Supplementary Material

Brominated flame retardants (BFRs) in $PM_{2.5}$ associated with various source sectors in southern China

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S1. Methods

S1.1 Instrumental parameters

Analysis of BFRs were performed on a Shimadzu GCMS-QP 2010 plus with electron capture negative ionization mass spectrometer (GC-NCI-MS). Tri- to hepta-BDEs were separated with a DB-XLB (30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column. 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 305 °C at 10 °C/ min (held for 7 min). For octa-BDEs through deca-BDEs, BTBPE and DBDPE, a DB-5HT (15 m × 0.25 mm i.d., 0.10 μm film thickness) column was used. The oven 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 finally to 310 °C at 10 °C/min (held for 10 min). The carrier gas was Helium with a flow rate of 2.0 mL/min. The ion source, quadrupole and interface temperatures were set to 200 °C, 150 °C and 290 °C, respectively. For all the targets, injection of 1 μL sample was performed with an automatic sampler in the splitless mode.

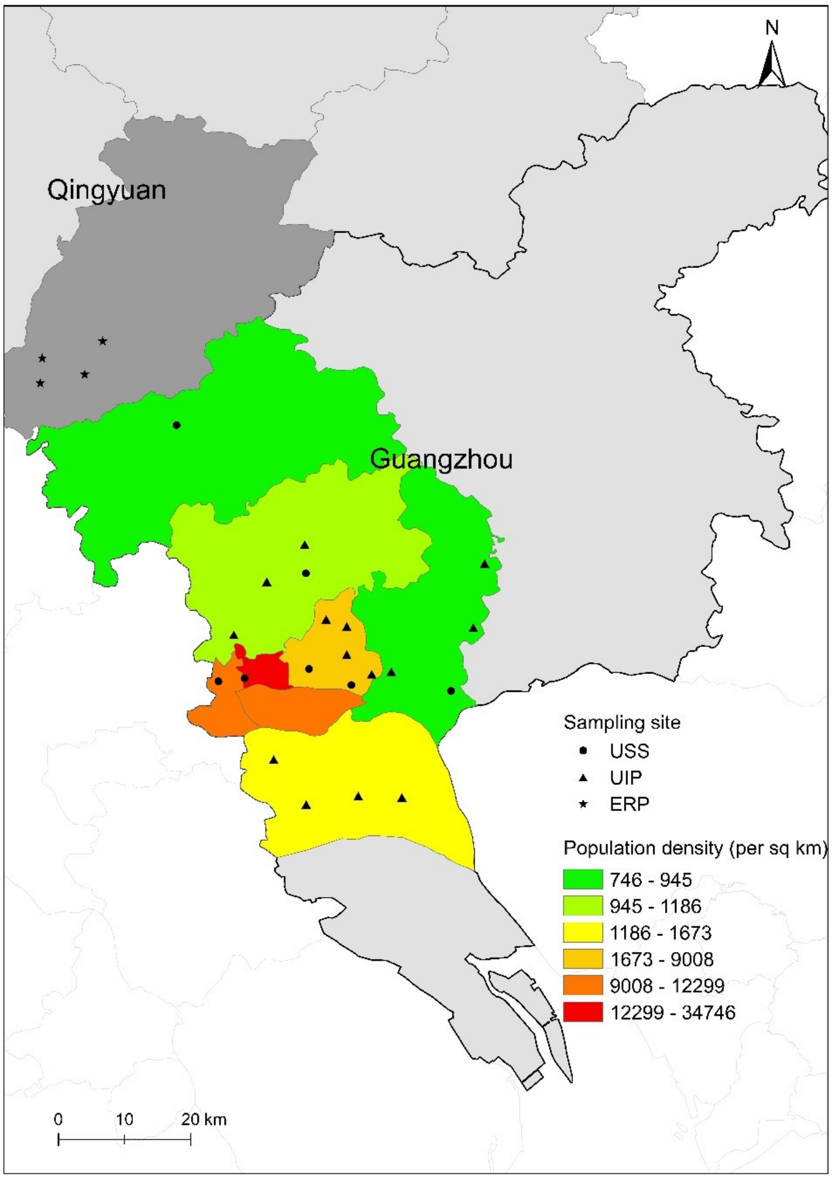

Fig. S1 Map of sampling sites in southern China.

Table S1. Site description.

