxhlet extraction were processed using the same procedure applied to each batch of 10 field samples. No target compounds were detected in procedural blanks, and the mean reproducibility of the spiked blanks was acceptable (recoveries of 90.5 ± 6.2%), indicating that minimal depletion of target compounds occurred during the experiment. Average surrogate recoveries in the 88 samples were 72.4 ± 13.8% for TCmX, 72.9 ± 6.3% for PCB30, 82.6 ± 9.3% for PCB198, and 80.8 ± 12.8% for PCB209. The reported PCB concentrations were not adjusted based on surrogate recoveries.

3. Results and discussion

3.1. Occurrence and distribution of PCBs

The total concentrations of 32 PCBs in each sampling site are listed in the Supporting Information (Table S1). The total concentrations of 32

PCBs ($\sum_{32}$PCB) in the study area ranged from 0.3 to 11.9 ng/g dry weight (dw), with a mean value of 2.9 ng/g dw. The PCB levels measured in this study were lower than those of sediments in other heavily polluted estuaries in China, such as the Haihe (n.d.–253 ng/g), Minjiang (15.14–57.93 ng/g), Liaohe (1.85–1075.60 ng/g), and Nanpaiwu river estuaries (n.d.–64 ng/g) (Hu et al., 2005; Zhang et al., 2010; Zhang et al., 2003; Zhao et al., 2010), as well as the Pearl River Estuary and coastal sediments around Hong Kong (43–461 ng/g) (Zhou et al., 1999). Additionally, the PCB concentrations in the study area were much lower than those reported in some urbanized and harbor areas around the world, such as Naples harbor, Italy (10–899 ng/g) (Sprovieri et al., 2007), Narragansett Bay, USA (20.8–1760 ng/g) (Hartmann et al., 2004), Shuaiba industrial area, Kuwait (0.4–84 ng/g) (Gevao et al., 2006), and Alexandria harbor, Egypt (0.9–1210 ng/g) (Breivik et al., 2002). Table S3 compares the PCB concentrations in this study with other areas worldwide. Overall, the PCB concentrations in the YRE and inner shelf of the ECS fell into the low to moderate levels of the global ranges (0.2–400 ng/g) in estuaries and adjacent surface sediments (Mai et al., 2005).

It has been reported that the YRE and inner shelf of the ECS serve as a significant sink for fine-grained sediments and associated hydrophobic organic pollutants from Yangtze River discharge (Guo et al., 2007). Relatively high levels of PCBs were observed at sites in the outer YRE (e.g., sites A4-6, A4-7) and in the mud area adjacent to Hangzhou Bay (e.g., sites A7-3 and A9-3) (Fig. 2a). Central mud areas are burdened with high PCB accumulation, similar to the findings for DDTs (Hu et al., 2011) and PAHs in the ECS (Lin et al., 2013). This could be attributed to the enhanced flocculation effect in the river-sea mixing zone and gravitational sedimentation of PCB-containing particles derived from the Yangtze River (Chen et al., 2006).

The higher concentration of Σ_{32}PCBs was also detected at sites near the central Zhejiang province coast (Fig. 2a). Compared with the YRE (transects A1–A9; Fig. 2a), transects from the inshore toward the offshore (A10–DH7) area of the inner shelf of the ECS were characterized by a decreasing PCB concentration gradient. A statistically significant reverse correlation was observed between log (Σ_{32}PCB concentration) in the inner shelf of the ECS and distance from the coastline ($R^2 = 0.37$, $p < 0.01$) (Fig. 3a, b). This spatial inconsistency suggests source dependence of the PCB distribution on the inner shelf of the ECS, primarily due to significant land-based inputs (Chen et al., 2002; Fan et al., 2014).

Fig. 2e and f present the spatial distributions of the sediment properties of grain size (Φ) and total organic carbon (TOC), respectively. Although, the sediments both in the YRE (transects of A1–A9) and in the inner shelf of the ECS (transects of A10–DH7) showed a dominance of silt and clay (Fig. 2e), the correlation of PCBs with TOC and sediment grain size spatially varied in the YRE and the inner shelf of the ECS. In the YRE (transects A1–A9), consistent with results for other POPs (including PBDEs, DDTs, and PAHs) (Gevao et al., 2006; Hu et al., 2011; Li et al., 2012), the weak correlations were observed between TOC or MD and log (Σ_{32}PCBs concentrations) (Fig. 3c and e), indicating that the distribution of PCBs was not constrained primarily by physicochemical factors of the sediments. This finding is likely linked to the marginal

