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Short-range transport of contaminants released from e-waste recycling site in South China†‡

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The transport behaviors of a suite of contaminants released from electronic waste (e-waste) recycling operations, including polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and heavy metals, were evaluated by analyzing the contaminant residues in surface soils sampled in the surrounding area of an e-waste recycling site in South China. Concentrations of PBDEs and PCBs in the soil samples ranged from 0.565 to 2908 ng g⁻¹ dw and from 0.267 to 1891 ng g⁻¹ dw, respectively, while soil residues were 0.082–2.56, 3.22–287, and 16.3–162 µg g⁻¹ dw for Cd, Cu, and Pb, respectively. Concentrations of PBDEs and PCBs in soil decreased with increasing distance from the source of pollution, indicating possible PBDE and PCB contamination in the surrounding areas due to the short-range transport of these compounds from the e-waste recycling site. Although no significant difference in the short-range transport potential among PBDE and PCB congeners was observed, reductions in concentrations of the highly-brominated-BDEs and highly-chlorinated-CBs were slightly quicker than those of their less-halogen-substituted counterparts. Conversely, heavy metals showed the lowest transport potential due to their low vapor pressure, and results showed metals would remain near the pollution source instead of diffusing into the surrounding areas. Finally, mass inventories in areas near the e-waste site were 0.920, 0.134, 0.860, 4.68, 757, and 673 tons for BDE209, PBDEs (excluding BDE209), PCBs, Cd, Cu, and Pb, respectively.

Introduction

Electronic waste (e-waste) has become a worldwide environmental problem due to the extensive use of electronic and electric products and their decreasing lifespan.^{1–3} As the fastest growing type of solid

waste, 20–50 million tons of e-waste is discarded yearly throughout the world, which accounts for 5% of the municipal solid waste.⁴ It was estimated that 50–80% of the global e-waste was illegally imported into Asia, from which 90% ended up in China.⁵ Most of the e-waste recycling sites in China are located in the south and east coast, including Guiyu,^{4,6,7} Longtang,^{8,9} and Taizhou.¹⁰ The commonly used e-waste dismantling and recycling operations at these sites include open acid stripping of chips, chipping and melting plastics, toner sweeping, open burning, and dumping of waste residues directly.^{1,2} As a result of the unprotected recycling techniques, a number of contaminants, such as persistent organic pollutants (POPs) (*e.g.* polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs)) and heavy metals (*e.g.* Pb and Cu), were released into the environment.^{1–3}

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Environmental impact

For more accurate evaluation of the risks of an electronic waste site to the surrounding area, the transport behaviors of the contaminants released from e-waste recycling activities need to be understood. The short-range transport potential of a suite of contaminants released from e-waste dismantling operations, including polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and heavy metals were evaluated by analyzing the contaminant residues in surface soils sampled in Longtang, an e-waste recycling site in South China, and its surrounding areas. Heavy metals showed the least transport potential due to their low vapor pressure. In contrast, it is evident that PBDE and PCB released from the e-waste recycling site would affect the surrounding areas due to the short-range transport of these compounds.

As brominated flame retardants, PBDEs are present in many electronic and electric products at levels ranging from 5 to 30%.¹¹ The release of PBDEs during the e-waste recycling activities has resulted in high concentrations of PBDEs in different environmental media including soil, sediment, biota tissue, and even human serum samples collected from the e-waste recycling sites in China.^{6,8,12–15} For instance, the sum concentrations of PBDEs in combusted residue and soil samples collected in Guiyu, which is one of the largest e-waste recycling sites in South China, were 33 000–97 400 and 2020–4250 ng g⁻¹ dw, respectively.¹⁵ The PCBs are another class of POPs that may be generated from the e-waste recycling operations, such as melting or open burning of obsolete transformers and electromotors. Recovery of valuable metals, such as Au, Ag, Al, and Cu, is the main purpose of e-waste recycling.¹⁶ Therefore, heavy metals are other major components of e-waste released contaminants and high concentrations of heavy metals were detected in water, sediment, and dust in the e-waste recycling areas.^{1,16,17}

Although the occurrence and distribution of contaminants released from e-waste recycling practices have been widely investigated, more studies are needed to understand their influence on the surrounding areas by short-range transport (SRT). In comparison to the definition of long range transport (LRT) which deals with the transport process in the long range even globally, SRT was refined in specific areas. It has been evident that POPs including PCBs and PBDEs would be subject to LRT,¹⁸ and different models have been developed to investigate their transport potential.^{19,20} The LRT model showed significantly greater transportability for chemicals with smaller sizes than those with larger sizes.¹⁰ Conversely, few studies have

addressed their SRT behaviors. Therefore, it is helpful to investigate the transport processes of these contaminants and understand their potential risks on surrounding areas resulting from the e-waste recycling practices. Reimer *et al.*^{21–24} studied the SRT of PCBs in the Canadian Arctic by comparing their congener patterns and showed PCBs would affect the surrounding environment up to 27 km. In addition, camphor tree leaves were used as biomonitors to evaluate diffusion of PBDEs from an e-waste recycling site to the surrounding regions in Southeast China, and results showed areas within 74 km may be influenced by PBDEs.¹⁰

Surface soil receives deposition of atmospheric contaminants and has been used to monitor SRT of PCBs in Canada.²⁴ In the current study soil samples collected in Longtang, a well-known e-waste recycling site in South China, and its surrounding area within a 40 km radius were analyzed for PBDEs, PCBs, and heavy metals to monitor their transport. The main objectives of the current study were to assess the SRT potential of PBDEs, PCBs, and heavy metals from an e-waste recycling site to the surrounding regions and in turn to evaluate the risks they may pose on the surrounding areas.

