

Cite this: *J. Environ. Monit.*, 2012, **14**, 3156

www.rsc.org/jem

PAPER

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†

Ting Zhang,^{abc} Ye-Ru Huang,^a She-Jun Chen,^{*b} Ai-Min Liu,^a Peng-Jun Xu,^a Nan Li,^a Li Qi,^a Yue Ren,^a Zhi-Guang Zhou^a and Bi-Xian Mai^b

Received 4th August 2012, Accepted 4th October 2012

DOI: 10.1039/c2em30648d

Atmospheric concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs), and polybrominated diphenyl ethers (PBDEs) were measured in Taizhou, a large electronic equipment waste (e-waste) recycling area in East China. The mean concentrations (in summer and winter) of PCDD/Fs (0.45 and 0.39 pg WHO-TEQ m⁻³, where WHO-TEQ is the toxic equivalent set by the World Health Organisation), PBDD/Fs (0.22 and 0.18 pg WHO-TEQ m⁻³), and PBDEs (270 and 225 pg m⁻³) in this region have declined compared with those in 2005, due to regulations on primitive e-waste recycling activities. However, these concentrations remain higher than the historically highest levels in Europe and North America. The congener profiles of 2,3,7,8-substituted PCDD/Fs were similar, with OCDD, 1,2,3,4,6,7,8-HpCDF, OCDF, and 1,2,3,4,6,7,8-HpCDD being the most abundant congeners at all sites. The PCDD/F homologue profiles in the present study were different from those typically observed at non-e-waste locations, indicating a distinct source in this region. Seasonal differences were found in the lower brominated PBDE profiles. These differences indicate that the PBDE emission sources in summer (*e.g.*, strong evaporation sources) differed from those in winter. However, the relatively steady congener profiles of the highly brominated PBDEs suggest that these PBDEs were controlled primarily by similar emission mechanisms. The lifetime excess cancer risks from exposure to PCDD/Fs and PBDD/Fs *via* inhalation ranged from 0.7×10^{-5} to 5.4×10^{-5} , or approximately 80 cancer cases in the Taizhou population.

1. Introduction

PCDD/F emissions are mainly the result of various industrial processes, the incineration of materials containing chlorine (*e.g.* municipal solid wastes), and natural processes such as volcanic eruptions and forest fires.^{1,2} Over the past few decades, these emissions have been dramatically reduced, mainly in Europe and North America, due to efforts from both industries and authorities.²⁻⁴ Nevertheless, these chemicals remain a concern because of their persistence in the environment and the highly toxic potential of some congeners.⁵ PBDEs are additive flame

^aState Environmental Protection Key Laboratory for Dioxin Pollution Control, National Research Center for Environmental Analysis and Measurement (CNEAC), Beijing 100029, China

^bState Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China. E-mail: chenshejun@gig.ac.cn; Tel: +86 20 8529 0146. Fax: +86 20 8529 0706

^cGraduate University of Chinese Academy of Sciences, Beijing 100049, China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2em30648d

Environmental impact

PCDD/Fs, PBDD/Fs, and PBDEs are important toxic pollutants that are released from uncontrolled e-waste recycling in developing countries. However, little is known about the contamination status of these compounds after the introduction of regulations on e-waste recycling by Chinese government. Air samples were collected in summer and winter in a large e-waste area (Taizhou) to investigate their current levels, composition profiles, and major sources. We also estimated the associated lifetime excess inhalation cancer risk for the population.

retardants that are extensively used in consumer products, including electronic equipment, textiles, furniture, and cars.⁶ PBDEs have been detected globally in various environmental media, wildlife and humans.^{7,8} Some PBDEs (tetra- through hepta-BDE congeners) have been included in the newly listed persistent organic pollutants (POPs) of the 2009 Stockholm Convention.⁹ PBDD/Fs, analogues of PCDD/Fs, are generated as unwanted by-products in various industrial and combustion processes,¹ but also as impurities in commercial deca-BDE mixtures,¹⁰ or from the photochemical degradation of brominated compounds.¹¹

Over the last decade, e-waste has emerged as a growing problem for many developing countries, such as China, India and African and Latin American countries,¹² where a considerable amount of e-waste (generated domestically or imported from overseas) is usually recycled using crude methods of disposal. As a result, a wide range of toxic compounds, including PCDD/Fs, PBDD/Fs, PBDEs, polychlorinated biphenyls and heavy metals, have been released into the environment and local people have been exposed to these compounds. Many studies have been conducted on the environmental occurrence of these contaminants associated with e-waste recycling in developing countries, and high levels have been reported.^{13–16} In recent years, the Chinese government has taken measures to regulate informal e-waste recycling activities to protect the environment and public health. These actions include building e-waste recycling industrial zones, reducing scattered backyard workshops, creating efficient facilities and banning the open burning of e-waste. It is therefore necessary to understand the current contamination status of e-waste areas in China since these regulations were put in place.

In the present study, we measured the concentration levels of PCDD/Fs, PBDD/Fs, and a number of brominated flame retardants (BFRs), including PBDEs, hexachlorobenzene (HCB) and pentabromoethylbenzene (PBEB), in the ambient air at various locations in Taizhou City. Taizhou began dismantling e-waste in the early 1980s and has become one of the largest e-waste processing centers in China. The number of e-waste dismantling workers in this region has been estimated at 50 000, with more than 150 000 involved in recycling.¹⁷ We aimed to investigate the current atmospheric levels, composition profiles, and major sources of these polyhalogenated compounds. We also aimed to estimate the lifetime excess inhalation cancer risk associated with exposure to PCDD/Fs and PBDD/Fs in local populations.

