

Supplementary Information

Atmospheric deposition of polybrominated dibenzo-*p*-dioxins and dibenzofurans in Guangzhou, China: seasonal variations and sources

By

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Method: Extract cleanup for co-analysis of PBDD/Fs and PCDD/Fs

Extract cleanup was accomplished successively with the following steps: (1) Sample extracts were pre-cleaned with 20 g 40% H₂SO₄/silica gel (70-230 mesh, Merck, Germany) in 100 mL hexane (Merck, Germany, pesticide quality grade), and stirred for 2 h. The entire content of the flask was filtered through a funnel with glass wool covered with 10 g Na₂SO₄. One hundred milliliters of hexane was used to rinse the flask and the slurry. (2) The filtrates were further cleaned on a multi-layer silica gel column (from up to bottom, containing 1 cm Na₂SO₄, 2 g neutral silica gel, 8 g 40% H₂SO₄/silica gel, 1 g neutral silica gel, 4 g 33% KOH/silica gel, 1 g neutral silica gel and glass wool), eluted successively with 20 mL hexane (to be discarded) and 100 mL 3% dichloromethane (Merck, Germany, pesticide quality grade)/hexane. (3) Finally the extract was loaded on a florisil (1g) column, eluted successively with 15 mL 5:95 dichloromethane/hexane (dioxin like-PCBs fraction) and 100 mL 1:1 dichloromethane/hexane (PCDD/Fs and PBDD/Fs fraction).

The last fraction were respectively concentrated with rotary evaporator, transferred into a 1.5 ml tear-drop vial, and then concentrated further with N₂, finally added with corresponding recovery standards. They were determined with GC/HRMS.

Table S1. Deposition fluxes ($\text{pg d}^{-1} \text{m}^{-2}$) of PBDD/Fs and PCDD/Fs in Guangzhou, China^a