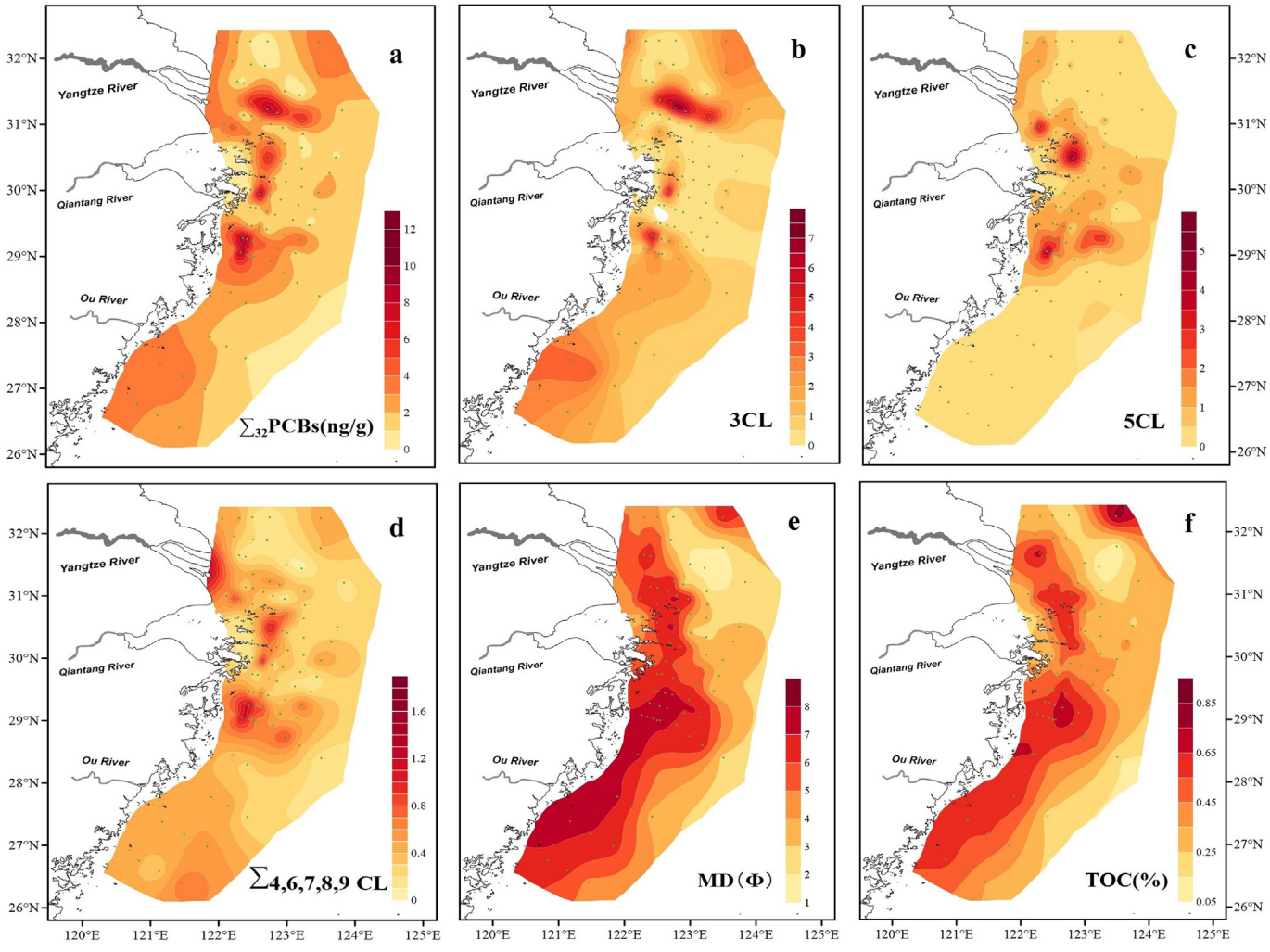

Fig. 2. Distribution patterns of Σ_{32}PCBs (pg/g dwt.), tri-CBs (pg/g dwt.), penta-CBs (pg/g dwt.), grain size median diameter (Φ), and TOC (%).

