Spatial distribution and implications to sources of halogenated flame retardants in riverine sediments of Taizhou, an intense e-waste recycling area in eastern China

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HIGHLIGHTS

- Residues of DPs were similar to the median of levels reported globally.
- Dec 604 stemmed from agrochemicals, while others from the use of flame retardants.
- Degradation of PBDEs and DP was evident.
- Distribution of DPs was influenced by a combination of diffuse and point sources.

GRAPHICAL ABSTRACT

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ABSTRACT

Concentrations and spatial distribution pattern of organohalogen flame retardants were investigated in the riverine surface sediments from Taizhou, an intensive e-waste recycling region in China. The analytes were *syn*- and *anti*- Dechlorane Plus (DP), Dechloranes 602, 603, and 604, a DP monoadduct, two dechlorinated DPs and 8 congeners of polybrominated diphenyl ethers (PBDEs). The concentrations of Σ_8 PBDEs, Σ DP, Σ Dec600s, and Σ DP-degradates ranged from <100 to 172,000, 100 to 55,000, not detectable (nd) to 1600, and nd to 2800 pg/g dry weight, respectively. BDE-209 and DP, both have been manufactured in China, had similar spatial distribution patterns in the study area, featured by distinctly recognizable hotspots some of which are in proximity to known e-waste dumping or metal recycling facilities. Such patterns were largely shared by Dec602 and dechlorinated DP, although their concentration levels were much lower. These major flame retardants significantly correlate with each other, and cluster together in the loading plot of principle component analysis. In contrast, most non-deca PBDE congeners do not correlate with DPs. Dec604 stood out having distinctly different spatial distribution pattern, which could be linked to historical use of mirex. Organic matter content of the sediment was not

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the dominant factor in determining the spatial pattern of pollution by halogenated flame retardants in the rivers of this study.

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1. Introduction

Dechlorane Plus (DP) is a highly chlorinated norbornene-based flame retardant used in electrical wire and cable coatings, computer and televisions connectors, and plastic roofing materials (OxyChem, 2011). DP was suggested as a potential substitute to decabromodiphenyl ether (deca-BDE) in some applications (European Commission, 2007). It is a high production volume (HPV) chemical in the United States (U.S. EPA, 2008). Other dechlorane series compounds, such as Dechlorane 602 (Dec602), Dechlorane 603 (Dec603), and Dechlorane 604 (Dec604) were also patented as flame retardants (FRs) in the 1970s (Shen et al., 2010, 2011a, 2011b). After the first detection of DP and Dec 600s (Dec602, 603, and 604) in the environment (Hoh et al., 2006; Shen et al., 2010), their occurrence has been reported all over the world (Sverko et al., 2008; Wang et al., 2016). DP analogs such as Dechlorane Plus monoadduct (DPMA), DP degradation products like undecachloropentacyclooctadecadiene (Cl₁₁-DP) and decachloropentacyclooctadecadiene (Cl₁₀-DP) have also been detected in the environment (Sverko et al., 2008; Wang et al., 2016).

Electrical and electronic equipment, such as cell phones, televisions, and computers, is one of the largest categories of consumer products containing flame retardants. Such equipment eventually becomes electronic waste (e-waste) and would be dismantled to recover useful components. Emissions from e-waste recycling activities have been identified as an important source of flame retardants to the ambient environment, and found to increase the health risk of local residents (Wang et al., 2016). For example, elevated DP levels have been found in abiota, biota, and human samples collecting from e-waste recycling regions (Ben et al., 2013; Chen et al., 2011; Li et al., 2014; Mo et al., 2013; Ren et al., 2009; Yu et al., 2010; Zheng et al., 2010).