2. Materials and methods

More detailed information on the materials and methods is available in the ESI.[†]

2.1 Sampling

Taizhou, located in Zhejiang Province in eastern China, has a subtropical monsoon climate characterized by northerly winds in winter (from November to February) and highly variable winds in summer (from June to August). The highest temperature appears in July and the lowest in January, with an annual average temperature of ~ 15 °C. Air samples were collected

concurrently at six sites in different districts of Taizhou (Fig. 1): an industrial zone site (IS), an e-waste site (ES), a historical e-waste site (HS), a residential site (RS), a suburban site (SS), and a background site (BS). The IS is located in a formal e-waste recycling center in Taizhou; the ES is located in a village where e-waste is manually dismantled in domestic workshops; the HS is located in a village where a large amount of e-waste was previously recycled using primitive methods; and the RS, SS and BS are located in the city center, beside a reservoir, and near the shore, respectively. At each site, two 24 h air samples were taken in June 2010 and one 72 h air sample was taken in January 2012. The samples were collected from the rooftops of buildings (15–20 m above ground for the industrial zone and residential sites) or on the ground (1 m above the ground) for the others. Air samples (gaseous and particle phases) were collected using high-volume air samplers (HV-700F, SIBATA Corp. Japan). Air was drawn through quartz microfiber filters (QMFs) followed by polyurethane foam (PUF) at flow rates of 700 L min^{-1} (for samples in June) and 500 L min^{-1} (for samples in January).

Before sampling, the QMFs were baked at 600 °C for 4 h to remove potential organic impurities, and the PUFs were extracted by an accelerated solvent extractor (ASE, Dionex, USA), first with acetone, then with dichloromethane. After sampling, the samples were wrapped with aluminum foil, sealed in a zipper bag, and transported to the laboratory, where they were analyzed immediately.

2.2 Sample extraction and clean-up

The analytical method employed for the target compounds, PCDD/Fs, PBDD/Fs and PBDEs, is based on US Environmental Protection Agency (EPA) method 1613 for PCDD/Fs, in which isotope dilution is performed in combination



Fig. 1 Map of sampling locations in Taizhou, eastern China. The six sampling sites (★, IS: industrial zone site, ES: e-waste site, HS: historical e-waste site, RS: residential site, SS: suburban site, and BS: background site) cover four of the administrative districts of Taizhou (A: Jiaojiang, B: Luqiao, C: Huangyan, and D: Wenling).

with high-resolution capillary column gas chromatography (HRGC)/high resolution mass spectrometry (HRMS). This method was developed to analyze PBDD/Fs and PBDEs. The particle-loaded filters and PUF samples are extracted separately with toluene and a 1 : 1 mixture of hexane and dichloromethane using Accelerated Solvent Extractor (ASE) 300 (Dionex Corp., California) at 100 °C under a pressure of 1500 psi. A static time of 5 minutes and 2 cycles was employed. The extracts were combined and concentrated using a rotary evaporator and then solvent-exchanged with hexane. The extracts were divided into two equal fractions (one of which was used for a back-up). After being spiked with internal clean-up standards, ¹³C-labeled-substituted PCDD/Fs, PBDD/Fs, PBDEs, and HBB, the extracts were used in a liquid–liquid sulfuric acid extraction.

The extracts were further cleaned through a multilayer silica column and eluted with 200 mL hexane. Concentrated extracts were then fractionated with an activate carbon column (which was packed with 1 g anhydrate sodium sulfate, 1 g embedded activate carbon silica gel, and 1 g anhydrate sodium sulfate) by elution with 200 mL 25% hexane/dichloromethane (F1, containing PBDEs, HBB, and PBEB) and 250 mL toluene (F2, containing PCDD/Fs and PBDD/Fs). The fractions were concentrated with a rotary evaporator to 1 mL and transferred to a K-D manifold for concentration to near dryness with a gentle nitrogen stream.

2.3 Instrumental analysis

Sample analysis was performed using an Agilent HRGC coupled to a Micromass Autospec-Ultima NT HRMS using electron impact ionization. Before analysis, ¹³C-labeled PCDD/Fs, PBDD/Fs, and PBDEs were added to the extracts as instrumental internal standards. A DB-5MS (60 m × 0.25 mm in diameter, 0.25 μm film thickness) capillary column (J&W Scientific; CA, USA) was used to separate PCDD/Fs in the splitless injection mode. Due to the higher molecular weights of PBDD/Fs and PBDEs compared with PCDD/Fs, a DB-5HT (15 m × 0.1 mm in diameter, 0.1 μm film thickness) capillary column (J&W Scientific) in a pulse injection mode was applied to these. The target compounds included 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. The contents of organic and black carbons (OC and BC, respectively) in bulk particles were measured using a Thermal/Optical Carbon Analyzer (DRI 2001A, Desert Research Institute, USA).

2.4 Quality control

For each sample set, a field blank (clean PUF plugs and QMFs) was collected that was identical to that of the real samples, but without air drawn through it. The results showed that the PCDD/F congeners have background values below the detection limit of the method, or lower than 20% of the amount in the sample extracts. BDE47, 99 and 209 were detected in the field blanks in quantities lower than 20% of those in the samples, and these quantities were subtracted from the sample extracts.

The recoveries of the ¹³C-labeled PCDD/Fs ranging from 17% to 181% met the criteria of the EPA 1613 method for PCDD/Fs. The recoveries of the ¹³C-labeled PBDD/Fs ranged from 54% to

163%, except for ¹³C OBDD and ¹³C OBDF, which are quite unstable and are not reported here. The recoveries of most ¹³C-labeled PBDEs in the samples were between 61% and 150%, except for mono-BDEs and some di-BDEs, which had low recoveries of <40% due to their high volatility. The recoveries of ¹³C-labeled HBB, as an internal standard for both HBB and PBEB quantitation, ranged from 33% to 128%. For samples that did not meet the recovery criteria, reanalysis was performed using the back-up sample fractions.

