Supporting Information

Plant Uptake of Atmospheric Brominated Flame Retardants at E-Waste Site in Southern China

Mi Tian,[†,‡] She-Jun Chen,[*,†] Jing Wang,[†,‡] Yong Luo,[§] Xiao-Jun Luo,[†] Bi-Xian Mai[†]

[†]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640,
[‡]China and Graduate University of Chinese Academy of Sciences, Beijing 100049, China
[§]Guangdong Forestry Survey and Planning Institute, Guangzhou 510520, China

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Materials and methods

Sampling. The e-waste site (N 23.59, E 113.03) is located in an e-waste recycling area within an area of 330 km^2 (Figure S1), where large quantities of e-waste (~700 000 metric tons) is processed using primitive methods (e.g., mechanical shredding, acid processing, and open burning). The studied area has a subtropical climate, with an annual average temperature of ~22 °C.

Air samples were taken by drawing air through 20.3 × 25.4 cm glass fiber filters (GFFs) (Whatman, Maidstone, England), and subsequently through polyurethane foam (PUF) plugs(6.5 cm in diameter × 7.5 cm in thickness) for 24 h, using a high-volume air sampler at a rate of 0.25 m^3/min. A total of 60 pairs of samples (gas and particle) were collected simultaneously from each site on five consecutive days each month from July 2007 to June 2008. Prior to sampling, GFFs were baked at 450 °C for 12 h to remove any organic contaminants. PUF plugs were Soxhlet extracted with hexane and acetone (1:1) for 48 h. After sampling, loaded GFFs and PUFs were wrapped with prebaked aluminum foils, sealed with polyethylene bags, and then stored at -20 °C until extraction.

Chemicals. PBDEs (BDE7, 8, 11, 12, 13, 15, 17, 25, 28, 32, 33, 35, 47, 49, 66, 85, 99, 100, 116, 119, 138, 153, 154, 155, 166, 183, 190, 196, 197, 201, 202, 203, 206, 207, 208, and 209), polybrominated biphenyls (PBBs) (BB153 and 209), surrogate standards (BDE 77 and 181), and internal standards (BDE118 and 128)were purchased from Accustandards Inc. (New Heaven, US). PBEB, PBT, HBB, BTBPE, and DBDPE were obtained from Wellington Laboratories (Guelph, Canada). Internal standard (^{13}C-PCB 208) and surrogate standard (^{13}C-BDE 209) were purchased from Cambridge Isotope Laboratories (Andover, US). All organic solvents were redistilled using a glass system.

Sample Preparation. The GFFs were equilibrated in a desiccator for 24 h before and after sampling and weighed to obtain TSP concentrations. PUF plugs and GFF samples were spiked with BDE77, BDE118, and ^{13}C-BDE 209(GFFs only) and Soxhlet extracted with a 1:1 (V/V) mixture of hexane and acetone for 48 h. The extracts were concentrated to 1-2 mL with a rotary evaporator and then further purified in a multilayer alumina/silica column. The effluent eluted with 80 mL of hexane: dichloromethane (1:1, V/V) was finally concentrated to 200 μL under a gentle nitrogen stream.

Leaf samples obtained each month were rinsed with purified water to collect particles on the leaf surface and were filtered immediately through glass fiber filters (Whatman GFFs, 47 mm) that were baked at 450^{o}C for 4 h before use for BFR analysis. Each 10 g sample of leaves was ground with hydrous sodium sulfate and Soxhlet extracted as the air samples did after being spiked with BDE77, BDE118, and ^{13}C-BDE209. The plant extract was mixed with 60 mL concentrated sulfuric acid to remove lipids and then was liquid-liquid extracted with hexane using a teflon separatory funnel (NalgeNunc, Rochester, NY) for three times. The hexane extracts were then further purified in a multilayer alumina/silica column as the air samples. BDE118 and BDE128 were added as quantification standards.

