

Pollution profiles and risk assessment of PBDEs and phenolic brominated flame retardants in water environments within a typical electronic waste dismantling region

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Abstract The aim of this study was to assess the pollution profiles of various typical brominated flame retardants in water and surface sediment near a typical electronic waste dismantling region in southern China. We found that polybrominated diphenyl ethers (PBDEs), 2,4,6-tribromophenol (TBP), pentabromophenol (PeBP), tetrabromobisphenol A (TBBPA), and bisphenol A (BPA) were ubiquitous in the water and sediment samples collected in the study region. In water, Σ_{19} PBDEs (sum of all 20 PBDE congeners studied except BDE-209, which was below the detection limit) levels ranged from 0.31 to 8.9×10^2 ng L⁻¹. TBP, PeBP, TBBPA, and BPA

concentrations in the water samples ranged from not being detectable (nd—under the detection limit) to 3.2×10^2 (TBP), from nd to 37 (PeBP), from nd to 9.2×10^2 (TBBPA) and from nd– 8.6×10^2 ng L⁻¹ (BPA). In sediment, Σ_{19} PBDEs ranged from nd to 5.6×10^3 ng g⁻¹, while BDE-209 was the predominant congener, with a range of nd to 3.5×10^3 ng g⁻¹. Tri- to hepta-BDE concentrations were significantly ($p < 0.01$) correlated with each other, except for BDE-71 and BDE-183, and octa- to nona-BDEs concentrations were significantly ($p < 0.05$) correlated with each other, except for BDE-208. BDE-209 was not significantly correlated with tri- to nona-BDEs. Risk assessments indicated that the water and sediment across the sampling sites posed no estrogenic risk. However, different eco-toxicity risk degrees at three trophic levels did exist at most sampling sites.

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Introduction

With the ever-increasing rapid economic development and frequent turnover of electronic products, electronic waste (e-waste) is a major global problem. Millions of tons of e-waste are recycled in developing countries using underdeveloped dismantling methods

(Wong et al. 2007; Zhang et al. 2011). In addition to heavy metals of concern, various hazardous organic compounds are released into the environment during these dismantling processes (He et al. 2013; Liu et al. 2014). Brominated flame retardants (BFRs), used to reduce the flammability of electrical and electronic products and textiles, are among the organics which are recently receiving the most attention.

One type of BFR, namely, the organobromine compounds called polybrominated diphenyl ethers (PBDEs), has been the focus of particular concern (An et al. 2011; Bjorklund et al. 2012). PBDEs account for one-third of all used BFRs (Lopez et al. 2009), and some PBDE congeners are highly toxic and classified as persistent organic pollutants by the Stockholm Convention (de Wit et al. 2010). PBDE pollution has been widely reported in recent research articles, and extremely high PBDE levels have been detected in various environmental matrices, including air, sewage sludge, sediment, soil, and tissues of organisms, blood, and breast milk (Fujii et al. 2014; Tang et al. 2014).

Tetrabromobisphenol-A (TBBPA) accounts for another one-third of all used BFRs (Lopez et al. 2009). This phenolic compound has been found in various environmental samples, such as air, water, soil, sediment, wildlife, and human tissues (Labadie et al. 2010; Fujii et al. 2014), due to its persistent, lipophilic, and bioaccumulative properties (Reistad et al. 2005).

Notable progress has been made in detecting these contaminants in the global environment. Nevertheless, little is known about the levels of phenolic BFRs, including TBBPA, pentabromophenol (PeBP), and 2,4,6-tribromophenol (TBP), as well as of a debromination product of TBBPA, bisphenol A (BPA), in the river water and sediment within a recognized e-waste dismantling region.

Recent research suggests that exposure to phenolic BFRs is associated with various toxicities in organisms and human beings, including neurological toxicity, thyroid toxicity, embryo toxicity, teratogenicity, and carcinogenicity (Nakajima et al. 2009; Li et al. 2012). Furthermore, TBBPA can be biodegraded to yield lower levels of brominated organics and even lose its bromines to produce the well-known endocrine disruptor BPA (Ronen and Abeliovich 2000; Arbeli and Ronen 2003; An et al. 2011; Li et al. 2012; Liu et al. 2013; Zu et al. 2013). Several national regulatory bodies have implemented regulations restricting the

discharge of the phenolic BFRs, and TBP, PeBP, and TBBPA have been listed on the U.S. Environmental Protection Agency Office (USEPA) of Pollution Prevention and Toxics Master Testing List (NICNAS 2001). Polo et al. (2006) also included TBBPA as a priority substance in their risk assessment of phenolic flame retardants in water samples. Taking into account these adverse effects, we considered it is important to conduct a systematic risk assessment of the potential eco-toxicity and endocrine-disrupting activity associated with phenolic BFRs and PBDEs from e-waste dismantling activities.

In this study we investigated the pollution profiles of phenolic BFRs, BPA, and PBDEs in river water and sediment samples collected within an e-waste dismantling and recycling region, following long-term e-waste dismantling activities. We attempted to determine the source of PBDEs, TBP, PeBP, TBBPA, and BPA at these sites and evaluated BFR eco-toxicities on fish, daphnia, and green algae at three different trophic levels. The endocrine-disrupting activities of TBBPA and BPA were also assessed. Our findings may support future risk assessment and pollution control policies within e-waste dismantling regions.

Materials and methods

Materials

Standards of 20 PBDEs, TBP, PeBP, TBBPA, and BPA were obtained from AccuStandard Inc. (New Haven, CT). Surrogates, including [^{13}C]PCB141, [^{13}C]TBP, [^{13}C]TBBPA, and [^{13}C]BPA were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). A detailed description of these standards is provided in the Electronic Supplementary Material (ESM).

All solvents were high-performance liquid chromatography grade from CNW technologies (ANPEL Scientific Instrument Co., Ltd, Shanghai, China). LC- C_{18} (40–63 μm) and SAX sorbents were also supplied by CNW technologies. Oasis MAX (150 mg, 6 cc) cartridges were purchased from Waters Corp. (Milford, MA). LC-Florisil cartridges (1 g, 6 cc) and silylating reagent bis(trimethylsilyl)trifluoroacetamide/trimethylchlorosilane (BSTFA:TMCS; 99:1; Supelco-33148) were purchased from Sigma-Aldrich (Louis, MO). Neutral alumina (mesh size 100–200) and silica sorbents

(mesh size 300–400) were provided by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and used after Soxhlet extraction, activated and deactivated.

Study area and sample collection

The study was conducted in a small town in South China (23°327'N, 116°342'E) where e-waste has been treated for nearly 30 years. There are more than 300 companies and 3,000 individual recycling workshops, with an annual recycling capacity of 100,000 tons (Xing et al. 2009). Sampling site S1, an upriver reservoir, was used as the control site. Water and soil samples were collected from the study sites: (1) sampling sites S4, S5, and S14, where many individual e-waste recycling workshops were situated; (2) sampling sites S7, S8 and S9, where a number of clothing industries are situated; (3) sampling sites S2, S3 and S13, where a number of plastic industries are found; (4) sampling sites S6, S10, S11, S12 and S15, located in the surroundings of the aforementioned sampling sites. Results from water and soil samples collected at the control sites were compared to those collected from the study sites across the region (ESM Fig. S1; Table S1). Fourteen river water and surface sediment samples were collected using pre-cleaned amber glass bottles in November 2013. The sampling process is detailed in the ES SI.

Pretreatment procedure and instrument analysis

Pretreatment

Water samples were collected and filtered within 24 h through pre-baked (450 °C, 4 h) GF/F filters (diameter 142 mm). Aliquots of 0.01 and 0.5 L of the sample filtrate were used to determine dissolved organic carbon (DOC) and target pollutant concentrations, respectively. Filtrate for further testing was first spiked with recovery surrogates and left overnight for equilibration; the sample was then extracted using the solid phase extraction method (Labadie et al. 2010). A detailed description of this process is provided in the ESM. Mixed extracts were then dried under a gentle nitrogen stream and derivatized using 100 µL of BSTFA:TMCS at 60 °C for 1 h just before analysis.

For analysis of the sediment, 5-g samples of sieved sediment (mesh size 200) were spiked with recovery surrogates and then ultrasonically extracted with 20 mL

of hexane/acetone (1:1, v/v) for 40 min. During the extraction, HCl-activated copper granules were added to the sample to remove elemental sulfur. The sample was then centrifuged (1,000 rpm, 5 min) and the supernatant was collected. This extraction process was repeated twice, following which all three extracts were combined, concentrated to 1 mL under a gentle nitrogen stream, and then cleaned up (Labadie et al. 2010).

Gas chromatography/mass spectrometry analysis

The samples were analyzed using an Agilent 7890A gas chromatography (GC) coupled with an Agilent 5975C mass spectrometer (MS) using negative chemical ionization (NCI) in selective ion-monitoring mode (Agilent Technologies, Santa Clara, CA). Retention time and characteristic ions were used to differentiate PBDE congeners. Quantification of tri- to hepta-BDEs was performed using a HP-5 ms (30 m × 0.32 mm, film thickness 0.5 µm) column with helium carrier gas. Injection volume was 1 µL in the splitless mode. For BDE congeners BDE-196, BDE-197, BDE-203, BDE-206, BDE-207, BDE-208, and BDE-209, a DB-5HT (15 m × 0.25 mm, film thickness 0.10 µm) capillary column was used. Ions m/z 79 and 81 were monitored for tri- to nona-BDEs, and m/z 79, 81, 486.7 and 488.7 were monitored for BDE-209. For the recovery surrogate standard, m/z 372 and 374 were monitored for [¹³C]PCB141.