2.5 Exposure and risk assessment

The inhalation exposure to these polyhalogenated compounds for populations living in the different districts of Taizhou (Fig. 1) was calculated based on the air concentrations measured in this study using the following equation:

$$\text{inhalation dose (pg kg}^{-1} \text{ per day)} = \frac{C_i \times IR \times ET \times EF \times ED \times AF}{BW \times AT} \quad (1)$$

where C_i is the concentration of pollutants in the air (pg TEQ m⁻³ or pg m⁻³), IR is the inhalation rate (m³ h⁻¹), ET is the exposure time (hours per day), EF is the exposure frequency (days per year), ED is the exposure duration (years), AF is the inhalation absorption fraction, BW is the body weight (kg), and AT is the averaging time (days). The mean air concentrations for each site were used for the evaluation, which represent both the indoor and outdoor air levels. The inhalation rate of 0.9 m³ h⁻¹ (95th percentile for adults) for long-term exposure recommended by the U.S. EPA was used.¹⁸ The exposure time, exposure frequency, and exposure duration were 24 hours per day, 330 days per year, and 70 years, respectively. The inhalation absorption factor was assumed to be 100% ($AF = 1$). A body weight of 70 kg for an adult and an averaging time of 365 days per year (25 550 days) were used.

The lifetime excess cancer risk of inhalation of PCDD/Fs and PBDD/Fs for a population was estimated by the following equation:

$$\text{cancer risk} = \text{inhalation dose} \times \text{inhalation cancer slope factor} \quad (2)$$

The inhalation cancer slope factor of 1.5×10^5 (mg kg⁻¹ d⁻¹)⁻¹ for 2,3,7,8-TCDD, calculated by the U.S. EPA, was used for both PCDD/Fs and PBDD/Fs.¹⁹ The cancer risks were estimated for the populations in the four administrative districts of Taizhou where the sampling sites are located.

3. Results and discussion

3.1 Concentrations and spatial variations

PCDD/Fs. Concentrations were present in both the particle and vapor phases. The total PCDD/F concentrations in the air at the sampling sites ranged from 7.13 to 106 pg m⁻³ in summer and from 11.1 to 61.2 pg m⁻³ in winter, with mean concentrations of 32.8 and 32.9 pg m⁻³, respectively (Table S1 in the ESI†). The mean dioxin-like TEQ concentrations of 2,3,7,8-substituted PCDD/Fs (obtained using the 2005 WHO toxic equivalent factors) in summer and winter were 0.45 and 0.39 pg TEQ m⁻³, respectively (Table 1). In both summer and winter, the

Table 1 Concentrations of PCDD/Fs (pg WHO-TEQ m⁻³), PBDD/Fs (pg WHO-TEQ m⁻³), and BFRs (pg m⁻³) in the air (gaseous and particle phases) of Taizhou, eastern China

Sampling site	PCDD/Fs	PBDD/Fs	PBDEs	BDE209	HBB	PBEB
<i>Summer (June)^a</i>						
Industrial zone site	0.907	0.331	500	213	29.4	3.78
E-waste site	0.606	0.124	278	114	7.76	0.59
Historical e-waste site	0.860	0.390	476	176	10.8	0.26
Residential site	0.191	0.309	118	65.5	3.06	0.11
Suburban site	0.096	0.152	159	85.0	45.7	0.41
Background site	0.051	0.013	86.5	45.2	17.7	0.16
<i>Winter (January)</i>						
Industrial zone site	0.704	0.686	541	326	11.5	0.32
E-waste site	0.361	0.0960	162	82.5	8.74	0.03
Historical e-waste site	0.488	0.126	409	100	13.8	0.03
Residential site	0.292	0.067	58.1	24.8	1.96	0.05
Suburban site	0.154	0.077	139	27.0	4.52	0.02
Background site	0.349	0.029	40.8	19.80	2.12	0.02

^a Average values.

concentrations measured at the industrial zone, historical e-waste, and e-waste sites (0.36–0.91 pg TEQ m⁻³) were significantly higher ($p \leq 0.007$) than those from the residential, suburban, and background sites (0.05–0.35 pg TEQ m⁻³). This finding clearly reveals that the increased atmospheric PCDD/F concentrations were associated with e-waste recycling. Although the e-waste recycling activities have been discontinued, emissions from contaminated media (such as e-waste scrap, e-waste burning remains, and/or soil) may remain an important source of PCDD/Fs in the air. The concentrations of PCDD/Fs in the winter samples from the industrial zone, historical e-waste, and e-waste sites were slightly lower than those in summer, whereas elevated concentrations (especially for total native PCDD/Fs) were found at the three non-point source sites (11.1–28.4 pg m⁻³) in winter compared to those in summer (7.13–15.4 pg m⁻³). This result is likely attributable to the increased coal and wood combustion for residential heating in winter, which has been shown to be a significant source of PCDD/Fs.^{20,21}

The average PCDD/F concentration (0.42 pg TEQ m⁻³) in the present study was 2-fold lower than that in the air in 2005 (1.10 pg TEQ m⁻³) from the same region (e-waste, urban, and rural sites) and was much lower than that from another e-waste site in 2005 (8.78 pg TEQ m⁻³).^{22,23} This result reflects a substantial reduction of atmospheric PCDD/F pollution, due to the regulations on e-waste recycling in recent years. However, our levels were higher than or comparable to the levels measured at Chinese urban sites, 0.14–0.50 pg TEQ m⁻³ (mean) in Shanghai and 0.08–0.17 pg TEQ m⁻³ in Beijing.^{24,25} PCDD/F concentrations in ambient air have substantially declined in the past few decades in Europe and North America. For example, the concentrations of PCDD/Fs in the atmosphere of the UK have declined from a peak level of 0.4 pg TEQ m⁻³ in the 1990s to <0.05 pg TEQ m⁻³ during the period 2005–2008,⁴ which is in very good agreement with the levels recently observed in the US, Spain, and Denmark.^{26–30} These measurements are generally one order of magnitude lower than the concentrations obtained in this study. The results indicate that, despite the regulations on e-waste recycling in Taizhou, the atmospheric PCDD/F levels are still relatively high and further measures are needed to reduce the pollution.