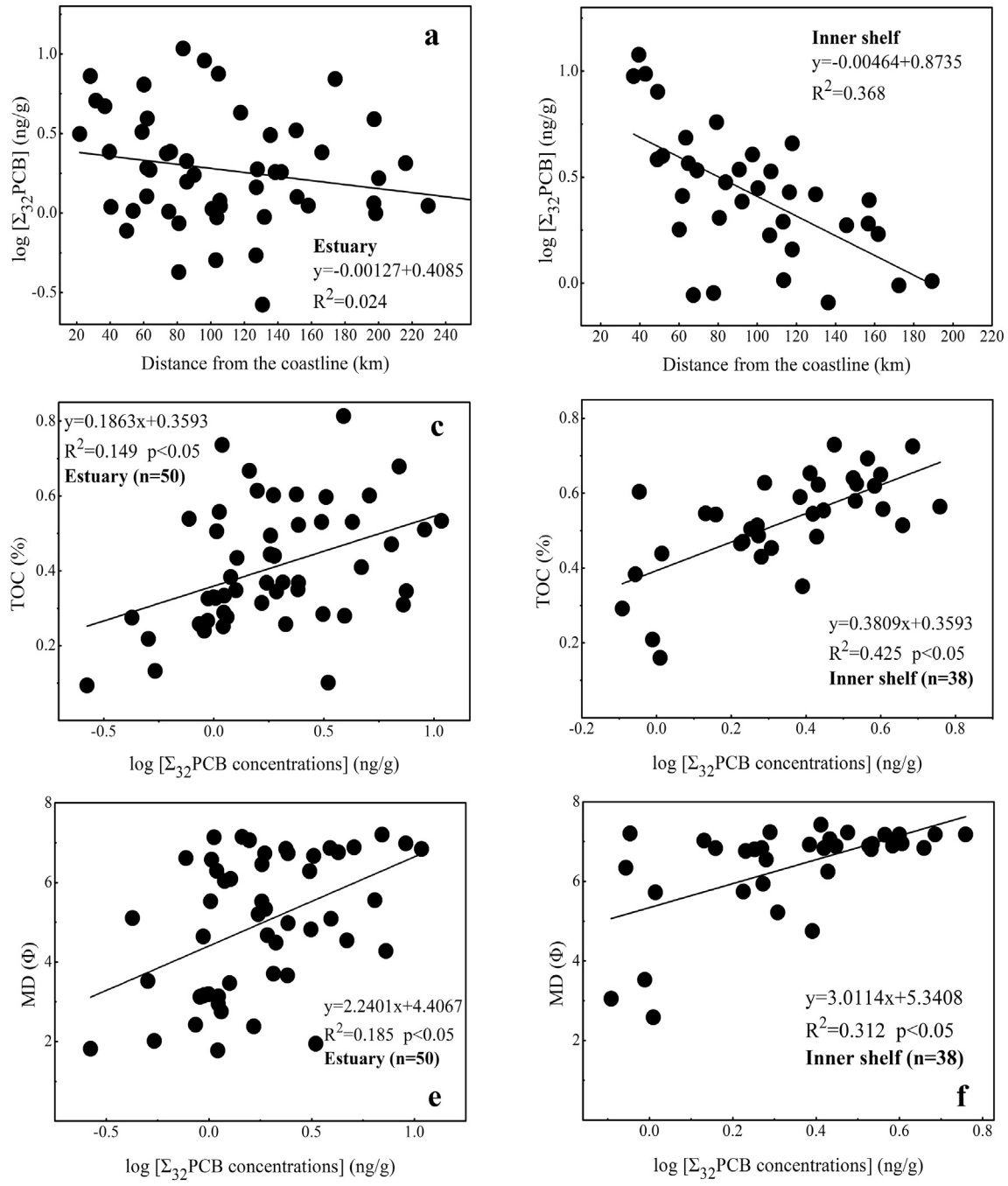

Fig. 3. Correlations of PCB concentrations with distance from the coastline, TOC contents of sediments, and median diameters of sediment particles of the YRE (a, c, e) and the inner shelf of the ECS (b, d, f).

filter process, which leads to a greater deposition of POP-associated particles at nearby sampling sites. With the dominance of Yangtze River input, relatively high deposition rates in the nearshore and outer YRE areas (up to 5 cm/a) led to a subtle sediment sorting effect on PCB occurrence (Huh and Su, 1999). Additionally, the complex hydrodynamic conditions in the YRE disrupt the regular adsorption behavior of PCBs on sediments.

In contrast, the relationships of PCBs with TOC content and sediment grain size were improved on the inner shelf of the ECS (transects A10–DH7), as shown in Fig. 3d and f, respectively. The large fraction of fluvial sediment (approximately 40%) from the Yangtze River system is readily deposited temporarily in the estuarine area north of 30°N. Then, induced by southwestward ocean currents triggered by the East Asian Monsoon, the remaining sedimentary material (approximately 32%) is believed to be redistributed and ultimately trapped on the inner shelf south of 30°N (Liu et al., 2007). Therefore, under the unique hydrodynamic conditions of the region, the natural resuspension-deposition process plays a considerable role in controlling the distribution of PCBs on the inner shelf of the ECS (Duan et al., 2013).

3.2. Deposition flux of PCBs

The total deposition flux of Σ_{32}PCBs in the Yangtze estuary and inner shelf, over an area of 85,000 km^2, was estimated to be 2.63 t/yr. The deposition fluxes of PCB 28 and PCB 52 were 0.3 t/yr and 0.05 t/yr in the same study area, respectively. As major congeners of the tri-CB and tetra-CB homologs, PCB 28 and PCB 52 are frequently detected in surface sediments globally. Jönsson et al. (2003) estimated that the burial

fluxes of PCB 28 and PCB 52 were 9.6 and 14 t/yr, respectively, in global continental shelf sediments (~2.72×10^7 km^2). Although the area of this study accounts for only ~0.3% of the global continental shelf, the total sedimentary burial flux was approximately ~1.5% of the global flux. The YRE and inner shelf of the ECS could serve as an important global sink for PCBs.