Materials and methods

Study site description and soil sample collection

Since the media exposure and prohibition of e-waste recycling activities in Guiyu, the center for the e-waste recycling business in South China gradually moved to Longtang, Qingyuan, which is located about 50 km north of Guangzhou, the capital of

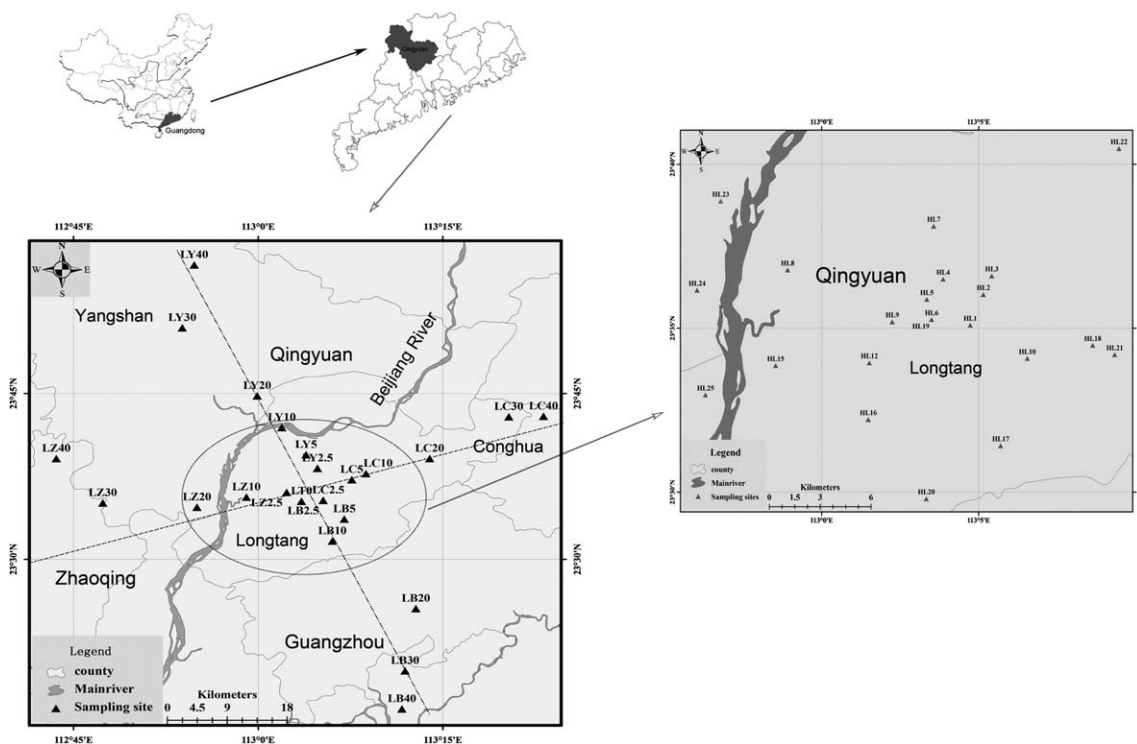


Fig. 1 Map of sampling sites surrounding the electronic waste site in Longtang, South China. Samples were collected in four directions, including LY (Longtang–Yangshan), LB (Longtang–Baiyun Mountain), LZ (Longtang–Zhaoqing), and LC (Longtang–Conghua).

Guangdong province. In the current study, Longtang and its surrounding areas within a radius of 40 km were chosen as the study regions (Fig. 1). Longtang has a history of approximately 30 years in recycling e-waste and currently houses more than 1300 workshops with 80 000 workers employed in the dismantling activities.²⁵ In order to recover metals such as Au, Cu, and Al, the e-wastes are dismantled and recycled using primitive and unprotected operations, like open burning, plastics peeling and melting, and acid leaching.⁵ As a result, a large amount of toxic chemicals (>1.7 million tons annually) were released into the atmosphere (semivolatile organics, e.g. PBDEs and PCBs) or waterways (acids with metals),²⁵ and the toxicants may reach various environmental media by precipitation or runoff. Additionally, the toxicants not only contaminated the local area, but also became a point source of contamination and pose a threat to the surrounding areas.

Dingan village in Longtang (23°35'16"N, 113°03'30"E) was selected as the center of the contamination source (site LT0) in the current study, and this village has been well known for the long-term and extensive practice of e-waste recycling activities. Surrounding the sampling center LT0, six circles with radii of 2.5, 5, 10, 20, 30, and 40 km and four radial lines with angles at approximately 90° were mapped. As shown in Fig. 1, the four directions extended to northwest (Longtang-Yangshan, LY), southeast (Longtang-Baiyun Mountain, Guangzhou, LB), southwest (Longtang-Zhaoqing, LZ), and northeast (Longtang-Conghua, LC), respectively. The cross points of the circles and the radial lines were referred to as the predetermined sampling sites to investigate the SRT potential of the contaminants released from the e-waste site. It should be noted that, however, in cases where the predetermined sampling sites were not reachable or the soil was heavily covered with vegetation, sampling was conducted in a nearby area of the predetermined site but with the same distance to the sampling center (Fig. 1). Except that the LT0 soil in Dingan Village was sampled in the e-waste recycling area, the remaining samples were collected in sites away from any burning activities to exclude other sources of contamination.