PBDD/Fs. The mean concentrations of total PBDD/Fs at the sampling sites were 58.9 (3.54–155) in summer and 73.7 pg m⁻³ (3.54–155) pg m⁻³ in winter (ESI Table S2†). The mean TEQ concentrations of 2,3,7,8-substituted PBDD/Fs in summer and winter were 0.22 and 0.18 pg TEQ m⁻³, respectively (Table 1). The spatial variations of the PBDD/F concentrations in winter were similar to those of the PCDD/Fs, for which the highest concentrations occurred at the industrial zone and the two e-waste sites (0.10–0.69 pg TEQ m⁻³), followed by those at the residential, suburban, and background sites (0.03–0.08 pg TEQ m⁻³). Nevertheless, a sample collected at the residential site in summer showed a comparable level (0.59 pg TEQ m⁻³) to those collected from the industrial zone and historical e-waste sites and was higher than those from the other three sites (0.03–0.30 pg TEQ m⁻³). The higher atmospheric concentration in the residential area may be attributable to atmospheric transport from the e-waste sites or the presence of PBDD/F sources in the urban area.

There are limited data on PBDD/F concentrations in ambient air in the literature. The total atmospheric concentrations of eight 2,3,7,8-substituted PBDD/Fs (0.70–1.36 pg m⁻³) in Shanghai are similar to those in our samples, but the most abundant congeners in our samples, 1,2,3,4,6,7,8-HpBDD/F, were not detected in Shanghai's air.²³ Our results are much lower than those reported at another e-waste site in 2005, which had concentrations of 4.53–26.9 pg TEQ m⁻³.²³

BFRs. The atmospheric concentrations of total PBDEs varied between 4.67 and 559 pg m⁻³ in summer and between 40.8 and 541 pg m⁻³ in winter, with comparable mean concentrations of 270 and 225 pg m⁻³, respectively. In both seasons, the total PBDE concentrations decreased in the following order: industrial zone site > historical e-waste site > e-waste site > suburban site > residential site > background site. The concentrations of HBB (0.71–35.5 pg m⁻³) and PBEB (0.02–4.60 pg m⁻³) followed this spatial distribution as well. The atmospheric concentration of PBDEs in the present study was lower than the mean concentrations of \sum_9 PBDEs measured in this region (2000 pg m⁻³) in 2005.²² Our PBDE concentrations at the e-waste sites were 1–2 orders of magnitude lower than those from other

e-waste sites in China, with mean levels of 21 500 pg m⁻³ in 2004 (\sum_{22} PBDEs), 8760 pg m⁻³ in 2005 (\sum_{11} PBDEs), and 3260 pg m⁻³ in 2007–2008 (\sum_{36} PBDEs).^{31–33} In addition to the increasingly stringent regulations on e-waste, the distance from the sampling sites to the e-waste recycling facilities and the recycling methods were factors influencing these levels. However, our measurements were generally higher than the concentrations commonly detected in global urban air (50–150 pg m⁻³) and rural/remote air (5–15 pg m⁻³).^{34–38} For HBB and PBEB, higher concentrations were found in summer (with means of 19.1 and 0.88 pg m⁻³) compared to winter (with means of 7.12 and 0.08 pg m⁻³). These HBB and PBEB concentrations were much lower than those reported from another e-waste site, with means of 138 and 41.0 pg m⁻³, respectively.³³

Correlations and cluster analysis. A correlation analysis was conducted for the concentrations of polyhalogenated compounds in the air samples and the OC and BC contents in the bulk atmospheric particles (ESI Table S3†). It can be seen that the concentrations of PCDD/Fs, PBDD/Fs, total PBDEs, and BDE209, which are present predominantly in particles, correlated strongly with each other ($p \leq 0.002$). The concentrations of both PCDD/Fs and PBDD/Fs displayed significant correlations with OC and BC, which all originate mainly from combustion processes,³⁹ but they did not correlate with HBB and PBEB, which are present largely in the gaseous phase.³² Interestingly, the PBDEs (especially the lower brominated congeners, data not shown) showed significant correlations with HBB and PBEB ($p \leq 0.022$) but not with OC and BC (for both total PBDEs and BDE209). The lack of correlations between PBDEs and OC and BC aerosols may suggest different sources or the influence of gas/particle partitioning or particle size distributions of PBDEs.

Cluster analysis (ESI Fig. S3†) indicated that the samples showed no specific clustering for either PBDEs or PCDD/Fs. For instance, samples from the suburban and background sites in summer may cluster with samples from the industrial zone, e-waste, or urban residential sites. This result suggests that the non-source sites are not affected by contaminants from a specific source or sources (such as e-waste, industrial or urban sources), but are most likely affected by a combination of these sources at different times.

3.2 Homologue and congener profiles

PCDD/Fs. The overall congener profiles of the 2,3,7,8-substituted PBDD/Fs were similar among the six sites, except for the relatively higher proportions of OCDD from the e-waste and residential sites (Fig. 2). The four most abundant congeners at all sites were OCDD, 1,2,3,4,6,7,8-HpCDF, OCDF and 1,2,3,4,6,7,8-HpCDD, which together accounted for 65% (on average) of the total 2,3,7,8-substituted PCDD/Fs; however, there were differences in their percentage contributions, especially between the e-waste-associated sites and the non-e-waste sites. The congener profiles were similar to those in the urban air of Beijing,²⁵ but they were more similar to the profiles in the air observed from another e-waste site in China.²³ The congener profiles obtained in this study were also similar to those in some smoke samples from the open burning of municipal solid waste,⁴⁰ but were different from emission profiles from the incineration of