According to Zhang et al. (2011), PCB concentrations in the water of the Yangtze River averaged ~3.36 ng/L. Thus, the annual average flux of PCBs is estimated to be ~3.21 t/yr from the Yangtze River to the sea based on an annual runoff flux of 900 km^3. In comparison, the ratio of the current PCB deposition flux in sediments to the total annual input from the Yangtze River is 0.82. Fig. 4 presents the contrasting results for deposition flux and Yangtze River inputs of PAHs, DDTs, HCHs and PCBs in the coastal ECS. It is notable that the ratio of the current PCB deposition flux in sediments to the annual input from the Yangtze River (0.82) was higher than those of PAHs (~0.65), DDTs (~0.51), and HCHs (~0.16) observed within the YRE and inner shelf of the ECS. The lowest ratio observed for HCHs is clearly due to their relatively high water solubility and low $logK_{ow}$ (3.7–3.94), which lead to weak affinity to sediments and limited deposition flux compared with other hydrophobic organic containments (Xiao et al., 2004). One study found that >70% of HCHs transported by the Yangtze River were volatilized into the air rather than deposited in the surface sediments of the coastal ECS (Li et al., 2017). Aside from HCHs, the physicochemical properties of PCBs are similar to those of PAHs and DDTs, with $logK_{ow}$ values ranging from 5.5 to 8.9 (Shen and Wania, 2005; Tobiszewski and Namiesnik, 2012). It is unlikely that PCBs have greater enrichment than PAHs and DDTs in sediments. Given that these pollutants are subjected to the same sedimentary processes during transport from the source to sink region, PCBs have specific important sources that do not exist for other land-based POPs in addition to Yangtze River inflows. Thus, other sources associated with the concurrent operation of e-waste recycling and unintentional emissions could make significant contributions to PCB loads in the sediments of the coastal ECS. Based on the reference ratios of 0.65 and 0.51, the observed ratio of 0.82 means that 21–39% (0.82–0.65/0.82–0.82–0.51/0.82) of PCBs were derived from sources other than Yangtze River inputs.

3.3. Mass inventory of PCBs

According to Eq. (2), the total mass inventory of Σ_{32}PCBs in the sediments of the YRE and inner shelf of the ECS was estimated to be 50 tons,

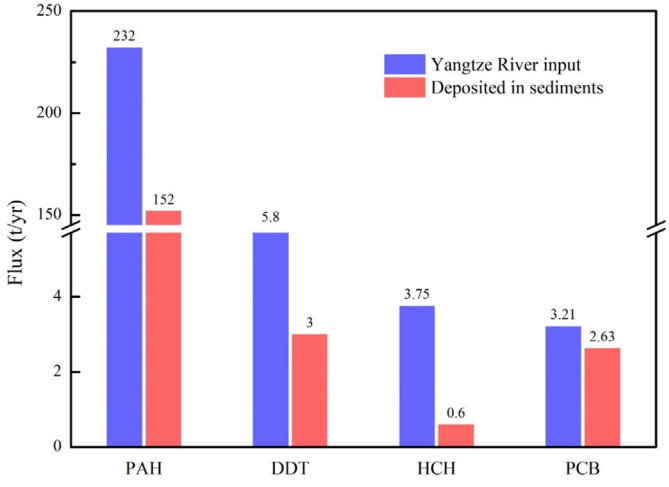

Fig. 4. Comparisons between Yangtze River input and typical POPs deposition flux in the sediments of Yangtze estuarine-inner shelf of the ECS. The datasets of Yangtze River input and deposition flux of PAHs are from Wang et al. (2007) and Lin et al. (2013), respectively; Yangtze River input and deposition flux of DDTs and HCHs are estimated according to the data from Lin et al. (2016); Yangtze River input of PCB is estimated according to the data from Zhang et al. (2010).

which is substantially lower than those estimated in the sediments of the five Great Lakes for Σ_{39}PCBs (500 tons, for Lakes Michigan, Superior, Huron, Ontario, and Erie) in the USA (Li et al., 2018). This comparison of PCB accumulation reflects the remarkable difference in the historical production and usage of PCBs between the USA (responsible for 46% of total global consumption) and China (responsible for only 1%) in the mid to late 20th century.