The study region is close to the Tropic of Cancer, and has mild temperatures and humid weather conditions all year long. The soil samples were collected in January and February in 2010. At each sampling site, three sub-samples of surface soil (0–5 cm) were collected in an area of about 10 m², combined and homogenized. The soil for analyzing PBDEs and PCBs was collected using a stainless steel spoon, mixed in a stainless steel pan and stored in a pre-cleaned glass jar, whereas the samples for analyzing heavy metals were sampled using a plastic spoon, homogenized in a plastic pan, and stored in plastic bags. The soil samples were transferred back to the laboratory and stored at –20 °C.

Chemicals and reagents

In the current study, 27 PBDEs (from dibromo- to decabromo-), 27 PCBs (from monochloro- to nonachloro-) and 12 heavy metals were evaluated as the contaminants released from the e-waste recycling practices. A complete list of the target contaminants can be found in Table S1 in the Electronic Supplementary Information (ESI),[†] and their respective

analytical methods are presented below. The stock solutions for PBDE and PCB standards were purchased from AccuStandard (New Haven, CT, USA), while the multi-element metal standards including Ag, As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, and Zn, were obtained from Agilent Technologies (Santa Clara, CA, USA). Decachlorobiphenyl (CB209) was added to all soil samples before extraction to be the surrogate for PBDE and PCB analysis, and it was purchased from Supelco (Bellefonte, PA, USA). Six internal standards (IS) were used for PBDE and PCB analysis, of which BDE69 and CB24 were obtained from AccuStandard and ¹³C-BDE139, ¹³C-CB141, ¹³C-CB208 and ¹³C-CB209 were from Cambridge (Andover, MA, USA).

The HPLC-grade hexane was purchased from Burdick and Jackson (Ulsan, Korea), while analytical grade dichloromethane and acetone were obtained from Tianjin Chemical Reagent Factory (Tianjin, China) and were redistilled before use. The high purity concentrated acids (HNO₃ and HF) were purchased from Beijing Chemical Reagent Factory (Beijing, China).

Sample preparation

PBDEs and PCBs. The soil samples for PBDE and PCB analysis were extracted using a CW-2000 ultrasound assisted microwave extractor (UAME, Xintuo Company, Shanghai, China) following a previously developed method²⁶ which is briefly described here. The soil samples were air-dried, ground and sieved through a 550-μm mesh sieve. Two grams of copper powder which was activated with concentrated HCl and sequentially washed with distilled water and acetone, was added to 25 g of soil in a 250-ml extraction flask to remove the sulfur interference. After adding 50 ng of surrogate CB209, the soil was extracted with 100 ml of a mixture of hexane : acetone (1 : 1, v/v) for 6 min. The ultrasound and microwave power settings were at 50 and 100 W, respectively. The extraction was repeated once with another 50 ml of extraction solvents. The extracts were filtered, combined, evaporated and solvent exchanged to 1 ml hexane using a rotary evaporator (IKA, Staufen, Germany).

The extract was cleaned using a column packed with 6 cm of 3% water-deactivated alumina, 12 cm of 3% water-deactivated silica gel and 2 cm anhydrous Na₂SO₄ from the bottom to the top. Before use, the absorbents alumina and silica gel were washed with acetone, dried, and baked at 180 and 250 °C, respectively, while the drying agent anhydrous Na₂SO₄ was baked at 450 °C for 4 h. After the sample was loaded, the column was washed with 5 ml of hexane (discharged), and the target contaminants were eluted out of the column with 75 ml of 30% dichloromethane in hexane (v/v). The eluents were concentrated and solvent exchanged to 0.1 ml hexane, and analyzed using gas chromatography/mass spectrometry (GC-MS) after adding 50 ng ml⁻¹ of each IS.

Heavy metals. To analyze the heavy metals, the soil samples were digested using a MARS microwave digestion system (CEM, Matthews, NC, USA) following USEPA method 3051.²⁷ After passing through a 150-μm mesh sieve, 0.200 g of air-dried soil was placed into a cell, and the digestion was performed with 9 ml of HNO₃ (~67%) and 3 ml of HF (~38%) under a microwave power of 1600 W. The temperature program for microwave digestion was set at 120 °C (3 min), then heated to 150 °C (3 min)

at 3 °C min⁻¹, then heated to 180 °C (10 min) at 3 °C min⁻¹. After digestion, the system was cooled down to 50 °C, and the digested solution was transferred to a 50 ml polyethylene terephthalate centrifuge tube. The digestion cell was then rinsed with triple distilled water three times and the rinses were combined with the digestion solution. The centrifuge tube containing the digested solution was then heated at 80 °C using an XT-9800 electric hot plate (Xingtuo). When the acid solution was evaporated to near dryness, 2 ml of HNO₃ was added to the tubes, and the solution was diluted to 100 ml with triple distilled water before analysis with inductively coupled plasma/MS (ICP/MS).

Instrumental analysis

PBDEs and PCBs. Analysis of PBDEs and PCBs was performed using a Shimadzu QP 2010 plus series GC-MS (Shimadzu, Japan) in negative chemical ionization (NCI) mode. A DB-5HT column (15 m × 0.25 mm, film thickness 0.1 μm) was used for separation of PBDEs whereas PCBs were analyzed using an Rtx-5MS column (30 m × 0.25 mm, film thickness 0.25 μm). Helium was used as the carrier gas and the flow rates were 1.5 and 1.0 ml min⁻¹ for the 15-m and 30-m columns, respectively.