Time (month/year)	04/05	05/05	06/05	07/05	08/05	09/05	10/05	11/05	12/05	01/06	02/06	03/06
Rainfall (mm)	209.1	395.2	581.5	131.5	371.2	128.9	0.0	2.6	1.6	9.5	99.3	96.6
Temperature (°C)	22.6	27.3	27.9	29.9	28.7	28.5	25.8	22.2	15.1	15.8	17.3	17.9
Sample No.	Yc4	Yc5	Yc6	Yc7	Yc8	Yc9	Yc10	Yc11	Yc12	Yc13	Yc14	Yc15
2378-TBDF	36.4	45.8	44.4	36.6	43.7	21.5	13.8	8.2	5.7	8.2	9.0	11.6
12378-PeBDF	15.1	17.3	18.6	14.3	22.3	8.2	5.5	5.9	3.0	3.6	4.2	5.8
23478-PeBDF	22.3	12.7	28.9	23.9	26.1	14.0	12.0	6.5	4.8	4.9	6.5	6.7
2378-TBDD	1.3	2.4	2.3	0.9	3.1	0.6	0.4	0.1	0.1	0.4	0.2	0.7
12378-PeBDD	0.6	0.5	0.7	0.9	1.1	0.4	ND	0.1	0.3	0.2	0.1	0.3
123478/123678-HxBDD	ND	ND	1.0	2.4	2.3	0.8	0.3	0.3	0.5	0.3	0.3	0.1
123789-HxBDD	0.7	ND	1.0	1.4	2.3	ND	0.2	0.3	0.5	0.3	0.2	0.3
Σ 2378-PBDD/Fs	76.4	78.7	96.9	80.4	100.9	45.6	32.3	21.5	14.9	17.7	20.4	25.5
I-TEQ (PBDD/Fs)	17.2	14.5	22.6	18.0	22.7	10.5	8.1	4.6	3.5	3.9	4.6	5.7
Σ 2378-PCDD/Fs	595	863	537	272	427	262	215	295	263	541	556	639
Σ PCDD/Fs	1953	2809	1581	2235	3325	829	590	798	729	1092	1680	2246
WHO ₉₈ -TEQ (PCDD/Fs)	31.4	50.3	24.8	31.5	46.5	14.0	8.3	9.8	8.9	10.3	21.7	32.1
I-TEQ (PCDD/Fs)	29.0	46.9	22.9	29.2	43.5	12.7	7.9	9.0	8.3	9.5	20.1	29.5
Time (month/year)	04/05	05/05	06/05	07/05	08/05	09/05	10/05	11/05	12/05	01/06	02/06	03/06
Sample No.	Ws4	Ws5	Ws6	Ws7	Ws8	Ws9	Ws10	Ws11	Ws12	Ws13	Ws14	Ws15
2378-TBDF	32.3	42.1	48.4	25.1	32.4	25.7	12.3	7.9	9.6	7.6	4.7	8.0
12378-PeBDF	10.4	25.9	22.6	9.2	19.9	12.7	2.9	3.1	4.6	4.2	2.8	4.2
23478-PeBDF	14.0	34.7	32.4	13.8	26.7	21.7	6.7	5.9	6.8	6.3	4.2	6.2
2378-TBDD	0.9	2.0	2.0	1.0	1.6	0.8	0.3	0.2	0.4	ND	ND	ND
12378-PeBDD	ND	1.0	ND	0.7	0.8	0.7	0.3	0.2	0.2	ND	ND	ND
123478/123678-HxBDD	ND	1.9	7.6	1.4	1.5	1.2	0.3	0.9	0.7	0.7	ND	ND
123789-HxBDD	ND	1.3	2.4	1.5	1.0	0.5	ND	1.6	0.5	0.6	ND	ND
Σ 2378-PBDD/Fs	57.5	108.9	115.2	52.5	83.8	63.4	22.7	19.9	22.7	19.7	12.6	19.0
I-TEQ (PBDD/Fs)	11.6	25.7	25.1	11.4	19.8	15.4	5.2	4.5	5.1	4.5	3.0	4.4
Σ 2378-PCDD/Fs	779	689	592	587	874	220	214	284	336	302	704	551
Σ PCDD/Fs	2912	2379	1760	1487	2337	675	568	735	769	880	1546	2084
WHO ₉₈ -TEQ (PCDD/Fs)	33.2	41.2	26.8	20.1	31.8	11.0	8.6	10.3	8.2	10.3	16.5	25.4
I-TEQ (PCDD/Fs)	30.3	37.7	24.7	18.8	29.3	9.8	8.1	9.4	7.7	9.4	15.3	23.1
Time (month/year)	04/05	05/05	06/05	07/05	08/05	09/05	10/05	11/05	12/05	01/06	02/06	03/06
Sample No.	Hz4	Hz5	Hz6	Hz7	Hz8	Hz9	Hz10	Hz11	Hz12	Hz13	Hz14	Hz15
2378-TBDF	31.9	43.7	75.3	25.2	31.2	17.0	14.4	6.0	5.2	6.1	5.7	7.7
12378-PeBDF	12.6	29.1	27.4	11.7	13.0	5.4	4.7	2.8	2.4	2.8	3.1	3.3
23478-PeBDF	16.3	22.4	34.5	23.5	16.8	10.8	9.1	4.3	4.4	5.1	4.5	4.7
2378-TBDD	1.5	2.4	1.7	1.0	1.5	0.5	0.3	ND	ND	ND	ND	0.5
12378-PeBDD	0.8	4.3	ND	2.3	1.0	0.5	0.4	ND	ND	ND	ND	ND
123478/123678-HxBDD	ND	ND	2.2	1.4	0.6	0.5	ND	0.5	ND	ND	ND	ND
123789-HxBDD	ND	3.6	1.8	0.9	0.6	0.5	0.3	1.0	ND	ND	ND	ND
Σ 2378-PBDD/Fs	63.1	105.5	142.7	66.0	64.6	35.2	29.3	15.0	12.9	15.0	13.9	16.6
I-TEQ (PBDD/Fs)	13.9	21.9	28.2	17.2	14.2	8.3	6.8	3.3	3.0	3.5	3.2	3.9
Σ 2378-PCDD/Fs	659	437	503	207	—	249	380	219	254	472	387	580
Σ PCDD/Fs	2347	1444	1381	1756	—	843	764	678	706	1288	1299	1949
WHO ₉₈ -TEQ (PCDD/Fs)	36.3	24.6	21.5	25.3	—	12.8	8.2	9.2	7.4	16.8	18.1	27.2
I-TEQ (PCDD/Fs)	33.1	23.1	20.1	23.4	—	11.6	7.8	8.4	6.9	15.6	16.5	24.7