Site	Industrial sector	Site	Industrial sector
Urban specific source sites			
WWTP	Wastewater treatment plant	CBN	Furnishings selling center
MSWIPP	Municipal waste incineration power plant	GD	Electronics shopping center
RRRP	Resources recycling and recovery	SL	Leather product making
XMK	Downtown residential area		
Urban industrial park sites			
CS	Electronics, hardware mould, and shoes	QH	Electronics, metals, and mould industries
DS	Electronic and electrical equipment, Automobile manufacturing	SB	Electronics, plastics and foam, and metals
GK	Machinery and clothing	SJ	Furniture, clock, electronics, and clothing
JLK	Chemical industry	JL	Automobile manufacturing and clothing
KML	Mechanical equipment manufacturing	XP	Household products, plastics and rubber, and electronics
LD	Metals, machinery, and papermaking	XK	Leather
MY	Electrical/electronic products, metals, building materials, clothing, and shoes	XZ	Chemical industry (coating and printing ink)
E-waste recycling parks			
ERP1	E-waste recycling	ERP3	E-waste recycling
ERP2	E-waste recycling	ERP4	E-waste recycling

Table S2. Summary of concentrations (pg/m^3) of BFRs in $PM_{2.5}$ at the USS, UIP, and ERP sites.

	USS[a]			UIP[a]			ERP[a]			DF(%) and MDL (pg/m^3)	
	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median		
BDE28	nd	nd	nd	nd	nd	nd	nd	nd	nd	0	0.04
BDE35	nd-0.36	0.14	0.16	nd-0.42	0.12	nd	nd-0.15	0.09	0.09	37	0.03
BDE37	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.7	0.05
BDE49	nd	nd	nd	nd	nd	nd	nd	nd	nd	0	0.03
BDE47	nd-0.55	0.14	nd	nd-0.86	0.25	0.23	nd-0.21	0.1	0.1	52	0.04
BDE66	nd-0.09	nd	nd	nd	nd	nd	nd	nd	nd	3.3	0.08
BDE100	nd-0.31	nd	nd	nd-0.07	nd	nd	nd	nd	nd	6.7	0.07
BDE99	nd-0.92	0.27	0.14	nd-1.22	0.29	0.26	nd	nd	nd	50	0.05
BDE85	nd	nd	nd	nd-0.23	nd	nd	nd-0.64	0.17	nd	8.3	0.03
BDE154	nd-0.6	0.25	0.18	nd-2.14	0.64	0.51	0.37-5.29	2.62	2.4	67	0.05
BDE153	nd-0.59	0.18	0.11	nd-0.78	0.18	0.15	1.67-30.2	15.0	14.0	85	0.03
BDE138	nd-2.33	0.45	0.08	nd-1.22	0.24	nd	nd-1.41	0.41	0.12	30	0.03
BDE183	0.30-5.75	1.48	0.62	0.11-6.35	0.95	0.68	11.0-181	84.4	72.8	95	0.02
BDE202	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.7	0.81
BDE197	nd-1.72	0.46	nd	nd-5.80	0.59	nd	2.88-47.0	22.8	20.7	45	0.15
BDE203	1.20-4.74	2.54	2.24	1.40-4.21	2.57	2.38	4.87-33.0	18.0	17.0	98	0.48
BDE196	1.02-3.61	2.47	2.46	1.76-4.89	2.88	2.70	4.39-32.9	18.6	18.5	100	0.43
BDE208	0.74-5.37	2.40	2.00	0.09-4.93	1.70	1.47	11.2-74.8	36.5	30.0	98	0.09
BDE207	1.91-8.00	4.26	3.61	1.04-8.06	3.44	3.38	16.0-129	61.7	50.9	100	0.32
BDE206	2.02-6.29	4.14	3.94	2.66-6.63	4.59	4.33	8.97-96.2	40.2	27.8	100	0.71
BDE209	17.7-56.8	36.7	36.3	13.4-86.9	42.8	41.5	159-1788	640	307	100	2.31
PentaBDEs[b]	0.12-3.21	1.52	1.42	0.42-3.73	1.74	1.59	2.51-35.8	18.4	17.6	100	-
OctaBDEs[b]	4.86-10.7	6.95	5.53	4.19-15.8	7.0	6.0	23.1-288	144	133	100	-
DecaBDEs[b]	31.4-67.9	47.5	443	17.2-97.3	52.5	53.4	195-2087	779	416	100	-
∑PBDEs	38.6-77.9	56.0	50.7	22-105	61.2	60.7	220-2356	941	595	100	-
DBDPE	50.3-113	71.3	63.4	27.9-455	121	65.0	55.8-517	241	196	100	8.91
BTBPE	1.88-5.83	3.32	3.09	1.73-6.29	3.16	2.94	nd-52.4	22.4	18.5	100	0.53
∑NBFRs	54.3-118	74.6	67.1	29.7-459	124	68.1	83.6-569	263	200	100	-
∑BFRs	96.2-196	131	118	66.5-543	186	141	267-2635	1205	921	100	-