Analysis of the derivatized TBP, PeBP, and TBBPA was also performed on a GC/MS (NCI mode) system equipped with a HP-5 ms (30 m × 0.32 mm, film thickness 0.5 µm) column. Ion fragments m/z 329.7 and 331.8 were monitored for TBP, m/z 335.7 and 337.8 for [¹³C]TBP, m/z 607 and 609 for TBBPA, and m/z 619 and 621 for [¹³C]TBBPA. The analysis of the derivatized BPA was performed as described in An et al. (2011b). Ion fragments m/z 357.2 and 372.2 were monitored for BPA and m/z 369.2 and 384.2 for [¹³C]BPA. The detailed analysis procedures are provided in the ESM.

Organic carbon measurement

Dissolved organic carbon content in water was measured using a Shimadzu TOC-VCPH analyzer (Shimadzu Corp., Kyoto, Japan), and total organic carbon (TOC) in sediment was determined using an elemental analyzer (CHNO Vario Ei III; ELEMENTAR

Analysensysteme, Hanau, Germany) after the carbonates had been removed with 10 % hydrochloric acid.

Quality assurance/quality control

No objective analytes were detected in the procedural blanks. Surrogate recoveries in all samples were 76.06 ± 9.27 % for [^{13}C]PCB141, 79.48 ± 13.57 % for [^{13}C]TBP, 83.12 ± 15.71 % for [^{13}C]TBBPA, and 90.00 ± 19.45 % for [^{13}C -BPA]. Recoveries of the 20 PBDE congeners ranged from 71.70 to 125.50 % [relative standard deviation (SD) <13.5 %] in three spiked blank samples and from 67.29 to 114.78 % (relative SD <9.2 %) in three spiked matrix samples. TBP, PeBP, TBBPA, and BPA recoveries ranged from 82.70 to 93.40 % (relative SD <14.8 %) in three spiked blank samples and from 78.20 to 100.26 % (relative SD <15.0 %) in three spiked matrix samples. Reported concentrations were not corrected by the surrogate recovery.

Risk assessment

Estrogenic activity assessment

Endocrine-disrupting activity of TBBPA and BPA in water was calculated using Eq. 1 (Sun et al. 2013b):

$$E_2EQ = E_2EF \times MEC \quad (1)$$

where E_2EQ represents 17β -estradiol equivalency, E_2EF represents the estrogenic equivalency factor of TBBPA (0.45×10^{-6}) and BPA (13.7×10^{-6}) (Kitamura et al. 2005). MEC is the measured environmental concentration (ng L^{-1}) of each organic compound. For sediment, it was assumed that pore water is the primary exposure route for aquatic organisms. Consequently, MEC in sediment was based on pore water concentration, calculated using the equilibrium partitioning approach in Eq. 2 (Di Toro et al. 1991):

$$C_{pw} = \frac{C_s}{f_{oc}K_{oc}} \quad (2)$$

where C_{pw} is the estimated pore water concentration (ng L^{-1}), C_s is the measured sediment concentration (ng g^{-1}), f_{oc} ($= 0.1$) is the fraction of organic carbon in the sediment sample (Cristale et al. 2013a), and K_{oc} is the partition coefficient for sediment organic carbon, predicted using Advanced Chemistry Development software (ACD/Labs, Toronto, ON, Canada).

The total E_2EQ of TBBPA and BPA based on the E_2EQ of single estrogenic activity was calculated using Eq. 3 (Sun et al. 2013b):

$$E_2EQ_{\text{Total}} = \sum E_2EQ_i = E_2EQ_{\text{TBBPA}} + E_2EQ_{\text{BPA}} \quad (3)$$

Eco-toxicity assessment

Eco-toxicity of the target compounds in the water and sediment samples was assessed using the risk quotient (RQ) on non-target organisms (Sánchez-Avila et al. 2012; Cristale et al. 2013b). At three trophic levels, the median lethal dose (LC_{50}) or half maximal effective concentration (EC_{50}) for fish, daphnia, and green algae associated with exposure to PBDEs, TBP, PeBP, TBBPA, and BPA were used to calculate the RQ as Eq. 4 (Cristale et al. 2013b):

$$RQ = \frac{MEC}{PNEC} = \frac{MEC}{EC_{50} \text{ or } LC_{50}/f} \quad (4)$$

where PNEC is the predicted no effect concentration (mg L^{-1}), estimated as a quotient of toxicological relevant concentration (EC_{50} or LC_{50}) with a security factor ($f = 1,000$). The software program ECOSAR (Ecological Structure Activity Relationships), recommended by the USEPA (Washington D.C.), was used to estimate the relative data because some EC_{50} and LC_{50} data are not available in the literature (Sánchez-Avila et al. 2012; Cristale et al. 2013a). For sediment, MEC was also based on pore water, estimated using Eq. 2. A sum of RQs was obtained from Eq. 5 (Cristale et al. 2013a):

$$RQ_{\text{Total}} = \sum RQ_i \quad (5)$$

Statistical analysis

Statistical analysis were carried out with PASW Statistics version 18 (IBM Co., Chicago, IL). $p < 0.05$ was considered to be statistically significant.

Results and discussion

PBDEs pollution

Levels and composition profiles of PBDEs

The concentration PBDEs in the water and sediment samples from all 15 study sites are given in Tables 1

and 2, respectively. PBDEs were detected in all samples, suggesting widespread contamination across the surveyed region. In water, Σ_{20} PBDE concentrations (the sum of the 20 PBDE congeners studied) ranged from 0.31 to 8.9×10^2 ng L⁻¹, with an average of 1.6×10^2 ng L⁻¹; BDE-209 was below the detection limit at all sites (Fig. 1a).

All PBDE congeners were found in the sediment samples, and the Σ_{20} PBDEs concentrations were much higher levels than those in the water samples. Σ_{20} PBDEs concentration in the sediment samples ranged from not detectable (nd; under the detection limit) to 6.0×10^3 ng g⁻¹, with an average of 2.8×10^3 ng g⁻¹ (Fig. 1b). The Σ_{20} PBDEs concentrations also varied across different sampling sites and within the same site across different matrices and were extremely low in both the water and sediment samples collected at control site S1, suggesting that the upriver reservoir was not contaminated with PBDEs.

The concentrations of the different PBDEs in sediment samples was very low at S11 and S12, sampling sites located upstream of the rivers and a good distance away from the e-waste dismantling workshops. One possible explanation for the low values is the very high DOC (32.53 and 50.39 mg L⁻¹, respectively) in the water and the low TOC (1.34 and 1.46 %, respectively) in the sediment (Tables 1, 2).

The highest Σ_{20} PBDEs concentration (8.9×10^2 ng L⁻¹) was found in water samples collected at S2, followed by S12 (3.3×10^2 ng L⁻¹), S7 (1.9×10^2 ng L⁻¹), and S15 (1.8×10^2 ng L⁻¹). A possible explanation for the relatively high Σ_{20} PBDEs pollution at these sites may be the presence of e-waste dismantling workshops, clothing industries (located at S7), and plastics industries (located at S2). S15 is located at a convergence of these sampling sites; as such, contaminants might be transported from other sources and sink here.

Sedimentation is an important fate mechanism for PBDEs in freshwater ecosystems (Malik et al. 2014). Sediments are composed of small organic and inorganic particles which show higher adsorption capacities for PBDEs due to their large surface area. In addition, the strong hydrophobic properties of PBDEs allow them to accumulate in sediment (Binelli et al. 2007). The most polluted sediment sample in our study was from S6 and S7, where Σ_{20} PBDEs concentrations were as high as 6.0×10^3 ng g⁻¹. This concentration is two to four orders of magnitude higher than the

lowest Σ_{20} PBDEs concentrations at S1, S11, and S12, which were located upstream of the polluted rivers and far from e-waste dismantling sites.

ESM Table S2 presents a comparison of the level of PBDE contamination determined in our water samples with levels reported in the literature. Few water-based datasets are available for study, likely because their partitioning and accumulation characteristics make other matrices more attractive for research purposes. We found, however, that the PBDE levels in our water samples were lower than those from sewage treatment plant water of the Pearl River Delta in China, but higher than those collected from Shihwa Lake in Korea (Moon et al. 2012) and the European Arctic (Möller et al. 2011). PBDE concentrations varied significantly in the water samples, depending on the degree of contamination and DOC content.

Table 3 provides a comparison of the levels of PBDE contamination in the sediment samples in our study with those of other studies. Although the PBDE congeners analyzed in our study differed somewhat from those of these other studies, BDE-28, -47, -99, -183, and -209 were consistently detected. The PBDE levels determined in our study closely correspond to levels found in surface sediment samples from a river in one of the more heavily industrialized polluted regions of south China (Zhang et al. 2009), but are slightly higher than those in surface sediment samples from the Pearl River Delta, China (Chen et al. 2013), Lake Chaohu of China (Wang et al. 2013), and Han River, Nakdong River, Geum River in Korea (Lee et al. 2012). PBDE levels in our sediment samples were one order of magnitude lower than those detected in Lake Shihwa in Korea (Moon et al. 2012), but two to four orders of magnitude higher than those detected in sediments of Coastal East China Sea (Li et al. 2012b), Goseong, Korea (Lee et al. 2014), White Lake and Muskegon Lake, Michigan, and San Francisco Bay, California, both USA (Bradley et al. 2011), Lake Maggiore, Italy (Mariani et al. 2008), and Monastir Bay, central Mediterranean region (Nouira et al. 2013). Overall, PBDE levels in the sediment samples collected at Asian locations were much higher than those in sediment samples collected on other continents.