Pulsed splitless injection was used to introduce 1 μl of extract into the column with a pulsed pressure at 250 kPa. The ion source and interface temperatures were set at 250 and 260 °C, respectively, and methane was used as the reaction gas for NCI. The oven temperature for PBDE analysis was set at 110 °C (5 min), then heated to 200 °C (4 min) at 40 °C min⁻¹, then heated to 260 °C (1 min) at 10 °C min⁻¹, then heated to 310 °C (15 min) at 15 °C min⁻¹. Meanwhile, the oven temperature for analyzing PCBs was set at 75 °C, held at 75 °C for 1 min, heated to 180 °C at 10 °C min⁻¹, held at 180 °C for 1 min, heated to 240 °C at 2 °C min⁻¹, held at 240 °C for 5 min, heated to 250 °C at 8 °C min⁻¹, then heated to 280 °C at 2 °C min⁻¹, and held at 280 °C for 10 min.

The ions were monitored in the selective ion monitoring (SIM) mode, and the most abundant ion was selected as the target ion for each compound. Identification of analytes was based on detection of target ion and qualifiers within the retention time window of 1%, while chemical quantification was based on IS calibration. The concentrations of the IS were kept constant at 50 ng ml⁻¹ for all samples, while the linear ranges of the calibration standards were 5–100, 2–200, 3–300, 4–400, 8–800, 10–1000 and 20–2000 ng ml⁻¹ for PCBs, bi- to penta-BDEs, hexa-BDEs, hepta-BDEs, octa-BDEs, nona-BDEs and BDE209, respectively.

Heavy metals. Twelve heavy metals including Ag, As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, and Zn, were assessed in the current study and the quantification was performed on an Agilent 7700 ICP/MS. Argon was used as the carrier gas with the circuit flow rate at 1 L min⁻¹. The RF power, S/C temperature, and analyzer pressure were set at 1550 W, 2 °C and 1 × 10⁻⁴ Pa, respectively. External calibration was used to quantify the target metals, and seven calibration standards in the range of 1–100 μg L⁻¹ were prepared in 2% HNO₃ solutions.

Quality assurance/quality control

A calibration standard check and solvent blank were injected after every 10 samples to make sure the relative differences

between the standard check and the calibration curve were less than 20% for all the target analytes. Simultaneously, two sets of quality control samples were included to verify the extraction and cleanup processes. Each set included a method blank (solvent only), a matrix blank (clean sand), a matrix spike, and a matrix spike duplicate. No detectable target compounds were observed in the blanks, and the recoveries of PBDEs and PCBs were 62–113% and 61–88%, respectively. In addition, to evaluate the efficiency of sample preparation processes, the surrogate CB209 was added to soil samples before extraction and its recoveries were from 65 to 99% for all samples.

Data analysis

The slopes of the regression lines were compared using an analysis of variance ($\alpha = 0.05$) coupled with a Dunnett's multiple comparison test using SAS 9.1 software (SAS Institute Inc., Cary, NC, USA).

Results and discussion

Occurrence and composition of e-waste related contaminants in soils

Concentrations. High concentrations of e-waste related contaminants were detected in soil samples collected near Longtang, and PBDE and PCB concentrations in all samples and the reporting limits (RLs) are presented in Table 1 and Tables S2 and S3 in the ESI.† As shown in Table 1, the sum concentrations of PBDEs and PCBs ranged from 0.565 to 2908 ng g⁻¹ dw and from 0.267 to 1891 ng g⁻¹ dw, respectively. The highest concentrations of sum PBDEs (2908 ng g⁻¹ dw) and sum PCBs (1891 ng g⁻¹ dw) were found in the center of the sampling circle, *i.e.* Dingan village (site LT0), whereas 0.565–65.1 and 0.267–449 ng g⁻¹ dw of sum PBDEs and sum PCBs, respectively, were detected in the surrounding areas. The results indicated that the e-waste dismantling and recycling operations conducted in Longtang have become a source of contamination of PBDEs and PCBs. Concentrations of PBDEs measured in the current study were comparable with other studies on PBDE concentrations in soils collected from the e-waste recycling areas of Longtang (122–3159 ng g⁻¹ dw),⁸ Taizhou (0.9–5469 ng g⁻¹ dw),¹² and Guiyu (34.7–4250 ng g⁻¹ dw).¹⁵ Similarly, as shown in Table 2 the highest sum concentration of heavy metals was also detected in the site LT0 at 812 μg g⁻¹ dw. Levels of heavy metals in soil released from e-waste recycling activities, including Ag, Cd, Co, Cr, Cu, Ni, Pb, and Zn, were also comparable with concentrations reported in previous studies on other e-waste recycling sites in China.^{1,16,17}

Composition. The demand for PBDEs in 2001 was approximately 67 000 tons all over the world³ and BDE209 accounted for 83.3% of all PBDEs and the percentage is still increasing.²⁸ Consistent to its usage, BDE209 was detected at the highest concentration in all soil samples and contributed 61–95% of all PBDEs in all samples with an exception of site LY4 (31%) (Fig. S1 in ESI†).

As shown in Fig. S1,‡ the composition of PCB congeners with different numbers of chlorines varied in different sampling sites. The percentage of the less-chlorine-substituted PCBs (mono- to

Table 1 The sum concentrations (ng g⁻¹ dry weight) of polybrominated diphenyl ethers (PBDE) and polychlorinated biphenyls (PCB) in different congener groups in soil samples^a

