Environmental Science
Processes & Impacts

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

Temporal trends of PCBs, PCDD/Fs and PBDEs in soils from an E-waste dismantling area in East China†

Cite this: *Environ. Sci.: Processes Impacts*, 2013, **15**, 1897

Pu Wang,[a] Haidong Zhang,[a] Jianjie Fu,[a] Yingming Li,[a] Thanh Wang,[a] Yawei Wang,[a] Daiwei Ren,[a] Patrick Ssebugere,[b] Qinghua Zhang*[a] and Guibin Jiang[a]

Received 10th June 2013
Accepted 1st August 2013

DOI: 10.1039/c3em00297g

rsc.li/process-impacts

The temporal trends of polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polybrominated diphenyl ethers (PBDEs) were investigated in soils from an E-waste dismantling area in East China between 2005 and 2011. Isotope dilution high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) was employed for the sample analysis. PCB levels declined as expected, while PCDD/Fs generally remained at a constant level during the sampling period, and PBDE concentrations tended to be slightly lower after 2007 although the decline was not statistically significant. The congener profiles indicated that lowly-halogenated congeners of these persistent organic pollutants (POPs) accounted for the decreasing levels and relative proportions of the POPs, suggesting that they have been gradually eliminated from the field soil over the years. However, the concentration levels of some heavy congeners (*e.g.*, CB-209, OCDD and OCDF) showed different trends from those of the lighter ones. The general tendencies of the three types of POPs in soils were consistent with those reported in other studies in this area. The results implied that the enhanced regulations and centralized dismantling action introduced in 2005 might exert a limited influence on these three types of POPs in soils during the sampling period.

Environmental impact

The environmental contamination associated with E-waste dismantling activities has been a topic of great concern during the past several decades. In China, two notorious E-waste recycling centers are hot spots for POPs research, which are respectively located in Guiyu, South China and Taizhou, East China. The present study was conducted to investigate the levels and distribution of PCBs, PCDD/Fs and PBDEs in soils from the Taizhou area to reflect the temporal tendency of POPs after stricter environmental regulations were introduced by local government in 2005. The results revealed that different temporal trends occurred for the different POPs, which were closely related to their historical emission and their chemical properties. The study will shed light on the contamination control for these POPs in E-waste dismantling areas.

1 Introduction

Electrical and electronic equipment pervades modern lifestyles and its usage and consumption is growing rapidly all over the world. In parallel, the life cycle of these electronic products is becoming shorter due to the fast turnover of products, resulting in a large amount of electronic waste (E-waste) both in developed and developing countries. E-waste is generally recycled for valuable materials, such as gold, silver, copper, platinum *etc.* However, primitive E-waste recycling activities have been considered a very important source of emissions of organic pollutants and heavy metals.[1,2] Many developed countries transported E-waste to developing regions such as Africa, India and China during the late 20th century, taking advantage of the lower labor costs and less stringent environmental regulations in these countries.[3] About 80% of the world's high-tech trash was exported to Asia, of which 90% flowed to China.[4] Although various multinational collaboration agreements were put into effect to ban or limit the movement of toxic substances, *e.g.* the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal (usually known as "the Basel Convention"), the amount of E-waste imported to China was still high in recent years. In Taizhou, a typical E-waste dismantling area in East China, up to 1.78 million tonnes of E-waste was imported in 2008 and the total recycling amount increased by more than 50% in 2009 compared to 2005.[5]

Numerous studies have reported high levels of various pollutants in E-waste dismantling areas, such as heavy metals

---

[a] *State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: qhzhang@rcees.ac.cn; Fax: +86-10-62849818; Tel: +86-10-62849818*

[b] *Department of Chemistry, Makerere University, P.O. Box 7062, Kampala, Uganda*

† Electronic supplementary information (ESI) available: Sampling information (Table S1), the temporal distribution of PCBs, PCDD/Fs and PBDEs in the soils over seven years (Fig. S1), relative distribution of the TEQ values of PCBs and PCDD/Fs (Fig. S2), the congener profiles of PCBs, PCDD/Fs and PBDEs in the soils (Fig. S3–S5), the trends of some congeners of PCBs, PCDD/Fs and PBDE in Taizhou soils over the years (Fig. S6–S8). See DOI: 10.1039/c3em00297g

and persistent organic pollutants (POPs) including polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs).[2,4] In China, the seriousness of environmental and human health problems has aroused great concern and finally contributed to stricter environmental laws and regulations from the Chinese authorities on illegal E-waste recycling activities. In the Taizhou area in 2005, the local government began to restrict the dismantling activities into specified zones and standardized the dismantling processes to protect the local environment. Even so, the large amounts of E-waste still posed a huge challenge for the environmental improvement of the local area.