Correlation of PBDEs with TOC

Dissolved organic carbon (in water) and TOC (in sediment) are principal factors controlling the sorption

Table 1 Concentrations of individual polybrominated diphenyl ethers in water samples

DOC of sites and PBDEs analyzed	Sampling sites ^a																			
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15					
DOC (mg L ⁻¹)	1.01	7.41	29.60	10.48	8.35	19.28	30.30	13.72	26.56	5.83	32.53	50.39	16.31	10.48	35.51					
PBDEs (ng L ⁻¹)																				
BDE-17	nd	2.8	nd	nd	1.5	nd	nd	0.49	13	nd	2.7	0.26	nd	4.2	nd					
BDE-28	nd	25	11	1.9	nd	8.5	nd	7.1	nd	0.27	0.08	nd	1.8	nd	0.06					
BDE-71	nd	nd	nd	nd	3.9	nd	8.9	5.7	14	nd	0.01	23	nd	nd	nd					
BDE-47	nd	2.0	3.5	3.7	6.7	2.5	nd	1.1 × 10 ²	22	nd	0.08	11	7.6	nd	nd					
BDE-66	nd	nd	nd	nd	4.9	nd	nd	nd	9.4	nd	nd	49	2.7	nd	nd					
BDE-100	nd	nd	nd	2.0	nd	nd	4.0	nd	0.64	nd	1.4	36	nd	nd	2.6					
BDE-99	0.29	nd	2.3	nd	nd	1.6	3.3	nd	6.8	nd	nd	nd	4.7	nd	1.4					
BDE-85	nd	nd	27	nd	2.4	27	22	nd	nd	0.75	32	57	nd	nd	10					
BDE-154	0.02	nd	nd	nd	nd	nd	48	nd	nd	nd	nd	nd	nd	nd	nd					
BDE-153	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	5.1	nd	nd					
BDE-138	nd	8.5 × 10 ²	3.1	nd	nd	3.3	nd	nd	nd	nd	nd	79	nd	14	nd					
BDE-183	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd					
BDE-190	nd	nd	nd	nd	nd	nd	22	nd	nd	nd	nd	nd	nd	nd	nd					
BDE-197	nd	4.3	3.7	0.43	2.7	3.1	7.9	6.9	0.98	0.20	5.5	19	3.7	4.0	6.7					
BDE-203	nd	nd	41	4.6	24	3.1	4.2	10	1.1	3.1	0.25	1.4	6.3	5.4	0.14					
BDE-196	nd	6.4	37	4.2	22	41	57	5.2	43	2.5	4.4	55	nd	42	1.6 × 10 ²					
BDE-208	nd	nd	5.1	4.4	nd	3.5	7.7	3.2	nd	nd	11	nd	4.9	6.2	nd					
BDE-207	nd	nd	nd	8.9	nd	2.8	3.6	2.2	nd	nd	5.4	nd	nd	7.5	nd					
BDE-206	nd	nd	nd	7.3	12	7.6	3.6	6.6	0.73	nd	nd	nd	4.4	0.34	nd					
BDE-209	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd					
Σ ₁₉ PBDEs ^b	0.31	8.9 × 10 ²	1.3 × 10 ²	37	79	1.0 × 10 ²	1.9 × 10 ²	1.5 × 10 ²	1.1 × 10 ²	6.8	62	3.3 × 10 ²	41	83	1.8 × 10 ²					
Σ ₂₀ PBDEs ^c	0.31	8.9 × 10 ²	1.3 × 10 ²	37	79	1.0 × 10 ²	1.9 × 10 ²	1.5 × 10 ²	1.1 × 10 ²	6.8	62	3.3 × 10 ²	41	83	1.8 × 10 ²					

PBDEs, Polybrominated diphenyl ethers; nd, under detection limit; DOC, dissolved organic carbon

^a Sampling site S1 is an upriver reservoir and control site; study sites S4, S5, and S14 are sites where many individual e-waste recycling workshops are situated; study sites S7, S8, and S9 are sites where a number of clothing industries are situated; study sites S2, S3, and S13 are where a number of plastic industries are found; sampling sites S6, S10, S11, S12, and S15 are located in the surroundings of the aforementioned sampling sites

^b Σ₁₉PBDEs, Sum of all quantified PBDE congeners except BDE-209

^c Σ₂₀, Sum of all 20 quantified PBDE congeners

Table 2 Concentrations of individual polybrominated diphenyl ethers in sediment samples

TOC of sites and PBDEs analyzed	Sampling sites ^a																			
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15					
TOC (%)	0.09	0.95	6.29	7.03	1.12	4.69	12.58	7.09	7.48	5.32	1.34	1.46	8.74	2.70	4.87					
PBDEs (ng g ⁻¹ , dw)																				
BDE-17	nd ^a	0.36	1.0 × 10 ²	4.6	0.99	93	3.5	3.9	5.5	2.0	0.04	0.05	38	1.3	13					
BDE-28	nd	1.6	2.2 × 10 ²	6.7	2.3	2.3 × 10 ²	7.1	7.4	11	4.1	nd	0.04	78	1.9	19					
BDE-71	nd	1.7	47	5.6	1.3	52	6.6 × 10 ²	38	5.3	2.8	nd	0.12	19	6.3	5.6					
BDE-47	nd	6.1	1.2 × 10 ³	23	17	1.7 × 10 ³	37	64	68	26	0.09	0.31	4.8 × 10 ²	15	1.1 × 10 ²					
BDE-66	nd	1.4	3.9 × 10 ²	7.3	4.6	5.1 × 10 ²	8.5	11	22	7.4	nd	0.09	1.6 × 10 ²	4.5	31					
BDE-100	nd	0.35	47	1.7	0.95	1.1 × 10 ²	17	8.8	5.7	1.9	nd	0.06	32	1.4	5.6					
BDE-99	nd	2.1	1.0 × 10 ³	16	18	1.9 × 10 ³	1.1 × 10 ²	68	78	26	0.13	0.36	5.0 × 10 ²	19	1.1 × 10 ²					
BDE-85	nd	nd	1.7 × 10 ²	1.2	2.3	1.8 × 10 ²	1.5 × 10 ²	5.5	11	2.9	nd	nd	72	2.4	14					
BDE-154	nd	0.79	41	3.4	1.4	91	21	14	7.5	4.6	nd	0.07	34	2.3	5.5					
BDE-153	nd	0.35	1.5 × 10 ²	8.3	3.8	4.0 × 10 ²	39	34	22	5.3	nd	0.1	1.1 × 10 ²	5.6	18					
BDE-138	nd	nd	58	1.4	1.2	78	6.9	5.6	5.1	1.3	nd	nd	28	1.1	7.9					
BDE-183	nd	3.1	32	33	8.2	89	5.3 × 10 ²	1.2 × 10 ²	27	9.8	nd	0.15	92	16	9.7					
BDE-190	nd	nd	7.2	3.3	1.1	11	22	13	3.2	1.1	nd	nd	8.8	1.9	1.0					
BDE-197	nd	30	9.7	83	79	24	75	2.2 × 10 ²	88	26	0.05	0.02	28	91	1.6					
BDE-203	nd	52	11	70	92	17	83	1.6 × 10 ²	1.0 × 10 ²	70	0.05	0.04	17	89	2.1					
BDE-196	nd	41	12	83	98	20	54	1.9 × 10 ²	83	54	0.02	nd	21	91	2.1					
BDE-208	nd	2.4 × 10 ²	37	2.7 × 10 ²	8.4 × 10 ²	26	90	1.1 × 10 ²	3.1 × 10 ²	1.7 × 10 ²	nd	nd	23	2.8 × 10 ²	9.6					
BDE-207	nd	3.6 × 10 ²	55	4.2 × 10 ²	1.3 × 10 ³	40	3.8 × 10 ²	2.5 × 10 ²	5.1 × 10 ²	2.6 × 10 ²	0.04	nd	45	4.8 × 10 ²	17					
BDE-206	nd	1.9 × 10 ²	47	2.1 × 10 ²	1.2 × 10 ³	36	1.7 × 10 ²	5.7 × 10 ²	6.3 × 10 ²	4.7 × 10 ²	nd	0.46	66	7.0 × 10 ²	15					
BDE-209	nd	3.6 × 10 ²	1.1 × 10 ³	7.4 × 10 ²	9.1 × 10 ²	3.7 × 10 ²	3.5 × 10 ³	1.4 × 10 ³	2.5 × 10 ³	8.7 × 10 ²	1.1	12	1.8 × 10 ³	1.0 × 10 ³	1.4 × 10 ³					
Σ ₁₉ PBDEs ^b	nd	9.4 × 10 ²	3.7 × 10 ³	1.3 × 10 ³	3.6 × 10 ³	5.6 × 10 ³	2.5 × 10 ³	1.9 × 10 ³	2.0 × 10 ³	1.2 × 10 ³	0.42	1.9	1.9 × 10 ³	1.8 × 10 ³	3.9 × 10 ²					
Σ ₂₀ PBDEs ^c	nd	1.3 × 10 ³	4.8 × 10 ²	2.0 × 10 ³	4.7 × 10 ³	6.0 × 10 ³	6.0 × 10 ³	3.3 × 10 ³	4.5 × 10 ³	2.0 × 10 ³	1.6	14	3.7 × 10 ³	2.9 × 10 ³	1.8 × 10 ³					