[a] USS, urban specific source; UIP, Urban industrial park; ERP, e-waste recycling park.

[b] PentaBDEs, sum of BDE 28, 35, 37,49, 47, 66, 100, 99, 85, 154, 152 and 138; OctaBDEs, sum of BDE 183, 202, 197, 203 and 196; DecaBDEs, Sum of BDE 208, 206, 207 and 209.

nd = not detected.

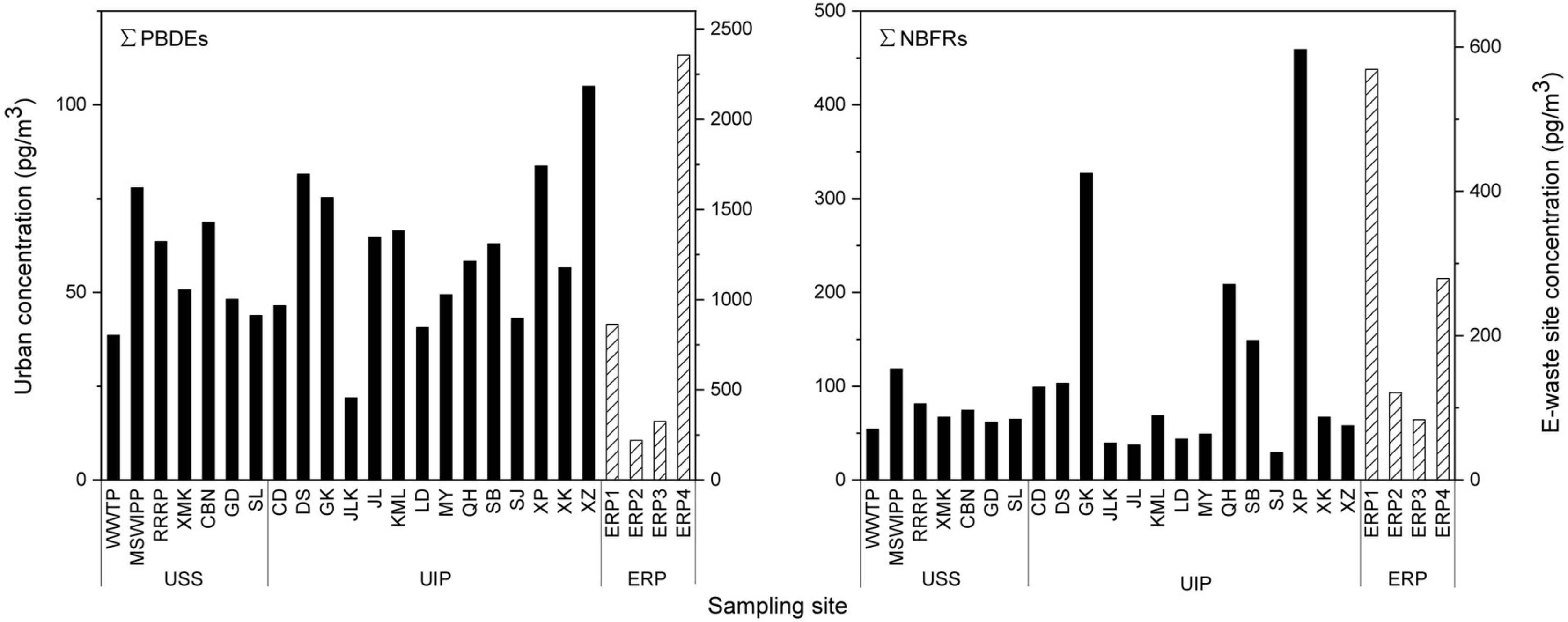

Fig. S2 Mean concentrations of ∑PBDEs and ∑NBFRs in $PM_{2.5}$ in the urban and e-waste regions. USS, urban specific source sites; UIP, urban industrial park sites; ERP, e-waste recycling park sites. The y-axis on the right is for ERP variables.