Extractable organic matter and water content of the leaves was also determined. About 10 g dry weight plant samples were Soxhlet extracted with a 1:1 (V/V) hexane/acetone for 24 h. The extracts were concentrated to 1-2 mL with a rotary evaporator and then dried at 60 °C until constant weight was obtained. The extractable lipid content was determined as a percentage of the sample dry weight. Approximately 10 g of the fresh plant samples was dried at 105 °C until constant weight was obtained to

determine water content.

Instrumental analysis. Analyses of relatively low molecular weight target compounds (di- through hepta-BDEs, PBT, PBEB, HBB, and PBB153) were performed on an Agilent 6980N gas chromatograph (GC) equipped with a DB-XLB (30 m×0.25 mm i.d., 0.25 μm film thickness) capillary column coupled with Agilent 5975B mass spectrometer (MS) in electron capture negative ionization (ECNI) mode. Initial column temperature was held at 110 °C for 1 min, and then programmed to 180 °C at 8 °C/min (held for 1 min), to 240 °C at 2 °C/min (held for 5 min), to 280 °C at 2 °C/min (held for 15 min), and to 310 °C at 10 °C/min (held for 5 min). The relatively large molecular weight compounds (octa- through deca-BDEs, DBDPE, BTBPT, and BB209) were analyzed by a Shimadzu 2010 GC-ECNI-MS system coupled with a DB-5HT (15 m × 0.25 mm i.d., 0.10 μm film thickness) column. The column temperature was initiated at 110 °C (held for 5 min), and increased to 200 °C at 20 °C /min (held for 4.5 min), and final reached 310 °C at 10 °C /min (held for 15 min). Methane was used as a chemical ionization moderating gas at an ion source pressure of 2.4 × 103 Pa and helium as the carrier gas at a flow rate of 1 mL/min. The ion source and interface temperatures were set to 200 and 290 °C, respectively. Injection of 1 μL sample was conducted with an automatic sampler in the splitless mode. Ions of m/z 79 and 81 were monitored for all compounds except for BDE209, ^{13}C-BDE 141, and ^{13}C-PCB208 for which m/z 486.7 and 488.7, m/z 372 and 374 and m/z 476 and 478 were recorded, respectively.

Table S1. Summary of Concentrations of BFRs in the gaseous and particle phases (pg/m^3), and particles (ng/g) at the E-waste Site in Southern China

	Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	Deca-	PBDEs	PBT	PBEB	HBB	BTBPE	DBDPE	PBBs	total
Gas (pg/m^3)																	
Jul. 2007	464	414	463	177	18.2	1.52	0.89	nd[a]	nd	1539	29	62.1	145	0.11	nd	2.92	1814 (1489-2348)
Aug. 2007	1166	1462	492	234	48.9	2.05	36	0.2	1.29	3443	77.2	239	275	0.9	nd	17.1	4090 (1351-7086)
Sep. 2007	25.1	21	16.1	11.3	2.22	0.92	25	0.11	0.32	102	3.78	5.26	15.3	0.55	nd	nd	128 (52.2-217)
Oct. 2007	105	127	123	29.2	3.47	1.55	4.3	nd	nd	394	10.7	12.2	108	nd	nd	9.16	534 (280-622)
Nov. 2007	85.4	67.6	35.8	5	1.09	1.61	2.58	nd	nd	199	6.17	5.96	36.9	0.19	nd	0.43	249 (71.6-394)
Jan. 2008	1668	862	107	16.6	8.79	13.3	22.8	nd	nd	2698	41.6	44	162	4.61	nd	1.07	2955 (888-6514)
Feb. 2008	106	74.8	30.1	4.39	2.06	1.43	nd	nd	nd	219	6.13	6.43	47.8	nd	nd	0.65	281 (37.9-530)
Mar. 2008	139	93.8	63.8	27	7.44	2.2	3.07	nd	nd	336	0.5	nd	11.3	80.1	nd	7.82	449 (259-610)
Apr. 2008	18.9	15.3	13.2	7.5	3.24	0.73	0.66	nd	nd	59.4	nd	nd	3.95	24.1	nd	0.67	91 (21.5-166)
Jun. 2008	647	472	202	81.9	11.5	2.12	nd	nd	nd	1416	26.6	35.7	127	0.08	nd	9.01	1616 (580-2804)
	Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	Deca-	PBDEs	PBT	PBEB	HBB	BTBPE	DBDPE	PBBs	total
Particle (pg/m^3)																	
Jul.2007	4.44	11.2	77.2	255	105	114	163	237	2020	2986	0.99	15.9	17.1	84.4	143	31.4	3279 (333-4202)
Aug.2007	14.7	8.54	42	446	224	218	362	337	4195	5846	1.58	1.84	17.1	140	102	57.2	6167 (1703-12427)
Sep.2007	0.32	0.82	6.92	22.6	12.4	16.2	28.6	81.5	341	510	nd	0.12	2.32	14.5	75.5	1.56	605 (311-983)
Oct.2007	3.57	4.95	44.3	191	107	57.9	101	237	1984	2731	0.51	0.57	26.3	36.9	114	169	3079 (1333-5331)
Nov.2007	3.67	9.31	71.5	188	132	163	111	190	975	1842	1.27	1.77	54.8	65	90.6	15.2	2071 (815-3573)
Jan.2008	29.9	251	311	568	286	292	220	158	1703	3818	19.6	21.3	183	146	287	86.2	4563 (1310-9992)
Feb.2008	2.7	12.9	65.6	123	43.4	59.9	80	130	1102	1619	0.97	1.22	40.5	19.9	137	10.8	1829 (1385-2533)
Mar.2008	3.77	25	150	461	236	192	245	327	1470	3109	4.64	3.43	117	113	635	81.9	4064 (931-10470)
Apr.2008	0.04	1.53	15.3	52.9	23.7	21.2	49.3	80.4	421	665	0.66	0.69	17.5	15.1	113	8.3	820 (97.0-2355)
Jun.2008	3.61	5.9	27.7	214	137	179	227	233	975	2002	1.99	0.69	16.6	62.8	206	62.2	2353 (796-3189)
	Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	Deca-	PBDEs	PBT	PBEB	HBB	BTBPE	DBDPE	PBBs	total
Gas and particle (pg/m^3)																	
Jul.2007	468	425	540	432	123	115	164	237	2020	4525	30	78	162	84.5	143	34.3	5093 (2681-5749)
Aug.2007	1181	1471	534	680	273	220	398	337	4196	9289	78.8	241	293	141	102	74.3	10257 (3053-18902)
Sep.2007	25.4	21.8	23	33.9	14.7	17.1	53.6	81.7	341	612	3.78	5.38	17.6	15	75.5	1.56	732 (419-1081)
Oct.2007	109	132	167	220	111	59.5	106	237	1984	3125	11.2	12.7	134	36.9	114	178	3613 (1612-5948)