TOC: Total organic carbon; dw, dry weight

^a For full description of sample site, see footnote to Table 1

^b Σ₁₉PBDEs refers the sum of all quantified PBDE congeners except BDE-209

^c Σ₂₀PBDEs refers the sum of all 20 quantified PBDE congeners

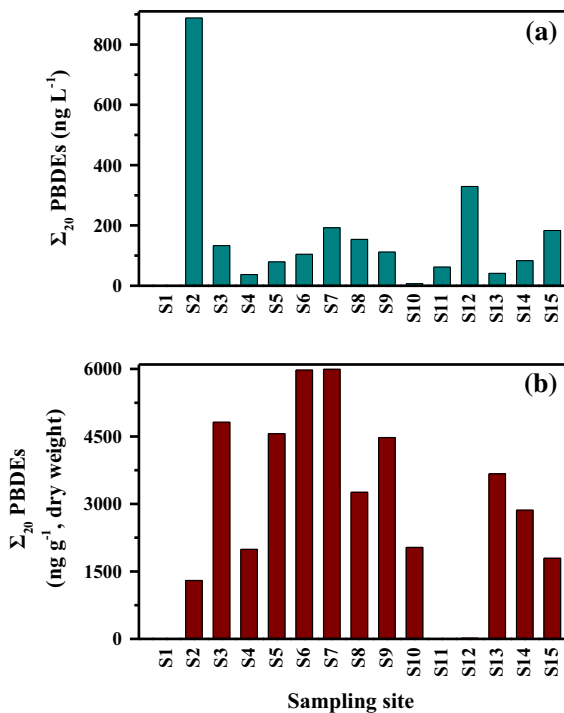


Fig. 1 Distribution of the sum of all 20 polybrominated diphenyl ethers (Σ_{20} PBDEs) in the water samples (a) and sediment samples (b). S1–S15 Sampling sites; see footnote to Table 1.

and subsequent partitioning of organics (Zhao et al. 2011), a process of diffusive dissolution in the organic matrix of organics compounds. Given the hydrophobic nature of PBDEs, their distribution in water/sediment may be strongly correlated with DOC or TOC. In our study area, the DOC in the water samples ranged from 1.01 to 50.39 mg L⁻¹, with an average of 19.85 mg L⁻¹. The TOC in the sediment samples ranged from 0.09 to 12.58 %, with an average of 4.80 %, respectively (Tables 1, 2). A regression analysis between PBDE concentration and the DOC or TOC revealed that Σ_{20} PBDEs concentrations in water were significantly positively correlated with DOC content ($R^2 = 0.70$). Similarly, Σ_{20} PBDEs and BDE-209 concentrations in the sediment samples were correlated with TOC content ($R^2 = 0.42$ and 0.74, respectively; Fig. 2). These results suggest that the amount of organic matter plays a significant role in PBDE transportation and distribution in water and sediment. These correlation results match previous studies (Malik et al. 2014).

PBDE congener patterns

PentaBDE, OctaBDE, and DecaBDE are three main types of PBDEs that were used previously in commercial products as additive flame retardants and still may be in use in some products. PentaBDE contains primarily BDE-47, BDE-99, BDE-100, BDE-153, and BDE-154; OctaBDE contains BDE-138, BDE-183, BDE-153, BDE-154, and octaBDEs; DecaBDE contains nonaBDEs and fully brominated BDE-209 (de Wit et al. 2010).

In our study, PentaBDE, OctaBDE, and other low-bromine PBDE congeners were the dominant polluted species in the water samples (74.06–100 %). The proportion of DecaBDE was very low (not detectable to 25.94 %, except at site S4, where it accounted for 55.23 % of all PBDE congeners; ESM Fig. S2). However, the percentage contribution of individual congeners to Σ_{20} PBDEs concentrations in the sediment samples differed from that in the water samples (Fig. 3, site S1 was excluded, due to no detectable PBDEs). The proportion of DecaBDE (53.04 – 92.71 %) in Σ_{20} PBDEs was clearly dominant in the sediment samples, with the exception of samples taken at S3 (25.57 %) and S6 (7.92 %). PBDEs with a relatively lower bromine content are more readily distributed in water, while PBDEs with a higher bromine content are more readily distributed in sediments. One possible explanation for this difference may be their different hydrophobic characteristics (PentaBDE and OctaBDE, with less bromine, are more hydrophilic than DecaBDE, with more bromine). Within the DecaBDE category, BDE-209 was the main congener, ranging from 41.65 to 97.13 % of total PBDEs, with the exception of samples collected at S2 (31.39 %) and S5 (21.63 %). This finding is in agreement with the lack of restrictions on DecaBDE production or use in most countries, whereas DecaBDE is a main element of BFR production in China (Yu et al. 2011).

The contributions of PentaBDE and OctaBDE congeners to Σ_{20} PBDEs in sediments were very low at most sampling sites. The exceptions were sediment samples collected at S3 and S6, where PentaBDE accounted for 52.29 % (S3) and 70.14 % (S6) of Σ_{20} PBDEs, respectively (Fig. 2). This may be due to the wide use of these pollutants, not only at e-waste recycling workshops, but also by the clothing industries near these two sites.

Table 3 Comparison of the levels of polybrominated diphenyl ether and tetrabromobisphenol A contamination in sediment samples of this study with those reported in previous studies

Location of sediment sampling	Levels detected	Sampling year	References
PBDEs (ng g⁻¹ dw)			
This study area, China	0–6.0 × 10 ³	2013	This study
Southern part, China	31–5.7 × 10 ³	2006	Bjorklund et al. (2012)
Pearl River Delta, China	3.7–2.5 × 10 ³	2009–2010	Bradley et al. (2011)
Lake Chaohu, China	2.4 × 10 ² –2.1 × 10 ³	2009	Chen et al. (2013)
The Coastal East China Sea, China	0.3–53	2006–2007	Chen et al. (2007)
Lake Shihwa, Korea	1.3–18700	2008	An et al. (2011)
Han River, Nakdong River, Geum River, Korea	0.46–1.8 × 10 ³	2005–2008	Commission (1996)
Goseong, Korea	0.05–11	2011	Commission (2003)
San Francisco Bay, U. S.	2.1–8.0	2007	Cristale et al. (2013)
White Lake and Muskegon Lake in Michigan, USA	0.4–3.9	2006	Cristale et al. (2013)
Lake Maggiore, Italy	0.06–2.6	2005	de Wit et al. (2010)
Monastir Bay, Tunisia, Central Mediterranean	0–0.1	2007–2008	Di Toro et al. (1991)
TBBPA (ng g⁻¹ dry weight)			
This study area, China	0–2.3 × 10 ²	2013	This study
South China, China	3.8–2.3 × 10 ²	2006	Bjorklund et al. (2012)
Pearl River Delta, China	0.06–3.0 × 10 ²	2009–2010	Du et al. (2013)
Catalonia, Spain	0–4.7 × 10 ²	2009	Feng et al. (2012)
Dongjiang River, South China	0–4.5 × 10 ²	2009	Binelli et al. (2007)

TBBPA tetrabromobisphenol A

PBDEs are hydrophobic and more readily adsorbed on organic sediment. Therefore, sediment contamination is a better indicator of long-term regional pollution. For insight into the complete regional pollution profile, we determined the average values of PBDE congeners in the sediment samples across all sites (ESM Fig. S3). PentaBDE, containing the tri- to hepta-BDE congeners, accounted for 22.36 % of Σ₂₀PBDEs, of which BDE-47 and BDE-99 were the two predominant species, accounting for 28.71 and 29.56 % of the PentaBDE congeners, respectively. Both BDE-47 and BDE-99 are also major contributors to the total PentaBDE congeners found in technical products (Alaee et al. 2003), and they can be easily released into environment during e-waste dismantling processes. A general finding was that BDE-47, BDE-99, BDE-100, BDE-153, and BDE-154 comprised a mean of 67.26 % of the PentaBDE congeners, similar to the composition of PentaBDE congeners in technical products (La Guardia et al. 2006).

Generally, BDE-183 is the major congener of the OctaBDE congeners found in technical products and is taken as an indicator of the presence of OctaBDE

congeners (Law et al. 2003). In our study, BDE-183 was not detected in any water samples, but it was present in most sediment samples (Tables 1, 2; Fig. 3), suggesting that OctaBDE congeners were previously processed in most parts of the study area. BDE-183 was present in the sediment samples, but not the water samples, primarily due to its hydrophobic properties. It is worth noting that other forms of octa-BDE congeners (BDE-196, BDE-197, BDE-203) and nona-BDE (BDE-206, BDE-207, BDE-208) congeners were detected in some of the water and sediment samples. The production and use of DecaBDE congeners are not restricted in many countries; this is particularly true in China, where DecaBDE is a main component in the production of BFRs.

Our results align well with those of previous studies where octa- and nona-BDEs were also detected in core sediments (Chen et al. 2007). One reasonable explanation is that the DecaBDE congeners found in technical products contain significant amounts of octa- and nona-BDEs. For example, two domestic technical DecaBDE products were found to contain 8.2–10.4 % (w/w) octa- and nona-BDEs (Chen et al.

