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Supplementary Information

PCDD/Fs, PBDD/Fs, and PBDEs in the air of an E-waste recycling area (Taizhou) in China: Current Levels, composition profiles, and potential cancer risks

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2. Materials and methods

Internal standards. The internal standards, 13C-labeled substituted PCDD/Fs (EPA-1613LCS, Wellington Lab, Canada), PBDD/Fs (BFR-LCS, Wellington Lab, Canada), PBDEs, and HBB (EDF-5382, Cambridge Isotope Laboratory, USA), the extracts were applied to a liquid-liquid sulfuric acid extraction. Specifically, the PCDD/F clean–up internal standards included 15 ^{13}C substituted PCDD/F congeners (5 PCDDs and 10 PCDFs) with toxic equivalent factors available. An amount of 1000 ng of every congener was spiked per example. The PBDD/F clean–up internal standards included 10 ^{13}C substituted PCDD/F congeners (5 PBDDs and 5 PBDFs) with spike amounts of 500-11,250 ng (congener specific) per sample. The internal standards for PBDEs included 16 ^{13}C substituted di-deca BDEs and HBB with spike amounts of 1000-10,000 ng (congener specific) per sample. For the instrumental internal standards, 2 ^{13}C substituted congeners for PCDD/Fs, 2 ^{13}C substituted congeners for PBDD/Fs, and 4 ^{13}C substituted congeners for PBDEs, were used.

Clean-up. The extracts were further cleaned through a multilayer silica column packed, from the bottom to the top, with 3 g anhydrate sodium sulfate, 1 g neutral silica gel, 3 g 2% NaOH silica gel, 1 g neutral silica gel, 4.5 g 44% sulfuric acid silica gel, 6 g 22% H_2SO_4 silica gel, 1 g neutral silica gel, and 2g anhydrate sodium sulfate and eluted with 200 mL hexane.

Instrumental analysis. Sample analysis was performed with an Agilent high resolution gas chromatography (HRGC) couple to a Autospec-Ultma NT high resolution mass spectrometry (HRMS) using electron impact ionization (ionizing energy 35ev at a resolution over 10000). Before analysis, 13C-labled PCDD/Fs, PBDD/Fs, and PBDEs were added to the extracts as instrumental internal standards. A DB-5MS (60 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column (J&W Scientific; CA, USA) was used for separating PCDD/Fs in splitless injection mode. Due to the higher molecular weights and unstable property of high brominated congeners of PBDD/Fs and PBDEs, comparing to PCDD/Fs, a DB-5HT (15 m × 0.1 mm i.d., 0.1 μm film thickness) capillary column (J&W Scientific) in a pulse injection mode was applied. Five-point calibration curve was used in the PCDD/Fs calibration curve, from 0.5 to 200 ng/mL; six-point calibration curve was used in the PBDD/Fs calibration curve, from 0.1 to 40 ng/mL; and five-point calibration curve was used in the PBDEs calibration curve, from 0.25-2.5 to 100-1000 ng/mL. The target compounds include 17 2,3,7,8-chlorine substituted PCDD/F congeners, 11 tetra- to octa- bromine substituted PBDD/Fs, 41 mono- to deca-BDEs, HBB, and PBEB.

OC and BC measurement. Two sub-samples (0.55 cm in diameter) were punched form each filter. OC and BC contents were measured by a Thermal/Optical Carbon Analyzer (DRI 2001A, Desert Research Institute, USA). The reported OC/BC values were the average of two piece measurements.

Data analysis. Pearson correlation analysis was applied to the concentration data. Cluster analysis was applied to the percentage contributions of PCDD/F homologues and PBDE congeners by the Ward method with squared Euclidean distance. Both were carried out using SPSS 16.0 for Windows (SPSS Inc., Chicago, IL).

TEQ concentration calculation. The TEQ concentrations for PCDD/Fs and

PBDD/Fs were calculated based on the $(WHO-TEF)_{2005}$ values for PCDD/Fs by equations

$$WHO-TEQ_i = C_i \times (WHO-TEF)_{2005} \quad (1)$$

$$\text{Total WHO}-\text{TEQ} = \sum_i WHO-TEQ \quad (2)$$

where $WHO-TEQ_i$ is the toxic equivalent quantity for congener i (PCDD/Fs or PBDD/Fs) derived from $(WHO-TEF)_{2005}$ values for PCDD/Fs (pg WHO-TEQ m^{-3}); C_i is the mass concentration of congener i (pg $m^{-3)}$; $(WHO-TEF)_{2005}$ are toxic equivalent factors for 17 PCDD/F congeners suggested by WHO (see Table a). Since no TEF value for PBDD/Fs available up to now, $(WHO-TEF)_{2005}$ values for PCDD/Fs were used for corresponding PBDD/F congeners.