Sites	∑bi-, tri-, tetra-, penta-BDE	∑hexa-, hepta-BDE	∑octa-, nona-BDE	BDE209	∑PBDEs	∑mono-, bi-, tri-CB	∑tetra-, penta-, hexa-CB	∑hepta-, octa-, nona-CB	∑PCBs
LT0	19.40	19.32	221.9	2648	2908	18.09	1608	265.4	1891
LY2.5	0.133	0.667	1.006	2.853	4.659	2.935	435.3	10.38	448.6
LY5	0.438	0.320	4.756	39.66	45.17	0.522	6.458	0.355	7.335
LY10	0.360	0.268	2.753	22.04	25.46	0.826	0.238	0.042	1.106
LY20	0.575	0.088	0.352	0.452	1.467	0.646	0.360	0.065	1.071
LY30	0.068	0.052	0.135	1.476	1.731	0.752	1.039	0.021	1.812
LY40	0.105	0.043	0.290	2.550	2.988	0.582	0.137	0.015	0.734
LB2.5	3.709	1.357	2.334	28.54	35.94	1.164	0.491	0.134	1.789
LB5	0.368	0.078	2.292	51.65	54.40	0.591	0.337	0.083	1.010
LB10	0.665	1.848	4.115	54.01	60.64	1.103	0.857	0.138	2.098
LB20	0.208	0.036	0.485	2.573	3.301	1.065	1.047	0.101	2.213
LB30	0.218	0.161	1.714	8.983	11.08	1.148	0.588	0.037	1.773
LB40	0.594	0.192	8.128	56.16	65.07	0.373	0.195	0.022	0.590
LZ2.5	0.019	0.058	0.326	1.781	2.184	6.956	89.63	12.36	108.9
LZ5	0.229	0.335	1.121	10.56	12.24	36.14	99.52	1.864	137.5
LZ20	0.022	0.012	0.070	0.461	0.565	0.199	0.058	0.011	0.267
LZ30	0.041	0.198	0.492	5.174	5.905	2.150	5.935	7.920	16.00
LZ40	0.158	0.309	0.377	2.876	3.720	2.001	0.729	0.026	2.755
LC2.5	3.709	1.357	2.334	55.22	62.62	1.164	0.491	0.134	1.789
LC5	0.201	0.124	1.754	12.60	14.68	1.536	36.92	29.22	67.68
LC10	0.217	0.121	2.454	20.21	23.00	0.453	0.522	0.098	1.073
LC20	0.104	0.066	0.331	2.566	3.066	1.053	4.536	7.716	13.30
LC30	0.299	0.125	2.866	19.67	22.96	0.452	1.356	0.048	1.856
LC40	0.498	0.052	1.633	7.448	9.632	1.665	0.808	0.056	2.528

^a LT (Longtang), LY (Longtang-Yangshan), LB (Longtang-Baiyun Mountain), LZ (Longtang-Zhaoqing), LC (Longtang-Conghua), 2.5 (2.5 km), 5 (5 km), 10 (10 km), 20 (20 km), 30 (30 km), and 40 (40 km).

Table 2 The reporting limits (RL, ×10⁻³ μg g⁻¹ dry weight) and concentrations of heavy metals (μg g⁻¹ dry weight) in soil samples^a

Sites	Ag	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	Zn
RL	0.014	0.011	0.0055	0.0033	0.028	0.16	0.071	0.019	0.018	0.057	0.035	0.41
LT0	1.374	9.615	1.343	3.637	19.84	287.5	0.393	136.2	12.91	162.5	1.044	174.9
LY2.5	0.220	24.06	2.564	6.600	28.98	21.78	0.197	376.4	16.32	41.70	0.357	95.80
LY5	0.278	14.66	0.237	1.647	39.14	17.84	0.127	117.8	8.615	30.82	0.892	29.73
LY10	0.257	28.99	1.268	6.033	26.86	19.08	0.219	338.8	13.80	45.45	0.420	72.24
LY20	0.198	31.19	0.303	6.184	40.69	17.18	0.107	112.9	19.67	39.64	0.701	54.14
LY30	0.230	6.891	0.203	2.415	17.88	6.096	0.104	121.2	6.760	30.64	0.597	33.22
LY40	0.088	6.143	0.086	11.97	10.83	15.25	0.054	286.8	8.235	24.51	0.574	44.88
LB2.5	0.167	9.433	0.227	3.732	10.91	28.89	0.329	223.2	6.758	56.89	0.409	26.49
LB5	0.287	7.682	0.401	3.861	7.241	15.59	0.190	188.1	4.417	59.79	0.430	38.03
LB10	0.335	11.45	0.195	2.136	19.33	10.66	0.135	45.19	7.414	29.73	1.418	30.07
LB20	0.362	16.86	0.847	7.444	54.06	20.58	0.135	204.4	18.86	60.23	0.899	126.0
LB30	0.280	8.542	0.153	2.005	40.44	9.697	0.153	40.00	9.118	23.11	0.697	63.26
LB40	0.255	12.34	0.206	2.918	34.90	14.39	0.173	54.03	12.72	28.72	0.727	52.91
LZ2.5	0.163	11.51	0.252	2.162	44.21	16.07	0.048	96.91	9.195	29.21	0.909	37.84
LZ5	0.240	56.72	0.130	1.184	20.51	13.68	0.182	33.59	3.607	25.27	0.549	11.23
LZ20	0.187	104.6	0.082	1.721	50.05	20.02	0.100	29.82	10.32	42.02	0.498	7.555
LZ30	0.178	14.55	0.194	4.886	21.80	13.41	0.125	115.6	9.396	18.98	0.378	30.61
LZ40	0.365	3.606	0.234	3.724	7.257	18.43	0.153	145.6	4.942	50.04	0.522	50.59
LC2.5	0.167	9.433	0.227	3.732	10.91	28.89	0.329	223.2	6.758	56.89	0.409	26.49
LC5	0.361	7.426	0.224	1.793	16.09	6.034	0.164	97.38	7.277	16.31	1.120	22.94
LC10	0.112	3.839	0.155	2.525	12.72	4.743	0.122	38.92	5.829	24.21	1.000	16.00
LC20	0.260	2.793	0.210	2.666	2.761	3.223	0.138	184.8	2.632	56.68	0.383	22.41
LC30	0.148	5.162	0.200	3.612	3.996	3.241	0.147	178.5	3.526	86.01	0.582	27.76
LC40	0.162	4.459	0.181	2.274	9.335	11.40	0.062	122.1	5.153	19.16	0.771	32.74