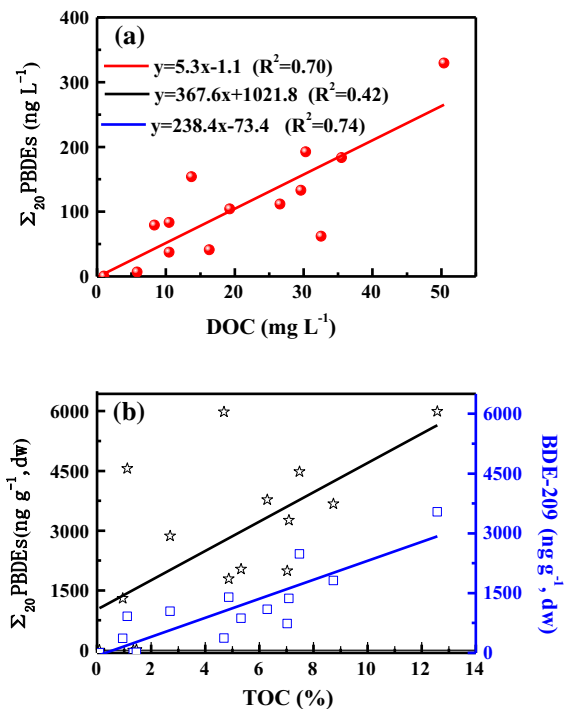


Fig. 2 Relationship between dissolved organic carbon (*DOC*) and Σ_{20} PBDEs in the water samples (a) and between total organic carbon (*TOC*) contents and Σ_{20} PBDEs as well as BDE-209 in the sediment samples (b). *dw* Dry weight

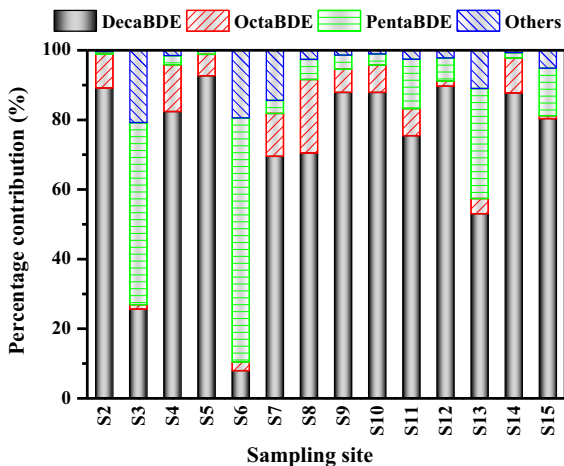


Fig. 3 Percentage contributions of individual congeners to Σ_{20} PBDEs concentrations in sediment collected at different sampling sites (S1–S15). *PentaBDE* BDE congeners BDE-47, -99, -100, -153, -154, *OctaBDE* BDE congeners BDE-138, -183, -153, -154 and octaBDEs, *DecaBDE* nonaBDEs and fully brominated BDE-209, *Others* PBDE congeners containing the remaining BDE congeners analyzed in this study (see Tables 1, 2)

2007); technical DecaBDE products from Europe (Bromakal 82-0DE) and North America (Saytex 102E) were also found to contain octa- and nona-BDEs—2.5 and 9.9 % (w/w), respectively (La Guardia et al. 2006). As such, it is considered that octa- and nona-BDEs in the environment are mainly derived from DecaBDE congeners in technical products and partially from the debromination of BDE-209 under UV light or anaerobic conditions (An et al. 2008; Du et al. 2013; Sun et al. 2013a).

Potential PBDEs sources and distributions were investigated by analyzing the pairwise correlations between PBDE congener concentrations in the sediment samples—most PBDEs were below the detection limit and could not be measured in water (Tables 4, 5). At all sampling sites, significant correlations were found for the relatively less highly brominated congeners (tri- to hepta-BDEs), except for BDE-71 and BDE-183, while BDE-209 showed relatively low or even negative correlations with the others. The low correlations between BDE-71 and other less highly brominated congeners may indicate that a portion of the BDE-71 detected derives from the debromination of other highly brominated congeners under UV light or anaerobic conditions. Comparatively, significant correlations were observed for highly brominated congeners (octa- and nona-BDEs), with the exception of BDE-208, while relatively low correlations were found between BDE-209 and the other congeners. This pattern may indicate that tri- to hepta-BDEs sources differ from BDE-183, octa- and nona-BDEs and BDE-209 sources. That is, BDE-209 exhibited a relatively moderate correlation with octa- and nona-BDEs, but not with tri- to hepta-BDEs, implying that tri- to hepta-BDEs were not BDE-209 debromination products and octa- and nona-BDEs were BDE-209 debromination products (Sun et al. 2013a; Huang et al. 2014b).

Pollution profiles of phenolic BFRs and BPA

The pollution profiles of phenolic BFRs and BPA other than PBDEs were also investigated (ESM Fig. S4). These pollutants were detected in all water and sediment samples, with the exception of the control site. The concentrations of these compounds in the water samples ranged from not detectable to 3.2×10^2 ng L⁻¹ (average of 1.1×10^2 ng L⁻¹) for TBP; from not detectable to 37 ng L⁻¹ (average of

Table 4 Correlation coefficient matrix for 12 tri- to hepta-BDEs and BDE-209 concentrations in sediment samples

BDE congener	BDE-17	BDE-28	BDE-71	BDE-47	BDE-66	BDE-100	BDE-99	BDE-85	BDE-154	BDE-153	BDE-138	BDE-183	BDE-209
BDE-17	1.000												
BDE-28	0.996**	1.000											
BDE-71	−0.037	1.000	1.000										
BDE-47	−0.037	−0.037	1.000	1.000									
BDE-66	0.999**	0.955**	0.948**	1.000	1.000								
BDE-100	0.948**	0.955**	1.000	0.948**	1.000	1.000							
BDE-99	0.769**	0.782**	0.769**	0.769**	0.769**	0.918**	1.000						
BDE-85	0.827**	0.622*	0.827**	0.607*	0.607*	0.607*	0.607*	1.000					
BDE-154	0.834**	0.680**	0.834**	1.000	1.000	0.856**	0.856**	1.000	1.000				
BDE-153	0.898**	0.860**	0.898**	0.856**	0.856**	0.797**	0.797**	0.988**	0.988**	1.000			
BDE-138	0.986**	0.986**	0.986**	0.954**	0.954**	0.954**	0.954**	0.954**	0.954**	0.954**	1.000		
BDE-183	0.976**	0.008	0.976**	0.109	0.109	0.109	0.109	0.109	0.109	0.109	0.060	1.000	
BDE-209	−0.079	0.789	−0.102	0.728	0.715**	0.004	−0.128	0.663	−0.125	0.670	−0.050	0.865	1.000

* Correlation is significant at $p < 0.05$; ** correlation is significant at $p < 0.01$

3.7 ng L^{−1}) for PeBP; from not detectable to 9.2 × 10² ng L^{−1} (average of 2.3 × 10² ng L^{−1}) for TBBPA; from not detectable to 8.6 × 10² ng L^{−1} (average of 4.0 × 10² ng L^{−1}) for BPA. The highest TBBPA and BPA concentrations (9.2 × 10² and 8.6 × 10² ng L^{−1}, respectively) were in samples from S5.

Comparatively, TBP, PeBP, TBBPA, and BPA pollution was only slight in the sediment samples, ranging from not detectable to 47 ng g^{−1} (average of 21 ng g^{−1}) for TBP; from not detectable to 25 ng g^{−1} (average of 3.1 ng g^{−1}) for PeBP; from not detectable to 2.4 × 10² ng g^{−1} (average of 84 ng g^{−1}) for TBBPA; from not detectable to 5.6 × 10² ng g^{−1} (average of 1.0 × 10² ng g^{−1}) for BPA. The highest concentrations of TBBPA and BPA (2.4 × 10² and 5.7 × 10² ng g^{−1}, respectively) were found in sediment sampled at S6.

TBBPA is the most widely used BFR worldwide (Shi et al. 2013), but its concentrations were lower than Σ₂₀PBDEs in all sediment samples and higher than Σ₂₀PBDEs in all water samples collected at all study sites. Two factors may explain this. First, compared with PBDEs (logK_{ow} ≥ 5.48), TBBPA (logK_{ow} = 4.50) is more hydrophilic and therefore migrates more easily in water. The pH values of the water samples across our study sites ranged from 7.1 to 8.5, which approximates or exceeds the pK_a of TBBPA (pK_a = 7.5; ESM Table S3) and thereby induces a relatively high aqueous solubility of TBBPA (Kuramochi et al. 2008). Second, TBBPA can be biodegraded and transformed into less brominated phenolic BFRs under anoxic and anaerobic conditions (An et al. 2011b; Liu et al. 2013; Huang et al. 2014a; Li et al. 2014).

Compared with available data on PBDEs, little information is available on TBBPA pollution. We found that TBBPA concentrations in our water samples were two orders of magnitude higher than those of Dongjiang River, South China (He et al. 2013; ESM Table S2), while the levels of TBBPA in the sediment samples were equivalent to those reported in South China (Zhang et al. 2009), the Pearl River Delta of China (Feng et al. 2012), and Catalonia, Spain (Gorga et al. 2013; Table 3). Similar to TBBPA, BPA was also detected in both the water and sediment samples across all sites, with the exception of control site S1, but its concentration was generally much higher at all sites than that of TBBPA (ESM Fig. S4),

Table 5 Correlation coefficient matrix for octa- to nona-BDEs and BDE-209 concentrations in sediment samples

BDE congener	BDE197	BDE203	BDE196	BDE208	BDE207	BDE206	BDE209
BDE-197	1.000	0.935**	0.972**	0.326	0.412	0.581*	0.346
BDE-203		1.000	0.969**	0.500	0.587*	0.737**	0.403
BDE-196			1.000	0.484	0.546*	0.718**	0.259
BDE-208				1.000	0.981**	0.882**	0.029
BDE-207					1.000	0.891**	0.182
BDE-206						1.000	0.147
BDE-209							1.000

* Correlation is significant at $p < 0.05$; ** correlation is significant at $p < 0.01$

possibly because a portion of the BPA can originate from the debromination of TBBPA through various biodegradation processes (An et al. 2011b; Huang et al. 2014a) and because BPA is widely used as an intermediate in the production of flame retardants and other products (Staples et al. 1998).