Nov.2007	93	87.6	100	135	62.3	52	83	194	1208	2015	8.11	8.51	85	25.3	96.2	39.9	2320 (886-3588)
Jan.2008	1698	1112	417	584	295	305	242	158	1703	6516	61.2	65.3	345	151	287	87.3	7518 (2313-16506)
Feb.2008	109	87.7	95.7	127	45.4	61.3	80	130	1102	1838	7.1	7.65	88.2	19.9	137	11.4	2110 (1423-2882)
Mar.2008	143	119	213	488	244	194	248	327	1470	3445	5.14	3.43	128	194	635	89.7	4513 (1258-10728)
Apr.2008	18.9	16.8	28.4	60.4	27	21.9	50	80.4	421	725	0.66	0.69	21.5	39.2	113	8.97	912 (119-2463)
Jun.2008	651	478	229	296	148	181	227	233	975	3418	28.6	36.4	144	62.9	206	71.3	3970 (1375-5993)
	Particle (ng/g) [b]																
	Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	Deca-	PBDEs	PBT	PBEB	HBB	BTBPE	DBDPE	PBBs	total
Jul.2007	14.9	37.8	256	858	355	383	557	787	6696	3.15	57.8	56.6	280	458	104	14.9	10904 (1404-15596)
Aug.2007	114	53.9	240	2747	1176	1339	2174	1868	20006	9.33	11.5	96.7	1152	653	337	114	31976 (19647-42680)
Sep.2007	4.75	18.9	120	384	190	272	529	1608	6394	nd	2.04	45.5	218	1603	27.7	4.75	11416 (7121-15807)
Oct.2007	13.0	18.0	168	718	381	217	378	935	7885	1.87	2.09	93.7	141	416	560	13.0	11927 (4627-24182)
Nov.2007	18.0	46.3	360	945	655	803	559	969	5095	6.37	8.76	275	324	480	75.9	18.0	10620 (3866-17357)
Jan.2008	159	1371	1849	3350	1711	1803	1326	989	9645	110	128	1087	918	1661	499	159	26604 (8422-42745)
Feb.2008	13.7	92.5	462	832	295	408	587	958	7299	7.93	8.59	283	150	1040	72.0	13.7	12508 (6963-18090)
Mar.2008	26.2	173	1045	3271	1831	1498	2024	2544	11439	38.1	25.0	906	898	4614	559	26.2	30889 (12704-68924)
Apr.2008	0.20	10.4	115	365	163	129	316	541	2682	4.49	4.83	124	83.1	737	50.2	0.20	5326 (679-12641)
Jun.2008	20.1	33.9	138	1088	706	945	1209	1272	5332	10.9	3.91	87.3	341	1179	366	20.1	12731 (5409-20311)

[a] Not detected.
[b] Concentration of BFRs in the atmospheric particle normalized to the particle mass.

Table S2. Total BFRs concentrations in the plants (ng/g dry weight), leaf surface particles (LSPs)(ng/g), and air (pg/m^3) at the e-waste site.

	plant		LSP		air		
	eucalyptus leaf	pine needle	eucalyptus leaf	pine needle	particle	gas	air
Jul.2007	51.8	40.4	2873	2779	3279	1814	5093
Aug.2007	30.6	50.1	6763	8951	6167	4090	10257
Sep.2007	81.3	114	18350	10998	605	128	732
Oct.2007	44.4	304	1197	2354	3079	534	3613
Nov.2007	121	254	1690	1832	2071	249	2320
Jan.2008	87.5	218	373	1777	4563	2955	7518
Feb.2008	134	546	21468	2904	1829	281	2110
Mar.2008	154	253	15941	6691	4064	449	4513
Apr.2008	151	120	n.a.[a]	n.a.	820	91	912
Jun.2008	128	174	3712	11110	2353	1616	3970

[a] Not available because of the absence of samples.

Table S3. Pearson Correlation coefficients (*r*) between BFR Concentrations in Plants and Relative Humidity and Wind speed at the E-waste Site.

	Eucalyptus foliage		Pine needles	
	wind speed	humidity	wind speed	humidity
Di-BDEs	0.020	0.060	0.050	-0.300
Tri-BDEs	-0.197	0.130	-0.030	-0.239
Tetra-BDEs	-0.227	0.160	-0.061	-0.227
Penta-BDEs	-0.095	0.039	-0.060	-0.280
Hexa-BDEs	-0.428	0.196	0.018	-0.433
Hepta-BDEs	-0.48	0.364	0.010	-0.359
Octa-BDEs	-0.214	0.295	-0.223	-0.043
Nona-BDEs	0.083	0.270	-0.352	0.133
Deca-BDEs	0.052	-0.093	-0.364	-0.049
PBT	0.053	-0.006	-0.074	-0.198
PBEB	0.118	-0.055	-0.090	-0.194
HBB	-0.200	0.082	-0.015	-0.274
BTBPE	-0.091	0.118	0.026	-0.296
DBDPE	0.076	-0.104	-0.287	0.067
ΣBFRs	0.006	0.043	-0.091	-0.253

Table S4. Pearson CorrelationCoefficients between log K_{PA} and Temperature (1/T) at the e-waste site.