^a LT (Longtang), LY (Longtang-Yangshan), LB (Longtang-Baiyun Mountain), LZ (Longtang-Zhaoqing), LC (Longtang-Conghua), 2.5 (2.5 km), 5 (5 km), 10 (10 km), 20 (20 km), 30 (30 km), and 40 (40 km).

tri-CBs) in all PCBs in the e-waste recycling site (LT0) and the nearby sites (LY1, LY2, LZ1, and LC2) was low and might be a result of the small quantity of usage. Conversely, they existed in greater portions in the remaining sites in the surrounding areas because of their relative high transport potential. The tetra-, penta-, and hexa-CB groups including the commonly used CB52, CB101, CB118, and CB153, also accounted for a large portion of total PCBs.

The transport potential of e-waste related contaminants

Heavy metals. Using concentrations of the e-waste related contaminants in soils, the current study investigated possible redistribution of metals, PBDEs, and PCBs from the e-waste site to the surrounding areas, *i.e.* their SRT potential. Compared to the POPs, heavy metals had less transport potential to the surrounding areas due to their low vapor pressures (Table 2). As aforementioned, the highest sum concentration of the 12 heavy metals was detected at the e-waste recycling site. Individually, only five metals, including Ag, Cu, Hg, Pb, and Zn, were detected at higher concentrations in the site LT0 than other surrounding sites. The highest concentrations of the remaining seven metals were scattered in other sites. In other words, the concentrations of metals jumped along the sampling lines and no distinct trend of metal concentration *versus* distance of sampling site to the e-waste site was observed. The results suggested that heavy metals released from e-waste recycling activities would stay in the original place rather than transport to the surrounding areas. The high concentrations of metals detected in other sampling sites might be possibly due to local pollution sources or possibly the high environmental background values. A previous study in Canada²² also reported no significant difference was observed for most inorganic elements, except for Pb, in plants collected at the source of contamination and the surrounding areas. Therefore, the following discussion on the SRT of contaminants only focuses on the two classes of POPs.

PBDEs *versus* PCBs. Wania and Dugani²⁰ compared the LRT potential of PCBs and less-brominated PBDEs and concluded that both classes of compounds had similar transport potential. Conversely, less LRT potential was observed for highly-brominated PBDEs. Conversely, the comparison of the SRT behavior of the two classes of POPs were limited, although two studies investigated PBDEs and PCBs individually.^{10,24} A term, namely “halo effect”, has been proposed to describe the emission of contaminants from the point source of contamination to the surrounding regions.²³ Zhao *et al.*¹⁰ reported that PBDEs from an e-waste recycling area in Southeast China showed a halo effect up to 74 km. Another study reported that a halo of 50 km resulted from the SRT of PCBs from a point source.²³ In the current study, surface soils were sampled in four directions around the e-waste site within 40 km in radius. Fig. 2 presents the relationships between the distance of sampling site from the e-waste site and the concentration of sum PBDEs or sum PCBs. As shown in Fig. 2, concentrations of PBDEs or PCBs in soils decreased with increasing distance from LT0 where the e-waste recycling workshops were located. In other words, the workshops served as a point source of pollution and both classes of POPs had diffused from the source to the surrounding regions.