Taizhou is a medium-sized city in China, located at the central coastal section of Zhejiang Province. By the end of 2014, Taizhou had a total population of 5.97 million. It has been one of the largest e-waste recycling areas in the world since the 1980s (Chi et al., 2011). E-waste recycling operations are mainly in the towns of Luqiao and Wenling in southern Taizhou (Li et al., 2014). Each year, approximately 2.2 million metric tons of e-waste is processed in Taizhou (Chan et al., 2007). Unregulated primitive manner of the operations and dumping of the residual waste has resulted in severe contamination of the local environment (Fu et al., 2011; Ma et al., 2009, 2011). Several studies have revealed the existence of DP, Dec602, and *anti*-Cl₁₁-DP in the living beings from Taizhou (Ben et al., 2013, 2014; Li et al., 2014; Wu et al., 2016). DP was also detected in the air (Sun et al., 2017) and in the floor particles of several e-waste recycling workshops in Taizhou (Zeng et al., 2016). However, little is known on the occurrence, spatial distribution, and sources of DP and its structurally related compounds in Taizhou's water environment.

In the present study, the concentrations of 8 DPs, including *syn*-DP, *anti*-DP, Dec602, Dec603, Dec604, DPMA, *anti*-Cl₁₀-DP and *anti*-Cl₁₁-DP in sediment samples from five main rivers in Taizhou were measured. Concentrations of selected congeners (BDEs 28, 47, 100, 99, 154, 153, 183, and 209) of polybrominated diphenyl ethers (PBDEs) were also measured to examine the correlations among flame retardants. The spatial distribution and the site-specific

contaminant patterns were analyzed to reveal potential sources of the targeted chemicals in the study area.

2. Materials and methods

2.1. Site description and sampling

Thirty-four surface sediment samples were collected during July 22–25, 2013, from five rivers, which run through the urban, industrialized, rural, or e-waste recycling areas of Taizhou and finally enter the East China Sea (ECS). A sampling map is shown in Fig. 1A, and site information is provided in Table S1 of Supplementary Material (SM). Sampling sites were chosen from the upstream to the downstream of each river within the study area, with 3–5 km apart between sites. Additional description of the rivers and sampling sites is provided in SM.

The top 5 cm of the sediments were taken with a stainless steel grab sampler and stored in stainless steel containers during transport under chilled conditions. All samples were freeze-dried, homogenized, passed through a 60 mesh sieve and kept at –20 °C before further analysis. Subsamples were analyzed for organic matter fraction (*f*_{OM}) using previously established method (Zhou et al., 2014), and the results are provided in Table S1.

2.2. Chemical analysis

Chemical information and details of laboratory procedures are given in Supplementary Material. A brief description is given below.

For each sample, 10 g freezing-dried sediment was spiked with surrogate standards (¹³C-PCB141 and ¹³C-PCB208), and Soxhlet-extracted. Anhydrous sodium sulfate and activated copper were added for removing water and elemental sulfur, respectively. The extract was concentrated by a rotary evaporator and the solvent was exchanged to 1–2 mL hexane. Cleanup of the extracts was conducted by the use of a glass column packed with Florisil, and target compounds were eluted with 40 mL of hexane:DCM (4:1). After volume reduction and solvent exchange to iso-octane, internal standard ¹³C-PCB202 was added before instrumental analyses.

All samples were quantitatively analyzed using an Agilent 7890/5973 gas chromatography – mass spectrometry (GC–MS) (Agilent Technologies, Santa Clara, California) with electron capture negative ionization. The GC was equipped with a DB-5HT capillary column (15 m × 0.25 mm × 0.10 μm; J&W Scientific). Identification of the compounds was performed by comparing their retention times and mass spectra with those of the standards. For each analyte, quantification was achieved via selected ion monitoring of the molecular ion with the most intensive isotopic abundance, and by use of a calibration curve based on the internal standard. All concentrations were normalized to dry weight (dw) and were not adjusted using surrogate recovery.

2.3. Quality control (QC)

For every set of 15 samples, a solvent blank and a procedure blank were run to check for interference and cross-contamination. The concentrations of *anti*-DP in all blanks were less than 0.5 pg/g dw, while those of other analytes were below their respective

Fig. 1. Sampling sites (A), and distributions of PBDEs (B), Σ DP and Σ DP-degradates (C), and Dec602 and Dec604 (D), in riverine sediments from Taizhou, China.

method detection limits (MDLs), which were estimated as ten times the signal-to-noise ratio and are summarized in Table S2. Five spike recovery experiments were conducted with sediment in which residues of target chemicals were close to or below their MDLs. The spiked recoveries of the analytes were in the range of 86–111% and their relative standard deviation was in the range of 3–12%. The recoveries of surrogates ^{13}C -PCB141 and ^{13}C -PCB208 were $87 \pm 13\%$ and $92 \pm 9\%$, respectively. All samples were extracted and analyzed in duplicate.