PCBs and technical penta- and octa-BDEs were produced in large amounts for industrial and commercial purposes, and their widespread use has led to their ubiquitous presence around the globe. Some of the most seriously affected areas are the E-waste areas.[2,6,7] PCDD/Fs are unintentional byproducts of certain industrial, non-industrial and natural processes, usually involving combustion sources. In Taizhou, primitive E-waste dismantling techniques such as circuit board baking, acid bathing and open burning prevailed and have caused serious PCDD/Fs contamination in the local area before a stricter environmental management policy was implemented.[8] Although several studies have been conducted to investigate the POPs contamination in the E-waste area of Taizhou, limited data could be found on the temporal trend of POPs distributions. Previously, we reported decreasing trends of PCDD/Fs, PCBs and PBDEs in rice hulls during the period 2005–2009, indicating that the enhanced regulations and centralized dismantling actions could have a positive environmental effect in regards to the release of POPs.[5] The sources of these pollutants in rice hulls could be attributed to uptake from both the soil and the atmosphere, while our previous results suggested that the latter transfer mechanism is the dominant contamination process in this annual plant.[5] This was in agreement with the argument that POPs measured in leaves could be mainly from atmospheric deposition.[9] In theory, uptake by plants from the atmosphere is important for chemicals with $\log K_{\mathrm{OA}} > 6$ and a $\log K_{\mathrm{AW}} > -6$, and uptake from soil is the main pathway for the chemicals with $\log K_{\mathrm{OW}} < 2.5$ and $\log K_{\mathrm{AW}} < -1$.[10] Soil is known to be one of the main disposal and landfill receptors for E-waste, as well as a main reservoir and re-emission source of the pollutants. POPs have longer half-lives in soil compared to in air,[11] which makes their elimination from the soil more difficult. These facts implied that the temporal trends of PCDD/Fs, PCBs and PBDEs in the soil system were probably inconsistent with those in the rice hulls (or air). Therefore, it is necessary to evaluate the POPs trends in soil to further investigate their spatio-temporal variation in E-waste dismantling areas.

This study investigated the temporal levels and distribution of PCBs, PCDD/Fs and PBDEs in soil samples from the Taizhou area during the period 2005–2011 (2005, 2007, 2009 and 2011), in order to understand the temporal tendency of POPs after the introduction of stricter environmental regulations. Relevant data on POPs distributions in the area was also reviewed and included in the analysis for a comprehensive comparison and understanding of POPs distribution trends in this E-waste area.

2 Experimental

2.1 Sites and samples

Taizhou is located in Zhejiang Province, East China. It is a famous place of agricultural production in China, indicating relatively effective land utilization. Taizhou has been involved in E-waste recycling for more than three decades, which is even longer than the disposal history of Guiyu, another major E-waste dismantling area in China. In this study, sampling campaigns were biennially arranged between August and October from 2005 to 2011. The soil samples were mainly collected around the Luqiao district which is an intensive E-waste dismantling region in Taizhou (Table S1 in the ESI†). Approximately 1 kg soil was pooled from 3–5 subsamples at depths of 0–10 cm in the surrounding area (area < 0.01 km^2). A total of 36 soil samples were obtained for the analysis of PCBs, PCDD/Fs and PBDEs, including six samples in 2005, thirteen in 2007, ten in 2009 and seven in 2011. All the samples were transferred to the lab in Beijing using an ice box and then stored at −20 °C in the freezer until analyzed.