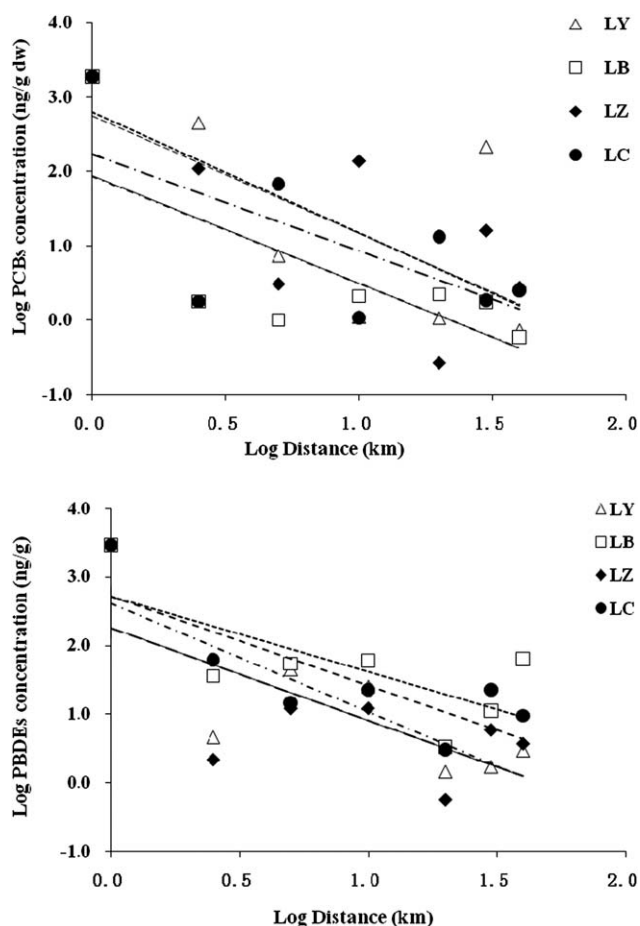


Fig. 2 The relationships of log sum polybrominated diphenyl ethers (PBDE) or polychlorinated biphenyls (PCB) concentrations (ng g^{-1} dry weight) *versus* log distance from the center of the circle (km). Samples were collected in four directions, including LY (Longtang-Yangshan), LB (Longtang-Baiyun Mountain), LZ (Longtang-Zhaoqing), and LC (Longtang-Conghua). The regression equations of PBDEs are as follows: LY: $y = -1.58x + 2.62$, $r^2 = 0.64$; LB: $y = -1.09x + 2.71$, $r^2 = 0.50$; LZ: $y = -1.35x + 2.26$, $r^2 = 0.46$; LC: $y = -1.30x + 2.72$, $r^2 = 0.65$. While the regression equations of PCBs are as follows: LY: $y = -2.12x + 3.01$, $r^2 = 0.85$; LB: $y = -1.45x + 1.94$, $r^2 = 0.51$; LZ: $y = -1.58x + 2.75$, $r^2 = 0.52$; LC: $y = -1.31x + 2.23$, $r^2 = 0.43$. Where, x represents log distance of the sampling site from the center, and y represents log concentration of PBDEs or PCBs.

The slopes of the regression lines for the four directions ranged from -1.09 to -1.58 and from -1.31 to -2.12 for PBDEs and PCBs, respectively, with r^2 values being 0.46 – 0.65 and 0.43 – 0.85 for PBDEs and PCBs, respectively. Statistical comparisons indicated no significant difference in the slopes of the regression lines for the same classes of contaminants among the four directions, or slopes between PBDEs and PCBs in the same direction. The weather and terrain may play an important role in SRT of contaminants.¹⁰ In the current study the sampling sites were in the subtropics and the direction of the wind changes when the season shifts in the area. The east-south wind in the summer changed to a west-north wind in the winter. Moreover, the altitudes of the sampling sites ranged from 7 to 209 m with the majority being <50 m. No prevailing wind and special terrain

effects may be the reason that no significant differences in transport were observed among the four directions. The results also showed the SRT potential for PBDEs and PCBs were not significantly different. Although no other study directly compared the SRT potential of these two classes of POPs, Zhao *et al.*¹⁰ compared their PBDE results with PCB data from Pier *et al.*,²³ and the results support our conclusion.

Among homologue groups. To evaluate the influence of volatility of different congeners on the SRT, the 27 PBDE congeners analyzed in the current study were divided into four groups (bi-, tri-, tetra-, and penta-BDE, hexa- and hepta-BDE, octa- and nona-BDE, and BDE209) while three groups for PCBs (mono-, bi-, and tri-CB, tetra-, penta-, and hexa-CB, and hepta-, octa-, and nona-CB) (Table S1†). The average concentrations in the four directions for all PBDE or PCB in the same congener group *versus* the distances of sampling sites from the e-waste site were plotted in Fig. 3. The slopes of the regression lines were -1.08 , -1.21 , -1.04 , and -1.28 for the groups of bi- to penta-BDE, hexa- and hepta-BDE, octa- and nona-BDE, and BDE209, respectively. While the slopes were -0.63 , -2.01 , and -1.74 for the mono- to tri-CB, tetra- to hexa-CB, and hepta- to nona-CB congener groups, respectively. There was no significant difference in the slopes for the highly and less brominated PBDEs, or chlorinated PCBs, which suggested that the SRT for the highly halogen-substituted PBDEs or PCBs was not significantly different from that of their less halogen-substituted counterparts even though their volatilities varied. Similar conclusions were presented by Zhao *et al.*,¹⁰ who reported that the characteristic travel distance (CTD), which represented the SRT potential, were not different for the less and highly brominated PBDEs.

On the other hand, concentrations of the highly halogen-substituted congeners decreased quicker than the less substituted ones, although the slopes of the regression lines are not significantly different among congener groups as discussed above (Fig. 3). Moreover, the trend of the changes in congener composition along the sampling sites was used to evaluate the difference in SRT potential among congeners as well. As shown in Fig. S1,† the percentage of BDE209 in total PBDEs slightly decreased with increasing distance from site LT0 which was indicated by the negative slopes for the regression line of Log percentage of BDE209 in all PBDEs *versus* sampling distance. In contrast, the percentages of other PBDE homologue groups in all PBDEs slightly increased with increasing distance from the e-waste site. The changes in composition of PBDE homologue groups suggested that BDE209 had less transport ability than other PBDEs. However, the decreasing trend was so subtle that it was not significantly different.

SRT *versus* LRT. The LRT potential models²⁰ suggested that the less bromine substituted PBDEs behaved in a similar manner to PCBs whereas the highly-brominated PBDEs had very low transportability to the remote areas. This is different from the similar SRT potential observed for all PBDE and PCB congeners in the current study and illustrated that the factors controlling the LRT and the SRT may be different. A variety of factors affect the transportability of organic compounds, such as chemical volatility, atmospheric or biota degradation, terrain, wind direction, and other weather conditions. For LRT potential, the chemical