2.4. Statistical analysis

Statistical analysis was performed with SPSS 17.0. For concentrations lower than the MDLs, half of the MDLs were used in calculation to avoid missing values. All concentration data and f_{OM} values were logarithm transformed for improved normality for statistical analysis. Pearson's correlation analysis was conducted to investigate the correlations among the concentrations of different analytes, as well as f_{OM} values of sediment samples. Principle component analysis (PCA) was used to gain more insight into the pollution pattern at different sites. Only compounds with detection frequencies greater than 50% were used for correlation and PCA analyses. The level of statistical significance was set at $p < 0.05$ unless otherwise specified.

3. Results and discussion

Table 1 presents a summary of measured concentrations for individual DP compounds as well as $\Sigma_8\text{PBDEs}$ (sum of BDEs 28, 47, 99, 100, 153, 154, 183 and 209). Table S2 provides detailed data for individual sites. DPMA was not detectable in any sediment samples; and thus is excluded in following discussion.

3.1. PBDEs

The concentration of $\Sigma_8\text{PBDEs}$ ranged from below 100 to 173,000 pg/g dw with an average of 12,000 pg/g dw (Table 1). A comparison with recently published data (sampling time from 2007 to present) indicates that sedimentary PBDEs concentrations in the rivers of Taizhou were generally comparable to those from other e-waste or urban sites in China, but distinctly lower than those from some heavily industrialized areas in Guangdong, South China (Dongjiang River and Zhujiang River) and Jinlin, North China (Songhua River) (Table S3).

The highest average $\Sigma_8\text{PBDEs}$ concentration 32,000 pg/g dw was found in the sediments from the YN River, which runs through an e-waste area (Table 1). The second highest mean $\Sigma_8\text{PBDEs}$ (7,000 pg/g dw) was found in the BT River, especially in the upper reaches adjacent to an industrial center, suggesting influence of industrial activities on PBDE levels in the sediments (Table 1). The

Table 1

Concentrations (mean and range, pg/g dry weight) and detection rates of DP related compounds and PBDEs in the riverine sediments from Taizhou in 2013.

Chemicals		YN (n = 10)	BT (n = 7)	NG (n = 7)	YNJ (n = 6)	JQ (n = 4)
Dec 602	Mean	50	9	16	nd ^b	1
	Range	nd–380	nd–60	nd–58	/	nd–3
	DR ^a	0.9	0.29	0.57	0	0.5
Dec 603	Mean	7	1	BDL	BDL	1
	Range	nd–43	nd–5	0	/	nd–1
	DR	0.3	0.14	0	0	0.5
Dec 604	Mean	381	261	165	Nd	413
	Range	nd–1500	nd–1520	36–580	/	nd–11601
	DR	0.6	0.29	1	0	
<i>anti</i> -Cl ₁₀ -DP	Mean	448	BDL	36	38	56
	Range	nd–2580	/	nd–250	nd–150	nd–171
	DR	0.8	0	0.14	0.5	0.5
<i>anti</i> -Cl ₁₁ -DP	Mean	133	39	19	14	7
	Range	2–580	nd–230	nd–43	nd–54	nd–13
	DR	1	0.57	0.57	0.67	0.75
<i>syn</i> -DP	Mean	3183	681	328	194	81
	Range	520–14280	440–2210	50–1130	38–630	27–170
	DR	1	1	1	1	1
<i>anti</i> -DP	Mean	11,867	3293	1263	490	225
	Range	510–40990	520–134,101	200–4490	180–1370	81–430
	DR	1	1	1	1	1
Σ Dec 600s ^c	Mean	438	271	181	Nd	414
	Range	112–16231	nd–1585	42–580	/	12–1161
	DR	1	0.43	1	0	1
Σ DPdegradates ^d	Mean	581	39	55	51	63
	Range	2–2860	nd–230	nd–69	nd–151	nd–184
	DR	1	0.57	0.71	0.33	0.75
Σ DP ^e	Mean	15,050	3974	1590	684	306
	Range	650–55270	650–15620	250–5620	228–2000	108–600
	DR	1	1	1	1	1
Σ ₈ PBDEs ^f	Mean	32,053	7278	5498	2885	2028
	Range	428–172,543	152–40546	73–20407	141–10656	88–4577
	DR	1	1	1	1	1