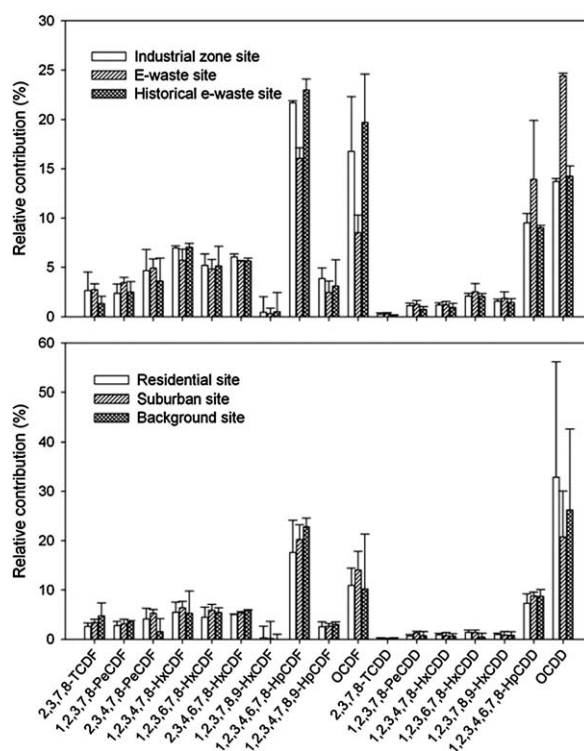


Fig. 2 Congener profiles of PCDD/Fs in the air (summer and winter) of Taizhou.

printed circuit board waste in a tubular reactor, as reported by Duan and Li *et al.*⁴¹

The PCDD/F homologue profiles (Fig. 3) in the present study were clearly different from the profiles typically observed in the ambient air from other locations in the world,^{25,42} in which declining homologue proportions for PCDFs and increasing proportions for PCDDs have been observed. This result is evidence of a different source of atmospheric PCDD/Fs in the studied area compared to other areas (*i.e.* e-waste source *versus* other sources). There were obvious differences in the homologue profile of the PCDD/Fs between summer and winter at nearly all the sites. In summer, the differences among the six sites were large, and no clear trends were observed compared with those in winter. Winter, however, had basically declining homologue proportions with increasing chlorination levels. These seasonal variations may be a result of different obsolete electronic products recycled at the sites or the different environmental variables (such as wind, temperature and humidity) in summer and winter. For instance, the wind directions in summer are more variable relative to winter (ESI Fig. S1†).

PBDD/Fs. The congener profiles of 2,3,7,8-substituted PBDD/Fs were dominated by 2,3,4,7,8-PeBDF, 1,2,3,4,6,7,8-HpBDF, and 1,2,3,4,7,8-HxBDF, which contributed an average of $52 \pm 3.7\%$, $36 \pm 7.1\%$, and $9.6 \pm 3.7\%$, respectively. There were large seasonal differences in the homologue profiles of the PBDD/Fs (ESI Fig. S2†). The homologue profiles were relatively constant across the sites in summer, while in winter the profiles were similar at the industrial zone, e-waste, and suburban sites and similar at the historical e-waste, residential, and background sites.