2.2 Analytical methods

The sample pretreatment including freeze-drying, grinding to a fine powder, extraction, a cleanup process, instrumental analysis, quality assurance and quality control and quantification followed the methods detailed in our previously published articles.[12,13] In brief, the sample extraction was performed using an accelerated solvent extraction unit (ASE, ASE300, Dionex, USA). The extract was then loaded into a multilayer silica column (from the bottom up with 1 g silica gel, 4 g basic silica gel, 1 g silica gel, 8 g acid silica gel, 2 g silica gel and 2 cm anhydrous sodium sulfate) and a basic alumina column (6 g basic alumina, 1 cm anhydrous sodium sulfate from the bottom up) for the cleanup. The target analytes were analyzed using high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC/HRMS). US EPA defined 68A-LCS and 1613-LCS, and PBDE-LCS (^{13}C-BDE-47, -99 and -153) standards were spiked into the samples for qualification and quantification, while EPA 1668A-IS and 1613-IS were utilized for the recovery calculations. The target compounds measured in all samples included twelve dioxin-like (dl-) PCBs, seven indicator PCBs and CB-209, seventeen 2,3,7,8-substituted PCDD/Fs and fourteen PBDEs (BDE-17, -28, -47, -66, -71, -85, -99, -100, -138, -153, -154, -183, -190 and -209).

2.3 Quality assurance and quality control

All the target compounds were quantified using HRGC/HRMS based on an isotope-dilution method. ^{13}C-labeled surrogated standards (68A-LCS, 1613-LCS, and PBDE-LCS) were spiked into the sample for qualification and quantification, and ^{13}C-labeled injection standards (EPA 68A-IS and 1613-IS) were used for the recovery calculations. In the samples, the recoveries of 68A-LCS, 1613-LCS and PBDE-LCS were in the range of 35–142%, 28–107% and 30–110%, respectively, which all met the requirements of US EPA methods 1668A, 1613B and 1614. The limit of detection (LOD) was defined as where the signal-to-noise ratio

$(S/N) = 3:1$ and they ranged between 0.04 and 10.1 pg g^{-1} for PCBs, 0.06–8.67 pg g^{-1} for PCDD/Fs and 0.09–14.0 pg g^{-1} for PBDEs (excluding BDE-209), respectively; the LOD for BDE-209 varied from 23.5–331 pg g^{-1}. Laboratory blanks were processed in parallel with each batch of the samples and some congeners (*e.g.*, CB-28, -118, -138 and -153, BDE-47 and -99, and OCDD) were detected at relatively low levels (<15% of the lowest concentration in each batch of the samples). The reported soil concentrations were not blank corrected.

3 Results and discussion

3.1 The general distribution of PCBs, PCDD/Fs and PBDEs

The overall concentrations of PCBs, PCDD/Fs and PBDEs in the soil samples are listed in Table 1. Generally, PCB levels showed a decreasing tendency over the sampling period of seven years. The mean concentrations of the sum of 19 PCB congeners ($\sum_{19}$PCBs) varied from 47.8 ng g^{-1} dry weight (dw) in 2005 to 11.7 ng g^{-1} dw in 2011, corresponding to mean toxicity values of 5.81 pg WHO-TEQ_{2005} g^{-1} in 2005 and 1.67 pg WHO-TEQ_{2005} g^{-1} in 2011. The concentrations were much lower than those in previous studies in the same area. Zhao *et al.*[14] found that the concentration was 739 ng g^{-1} dw and the TEQ value was up to 57 pg g^{-1} in 2003. Chu *et al.*[15] observed that the concentration in soils was up to 1100 ng g^{-1} dw in 1993. However, the PCB levels in this study are comparable to those reported by Liu *et al.*[16] and Leung *et al.*[17] in the soils from Guiyu, another major E-waste dismantling area in South China. Compositional analysis indicated that the indicator PCBs represented high proportions of the $\sum_{19}$PCBs (>80%) except for at one sampling site (Hengjie) in 2009 (about 45%). Thereinto, CB-28, -138 and -153 were the main congeners and contributed about 30%, 13% and 11% of the $\sum_{19}$PCBs, respectively. CB-126 was the major contributor to the $\sum$TEQs of the PCBs (>90%). This result is similar to those reported by Bi *et al.*[18] and Shen *et al.*[19] in this area.