^a DR: detection rate.^b nd: not detected. ^c Σ Dec 600s: sum of Dec 602, 603 and 604.^d Σ DPdegradates: sum of *anti*-Cl₁₀-DP and *anti*-Cl₁₁-DP.^e Σ DP: sum of *anti*-DP and *syn*-DP.^f Σ ₈PBDEs: sum of PBDEs 28, 47, 99, 100, 153, 154, 183, and 209.

NG River passes over a large residence area with high population density and has an average Σ ₈PBDEs concentration of 5,000 pg/g dw (Table 1). In contrast, the PBDE concentrations were lower in the sediment from rural and less industrialized areas, where the mean Σ ₈PBDEs were 2,800 and 2,000 pg/g dw for the YNJ River, and the JQ River, respectively (Table 1).

Large variability in Σ ₈PBDEs was observed among sites in some individual rivers (Fig. 1B). In the YN River, for example, the highest Σ ₈PBDEs (173,000 pg/g dw) was found at site YN-5, a location very close to the Fengjiang Metal Recycling Base. Site YN-8, downstream of YN-5 (Fig. 1B), also had a much higher Σ ₈PBDEs concentration (12,500 pg/g dw) than the upstream site YN-4 (980 pg/g dw), reiterating the influence of this metal recycling facility. The sources of the relatively high PBDE levels observed at sites YN-1 and YN-3 in the upstream Luqiao district are not clear, but may include drainage outlets which have acted as point sources. The low levels of PBDEs at sites YN-6 and YN-7 were not expected. These sites were from two artificial pools (surface area about 50 m²) within the Fengjiang Metal Recycling Base. With no drainage pipes, surface runoff and air deposition were likely to be the only inputs of pollutants to these pools. PBDE levels in the sediment of the NG River seem to be highly affected by the YN River, as Σ ₈PBDEs was low at sites (NG-1 through NG-5) located upstream of the junction near YN-3, and decreased as the river flowed east-wards towards NG-6 and NG-7 after it passed the junction (Fig. 1B). In the BT River, the highest Σ ₈PBDEs was observed at site BT-2 (40,000 pg/g dw); while other sites had Σ ₈PBDEs ranging from 150 to 5,800 pg/g dw

(Fig. 1B). BT-2 is in close proximity to an industrial center; in addition, frequent open burning of residential waste in a nearby backyard could be an important contributor to the observed high PBDE level as well. Among the sites in the YNJ River, significantly higher Σ ₈PBDEs was observed at YNJ-6, which is near an e-waste dumping area and likely to receive its leachate (Fig. 1A).

At all sites, decabromodiphenyl ether (BDE209) outweighed other PBDE congeners in large margins (Fig. 1B), and was also much higher than all other target compounds of this work. It accounted for 95%–99% of Σ ₈PBDEs at all nine PBDE “hotspots”-where Σ ₈PBDEs was higher than 5 ng/g dw (Table S1). Similar predominance of PBDEs by BDE209 in sediment was reported for other waters (Ma et al., 2012; Wang et al., 2011a). Deca-BDE, in which 92–97% is BDE209 (La Guardia et al., 2006), is the only PBDE product that was made in significant amount in China. The high hydrophobicity of BDE209 (log Kow >9, Darnerud et al., 2001) also contribute to its stronger affinity to sediment in comparison of other PBDE congeners.