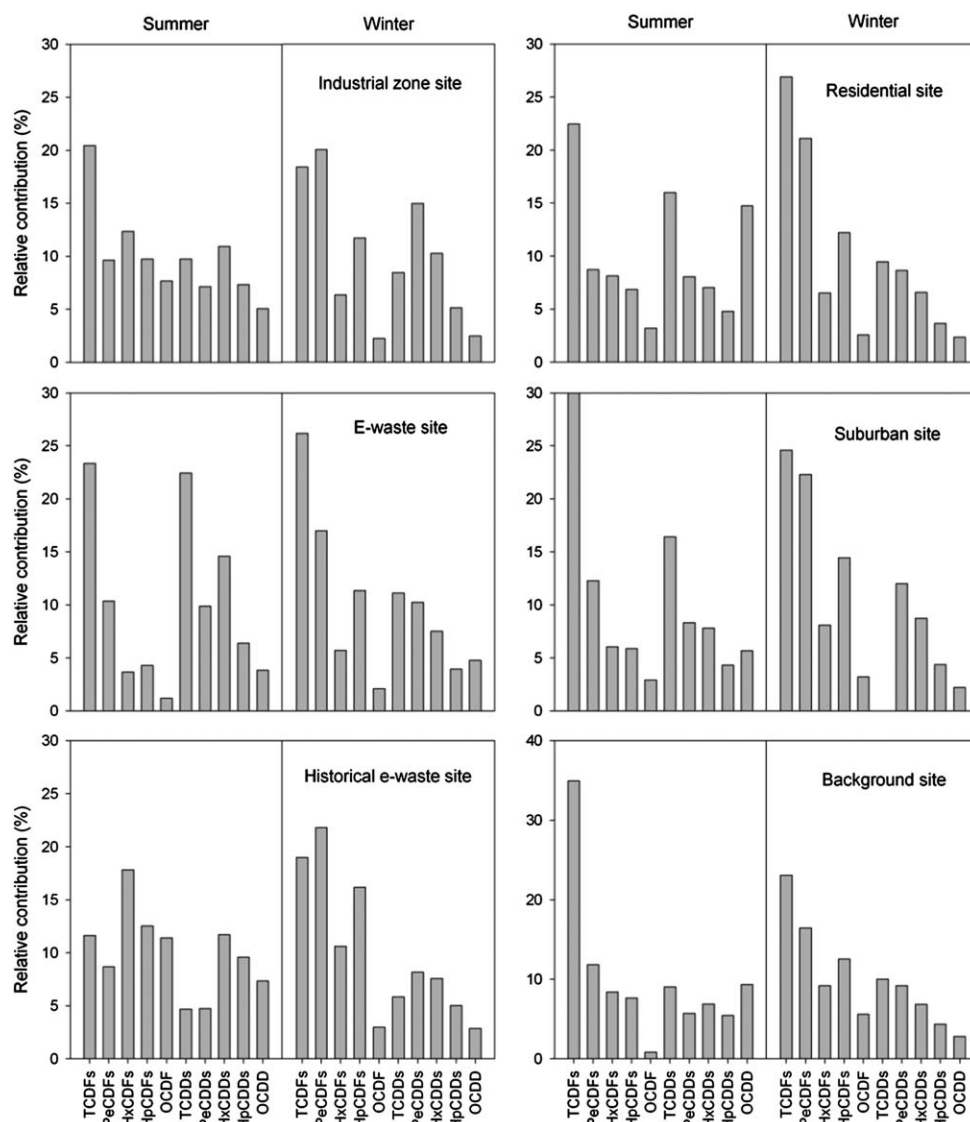


Fig. 3 Homologue profiles of PCDD/Fs in the air in summer and winter at different sites in Taizhou.

PBDEs. The PBDE congener profiles for lower and highly brominated PBDEs in summer and winter are displayed in Fig. 4. It is interesting that the congener profiles of the major lower brominated PBDEs that are mainly from technical penta-BDE products were consistent across the sites in summer. Nevertheless, there were obviously elevated contributions of BDE47 and decreased contributions of BDE99 (two major congeners in technical products) at the background and suburban sites, which could be due to the preferred atmospheric transport of BDE47 or the photodegradation of BDE99 into BDE47 during transport, which have both been observed previously.^{43,44} By comparison, the profiles in winter for the lower brominated PBDEs varied spatially, in contrast to the results for the PCDD/F homologue profiles. A possible interpretation is the different sources of these two classes of compounds. PCDD/Fs are related largely to combustion processes, while PBDEs may be released into the environment *via* various pathways, including manufacturing processes, evaporation from related products or contaminated environmental media (especially for lower brominated

congeners), and the combustion or weathering processes of related products. The difference in the lower-brominated PBDE profiles between summer and winter may reflect their different emission mechanisms in the two seasons. The constant PBDE congener profiles in summer may be attributable to strong evaporation sources due to high ambient temperatures, which was demonstrated in our previous study.³³ In winter, the PBDEs contributed from other sources increased, affecting their air profiles. This result is supported by the higher concentrations of lower brominated PBDEs in summer (averaged 94.5 pg m^{-3}) relative to winter (63.4 pg m^{-3}). This seasonal difference was not observed for the highly brominated PBDEs, which showed similar percentage contributions across the sites in each season. The exception was BDE209 (the most abundant congener), with contributions varying from 28% to 59% in summer and from 20% to 62% in winter. Furthermore, the atmospheric concentrations of highly brominated PBDEs in summer (averaged 165 pg m^{-3}) were comparable to those in winter (147 pg m^{-3}). The relatively steady profiles and concentrations of the highly brominated

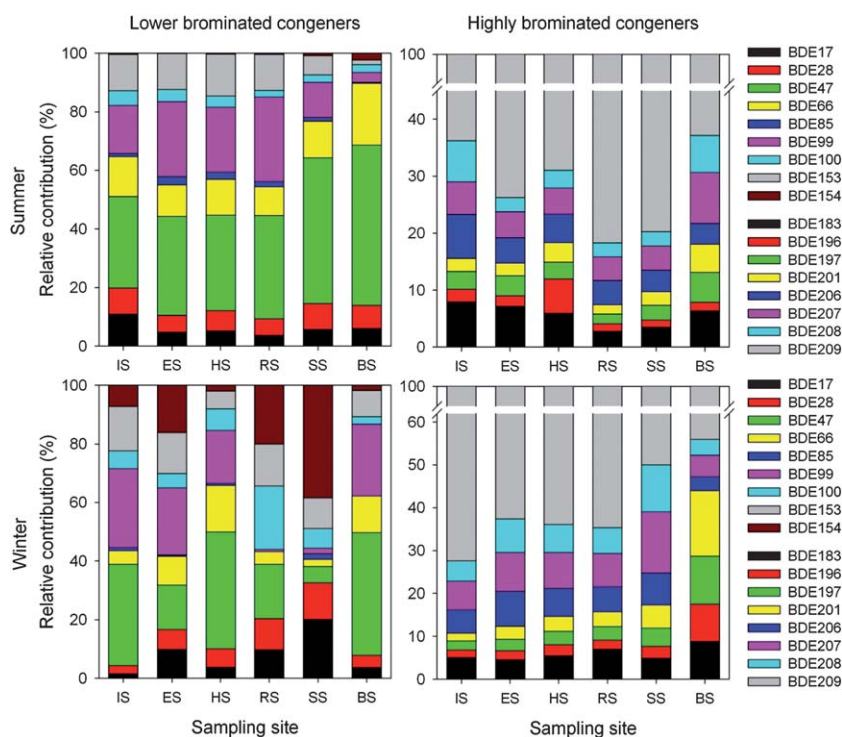


Fig. 4 Congener profiles of the major lower and highly brominated PBDEs in the air at the different sites in Taizhou. IS: industrial zone site, ES: e-waste site, HS: historical e-waste site, RS: residential site, SS: suburban site, BS: background site.

PBDEs indicate that the PBDEs in the air of this region were controlled primarily by similar emission mechanisms.