For the PCDD/Fs, the sum concentrations of 17 2,3,7,8-substituted congeners and their TEQ values were in the range of 0.27–1.46 ng g^{-1} dw and 0.85–20.8 pg WHO-TEQ_{2005} g^{-1}, respectively. In spite of large variations in the concentrations, a constant trend was observed over the seven years (annual mean concentrations between 0.60 and 0.71 ng g^{-1} dw). The concentrations are comparable to those found in the agricultural soils of Guiyu in South China[16,20] and the results from Taiwan.[21] However, they were lower than those reported by Kobayashi *et al.*[22] and Seike *et al.*[23] in Japanese paddy soils, as well as in Korean soils as reported by Im *et al.*[24] and Kim *et al.*[25] Congener profiles showed that octachlorodibenzo-*p*-dioxin (OCDD) accounted for approximately 80% of the concentrations of the $\sum_{17}$PCDD/Fs, followed by 1,2,3,4,6,7,8-hepta CDD (1,2,3,4,6,7,8-HpCDD, 7% of the $\sum_{17}$PCDD/Fs). Among the PCDF homologues, octachlorodibenzofuran (OCDF) and 1,2,3,4,6,7,8-hepta CDF (1,2,3,4,6,7,8-HpCDF) were the predominant congeners, both of which contributed more than 50% to the $\sum_{10}$PCDFs. In addition, the concentrations of PCDFs were generally higher than PCDDs except for OCDD and 1,2,3,4,6,7,8-HpCDD. This congener pattern was similar to that observed by Shen *et al.*[19] in the same region, and was also comparable to the PCDD/Fs distribution in the soils of Guiyu,[16,20] suggesting a common source of PCDD/Fs emission involving combustion of E-waste in the E-waste areas.

In case of PBDEs, the concentrations of the $\sum_{14}$PBDEs ranged from 0.49–15.4 ng g^{-1} dw and higher mean values were obtained in 2005 and 2007 (Table 1). These levels were lower than those reported in the Guiyu area. Leung *et al.*[20] indicated that PBDE concentrations in the surface soils from Guiyu ranged from 34.7 to 4250 ng g^{-1} dw; Liu *et al.*[16] reported that the concentrations of $\sum_{19}$PBDEs were in the range 0.40–789.49 ng g^{-1} dw. Additionally, an investigation from Qingyuan, an E-waste dismantling area near Guiyu, showed that the total PBDE concentrations ranged from 191 to 9156 ng g^{-1} dw in road soils and from 2.9 to 207 ng g^{-1} dw in farmland soils,[26] which was up to two orders of magnitude higher than the present results for Taizhou. However, the PBDE concentrations in this study were at relatively high levels compared with many results from Europe as summarized by Law *et al.*[27] In this study, BDE-209 generally had the greatest contribution to the $\sum$PBDEs with a concentration range from no detection to 13.7 ng g^{-1} dw. Its proportions of the $\sum$PBDEs were up to 92%, indicating the prevalence of commercial deca-BDE. Furthermore, BDE-47, -99 -153 and -183 were the dominant congeners and accounted for 13%, 9%, 6% and 6% of the $\sum_{13}$PBDEs (excluding BDE-209), respectively. The abundance of these signature congeners from commercial deca-, penta- and octa-BDE elucidated the predominant commercial source of PBDEs in this E-waste dismantling area.

3.2 Temporal trends of POPs

Statistical analyses were processed using the software SPSS 13.0 and the differences between the concentrations in each year were investigated using One-Way ANOVA. The temporal trend of PCB concentrations over the period 2005–2011 is

Table 1 The concentrations of PCBs, PCDD/Fs and PBDEs in the soil samples (pg g^{-1} dw)