Table S3. Comparison of $PM_{2.5}$-bound BFRs concentrations (pg/m^3) in the present study with literature data.

Location (Year)	PBDEs		BDE209		DBDPE		BTBPE		Refs.
	Range	Mean (median)	Range	Mean (median)	Range	Mean (median)	Range	Mean (median)	
Urban site									
Shanghai, China (2012-2013)		51.8		15.6					1
Chinese cities (2013-2014)	0.01-1000	35	0.01-1010	24.7 (1.31)	0.24-1020	50 (7.51)	0.03-4.38	0.64 (0.42)	2
Guangzhou, China (2013-2014)	2.51-7031	839 (375)	0.14-6797	792 (324)	0.12-6211	703（365)	0.11-12.0	1.64（0.70）	3
Shenzhen, China (2014-2015)	1.33- 319	33.5 (14.6)	1.17-231	24.8 (10.5)					4
Hong Kong, China (2016)	100-640			37					5
Beijing, China (2016-2017)			4.64-92.9	47.0 (11.0)	<0.11-100	16.1 (10.8)	<0.03-1.23	0.18 (0.10)	6
Tianjin, China (2016-2017)			1.3-35.0	8.76 (5.80)	0.33–57.7	6.68 (1.48)	0.001–1.01	0.12 (0.06)	6
Shijiazhuang, China (2016-2017)			5.32-104	25.9 (12.0)	0.93–51.4	12.1 (7.51)	<0.01–3.79	0.48 (0.20)	6
Dalian, China (2016-2017)	245-19610	4294	244-19600	4291			0.03–1.23	7.7 (1.5)	7
Karachi, Pakistan (2020)	15.1-183			87.0					8
Rural/remote site									
The East China Sea, China (2012)	1.3-33.8	8.07	0.75-31.8	7.1				2.32	9
Zhaoqing, China (2013-2014)	9.19-242	67.4 (52.4)	4.59-121	42.2 (32.5)	0.47-33.9	6.53 (5.09)	0.12–20.2	2.91 (2.45)	3
Rural site, China (2016-2017)			0.88-14.4	5.10 (3.61)	0.92–33.9	14.7 (10.9)	<0.14	0.04 (0.03)	6
E-waste site									
E-waste site, China (2018)		16100		652					10

nd = not detected.