3.3 Estimation of inhalation cancer risk

The estimated daily intakes (EDI) of PCDD/Fs and PBDD/Fs via inhalation and the associated potential cancer risks are given in Table 2. The EDIs were highest for people living in the industrial zone ($0.36 \text{ pg TEQ kg}^{-1} \text{ dw}$ (dry weight)) and around the historical e-waste site ($0.29 \text{ pg TEQ kg}^{-1} \text{ dw}$). The lowest EDIs were determined for people in rural and suburban areas ($0.05\text{--}0.07 \text{ pg TEQ kg}^{-1} \text{ dw}$). The lifetime excess cancer risk ranged from 0.7×10^{-5} to 5.4×10^{-5} (i.e., 7–54 cases per million people) for the Taizhou residents. In addition, we estimated the potential cancer cases in the four districts by multiplying the

cancer risks by the populations in corresponding districts. Average estimated risks were used for districts that housed one more sampling sites. The predicted cancer cases associated with exposure to airborne PCDD/Fs and PBDD/Fs are 35, 26, 13, and 7 for the districts of Wenling, Luqiao, Jiaojiang, and Huangyan, respectively. The cancer risks estimated in the present study were within the range of 1.0×10^{-6} to 1.0×10^{-4} considered acceptable by the U.S. EPA,⁴⁵ suggesting a limited cancer risk from inhalation exposure to these chemicals for Taizhou residents. However, it should be noted that the estimations do not represent the cancer risks for e-waste dismantling workers in this region, who may have a much higher inhalation cancer risk than the general residents.

4. Conclusions

This work presents, for the first time, the status of PCDD/F, PBDD/F, and PBDE contamination in the air of an e-waste area (Taizhou) in eastern China after regulations were implemented on e-waste recycling. The current atmospheric concentrations in this region have substantially declined compared with those before the regulations; however, they are still higher than the historically highest levels in Europe and North America. The congener profiles of 2,3,7,8-substituted PBDD/Fs were generally constant in the air, but the PCDD/F homologue profiles varied seasonally and spatially, indicating that e-waste recycling is the primary source of these polyhalogenated compounds in the air of this region. The PBDE profiles suggest that evaporation may be a major source of lower-brominated BDE congeners in summer, while there were no clear seasonal differences in the emission mechanism for highly brominated PBDEs. The lifetime excess cancer risks associated

Table 2 Estimated daily intake of PCDD/Fs ($\text{pg TEQ kg}^{-1} \text{ dw}$), PBDD/Fs ($\text{pg TEQ kg}^{-1} \text{ dw}$), and PBDEs ($\text{pg kg}^{-1} \text{ dw}$) and potential cancer risk via inhalation exposure to PCDD/Fs and PBDD/Fs

Sampling site	Daily inhalation intake			Cancer risk ^a
	PCDD/Fs	PBDD/Fs	PBDEs	
Industrial zone site	0.23	0.13	143.4	5.4×10^{-5}
E-waste site	0.15	0.03	66.8	2.7×10^{-5}
Historical e-waste site	0.21	0.08	126.5	4.3×10^{-5}
Residential site	0.06	0.06	27.4	1.9×10^{-5}
Suburban site	0.03	0.04	42.5	1.0×10^{-5}
Background site	0.04	0.01	19.9	0.7×10^{-5}

^a For the total of PCDD/Fs and PBDD/Fs using the same inhalation cancer slope factor of $1.5 \times 10^5 \text{ (mg kg}^{-1} \text{ d}^{-1})^{-1}$ for 2,3,7,8-TCDD.

with inhalation exposure to PCDD/Fs and PBDD/Fs ranged from 0.7×10^{-5} to 5.4×10^{-5} , corresponding to approximately 80 cancer cases in the Taizhou population.

Acknowledgements

This work was supported by the National Basic Research Program of China (2009CB421602), the National Natural Science Foundation of China (21077134), and the China Ministry of Environmental Protection's Special Funds for Scientific Research on Public Welfare (201009026). The authors greatly appreciate the Taizhou Environmental Monitoring Station for their help with air sampling.