Table a. The WHO-TEFs of 17 PCDD/F congeners suggested by WHO.

PCDD/Fs congener	WHO-TEFs
2378-TCDF	0.1000
12378-PeCDF	0.0300
23478-PeCDF	0.3000
123478-HxCDF	0.1000
123678-HxCDF	0.1000
123789-HxCDF	0.1000
234678-HxCDF	0.1000
1234678-HpCDF	0.0100
1234789-HpCDF	0.0100
OCDF	0.0003
2378-TCDD	1.0000
12378-PeCDD	1.0000
123478-HxCDD	0.1000
123678-HxCDD	0.1000
123789-HxCDD	0.1000
1234678-HpCDD	0.0100
OCDD	0.0003

Table S1. Concentrations of 17 2,3,7,8-substituted PCDD/Fs and native homologues(pg m^{-3}), in the air (gaseous and particle-phases) of Taizhou, eastern China.

Sampling site	**2,3,7,8-substituted PCDD/Fs**			**native homologues**		
	Summer		Winter	Summer		Winter
	June 2-3	June 3-4	Jan 11-14	June 2-3	June 3-4	Jan 11-14
Industrial zone site	18.3	14.8	11.2	33.4	80.2	61.2
E-waste site	14.3	6.43	6.33	10.6	36.0	31.9
Historical e-waste site	21.1	19.5	8.46	45.7	35.7	40.0
Residential site	5.32	4.95	4.62	15.4	14.7	24.8
Suburban site	1.43	2.07	2.47	7.13	8.79	11.1
Background site	0.476	1.74	7.18	1.48	9.05	28.4

Table S2. Concentrations of 17 2,3,7,8-substituted PBDD/Fs and native homologues(pg m^{-3}), in the air (gaseous and particle-phases) of Taizhou, eastern China.

Sampling site	**2,3,7,8-substituted PBDD/Fs**			**native homologues**		
	Summer		Winter	Summer		Winter
	June 2-3	June 3-4	Jan 11-14	June 2-3	June 3-4	Jan 11-14
Industrial zone site	6.50	21.1	16.2	104	155	170
E-waste site	1.69	4.34	3.44	36.9	58.9	59.0
Historical e-waste site	5.37	8.99	5.98	92.4	79.0	132
Residential site	0.434	3.21	2.39	21.1	55.8	39.1
Suburban site	0.259	7.32	1.60	6.18	81.0	21.9
Background site	0.080	0.784	1.37	3.54	13.2	19.9

Table S3. Pearson correlation coefficients for the target compounds.

	PBDD/Fs	PBDEs	BDE209	HBB	PBEB	OC	BC
PCDD/Fs	0.629**[a]	0.671**	0.592**	0.268	0.253	0.506* [b]	0.674**
PBDDFs		0.833**	0.771**	0.396	0.361	0.512*	0.564*
PBDEs			0.914**	0.544**	0.552*	0.327	0.430
BDE209				0.536*	0.607**	0.382	0.344
HBB					0.587**	0.142	0.208
PBEB						-0.272	0.077

[a] The correlations are significant at p <0.05.

[b] The correlations are significant at p <0.01.