In a previous study, the total mass inventory of DDTs (official ban since 1983) was estimated at 160 tons in the sediments of the study area (Lin et al., 2016). Despite the much lower historical production of PCBs (10,000 tons) than that of DDTs (400,000 tons) in China (Wei et al., 2007), the total mass inventory of PCBs was equivalent to one-third of the mass inventory of DDTs observed in the YRE and inner shelf of the ECS. From a source-to-sink perspective, these relatively large amounts of sedimentary PCBs can be attributed to the abandonment of PCB-containing electrical equipment in surface or underground mines mainly located in Southeast China, which can result in greater PCB contamination of ground and surface waters and continuous input into the sea. Additionally, the large amount of PCBs released from e-waste recycling into the coastal area may be a potential source of PCBs in the sediment. Due to the proximity of e-waste dismantling plants and the drainage basins of local coastal rivers (such as the Qiantang and Ou) to the coastal ECS, PCBs can be more directly constrained in sediments near source regions along the inner shelf of the ECS.

3.4. Implication for contribution of e-waste dismantling emissions to the inner shelf of the ECS

In this study, the highest level of PCBs in the inner shelf was detected in the central part of the coastal mud area (A13-2, near Taizhou in Zhejiang province) where high levels of DDTs and HCHs were not observed in these sediments (Hu et al., 2011), but where elevated PBDE levels were found due to local discharge and emissions from e-waste dismantling (Li et al., 2012). This inconsistency on the inner shelf of the ECS suggests that the occurrence of PCBs could be strongly influenced by land-derived PCB inputs associated with local e-waste dismantling rather than re-suspension and transport of PCBs originating from the YRE. China has become the largest recipient of e-waste in the world. In 2006, >80% of global e-waste was imported to Asia, about 90% of which was destined for China (Xinhua News Agency of China, 2006). Materials leaked from recycling/dismantling processes of dismantled electric power transformers and capacitors, as well as the open burning of printed circuit boards and electric wires, have resulted in higher concentrations of PCBs in the country (Shen et al., 2007). Reported atmospheric PCB levels near Taizhou (a typical e-waste dismantling region) were 54 times those of the reference urban site (Han et al., 2010). Although commercial production of PCBs has been prohibited, the booming e-waste recycling and other potential unintentional releases from anthropogenic activities are still important drivers of environmental PCB levels.

Table S4 lists the PCB concentrations of various homologs. The average homolog proportions of PCBs measured in all surface sediment samples of this study were, in decreasing order: tri-CBs (48.8%) > penta-CBs (33.4%) > hexa-CBs (7.1%) > tetra-CBs (4.9%) > hepta-CBs (2.9%) > octa-CBs (0.7%) > nona-CBs (0.3%). Sum of tri-CBs and penta-CBs accounted for up to 82.2% of total PCB concentrations. Approximately 10,000 tons of PCBs were manufactured in China during the period of 1965–1974, with 9000 tons known as #1 PCB (dominated by tri-CBs) and 1000 tons known as #2 PCB (dominated by penta-CBs) (Xing et al., 2005). The #1 and #2 PCBs were primarily used in power capacitors and as a paint additive, respectively (China SEPA, 2003). The distribution patterns of tri-CBs (Fig. 2b) are similar to those of Σ_{32}PCBs (Fig. 2a), with high occurrences in the YRE and the Ou River estuary, suggesting that tri-CBs in this region are largely derived from historical usage of Chinese commercial PCB mixtures as well as the release of PCB-

contained products produced abroad through the pathways of riverine runoff. However, the percentage of penta-CBs (~33.4%) in this study was considerably greater than those in transformer oil (total, 5%) and PCB products (total, 10%) produced in China during the 1960s (Jiang, 2007). The PCB congeners' profile (dominance of tri- and penta-CBs) showed the similar constitution with several previous studies, which reported the dominance presence of tri- and penta-CBs in the atmosphere (total, 65%) (Han et al., 2010), soil (total, 50%) (Tang et al., 2010), water (total, 32.4%), and plant samples (total, 36.4%) (Zhang et al., 2016) collected near the e-waste disposal center in Taizhou (Zhejiang province). In fact, there have several studies demonstrated that the emissions from local e-wastes dismantling could be the significant contributor of PCBs in the coastal ECS (Fan et al., 2014; Wang et al., 2016). Furthermore, with greater volatility and water solubility, tri-CBs are more easily transported by air and water, traveling further from the estuary and inshore area. In this study, however, more penta-CBs accumulated near the central Zhejiang province coast and the inner portion of Hangzhou Bay (Fig. 2c), which are not the major mud depositional areas for Yangtze runoff. This provides further evidence that the emissions from booming e-waste recycling and incineration activities near the coast may have a significant contribution to the sedimentary PCBs in the study area.