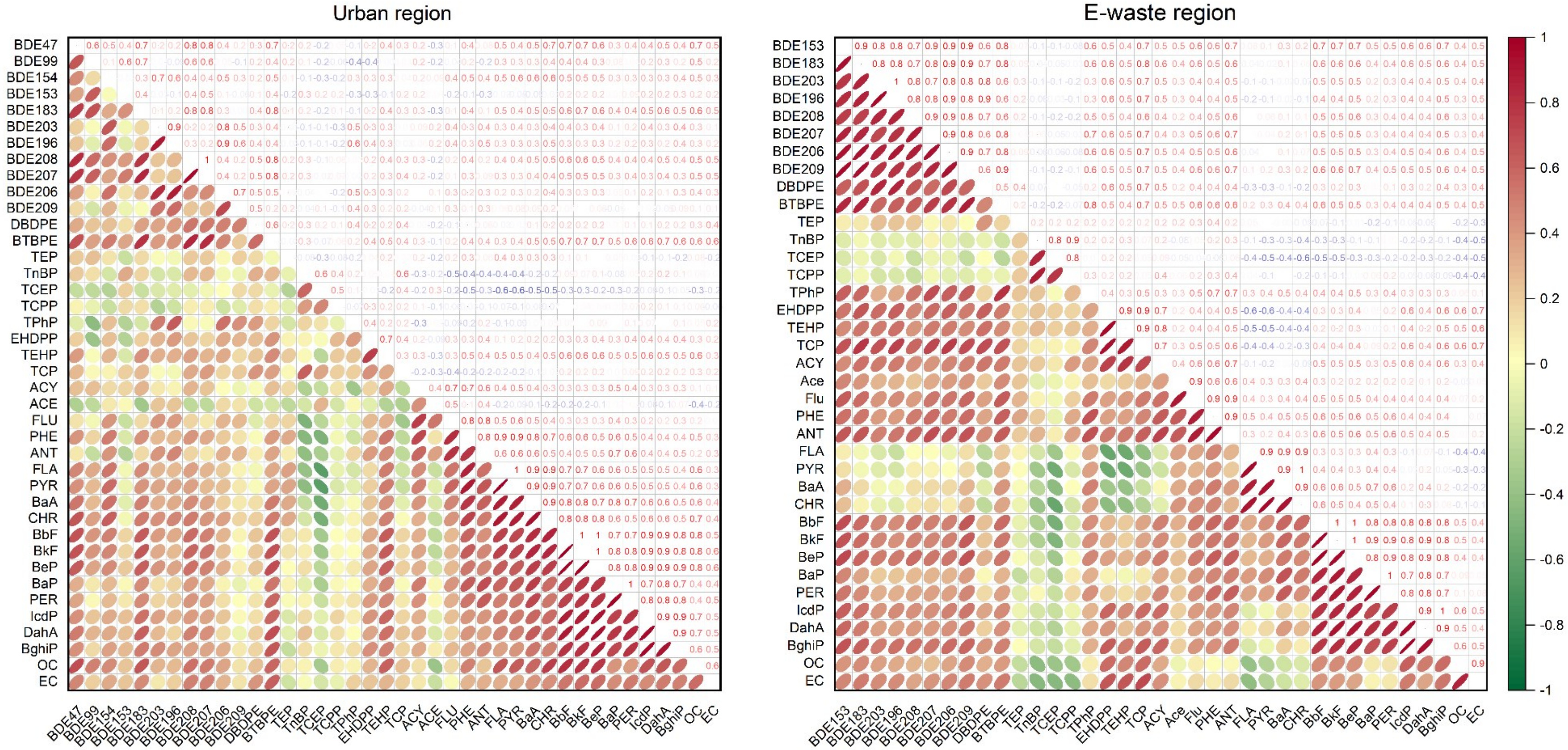

Fig. S3 Correlation matrix for the BFRs, OPEs, PAHs, OC and EC in $PM_{2.5}$ in the urban region and e-waste recycling region. A confidence level of 95% was applied.