Compared with TBBPA, PeBP concentrations were much lower or below the detection limit at some sampling sites (S1, S2, S3, S9 and S10 in water, and S1, S4, S7, S11 and S12 in sediment) (ESM Fig. S4). Although TBP was detected in the water samples (except S1) and sediment samples (except S1 and S7) at almost all sites, its concentrations were lower than those of TBBPA. Only sporadic studies have reported the pollution of PeBP and TBP. Examples include a study of TBP pollution in indoor air and dust samples from two modern homes in Japan (Takigami et al. 2009) and a study assessing TBP in the breast milk and serum of Okinawans (Fujii et al. 2014). No reports are available for water and sediment samples.

Risk assessment of PBDEs and phenolic BFRs

Estrogenic activity assessment

It is well-known that TBBPA and BPA are linked with endocrine-disrupting activities (Li et al. 2012a) and can mimic or antagonize the biological function of natural hormones (Kitamura et al. 2005). The European Commission has set the threshold of endocrine disrupting effects at $1 \text{ ng E}_2 \text{ L}^{-1}$, meaning that when the total E_2EQ of any individual endocrine-disrupting chemical exceeds $1 \text{ ng E}_2 \text{ L}^{-1}$, that chemical may affect the endocrine systems of aquatic organisms in the receiving water environments (EU Commission 1996). We found that TBBPA and BPA had stronger

estrogenic activities in the water samples than in the sediment samples at all sites except the control site (Fig. 4). Nevertheless, even the highest $\text{E}_2\text{EQ}_{\text{Total}}$ in our study ($12,196.57 \times 10^{-6} \text{ ng E}_2 \text{ L}^{-1}$ in water at S5 and $1,035.78 \times 10^{-6} \text{ ng E}_2 \text{ L}^{-1}$ in sediment at S6) was far less than $1 \text{ ng E}_2 \text{ L}^{-1}$, suggesting there was no estrogenic risk from TBBPA and BPA pollution at our study site. This result is consistent with the results of Jin et al. (2013).

Conversely, BPA was a definite contributor of total estrogenic activities, with E_2EQ levels that were two- to four orders of magnitude higher than those of TBBPA, although the concentration discrepancy between TBBPA and BPA in the water and sediment samples was not as large. This result may be due to the relatively higher estrogenic equivalency factor of BPA (13.7×10^{-6}) compared to TBBPA (13.7×10^{-6}) (Kitamura et al. 2005).

Eco-toxicity assessment

In addition to estrogenic activity, we also assessed the eco-toxicity of PBDEs and phenolic BFRs using the recommendation from the Technical Guidance Document on Risk Assessment (EU Commission 2003). Taking into account the possible joint effects of those compounds with a similar mode of action (Ginebreda et al. 2010), we obtained a summed RQ of each individually detected compound at each site. Figure 5 shows the total eco-toxicities of PBDEs, phenolic BFRs, and BPA at three trophic levels in water samples collected at all sites. With the exception of samples collected at S1 and S10, all samples exhibited expected potential adverse effects ($\text{RQ}_{\text{Total}} \geq 100$) on the three evaluated organisms (Marcus et al. 2010). No eco-toxicity was found at the control site, but at S10

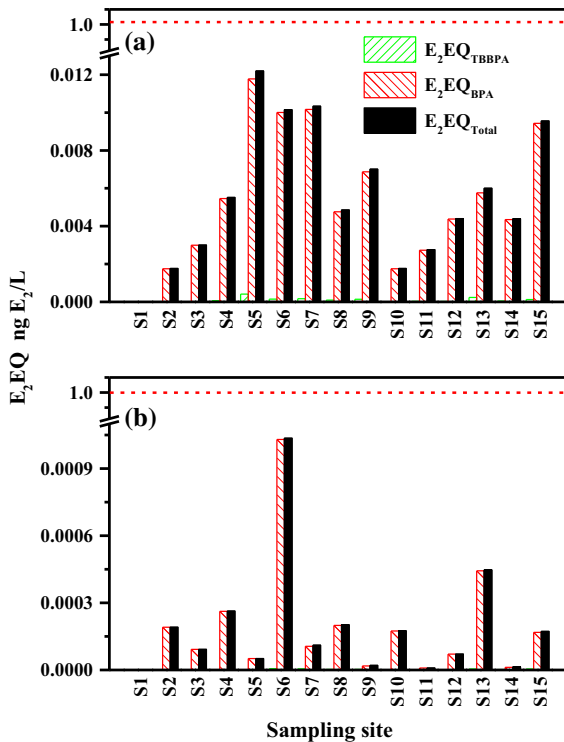


Fig. 4 The estimated 17β-estradiol equivalency quantity (E_{EQ2}) of tetrabromobisphenol A (TBBPA) and bisphenol A (BPA) in the water samples (a) and sediment samples (b). S1–S15 Sampling sites

we did detect expected potential adverse effects ($RQ_{Total} \geq 100$) on fish and daphnia, and potential adverse effects ($10 \leq RQ_{Total} < 100$) on green algae (Marcus et al. 2010).

ESM Figure S5 also presents the risk assessment of PBDEs, phenolic BFRs, and BPA at each sediment sample for the three evaluated organisms. Similar to the water eco-toxicities, the control sample showed no risk at the three trophic levels, but the eco-toxicity of the sediment collected at S11 and S12 indicated small potential adverse effects ($1.0 \leq RQ_{Total} < 10$) on fish as well as daphnia; the other sampling sites revealed the expected potential adverse effects ($RQ_{Total} \geq 100$) on fish and daphnia. One explanation may be the high DOC (32.53 and 50.39 $mg L^{-1}$, respectively) in water and low TOC (1.34 and 1.46 %, respectively) in sediment at S11 and S12, allowing more organics to dissolve in the water and be transported to other places.

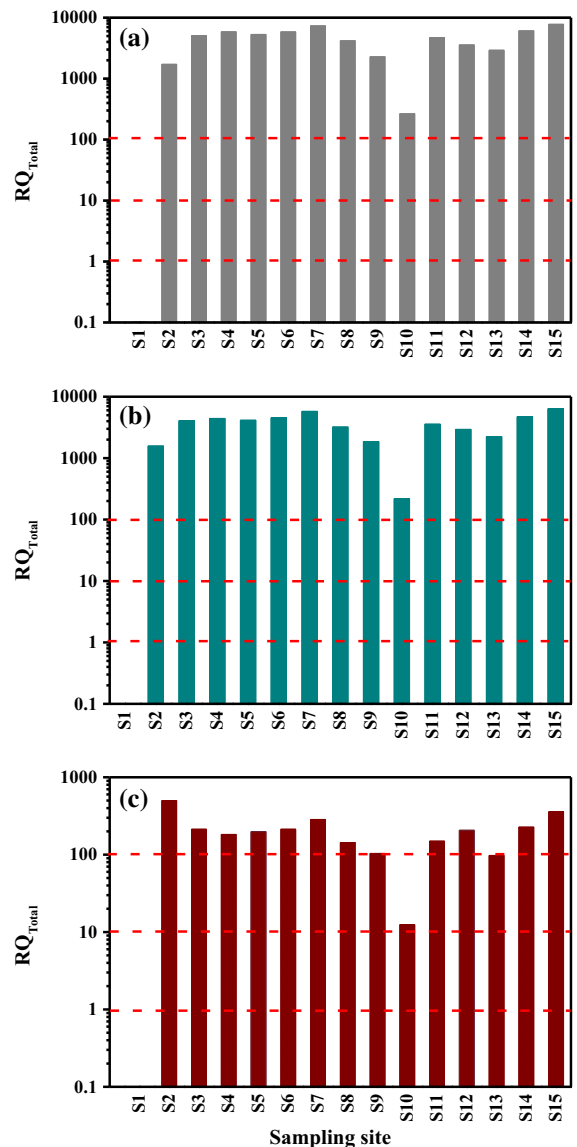


Fig. 5 Total risk quotient (RQ_{Total}) of PBDEs, pentabromophenol (PeBP), 2,4,6-tribromophenol (TBP), TBBPA, and BPA for fish (a), daphnia (b), green algae (c) in water. S1–S15 Sampling sites

The results across the three evaluated organisms suggested that green algae is least affected by BFRs. Some studies have indicated that BFRs can be accumulated and magnified in biota (de Wit et al. 2010; Fujii et al. 2014); as such, additional study is needed to better understand the bioaccumulation, as well as the toxicology, of these BFRs in the environment.

Conclusion

The dismantling of e-waste has become a source of a variety of toxic and persistent chemicals, including PBDEs, TBP, PeBP, TBBPA, and BPA. Our results indicate that these contaminants can disperse widely as they were found throughout our surveyed region. PBDEs were mainly present in the sediment samples; tri- to nona-BDEs (instead of BDE-209) were mainly detected in the water samples, with BDE-209 being the dominant congener in the sediment. TBP, PeBP, TBBPA, and BPA were also detected in water and sediments. TBBPA concentrations were lower than Σ_{20} PBDEs concentrations in the sediment. BPA was detected in the water and sediment samples collected at all sites except the control, and its concentrations were much higher than those of TBBPA at most sites. TBP and PeBP were detected in both the water and sediment samples collected at almost all sites, at concentrations that were lower than TBBPA levels or below the detection limit at most sites. Estrogenic activity assessment showed that no estrogenic risk could be expected from the water and sediment based on TBBPA and BPA estrogenic activity, while eco-toxicity assessment at three representative trophic levels showed that different risks were present at most sampling sites. Monitoring these compounds over time will help researchers better understand the usage, emission, toxicity, transformation, and effective decontamination of these pollutants.