In commercial Penta-BDE formulation, BDE28 is a minor components (<0.25%) (La Guardia et al., 2006). In about half of the samples of this work, enrichment of BDE28 was observed, and it is likely an indication of debromination of higher PBDE congeners during the lifespan of PBDE-containing products and their end-of-life disposals. Given that China has no commercial scale production of the Penta-BDE mixture (Wang et al., 2007), all non-deca PBDEs found in this work would originate from imported e-wastes or the in situ debromination of Deca-BDE components.

3.2. DP

Both *anti*-DP and *syn*-DP were detected in the sediments at all sites (Table 1 and Table S2). Concentrations of $\sum$ DP (sum of *syn*-DP and *anti*-DP) ranged from 100 to 55,000 pg g⁻¹dw with an average of 5600 pg g⁻¹dw. The sediment levels of $\sum$ DP in the rivers from Taizhou were one to three orders of magnitude higher than those reported for many other water bodies in China and other areas, but lower than those in Lake Ontario, North America (Yang et al., 2011), and a reservoir near another e-waste recycling place (Qingyuan) in South China (Table S4).

The spatial distribution pattern of DP in sediment (Fig. 1C) was generally similar to that of PBDEs (Fig. 1B). The river averages of $\sum$ DP were in the rank order that e-waste areas (the YN River) > industrial/urban areas (the BT River and NG River) > agricultural areas/suburban areas (the YNJ River and JQ River) (Table 1, Fig. 1A). The sampling sites near potential point-sources (YN-1, YN-3, YN-5, YN-8, BT-2, and YNJ-6) exhibited higher levels of both $\sum_8$ PBDEs and $\sum$ DP than other locations (Table S2, Fig. 1A), suggesting similar sources of PBDEs and DP in the study area. However, the opposite was observed at lower reach of the YN River (from YN-8 to YN-10) where $\sum_8$ PBDEs was decreasing while $\sum$ DP increasing (Table S2, Fig. 1A). DP discharge sources are suspected near YN-10 but future confirmation is needed.

Isomers *syn*-DP and *anti*-DP may differ in their environmental persistence and long range transport potential (Yang et al., 2011). The fractional abundance of the *anti*-isomer (f_{anti}) is defined as the concentration of *anti*-DP relative to total DP. In industrial formulations of the technical DP mixtures manufactured by AnPon (Huai'an, China) and OxyChem (Houston, Texas, USA), the f_{anti} values are in the range of 0.65–0.80 (Hoh et al., 2006; Li et al., 2013; Tomy et al., 2007; Wang et al., 2010a). In environmental samples, f_{anti} tends to decline at locations farther away from DP emission sources, due to the enrichment of *syn*-DP during atmospheric transport (Wang et al., 2016; Yang et al., 2011). The f_{anti} values in the sediment samples of this work were in the range of 0.69–0.86, which is not different from the range in the original DP mixture, reflecting the proximity of the sampling sites to discharge sources.

3.3. Dec 600s

The Dec-600s, including Dec602, Dec603, and Dec604, in sediments were first detected in the Laurentian Great Lakes (Shen et al., 2010, 2011a, 2011b; Yang et al., 2011). They have also been found in various environmental samples in China (Jia et al., 2011; Peng et al., 2014; Sun et al., 2013; Wang et al., 2010a). In the sediment of this work, both Dec602 and Dec604 were detected in about half of the samples. The concentration of Dec604 was found to vary considerably, ranging from nd to 1500 pg/g dw with a mean of 250 pg/g dw. Dec602 concentrations ranged from nd–380 pg/g dw with a mean of 20 pg/g dw. Dec603 was found to be above its detection limit of 0.4 pg/g dw in only seven samples (detection rate 20%), with the highest being 43 pg/g dw at site YN-8. The sum of Dec602, Dec603, and Dec604 ($\sum$ Dec600s) ranged from nd to 1600 pg/g dw, much lower than $\sum_8$ PBDEs and $\sum$ DP.