Continued

Time (month/year)	04/05	05/05	06/05	07/05	08/05	09/05	10/05	11/05	12/05	01/06	02/06	03/06
Sample No.	Cb4	Cb5	Cb6	Cb7	Cb8	Cb9	Cb10	Cb11	Cb12	Cb13	Cb14	Cb15
2378-TBDF	17.5	39.5	28.9	28.0	35.0	13.7	16.9	5.8	6.8	5.1	5.3	6.4
12378-PeBDF	8.0	12.4	9.4	11.3	14.1	5.6	8.3	2.6	2.7	2.0	3.5	3.1
23478-PeBDF	12.2	15.8	18.2	10.6	13.2	8.0	8.2	3.7	3.4	2.6	5.0	4.2
2378-TBDD	0.5	1.8	0.7	3.4	4.2	0.5	0.3	0.1	0.4	0.3	0.1	0.2
12378-PeBDD	0.3	0.5	0.9	1.6	2.0	0.5	ND	0.2	0.2	0.2	0.2	0.4
123478/123678-HxBDD	0.3	ND	ND	0.5	0.6	0.3	0.8	1.2	0.1	0.1	0.3	0.2
123789-HxBDD	0.5	1.5	0.6	1.7	2.2	ND	0.6	1.0	0.3	0.2	0.1	0.1
∑2378-PBDD/Fs	39.3	71.4	58.6	57.1	71.3	28.6	35.0	14.6	14.0	10.5	14.6	14.5
I-TEQ (PBDD/Fs)	9.0	14.6	13.6	13.1	16.3	6.5	6.7	3.0	3.1	2.3	3.5	3.3
∑2378-PCDD/Fs	383	462	—	—	436	236	161	257	175	359	612	504
∑PCDD/Fs	1271	1510	—	—	2784	633	408	631	405	785	1663	1649
WHO ₉₈ -TEQ (PCDD/Fs)	18.9	24.0	—	—	42.0	10.5	6.8	9.4	4.8	8.3	21.9	21.9
I-TEQ (PCDD/Fs)	17.1	22.0	—	—	39.0	9.5	6.4	8.7	4.4	7.9	20.2	19.7

^a —: PCDD/Fs were not analyzed. ND: not detected.

Table S2. Relative proportion (%) of PBDD/Fs in bulk deposition and sources

	Bulk deposition ^a	E-waste air ^b	Stack flue gas				
			IWIs ^c	MSWIs ^c	Batch MSWIs ^c	Carbon steel EAFs ^d	Stainless steel EAFs ^d
2378-TBDF	45	49	42	15	13	11	17
12378-PeBDF	20	19	23	11	12	12	12
23478-PeBDF	28	22	23	27	22	10	28
2378-TBDD	1.8	3.2	4.5	2.8	2.2	4.0	4.2
12378-PeBDD	1.2	2.8	5.5	4.5	11	5.8	12
1234/678-HxBDD	1.6	2.6	2.4	30	25	46	18
123789-HxBDD	1.8	1.5	3.9	13	14	11	8.4

^a this study. ^b data from ref 10. ^c data from ref 11. ^d data from ref 12.