	Eucalyptus leaf		Pine needles	
	A[a]	B[a]	A	B
BDE7	0.150[a]	0.749	0.423	0.710
BDE8	0.333	0.795*[b]	0.439	0.740
BDE13	0.275	0.723	0.416	0.626
BDE15	0.213	0.658	0.328	0.624
BDE17	0.215	0.846*	0.359	0.822*
BDE28	0.339	0.892*	0.469	0.847*
BDE47	0.377	0.759*	0.515	0.786*
BDE66	0.255	0.697	0.440	0.737
BDE85	0.571	0.373	0.646*	0.286
BDE99	0.310	0.638	0.455	0.665
BDE100	0.374	0.618	0.466	0.736
BDE138	-0.591	-0.107	0.195	-0.248
BDE153	0.088	0.553	0.366	0.574
BDE154	0.031	0.529	0.316	0.543
BDE183	-0.112	0.592	0.270	0.621
BDE196	0.269	0.485	0.503	0.613
BDE197	0.071	0.450	0.475	0.693
BDE201	0.136	0.636	0.383	0.738
BDE203	0.200	0.378	0.498	0.595
BDE206	-0.063	-0.191	0.399	0.206
BDE207	0.047	0.084	0.460	0.564
BDE208	-0.091	0.193	0.435	0.466
BDE209	0.147	0.427	0.411	0.681

[a] A, for all the samples; B, For samples except for those from winter (from Nov. 2007 to Feb. 2008).
[b] *, Correlation is significant at the 0.05 level (2-tailed).

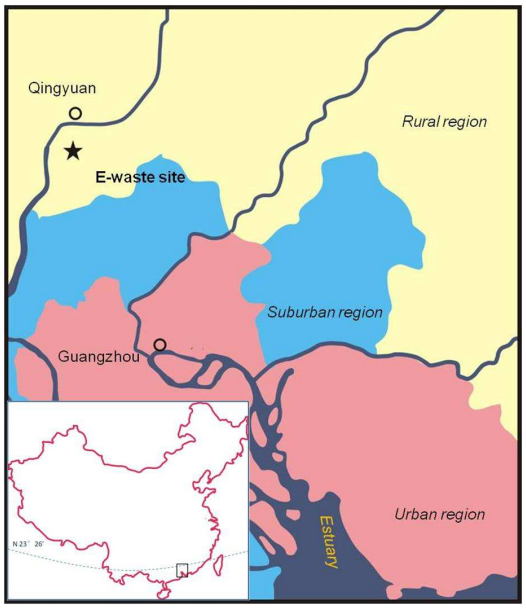

Figure S1. Map of sampling site (e-waste site) in southern China.

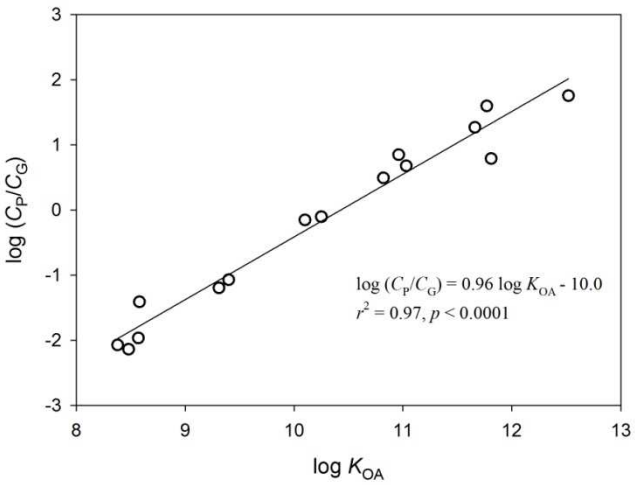

Figure S2. Regression for log (C_P/C_G) = log K_{OA} + log ($B\times TSP$) of the data in the present study.