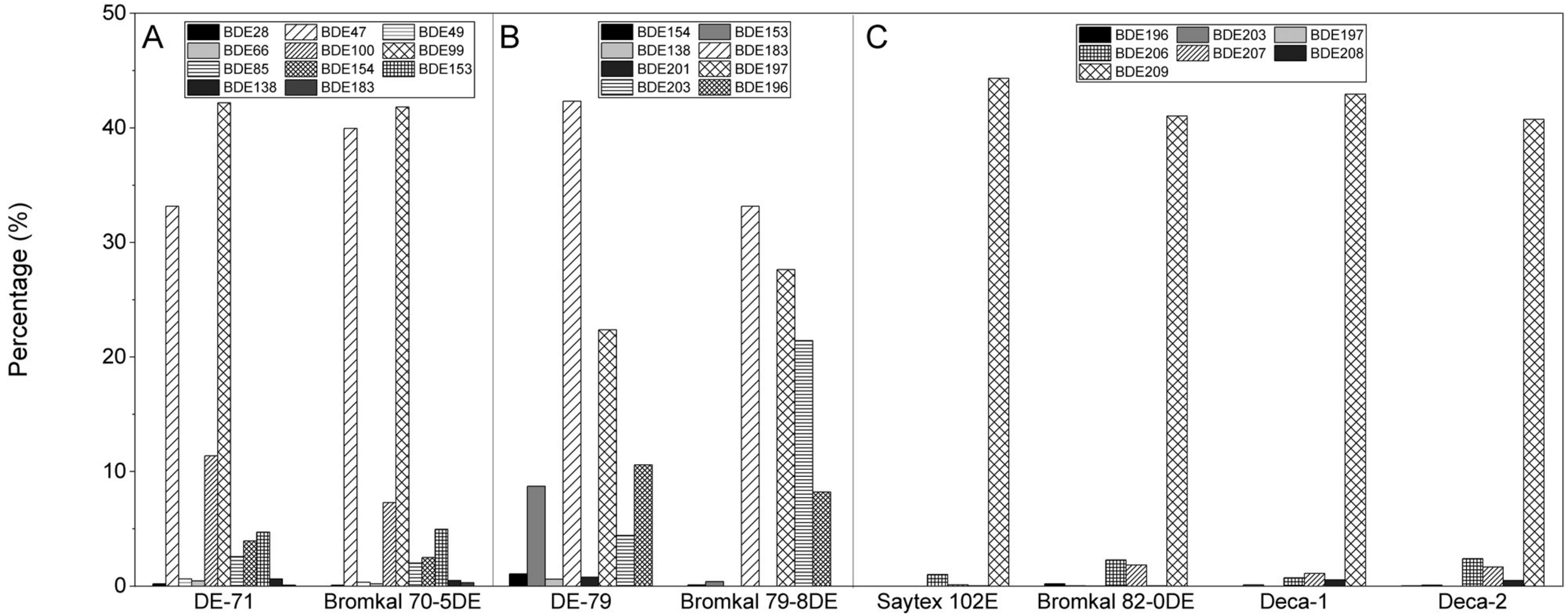

Fig. S4 Compositions of PBDEs in the commercial mixtures: congener profiles of c-PentaBDE (A), congener profiles of c-OctaBDE (B), congener profiles of c-DecaBDE (C). Data are from the literature[11], except for those of Deca-1 and -2 (two decaBDE mixtures produced in China) which are from the literature[12] .

Table S4. Physicochemical properties of selected target BFRs and PAHs[a].

Compd.	Mol wt	Log K_{OW}	VP (Pa) [b]	S (mg/L) [c]	Log K_{OA}	Half-life (d)	P_{OV} (hr)
BDE28	406.9	5.88	0.00122	0.02642	9.396	7.57	1810
BDE47	485.8	6.77	0.000211	0.001461	10.686	10.661	5740
BDE66	485.8	6.77	0.000815	0.001461	10.686	10.579	5740
BDE99	564.69	7.66	4.13 E-06	0.000394	11.157	19.439	5370
BDE100	564.69	7.66	0.000144	7.86E-05	11.977	14.856	6770
BDE153	643.59	8.55	2.48 E-05	4.15E-06	13.265	46.163	7170
BDE154	643.59	8.55	2.48 E-05	4.15E-06	13.265	28.885	7140
BDE183	722.48	9.44	4.21E-06	2.16E-07	14.554	64.327	7220
BDE196	801.38	10.33	6.99E-07	1.11E-08	15.845	98.714	7240
BDE203	801.38	10.33	164	2.68E-07	14.225	93.62	7380
BDE206	880.28	11.22	1.14E-07	5.63E-10	17.134	161.004	7250
BDE207	880.28	11.22	1.14E-07	5.63E-10	17.134	141.472	7250
BDE208	880.28	11.22	1.14E-07	5.63E-10	17.134	161.004	7250
BDE209	959.17	12.11	6.32E-07	2.84E-11	18.423	317.534	7260
DBDPE	971.23	13.64	9.33E-09	1.16E-12	19.221	4.466	6880
Nap	128.18	3.17	39.9	31	5.045	0.495	873
Acy	152.2	3.94	4.15	16.1	6.272	0.142	447
Ace	154.21	4.15	1.36	3.9	6.044	0.16	1000
Flu	166.22	4.02	0.619	1.69	6.585	1.208	471
Phe	178.24	4.35	0.0875	1.15	7.222	0.823	1790
Ant	178.24	4.35	0.0659	0.0434	7.093	0.267	1800
Fla	202.26	4.93	0.00811	0.26	8.601	0.366	2350
Pyr	202.26	4.93	0.0106	0.135	8.193	0.214	2340
BaA	228.3	5.52	0.000107	0.0094	9.069	0.214	3130
Chr	228.3	5.52	0.000168	0.00345	9.48	0.214	3360
BbF	252.32	6.11	0.00173	0.0015	10.351	0.576	4360
BkF	252.32	6.11	1.02E-05	0.0008	10.732	0.199	4200
BeP	252.32	6.11	2.45E-05	0.0063	11.351	0.214	4140
BaP	252.32	6.11	0.000107	0.00162	10.859	0.214	4220
Per	252.32	6.11	0.000203	0.0004	10.076	0.214	4200
IcdP	276.34	6.7	4.44E-07	0.00019	11.547	0.166	4630
DahA	278.36	6.7	3.33E-05	0.00249	11.779	0.214	4690
BghiP	276.34	6.7	4.24E-06	0.00026	11.499	0.123	4590

[a] The physicochemical properties were estimated using US EPA EPI program.
[b] Liquid/subcooled vapor pressure at 25 °C.
[c] Water solubility at 25 °C.

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