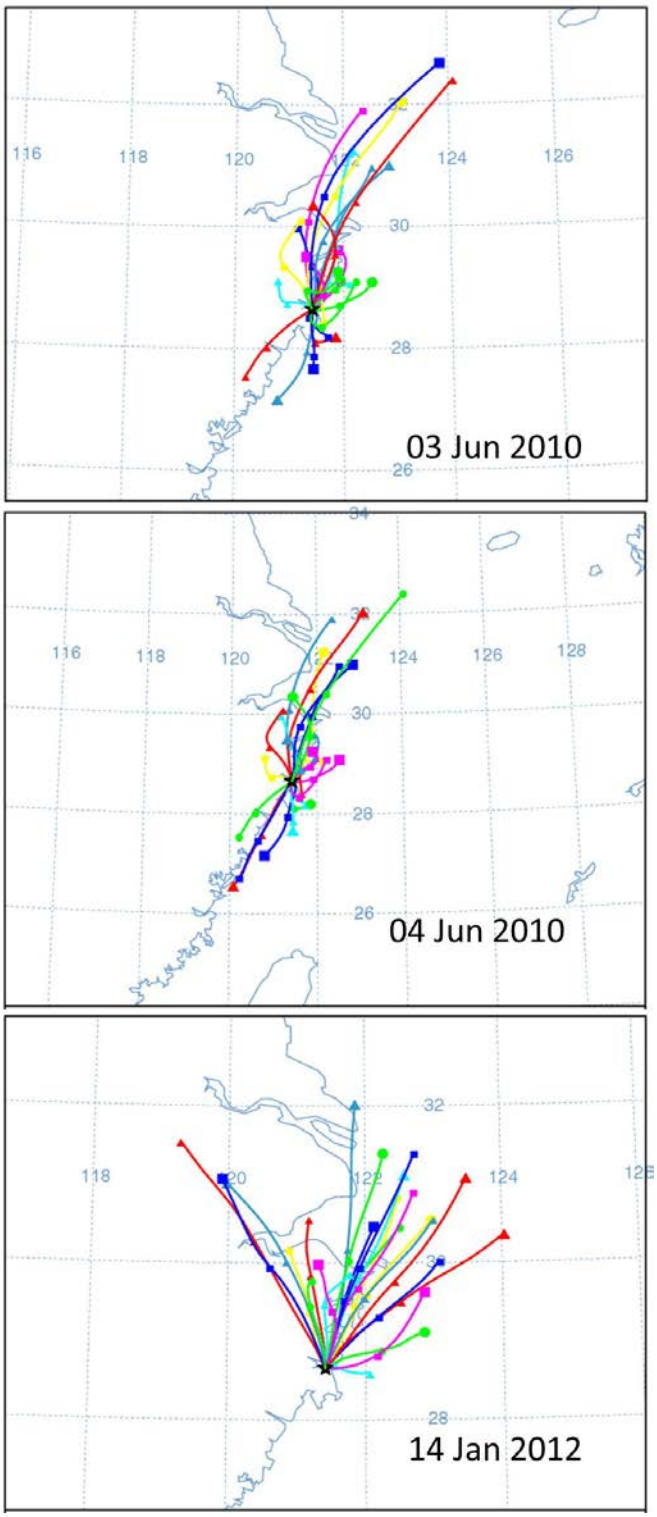

Fig. S1 The NOAA HYSPLIT backward trajectories (12 h) for Taizhou at 12 UTC on 3-4 Jun, 2010 and 14 Jan 2012 produced on the website of NOAA (http://www.noaa.gov/).