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References

- Alaee, M., Arias, P., Sjödin, A., & Bergman, Å. (2003). An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environment International*, 29(6), 683–689.
- An, T. C., Chen, J. X., Li, G. Y., Ding, X. J., Sheng, G. Y., Fu, J. M., et al. (2008). Characterization and the photocatalytic activity of TiO₂ immobilized hydrophobic montmorillonite photocatalysts degradation of decabromodiphenyl ether (BDE 209). *Catalysis Today*, 139(1–2), 69–76.
- An, T. C., Zhang, D. L., Li, G. Y., Mai, B. X., & Fu, J. M. (2011a). On-site and off-site atmospheric PBDEs in an electronic dismantling workshop in south China: Gas-particle partitioning and human exposure assessment. *Environmental Pollution*, 159(12), 3529–3535.
- An, T. C., Zu, L., Li, G. Y., Wan, S. G., Mai, B. X., & Wong, P. K. (2011b). One-step process for debromination and aerobic mineralization of tetrabromobisphenol-A by a novel *Ochrobactrum* sp. T isolated from an e-waste recycling site. *Bioresource Technology*, 102(19), 9148–9154.
- Arbeli, Z., & Ronen, Z. (2003). Enrichment of a microbial culture capable of reductive debromination of the flame retardant tetrabromobisphenol-A, and identification of the intermediate metabolites produced in the process. *Bio-degradation*, 14(6), 385–395.
- Binelli, A., Sarkar, S. K., Chatterjee, M., Riva, C., Parolini, M., Bhattacharya, B. D., et al. (2007). Concentration of polybrominated diphenyl ethers (PBDEs) in sediment cores of Sundarban mangrove wetland, northeastern part of Bay of Bengal (India). *Marine Pollution Bulletin*, 54(8), 1220–1229.
- Bjorklund, J. A., Thuresson, K., Cousins, A. P., Sellstrom, U., Emenius, G., & de Wit, C. A. (2012). Indoor air is a significant source of tri-decaborinated diphenyl ethers to outdoor air via ventilation systems. *Environmental Science and Technology*, 46(11), 5876–5884.
- Bradley, P. W., Wan, Y., Jones, P. D., Wiseman, S., Chang, H., Lam, M. H., et al. (2011). PBDEs and methoxylated analogues in sediment cores from two Michigan, USA, inland lakes. *Environmental Toxicology and Chemistry*, 30(6), 1236–1242.
- Chen, S. J., Feng, A. H., He, M. J., Chen, M. Y., Luo, X. J., & Mai, B. X. (2013). Current levels and composition profiles of PBDEs and alternative flame retardants in surface sediments from the Pearl River Delta, southern China: Comparison with historical data. *Science of the Total Environment*, 444, 205–211.
- Chen, S. J., Luo, X. J., Lin, Z., Luo, Y., Li, K. C., Peng, X. Z., et al. (2007). Time trends of polybrominated diphenyl ethers in sediment cores from the Pearl River Estuary, South China. *Environmental Science and Technology*, 41(16), 5595–5600.
- EU Commission. (1996). Technical guidance document in support of commission directive 93/67/EEC on risk assessment for new notified substances and commission regulation (EC) No. 1488/94 on risk assessment for existing substances. *Office for Official Publications of the European Communities, Luxembourg*, pp. 328–334.
- EU Commission. (2003). Technical guidance document on risk assessment in support of commission Directive 93/67/EEC on risk assessment for new notified substances and commission regulation (EC) No 1488/94 on risk assessment for existing substances. Directive 98/8/EC of the European parliament and of the council concerning the placing of biocidal products on the market. Part II. Office for Official Publications of the European Communities, Luxembourg.
- Cristale, J., García Vázquez, A., Barata, C., & Lacorte, S. (2013a). Priority and emerging flame retardants in rivers: Occurrence in water and sediment, *Daphnia magna* toxicity and risk assessment. *Environment International*, 59, 232–243.

- Cristale, J., Katsoyiannis, A., Sweetman, A. J., Jones, K. C., & Lacorte, S. (2013b). Occurrence and risk assessment of organophosphorus and brominated flame retardants in the River Aire (UK). *Environmental Pollution*, *179*, 194–200.
- de Wit, C. A., Herzke, D., & Vorkamp, K. (2010). Brominated flame retardants in the Arctic environment—Trends and new candidates. *Science of the Total Environment*, *408*(15), 2885–2918.
- Di Toro, D. M., Zarba, C. S., Hansen, D. J., Berry, W. J., Swartz, R. C., Cowan, C. E., et al. (1991). Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environmental Toxicology and Chemistry*, *10*(12), 1541–1583.
- Du, W. C., Ji, R., Sun, Y. Y., Zhu, J. G., Wu, J. C., & Guo, H. Y. (2013). Fate and ecological effects of decabromodiphenyl ether in a field lysimeter. *Environmental Science and Technology*, *47*(16), 9167–9174.
- Feng, A. H., Chen, S. J., Chen, M. Y., He, M. J., Luo, X. J., & Mai, B. X. (2012). Hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) in riverine and estuarine sediments of the Pearl River Delta in southern China, with emphasis on spatial variability in diastereoisomer- and enantiomer-specific distribution of HBCD. *Marine Pollution Bulletin*, *64*(5), 919–925.
- Fujii, Y., Nishimura, E., Kato, Y., Harada, K. H., Koizumi, A., & Haraguchi, K. (2014). Dietary exposure to phenolic and methoxylated organohalogen contaminants in relation to their concentrations in breast milk and serum in Japan. *Environment International*, *63*, 19–25.
- Ginebreda, A., Muñoz, I., de Alda, M. L., Brix, R., López-Doval, J., & Barceló, D. (2010). Environmental risk assessment of pharmaceuticals in rivers: Relationships between hazard indexes and aquatic macroinvertebrate diversity indexes in the Llobregat River (NE Spain). *Environment International*, *36*(2), 153–162.
- Gorga, M., Martínez, E., Ginebreda, A., Eljarrat, E., & Barcelo, D. (2013). Determination of PBDEs, HBB, PBEB, DBDPE, HBCD, TBBPA and related compounds in sewage sludge from Catalonia (Spain). *Science of the Total Environment*, *444*, 51–59.
- He, M. J., Luo, X. J., Yu, L. H., Wu, J. P., Chen, S. J., & Mai, B. X. (2013). Diastereoisomer and enantiomer-specific profiles of hexabromocyclododecane and tetrabromobisphenol A in an aquatic environment in a highly industrialized area, South China: Vertical profile, phase partition, and bioaccumulation. *Environmental Pollution*, *179*, 105–110.
- Huang, H. W., Chang, B. V., & Lee, C. C. (2014a). Reductive debromination of decabromodiphenyl ether by anaerobic microbes from river sediment. *International Biodeterioration and Biodegradation*, *87*, 60–65.
- Huang, D. Y., Zhao, H. Q., Liu, C. P., & Sun, C. X. (2014b). Characteristics, sources, and transport of tetrabromobisphenol A and bisphenol A in soils from a typical e-waste recycling area in South China. *Environmental Science and Pollution Research*, *21*(9), 5818–5826.
- Jin, S. W., Yang, F. X., Xu, Y., Dai, H. P., & Liu, W. P. (2013). Risk assessment of xenoestrogens in a typical domestic sewage-holding lake in China. *Chemosphere*, *93*(6), 892–898.
- Kitamura, S., Suzuki, T., Sanoh, S., Kohta, R., Jinno, N., Sugihara, K., et al. (2005). Comparative study of the endocrine-disrupting activity of bisphenol A and 19 related compounds. *Toxicological Sciences*, *84*(2), 249–259.
- Kuramochi, H., Kawamoto, K., Miyazaki, K., Nagahama, K., Maeda, K., Li, X. W., et al. (2008). Determination of physicochemical properties of tetrabromobisphenol A. *Environmental Toxicology and Chemistry*, *27*(12), 2413–2418.
- La Guardia, M. J., Hale, R. C., & Harvey, E. (2006). Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-pbde technical flame-retardant mixtures. *Environmental Science and Technology*, *40*(20), 6247–6254.
- Labadie, P., Tlili, K., Alliot, F., Bourges, C., Desportes, A., & Chevreuil, M. (2010). Development of analytical procedures for trace-level determination of polybrominated diphenyl ethers and tetrabromobisphenol A in river water and sediment. *Analytical and Bioanalytical Chemistry*, *396*(2), 865–875.
- Law, R. J., Alaei, M., Allchin, C. R., Boon, J. P., Lebeuf, M., Lepom, P., & Stern, G. A. (2003). Levels and trends of polybrominated diphenylethers and other brominated flame retardants in wildlife. *Environment International*, *29*(6), 757–770.
- Lee, H. J., An, S., & Kim, G. B. (2014). Background level and composition of polybrominated diphenyl ethers (PBDEs) in creek and subtidal sediments in a rural area of Korea. *Science of the Total Environment*, *470–471*, 1479–1484.
- Lee, I. S., Kim, K. S., Kim, S. J., Yoon, J. H., Choi, K. H., Choi, S. D., & Oh, J. E. (2012). Evaluation of mono- to decabrominated diphenyl ethers in riverine sediment of Korea with special reference to the debromination of DeBDE209. *Science of the Total Environment*, *432*, 128–134.
- Li, Y., Lin, T., Chen, Y., Hu, L., Guo, Z., & Zhang, G. (2012a). Polybrominated diphenyl ethers (PBDEs) in sediments of the coastal East China Sea: Occurrence, distribution and mass inventory. *Environmental Pollution*, *171*, 155–161.
- Li, F. J., Wang, J. J., Nastold, P., Jiang, B. Q., Sun, F. F., Zenker, A., et al. (2014). Fate and metabolism of tetrabromobisphenol A in soil slurries without and with the amendment with the alkylphenol degrading bacterium *Sphingomonas* sp strain TTNP3. *Environmental Pollution*, *193*, 181–188.
- Li, G. Y., Zu, L., Wong, P. K., Hui, X., Lu, Y., Xiong, J. K., & An, T. C. (2012b). Biodegradation and detoxification of bisphenol A with one newly-isolated strain *Bacillus* sp. GZB: Kinetics, mechanism and estrogenic transition. *Bioresour Technol*, *114*, 224–230.
- Liu, F., Liao, C. Y., Fu, J. J., Lv, J. G., Xue, Q. Z., & Jiang, G. B. (2014). Polycyclic aromatic hydrocarbons and organochlorine pesticides in rice hull from a typical e-waste recycling area in southeast China: Temporal trend, source, and exposure assessment. *Environmental Geochemistry and Health*, *36*(1), 65–77.
- Liu, J., Wang, Y. F., Jiang, B. Q., Wang, L. H., Chen, J. Q., Guo, H. Y., & Ji, R. (2013). Degradation, metabolism, and bound-residue formation and release of tetrabromobisphenol A in soil during sequential anoxic-oxic incubation. *Environmental Science and Technology*, *47*(15), 8348–8354.
- Lopez, P., Brandsma, S. A., Leonards, P. E. G., & De Boer, J. (2009). Methods for the determination of phenolic brominated flame retardants, and by-products, formulation