Among the rivers, the average $\sum$ Dec-600s was about 400 pg/g dw in both YN River and JQ River, which was 1.5–2.4 times higher than those in the BT River and the NG rivers; whereas Dec-600s were not detected in the sediment samples from the YNJ River (Table 1 and Fig. 1D). Sites YN-7, YN-8, BT-2, and JQ-2 have accumulated $\sum$ Dec-600s orders of magnitude higher than the other sites (Table S2; Fig. 1B). These hotspots for Dec-600s (Fig. 1D) do not overlapped with the hotspots for PBDEs and DP (YN-1, YN-3, YN-5, YN-8, BT-2, and YNJ-2), implying different origins and/or time trends. Li et al. (2015) reported that DP in indoor dust from China is

dominated by its use as a flame retardant in consumer goods, while Dec-600s is associated with agricultural discharges.

The concentrations of Dec602 and Dec603 measured in this work are in the range reported from northern and eastern China (Table S4). However, Dec604 was not detected in sediment studies from China prior to this work (Table S4). We found Dec604 had a higher concentrations than Dec602 and Dec603 in most samples, and contributed >70% of $\sum$ Dec-600s at sites YN-7, YN-8, BT-2, and JQ-2. To our knowledge, China has not manufactured Dec604 to date. However, it was reported as an impurity (2%) in a commercial product of mirex (U.S. Department of Health and Human Services, 1990), one of the two organochlorine pesticides used in China for termite control until 2009 (Wang et al., 2010b). A total of 869 kg of mirex was used in Zhejiang province from 1997 to 2001 (Global Environment Facility, 2006); an estimated 1.5 metric tonnes of mirex remains in the environment of Zhejiang, most of which are in soil and sediment (Wang et al., 2010b). The elevated concentrations of Dec604 could be attributed, at least partially, to the historical use of mirex in China.

3.4. Dechlorinated DP

Two DP-like compounds were first observed in the surficial sediments from the Niagara River and Lake Ontario (Sverko et al., 2008). They have one and two less chlorine atoms than DP, thus are labeled as Cl₁₁-DP and Cl₁₀-DP, respectively. These compounds can form from the decomposition of DP during instrumental analyses if a “dirty” glass liner is used in GC inlet (Sverko et al., 2008). To avoid false positive detection in the collected sediments, the GC inlet liner used in this work was replaced frequently. Moreover, a QC standard (including *syn*-DP, *anti*-DP, *anti*-Cl₁₀-DP and *anti*-Cl₁₁-DP, 20 ng/mL each) was analyzed daily to examine the possible DP decomposition within the GC instrument. The deviations were less than 10% for all target compounds in all cases, indicating negligible effect on the results for the sediment from the operations of the GC-MS system. Only the anti isomers of Cl₁₀-DP and Cl₁₁-DP were analyzed in this work.

The concentration sum of *anti*-Cl₁₀-DP and *anti*-Cl₁₁-DP ($\sum$ DP-degradates) ranged from nd to 2800 pg/g dw. These were significantly higher than those in the coastal sediments of the Yellow Sea, North China (nd–0.04 ng/g dw) (Zhao et al., 2011). As shown in Table 1 and Fig. 1C, $\sum$ DP-degradates in the YN River was at least 10

Fig. 2. Loading plot of the concentrations of PBDEs and DP related compounds in all sediment samples from the principal component analysis.

Table 2Pearson correlation matrix (two-tailed) for concentrations of DP related compounds, PBDEs, and f_{OM} in sediment Samples.

	f_{OM}	Dec 602	Dec 604	<i>anti</i> -Cl ₁₁ -DP	<i>syn</i> -DP	<i>anti</i> -DP	BDE 28	BDE 47	BDE 100	BDE 99	BDE 153
Dec 602	0.442**										
Dec 604	0.380*	0.217									
<i>anti</i> -Cl ₁₁ -DP	0.367*	0.770**	0.080								
<i>syn</i> -DP	0.283	0.700**	0.037	0.700**							
<i>anti</i> -DP	0.334	0.727**	0.073	0.672**	0.989**						
BDE 28	0.196	0.575**	−0.086	0.469**	0.658**	0.681**					
BDE 47	− 0.392*	0.141	− 0.369*	0.059	0.200	0.184	0.325				
BDE 100	−0.300	0.072	− 0.418*	0.262	0.251	0.196	0.424*	0.726**			
BDE 99	−0.190	0.288	− 0.438**	0.286	0.367*	0.353*	0.369*	0.765**	0.600**		
BDE 153	−0.187	0.313	−0.325	0.253	0.414*	0.391*	0.470**	0.615**	0.539**	0.438**	
BDE 209	0.476**	0.570**	0.007	0.660**	0.610**	0.592**	0.516**	−0.001	0.270	0.215	0.184