4. Conclusion

High levels of PCBs were observed in sediments in an inshore area off Zhejiang province, with a distribution pattern that shows a generally decreasing tendency in the offshore direction in the coastal ECS. Differential chlorine-dependent distribution suggests that the PCB contamination in the YRE and inner shelf of the ECS was tightly controlled by both Yangtze River input and local sources (e.g. e-waste dismantling) along the coast. This distribution pattern was in contrast to other legacy persistent organic pollutants (i.e., PAHs, HCHs, and DDTs), and the latter ones largely depend on Yangtze River inputs in the coastal ECS.

We estimated that about 21–39% of PCBs deposited in the study area originate from e-waste dismantling/recycling and other unintentional PCB sources, rather than from Yangtze River input. The total deposition flux and mass inventory of PCBs in the coastal ECS area of 85,000 km^2 were estimated to be 2.63 t/yr and 50 t, respectively. In addition, higher proportion of penta-CBs (compared with tri-CBs) was observed near the central Zhejiang Coast, suggesting a significant contribution of PCB emissions from e-waste dismantling to the coastal ECS.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NSFC) (Nos.: 41376051, 41722603, 41676034, 41676063 and 41521064), and in part supported by the Basic Scientific Fund for National Public Research Institutes of China (2017S01). We thank the crews of the R/V Runjiang 1 and Kexue 3 for sampling assistance. We also thank Lu Qiu and Jun Ye for their technical assistance in this study. Anonymous reviewers should be sincerely appreciated for their constructive comments that greatly improved this work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.08.076.

References

Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2002. Towards a global historical emission inventory for selected PCB congeners—a mass balance approach. Sci. Total Environ. 290, 199–224.

Chen, J., Xia, X., Ye, X., Jin, H., 2002. Marine organic pollution history in the Changjiang Estuary and Zhejiang coastal area—HCHs and DDTs stratigraphical records. Mar. Pollut. Bull. 45, 391–396.

Chen, S.-J., Luo, X.-J., Mai, B.-X., Sheng, G.-Y., Fu, J.-M., Zeng, E.Y., 2006. Distribution and mass inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in sediments of the Pearl River Estuary and the northern South China Sea. Environ. Sci. Technol. 40, 709–714.

China SEPA, 2003. Building the Capacity of the People's Republic of China to implement the Stockholm Convention on POPs and Develop a National Implementation Plan, GEF Project Brief (GF/CPR/02/010).

Cui, S., Qi, H., Liu, L.-Y., Song, W.-W., Ma, W.-L., Jia, H.-L., Ding, Y.-S., Li, Y.-F., 2013. Emission of unintentionally produced polychlorinated biphenyls (UP-PCBs) in China: has this become the major source of PCBs in Chinese air? Atmos. Environ. 67, 73–79.

Duan, X., Li, Y., Li, X., Li, M., Zhang, D., 2013. Distributions and sources of polychlorinated biphenyls in the coastal East China Sea sediments. Sci. Total Environ. 463–464, 894–903.

Fan, Y., Lan, J., Li, H., Cao, Y., Zhao, Z., Wang, J., Zhao, M., Jiang, G., 2014. Use of lipid biomarkers for identification of regional sources and dechlorination characteristics of polychlorinated biphenyls in the East China Sea. Sci. Total Environ. 490, 766–775.

Gao, S., Chen, J., Shen, Z., Liu, H., Chen, Y., 2013. Seasonal and spatial distributions and possible sources of polychlorinated biphenyls in surface sediments of Yangtze Estuary, China. Chemosphere 91, 809–816.

Gevao, B., Beg, M.U., Al-Omair, A., Helaleh, M., Zafar, J., 2006. Spatial distribution of polychlorinated biphenyls in coastal marine sediments receiving industrial effluents in Kuwait. Arch. Environ. Contam. Toxicol. 50, 166–174.

Guo, Z., Lin, T., Zhang, G., Zheng, M., Zhang, Z., Hao, Y., Fang, M., 2007. The sedimentary fluxes of polycyclic aromatic hydrocarbons in the Yangtze River Estuary coastal sea for the past century. Sci. Total Environ. 386, 33–41.

Han, W., Feng, J., Gu, Z., Wu, M., Sheng, G., Fu, J., 2010. Polychlorinated biphenyls in the atmosphere of Taizhou, a major e-waste dismantling area in China. J. Environ. Sci. 22, 589–597.

Hartmann, P.C., Quinn, J.G., Cairns, R.W., King, J.W., 2004. Polychlorinated biphenyls in Narragansett Bay surface sediments. Chemosphere 57, 9–20.

Hiller, E., Zemanova, L., Sirotiak, M., Jurkovic, L., 2011. Concentrations, distributions, and sources of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in bed sediments of the water reservoirs in Slovakia. Environ. Monit. Assess. 173, 883–897.

Hong, Q., Wang, Y., Luo, X., Chen, S., Chen, J., Cai, M., Cai, M., Mai, B., 2012. Occurrence of polychlorinated biphenyls (PCBs) together with sediment properties in the surface sediments of the Bering Sea, Chukchi Sea and Canada Basin. Chemosphere 88, 1340–1345.