- intermediates and decomposition products of brominated flame retardants in water. *Journal of Chromatography A*, 1216(3), 334–345.
- Malik, R. N., Mehboob, F., Ali, U., Katsoyiannis, A., Schuster, J. K., Moeckel, C., & Jones, K. C. (2014). Organo-halogenated contaminants (OHCs) in the sediments from the Soan River, Pakistan: OHCs (adsorbed TOC) burial flux, status and risk assessment. *Science of the Total Environment*, 481, 343–351.
- Marcus, M. D., Covington, S., Liu, B., & Smith, N. R. (2010). Use of existing water, sediment, and tissue data to screen ecological risks to the endangered Rio Grande silvery minnow. *The Science of the Total Environment*, 409(1), 83–94.
- Mariani, G., Canuti, E., Castro-Jiménez, J., Christoph, E. H., Eisenreich, S. J., Hanke, G., et al. (2008). Atmospheric input of POPs into Lake Maggiore (Northern Italy): PBDE concentrations and profile in air, precipitation, settling material and sediments. *Chemosphere*, 73[Suppl 1], S114–S121.
- Möller, A., Xie, Z., Sturm, R., & Ebinghaus, R. (2011). Polybrominated diphenyl ethers (PBDEs) and alternative brominated flame retardants in air and seawater of the European Arctic. *Environmental Pollution*, 159(6), 1577–1583.
- Moon, H. B., Choi, M., Yu, J., Jung, R. H., & Choi, H. G. (2012). Contamination and potential sources of polybrominated diphenyl ethers (PBDEs) in water and sediment from the artificial Lake Shihwa, Korea. *Chemosphere*, 88(7), 837–843.
- Nakajima, A., Saigusa, D., Tetsu, N., Yamakuni, T., Tomioka, Y., & Hishinuma, T. (2009). Neurobehavioral effects of tetrabromobisphenol A, a brominated flame retardant, in mice. *Toxicology Letters*, 189(1), 78–83.
- Nouira, T., Rizzo, C., Chouba, L., Budzinski, H., & Boussetta, H. (2013). Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in surface sediments from Monastir Bay (Tunisia, Central Mediterranean): Occurrence, distribution and seasonal variations. *Chemosphere*, 93(3), 487–493.
- National Industrial Chemicals Notification and Assessments Scheme (NICNAS). (2001). PBFs, P.F.R. Priority Existing Chemical Assessment Report No. 20. NICNAS/Australian Government, Marrickville.
- Polo, M., Llompарт, M., Garcia-Jares, C., Gomez-Noya, G., Bollain, M. H., & Cela, R. (2006). Development of a solid-phase microextraction method for the analysis of phenolic flame retardants in water samples. *Journal of Chromatography A*, 1124(1–2), 11–21.
- Reistad, T., Mariussen, E., & Fonnum, F. (2005). The effect of a brominated flame retardant, tetrabromobisphenol-A, on free radical formation in human neutrophil granulocytes: The involvement of the MAP kinase pathway and protein kinase C. *Toxicological Sciences*, 56, 95–104.
- Ronen, Z., & Abeliovich, A. (2000). Anaerobic-aerobic process for microbial degradation of tetrabromobisphenol A. *Applied and Environmental Microbiology*, 66(6), 2372–2377.
- Sánchez-Avila, J., Tauler, R., & Lacorte, S. (2012). Organic micropollutants in coastal waters from NW Mediterranean Sea: Sources distribution and potential risk. *Environment International*, 46, 50–62.
- Shi, Z. X., Jiao, Y., Hu, Y., Sun, Z. W., Zhou, X. Q., Feng, J. F., et al. (2013). Levels of tetrabromobisphenol A, hexabromocyclododecanes and polybrominated diphenyl ethers in human milk from the general population in Beijing, China. *Science of the Total Environment*, 452–453, 10–18.
- Staples, C. A., Dome, P. B., Klecka, G. M., Oblock, S. T., & Harris, L. R. (1998). A review of the environmental fate, effects, and exposures of bisphenol A. *Chemosphere*, 36(10), 2149–2173.
- Sun, C., Chang, W., Ma, W., Chen, C., & Zhao, J. (2013a). Photoreductive debromination of decabromodiphenyl ethers in the presence of carboxylates under visible light irradiation. *Environmental Science and Technology*, 47(5), 2370–2377.
- Sun, Y., Huang, H., Sun, Y., Wang, C., Shi, X. L., Hu, H. Y., et al. (2013b). Ecological risk of estrogenic endocrine disrupting chemicals in sewage plant effluent and reclaimed water. *Environmental Pollution*, 180, 339–344.
- Takigami, H., Suzuki, G., Hirai, Y., & Sakai, Si. (2009). Brominated flame retardants and other polyhalogenated compounds in indoor air and dust from two houses in Japan. *Chemosphere*, 76(2), 270–277.
- Tang, Z. W., Huang, Q. F., Cheng, J. L., Yang, Y. F., Yang, J., Guo, W., et al. (2014). Polybrominated diphenyl ethers in soils, sediments, and human hair in a plastic waste recycling area: A neglected heavily polluted area. *Environmental Science and Technology*, 48(3), 1508–1516.
- Wang, X. W., Xi, B. D., Huo, S. L., Deng, L., Pan, H. W., Xia, X. F., et al. (2013). Polybrominated diphenyl ethers occurring in major inflowing rivers of Lake Chaohu (China): Characteristics, potential sources and inputs to lake. *Chemosphere*, 93(8), 1624–1631.
- Wong, C. S. C., Duzgoren-Aydin, N. S., Aydin, A., & Wong, M. H. (2007). Evidence of excessive releases of metals from primitive e-waste processing in Guiyu. *China. Environmental Pollution*, 148(1), 62–72.
- Xing, G. H., Chan, J. K. Y., Leung, A. O. W., Wu, S. C., & Wong, M. H. (2009). Environmental impact and human exposure to PCBs in Guiyu, an electronic waste recycling site in China. *Environment International*, 35(1), 76–82.
- Yu, Z. Q., Liao, R., Li, H. R., Mo, L. G., Zeng, X. Y., Sheng, G. Y., & Fu, J. M. (2011). Particle-bound Dechlorane Plus and polybrominated diphenyl ethers in ambient air around Shanghai, China. *Environmental Pollution (Barking, Essex: 1987)*, 159(10), 2982–2988.
- Zhang, D. L., An, T. C., Qiao, M., Loganathan, B. G., Zeng, X. Y., Sheng, G. Y., & Fu, J. M. (2011). Source identification and health risk of polycyclic aromatic hydrocarbons associated with electronic dismantling in Guiyu town, South China. *Journal of Hazardous Materials*, 192(1), 1–7.
- Zhang, X. L., Luo, X. J., Chen, S. J., Wu, J. P., & Mai, B. X. (2009). Spatial distribution and vertical profile of polybrominated diphenyl ethers, tetrabromobisphenol A, and decabromodiphenylethane in river sediment from an industrialized region of South China. *Environmental Pollution*, 157(6), 1917–1923.
- Zhao, X., Zhang, H., Ni, Y., Lu, X., Zhang, X., Su, F., et al. (2011). Polybrominated diphenyl ethers in sediments of the

Daliao River Estuary, China: Levels, distribution and their influencing factors. *Chemosphere*, 82(9), 1262–1267.

[Zu, L., Li, G. Y., An, J. B., Li, J. J., & An, T. C. \(2013\). Kinetic optimization of biodegradation and debromination of](#)

[2,4,6-tribromophenol using response surface methodology. *International Biodeterioration and Biodegradation*, 76, 18–23.](#)