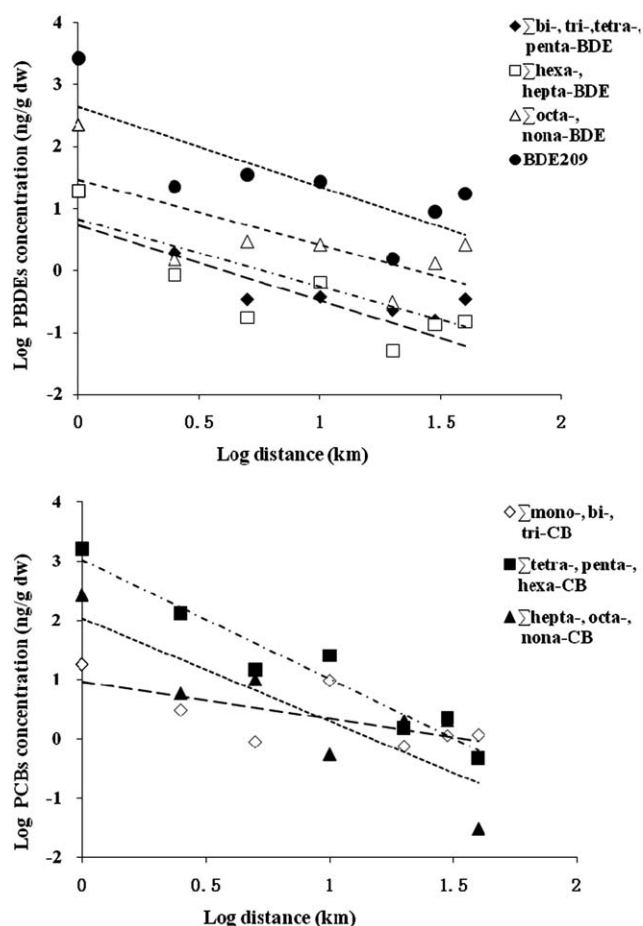


Fig. 3 The relationships of log concentrations of polybrominated diphenyl ethers (PBDE) or polychlorinated biphenyls (PCB) in different groups (ng g^{-1} dry weight) *versus* log distance from the circle centre (km) of the average of the four directions. The regression equations of PBDEs are $y = -1.08x + 0.82$, $r^2 = 0.77$; $y = -1.21x + 0.73$, $r^2 = 0.70$; $y = -1.04x + 1.45$, $r^2 = 0.49$; $y = -1.28x + 2.63$, $r^2 = 0.59$ for \sum bi-, tri-, tetra-, penta-BDE, \sum hexa-, hepta-BDE, \sum octa-, nona-BDE, and BDE209, respectively. While the regression equations of PCBs are $y = -0.63x + 0.96$, $r^2 = 0.46$; $y = -2.01x + 3.01$, $r^2 = 0.94$; $y = -1.74x + 2.04$, $r^2 = 0.72$ for \sum mono-, bi-, tri-CB, \sum tetra-, penta-, hexa-CB, and \sum hepta-, octa-, nona-CB, respectively. Where, x represents log distance of the sampling site from the center, and y represents log concentration of PBDEs or PCBs.

characteristics including volatility and degradation potential are the key factors because chemicals transport to a long range in a long time period. However, other environmental factors, such as terrain along the transport path or the weather conditions may contribute more to the SRT than the LRT. Additionally, highly brominated PBDEs preferentially sorbed to suspended particles due to their low volatility, therefore, their transport potential is also controlled by the transport behavior of the particles.²⁰ For this reason, the wet and/or dry deposition of the particles sorbed with the contaminants might result in contamination in the nearby areas. The study area had humid weather and wet deposition may play an important role in the SRT of the POPs from the e-waste recycling site to the surrounding areas.

Overall, the e-waste site had become a point pollution source for a suite of POPs, including PBDEs and PCBs. Results

illustrated that PBDEs, both less and highly brominated congeners, had similar transport potential to the surrounding areas in a short range as the PCBs. Conversely, heavy metals had the least transport potential and the e-waste practice is not the reason for the heavy metal contamination in the surrounding areas.

Risks of e-waste related contaminants to the surrounding areas

Soil served as a major reservoir for many contaminants and might become a second source of pollution by re-emission and transport. Therefore, knowing the mass inventory of contaminants in soil helps to assess the risk of soil being a pollution source to surrounding regions. In the current study, an additional 21 soil samples were collected within an 8 km-radius circle of the e-waste site (Dingan village) and soil concentrations of PBDE, PCBs, and heavy metals are presented in Tables S4–S6 in the ESI.† Mass inventories of BDE209, sum PBDEs (excluding BDE209), sum PCBs, and sum metals were estimated in this area using eqn (1)²⁹:

$$I = \sum kCA\rho d \quad (1)$$

Where I is the mass inventory (tons), C is the average concentration of the target contaminants (ng g^{-1} dw) in the sampling region, A is the area of sampling region (km^2), d is the depth of soil sampled (cm), ρ is the dry soil density (g cm^{-3}), and k is the unit conversion factor. In the current study, A was 201 km^2 , d was 5 cm , and ρ (1.5 g cm^{-3}) was derived from Zou *et al.*²⁹ The calculated mass inventories of BDE209, sum PBDEs, sum PCBs and sum metals were 0.920, 0.134, 0.860 and 1434 tons, respectively. For three representative metals, including Cd, Cu, and Pb, the inventories were estimated as 4.68, 757, and 673 tons, respectively. The high estimated mass inventories suggested severe contamination to the local environment from e-waste dismantling and recycling activities and it may be a threat to the surrounding areas due to the SRT potential of the POPs.

Conclusion

High concentrations of PBDEs, PCBs, and heavy metals in soils in an e-waste site revealed that the e-waste recycling activities had caused severe local contamination. Furthermore, POPs, including PBDEs and PCBs, were transported from the pollution source to the surrounding areas, potentially threatening these areas. Although there was no significant difference in SRT behavior between highly and less halogenated PBDE or PCB congeners, BDE209 showed slightly less transport potential than other PBDEs. In contrast, no trend in SRT was observed for heavy metals indicating heavy metals from e-waste recycling practice would only be a local problem.

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