Hu, J., Wan, Y., Shao, B., Jin, X., An, W., Jin, F., Yang, M., Wang, X., Sugisaki, M., 2005. Occurrence of trace organic contaminants in Bohai Bay and its adjacent Nanpaiwu River, North China. Mar. Chem. 95, 1–13.

Hu, L.M., Lin, T., Shi, X.F., Yang, Z.S., Wang, H.J., Zhang, G., Guo, Z.G., 2011. The role of shelf mud depositional process and large river inputs on the fate of organochlorine pesticides in sediments of the Yellow and East China seas. Geophys. Res. Lett. 38 (n/a-n/a).

Huh, C.-A., Su, C.-C., 1999. Sedimentation dynamics in the East China Sea elucidated from ^{210}Pb, ^{137}Cs and $^{239,240}Pu$. Mar. Geol. 160, 183–196.

Jiang, Q., 2007. Characteristics of PCB congeners and homologues in Chinese transformer oil. China Environ. Sci. Ed. 27, 608.

Jönsson, A., Gustafsson, Ö., Axelman, J., Sundberg, H., 2003. Global accounting of PCBs in the continental shelf sediments. Environ. Sci. Technol. 37, 245–255.

Li, Y., Lin, T., Chen, Y., Hu, L., Guo, Z., Zhang, G., 2012. Polybrominated diphenyl ethers (PBDEs) in sediments of the coastal East China Sea: occurrence, distribution and mass inventory. Environ. Pollut. 171, 155–161.

Li, Y., Lin, T., Hu, L., Feng, J., Guo, Z., 2016. Time trends of polybrominated diphenyl ethers in East China Seas: response to the booming of PBDE pollution industry in China. Environ. Int. 92, 507–514.

Li, Z., Lin, T., Li, Y., Jiang, Y., Guo, Z., 2017. Atmospheric deposition and air-sea gas exchange fluxes of DDT and HCH in the Yangtze River Estuary, East China Sea. J. Geophys. Res. Atmos. 122, 7664–7677.

Li, A., Guo, J., Li, Z., Lin, T., Zhou, S., He, H., Ranansinghe, P., Sturchio, N.C., Rockne, K.J., Giesy, J.P., 2018. Legacy polychlorinated organic pollutants in the sediment of the Great Lakes. J. Great Lakes Res. 44, 682–692.

Lin, T., Hu, L., Guo, Z., Zhang, G., Yang, Z., 2013. Deposition fluxes and fate of polycyclic aromatic hydrocarbons in the Yangtze River estuarine-inner shelf in the East China Sea. Glob. Biogeochem. Cycles 27, 77–87.

Lin, T., Nizzetto, L., Guo, Z., Li, Y., Li, J., Zhang, G., 2016. DDTs and HCHs in sediment cores from the coastal East China Sea. Sci. Total Environ. 539, 388–394.

Liu, J.P., Li, A.C., Xu, K.H., Velozzi, D.M., Yang, Z.S., Milliman, J.D., DeMaster, D.J., 2006. Sedimentary features of the Yangtze River-derived along-shelf clinoform deposit in the East China Sea. Cont. Shelf Res. 26, 2141–2156.

Liu, J.P., Xu, K.H., Li, A.C., Milliman, J.D., Velozzi, D.M., Xiao, S.B., Yang, Z.S., 2007. Flux and fate of Yangtze River sediment delivered to the East China Sea. Geomorphology 85, 208–224.

Liu, A., Wang, Y., Xian, M., Zhao, Z., Zhao, B., Wang, J., Yao, P., 2017. Characterization of polychlorinated biphenyl congeners in surface sediments of the Changjiang Estuary and adjacent shelf by high-resolution sampling and high-resolution mass spectrometry. Mar. Pollut. Bull. 124, 496–501.

Mai, B., Zeng, E.Y., Luo, X., Yang, Q., Zhang, G., Li, X., Sheng, G., Fu, J., 2005. Abundances, depositional fluxes, and homologue patterns of polychlorinated biphenyls in dated sediment cores from the Pearl River Delta, China. Environ. Sci. Technol. 39, 49–56.

Savinov, V.M., Savinova, T.N., Matishov, G.G., Dahle, S., Næs, K., 2003. Polycyclic aromatic hydrocarbons (PAHs) and organochlorines (OCs) in bottom sediments of the Guba Pechenga, Barents Sea, Russia. Sci. Total Environ. 306, 39–56.

Shen, L., Wania, F., 2005. Compilation, evaluation, and selection of physical–chemical property data for organochlorine pesticides. J. Chem. Eng. Data 50, 742–768.