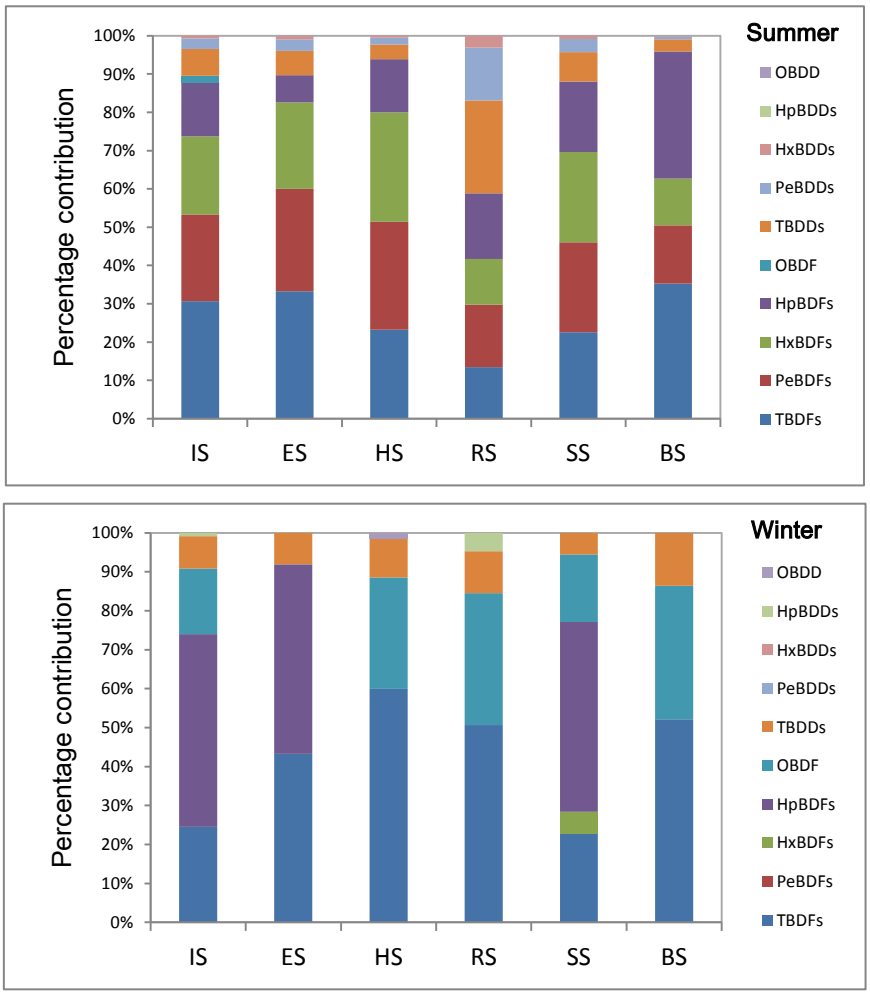

Fig. S2 Homologue profiles of PBDD/Fs in the air in summer and winter at different sites in Taizhou.

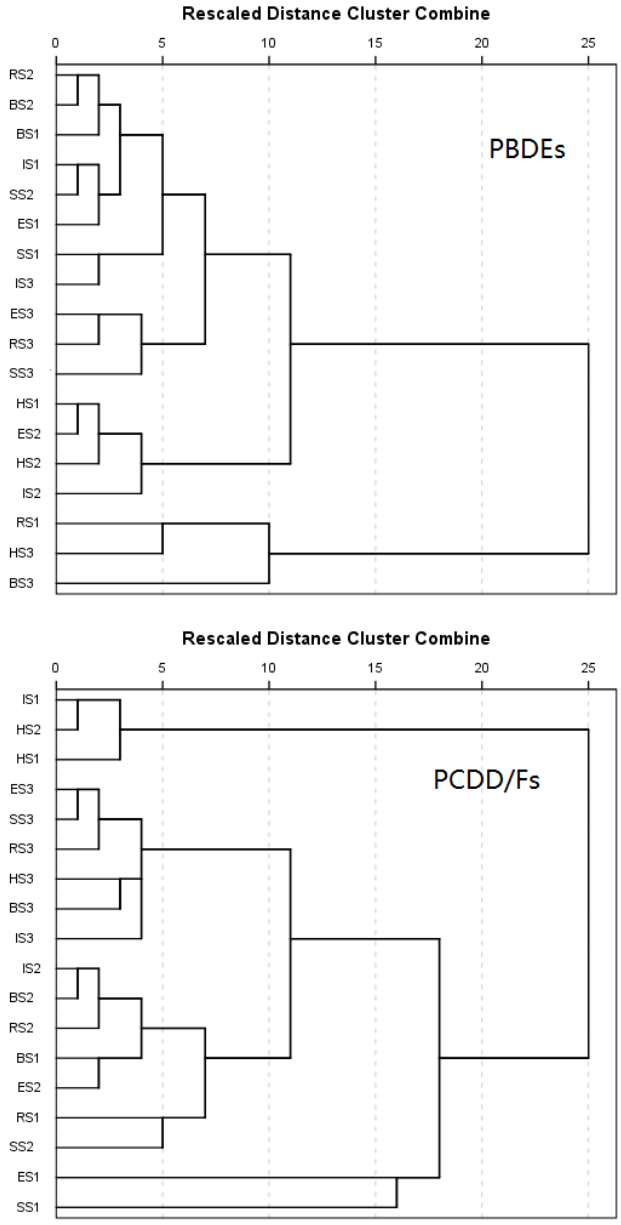

Fig. S3 Dendrogram of hierarchical cluster analysis for PCDD/F homologues and PBDE congeners.