References

- 1 C. Melber and J. Kielhorn, *Environmental Health Criteria 205, Polybrominated Dibenzo-p-Dioxins and Dibenzofurans*, 1998, <http://www.inchem.org/documents/ehc/ehc/ehc205.htm>.
- 2 U. Quass, M. Fermann and G. Bröker, *Chemosphere*, 2004, **54**, 1319–1327.
- 3 U. S. EPA, *An Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the U.S. for the Years 1987, 1995, and 2000* (Final, Nov 2006), <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=159286>.
- 4 A. Katsoyiannis, R. Gioia, A. J. Sweetman and K. C. Jones, *Environ. Sci. Technol.*, 2010, **44**, 5735–5740.
- 5 M. Van den Berg, L. Birnbaum, A. T. Bosveld, B. Brunström, P. Cook, M. Feeley, J. P. Giesy, A. Hanberg, R. Hasegawa, S. W. Kennedy, T. Kubiak, J. C. Larsen, F. X. van Leeuwen, A. K. Liem, C. Nolt, R. E. Peterson, L. Poellinger, S. Safe, D. Schrenk, D. Tillitt, M. Tysklind, M. Younes, F. Waern and T. Zacharewski, *Environ. Health Perspect.*, 1998, **106**, 775–792.
- 6 S. Batterman, C. Godwin, S. Chernyak, C. R. Jia and S. Charles, *Environ. Int.*, 2010, **36**, 548–556.
- 7 I. Watanabe and S. Sakai, *Environ. Int.*, 2003, **29**, 665–682.
- 8 A. Covaci, S. Harrad, M. A. E. Abdallah, N. Ali, R. J. Law, D. Herzke and C. A. de Wit, *Environ. Int.*, 2011, **37**, 532–556.
- 9 UNEP, Stockholm Convention text and annexes as amended in 2009, <http://chm.pops.int/Convention/tabid/54/language/en-US/Default.aspx#convtext>.
- 10 M. Ren, P. A. Peng, Y. Cai, D. Chen, L. Zhou, P. Chen and J. Hu, *Environ. Pollut.*, 2011, **159**, 1375–1380.
- 11 J. Eriksson, N. Green, G. Marsh and Å. Bergman, *Environ. Sci. Technol.*, 2004, **38**, 3119–3125.
- 12 UNEP, *Urgent Need to Prepare Developing Countries for Surge in E-Wastes*, 2010, <http://www.unep.org/Documents.Multilingual/Default.asp?DocumentID=612&ArticleID=6471>.
- 13 A. O. W. Leung, W. J. Luksemburg, A. S. Wong and M. H. Wong, *Environ. Sci. Technol.*, 2007, **41**, 2730–2737.
- 14 J. Ma, R. Addink, S. Yun, J. P. Cheng, W. H. Wang and K. Kannan, *Environ. Sci. Technol.*, 2009, **43**, 7350–7356.
- 15 D. Muenhor, S. Harrad, N. Ali and A. Covaci, *Environ. Int.*, 2010, **36**, 690–698.
- 16 M. Tian, S.-J. Chen, J. Wang, T. Shi, X.-J. Luo and B.-X. Mai, *Environ. Sci. Technol.*, 2011, **45**, 4696–4701.
- 17 J.-J. Fu, Y.-W. Wang, L.-J. Zhou, A.-X. Zhang and G.-B. Jiang, *Progr. Chem.*, 2011, **23**, 1755–1768.
- 18 U. S. EPA, *Exposure Factors Handbook Chapter 6-Inhalation Rates*, 1997, <http://www.epa.gov/ncea/efh/pdfs/efh-chapter06.pdf>.
- 19 U. S. EPA, *Health Effects Assessment Summary Tables*, FY 1997 Update, Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Cincinnati, OH, 1997.
- 20 P. Samaras, G. Skodras, G. P. Sakellaropoulos, M. Blumenstock, K. W. Schramm and A. Kettrup, *Chemosphere*, 2001, **43**, 751–755.
- 21 G. Skodras, A. Palladas, S. P. Kaldis and G. P. Sakellaropoulos, *Chemosphere*, 2007, **67**, S191–S197.
- 22 Y. M. Li, G. B. Jiang, Y. W. Wang, P. Wang and Q. H. Zhang, *Chin. Sci. Bull.*, 2008, **53**, 521–528.
- 23 H. R. Li, L. P. Yu, G. Y. Sheng, J. M. Fu and P. A. Peng, *Environ. Sci. Technol.*, 2007, **41**, 5641–5646.
- 24 H. R. Li, J. L. Feng, G. Y. Sheng, S. L. Lü, J. M. Fu, P. A. Peng and R. Man, *Chemosphere*, 2008, **70**, 576–583.
- 25 Y. Li, G. Jiang, Y. Wang, Z. Cai and Q. Zhang, *Atmos. Environ.*, 2008, **42**, 2037–2047.
- 26 M. Venier, J. Ferrario and R. A. Hites, *Environ. Sci. Technol.*, 2009, **43**, 1036–1041.
- 27 O. Correa, H. Rifai, L. Raun, M. Suarez and L. Koenig, *Atmos. Environ.*, 2004, **38**, 6687–6699.
- 28 E. Abad, K. Martínez, L. Gustems, R. Gómez, X. Guinart, I. Hernández and J. Rivera, *Chemosphere*, 2007, **67**, 1709–1714.
- 29 M. F. Hovmand, J. Vikelsøe and H. V. Andersen, *Atmos. Environ.*, 2007, **41**, 2400–2411.
- 30 H. Fiedler, H. Rottler, L. Peichl, G. Knetsch and A. Basler, *Organohalogen Compd.*, 2000, **45**, 264–268.
- 31 W. J. Deng, J. S. Zheng, X. H. Bi, J. M. Fu and M. H. Wong, *Environ. Int.*, 2007, **33**, 1063–1069.
- 32 D. Chen, X. Bi, J. Zhao, L. Chen, J. Tan, B. Mai, G. Sheng, J. Fu and M. Wong, *Environ. Pollut.*, 2009, **157**, 1051–1057.
- 33 M. Tian, S. J. Chen, J. Wang, X. B. Zheng, X. J. Luo and B. X. Mai, *Environ. Sci. Technol.*, 2011, **45**, 8819–8825.
- 34 R. A. Hites, *Environ. Sci. Technol.*, 2004, **38**, 945–956.
- 35 R. G. M. Lee, G. O. Thomas and K. C. Jones, *Environ. Sci. Technol.*, 2003, **38**, 699–706.
- 36 B. Cetin and M. Odabasi, *Environ. Sci. Technol.*, 2007, **41**, 785–791.
- 37 M. Venier and R. A. Hites, *Environ. Sci. Technol.*, 2008, **42**, 4745–4751.
- 38 Y. Su, H. Hung, K. A. Brice, K. Su, N. Alexandrou, P. Blanchard, E. Chan, E. Sverko and P. Fellin, *Atmos. Environ.*, 2009, **43**, 6230–6237.
- 39 W. F. Cooke, C. Liousse, H. Cachier and J. Feichter, *J. Geophys. Res.*, 1999, **104**, 137–222.
- 40 T. Zhang, H. Fiedler, G. Yu, G. S. Ochoa, W. F. Carroll Jr, B. K. Gullett, S. Marklund and A. Touati, *Chemosphere*, 2011, **84**, 994–1001.
- 41 H. Duan, J. Li, Y. Liu, N. Yamazaki and W. Jiang, *Environ. Pollut.*, 2012, **161**, 185–191.
- 42 R. Lohmann and K. C. Jones, *Sci. Total Environ.*, 1998, **219**, 53–81.
- 43 L. Fang, J. Huang, G. Yu and L. Wang, *Chemosphere*, 2008, **71**, 258–267.
- 44 R. M. Dickhut, A. Cincinelli, M. Cochran and H. Kylin, *Environ. Sci. Technol.*, 2012, **46**, 3135–3140.
- 45 U.S.EPA, http://www.epa.gov/region8/r8risk/hh_risk.html.