Shen, C., Huang, S., Wang, Z., Qiao, M., Tang, X., Yu, C., Shi, D., Zhu, Y., Shi, J., Chen, X., 2007. Identification of Ah receptor agonists in soil of e-waste recycling sites from Taizhou area in China. Environ. Sci. Technol. 42, 49–55.

Sprovieri, M., Feo, M.L., Prevedello, L., Manta, D.S., Sammartino, S., Tamburrino, S., Marsella, E., 2007. Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy). Chemosphere 67, 998–1009.

Tang, X., Shen, C., Shi, D., Cheema, S.A., Khan, M.I., Zhang, C., Chen, Y., 2010. Heavy metal and persistent organic compound contamination in soil from Wenling: an emerging e-waste recycling city in Taizhou area, China. J. Hazard. Mater. 173, 653–660.

Tobiszewski, M., Namiesnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environ. Pollut. 162, 110–119.

UNEP, C, 2001. Stockholm Convention on Persistent Organic Pollutants (POPs). UNEP Chem, Geneva.

Wang, J.Z., Guan, Y.F., Ni, H.G., Luo, X.L., Zeng, E.Y., 2007. Polycyclic aromatic hydrocarbons in riverine runoff of the Pearl River Delta (China): concentrations, fluxes, and fate. Environ. Sci. Technol. 41, 5614–5619.

Wang, H.S., Du, J., Leung, H.M., Leung, A.O., Liang, P., Giesy, J.P., Wong, C.K., Wong, M.H., 2011. Distribution and source apportionments of polychlorinated biphenyls (PCBs) in mariculture sediments from the Pearl River Delta, South China. Mar. Pollut. Bull. 63, 516–522.

Wang, X., Xu, H., Zhou, Y., Wu, C., Kanchanopas-Barnette, P., 2016. Spatial distribution and sources of polychlorinated biphenyls in surface sediments from the Zhoushan Archipelago and Xiangshan Harbor, East China Sea. Mar. Pollut. Bull. 105, 385–392.

Wei, D., Kameya, T., Urano, K., 2007. Environmental management of pesticidal POPs in China: past, present and future. Environ. Int. 33, 894–902.

Wu, J., Teng, M., Gao, L., Zheng, M., 2011. Background air levels of polychlorinated biphenyls in China. Sci. Total Environ. 409, 1818–1823.

Xiao, H., Li, N., Wania, F., 2004. Compilation, evaluation, and selection of physical-chemical property data for α-, β-, and γ-hexachlorocyclohexane. J. Chem. Eng. Data 49, 173–185.

Xing, Y., Lu, Y., Dawson, R.W., Shi, Y., Zhang, H., Wang, T., Liu, W., Ren, H., 2005. A spatial temporal assessment of pollution from PCBs in China. Chemosphere 60, 731–739.

Xinhua News Agency of China, 2006. China suffers from hazardous waste. www.china.org.cn/english/environment/192237.htm (accessed February 2018).

Yang, Z., Wang, H., Saito, Y., Milliman, J.D., Xu, K., Qiao, S., Shi, G., 2006. Dam impacts on the Changjiang (Yangtze) River sediment discharge to the sea: the past 55 years and after the Three Gorges Dam. Water Resour. Res. 42.

Zhang, Z.L., Hong, H.S., Zhou, J.L., Huang, J., Yu, G., 2003. Fate and assessment of persistent organic pollutants in water and sediment from Minjiang River Estuary, Southeast China. Chemosphere 52, 1423–1430.

Zhang, H., Zhao, X., Ni, Y., Lu, X., Chen, J., Su, F., Zhao, L., Zhang, N., Zhang, X., 2010. PCDD/Fs and PCBs in sediments of the Liaohe River, China: levels, distribution, and possible sources. Chemosphere 79, 754–762.

Zhang, L., Shi, S., Dong, L., Zhang, T., Zhou, L., Huang, Y., 2011. Concentrations and possible sources of polychlorinated biphenyls in the surface water of the Yangtze River Delta, China. Chemosphere 85, 399–405.

Zhang, Q., Zhu, J., Ye, J., Qian, Y., Chen, F., Wang, J., Zhao, M., 2016. Temporal trends and risk assessment of polychlorinated biphenyls and heavy metals in a solid waste site in Taizhou, China. Environ. Sci. Pollut. Res. 23, 438–446.

Zhao, L., Hou, H., Zhou, Y., Xue, N., Li, H., Li, F., 2010. Distribution and ecological risk of polychlorinated biphenyls and organochlorine pesticides in surficial sediments from Haihe River and Haihe Estuary Area, China. Chemosphere 78, 1285–1293.

Zhou, H.Y., Cheung, R.Y.H., Wong, M.H., 1999. Residues of organochlorines in sediments and tilapia collected from inland water systems of Hong Kong. Arch. Environ. Contam. Toxicol. 36, 424–431.