Values in bold are significant with a p value < 0.05* or < 0.01**.

times higher than in other four rivers. This is not surprising given that the YN River is also the most contaminated with DPs (Fig. 1C). The decomposition of DP may occur via pyrolytic reaction during the e-waste burning processes (Chen et al., 2011; Wang et al., 2011b).

Both *anti*-Cl₁₀-DP and *anti*-Cl₁₁-DP were detected in 15 of the 34 samples. Among the other samples, 12 had only *anti*-Cl₁₁-DP. The higher frequency of Cl₁₁-DP than Cl₁₀-DP in the sediment is in agreement with the findings in wild frogs from Taizhou (Li et al., 2014). The concentration ratio $\sum$ DP-degradates/*anti*-DP averaged 10%, which is close to those found in air (14%), plants (20%), and house dust (17.3%) from an electronic waste site in South China (Chen et al., 2011; Wang et al., 2011b). In addition, no significant difference in this ratio was observed among the five rivers of this work (ANOVA, $p = 0.18$). This may reflect the widespread existence of small backyard e-waste recycling workshops through out the Taizhou city.

3.5. Correlation analysis and principal component analysis (PCA)

Pearson correlation and PCA were conducted among individual target compounds as well as f_{OM} of the sediments. Dec603, *anti*-Cl₁₀-DP, BDE154, and BDE183 were excluded due to their low detection rates (<50%).

PCA extracted two components with eigenvalues greater than 1; PC1 and PC2 contributed 42.8% and 26.5% to the cumulative variances, respectively. In the loading plot (Fig. 2), the analytes are separated into two major groups. Group 1 includes *syn*-DP, *anti*-DP, *anti*-Cl₁₁-DP, Dec602, and BDE209. Concentrations of these compounds were also strongly correlated with each other by Pearson correlation analyses (Table 2). Particularly strong was the correlation between DP and BDE209 ($r = 0.592$ – 0.610 , $p < 0.0001$), suggesting that they share similar sources and histories of production and uses in the study area. Group 2 consists of non-deca PBDEs, although BDE28 is distanced from others to some extent. They were correlated with each other in most cases, but not with BDE 209 and most DP related compounds (Table 2). Dec604 is not associated with others in Fig. 2, and it does not correlate with any other DP related analytes (Table 2), suggesting distinctly different emission sources or environmental behavior of Dec604 in comparison with others.

Natural organic matter of sediment is an important variable that influences the distribution of hydrophobic organic compounds. In the samples of this study, f_{OM} varied from 0.24% to 6.21% with an average of 1.98%. It statistically significantly correlated with the dry weight based concentrations of BDE209, Dec602, Dec604, *anti*-DP, and *anti*-Cl₁₁-DP ($r = 0.367$ – 0.476 , $p = 0.004$ – 0.03 ; Table 2). Based on the r^2 of the correlations, f_{OM} explains 14%–23% of the variations in the concentration of these analytes. For other analytes, no

statistically significant correlations with f_{OM} were found ($p > 0.05$, Table 2). We conclude that, although organic matter of the sediments plays a role in retaining hydrophobic organics such as the analytes of this work, it is the potential point sources that dominates the spatial distribution of the target flame retardants in Taizhou's environment.

4. Conclusions

Combining the visualization of spatial distribution with the results of statistical analyses, we conclude that the spatial distribution of major flame retardants, particularly BDE209, DP, and Dec602, in the sediments of the Taizhou rivers is dominated by local point sources, which are associated with e-waste dumping and handling among others. Non-point, diffusive sources such as agricultural discharge is likely a major contributor to Dec604, which was not found in sediments in China prior to this work, and stood out as having a distinct spatial distribution pattern than known flame retardants in the riverine sediment of Taizhou.

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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.chemosphere.2017.06.104>.

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