	2005 ($n = 6$)				2007 ($n = 13$)				2009 ($n = 10$)				2011 ($n = 7$)			
	Min.	Max.	Mean	Median	Min.	Max.	Mean	Median	Min.	Max.	Mean	Median	Min.	Max.	Mean	Median
$\sum$PCDD/Fs	272	1458	627	538	282	1251	643	512	325	1166	600	484	407	1393	711	520
$TEQ_{PCDD/Fs}$	1.56	11.4	6.49	5.56	4.37	20.8	8.46	6.55	2.36	7.82	4.96	4.82	0.85	7.65	4.85	4.47
$\sum$PCBs	776	127 330	47 842	35 452	2111	82 566	43 299	38 015	2124	56 063	12 181	4169	612	28 927	11 747	5883
TEQ_{PCBs}	0.24	10.9	5.81	5.00	0.33	10.9	5.95	7.63	0.63	4.82	1.82	1.02	0.09	3.39	1.67	1.94
$\sum$PBDEs	489	14 926	4623	3137	1430	15 363	4469	3413	628	9639	3397	2086	1643	11 715	3805	2248

presented in Fig. S1.† Both the concentrations and TEQs showed markedly decreasing trends over the seven year period ($p = 0.009$ and 0.002). A similar trend was also observed for the proportions of dl-PCBs in total TEQ values (Fig. S2†) and for most of the individual congeners except for CB-209 (Fig. S3†). Considering that CB-209 has a larger molecular size, lower volatility, higher stability in the environment and is mainly sorbed to air particulates, the atmospheric deposition and long-term persistence in the soil could be an explanation for this phenomenon in the soil samples. It was noted that the percentages of lighter PCB congeners tended to be lower over the years (Fig. 1). For instance, the ratios of CB-28/indicator PCBs decreased from 50% in 2005 to 30% in 2011. On the other hand, the heavier congeners showed an increasing contribution to the $\sum$PCBs, *e.g.*, the proportions of CB-180 among the indicator PCBs increased from 3.0% in 2005 to 4.2% in 2011.

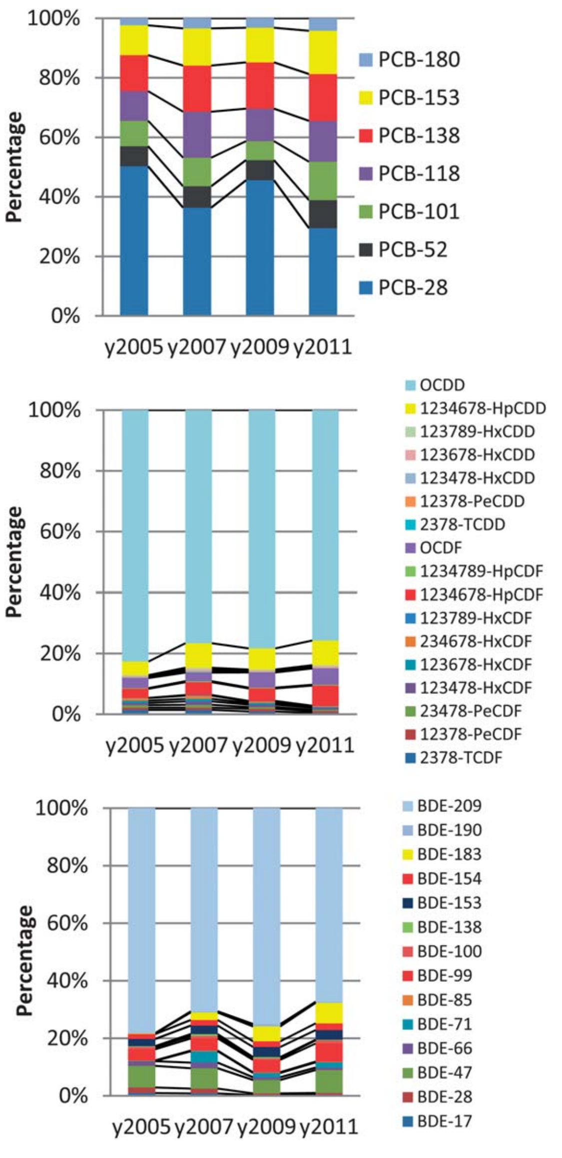

Fig. 1 The distribution patterns of PCBs, PCDD/Fs and PBDEs.

For the PCDD/Fs, a constant level was observed for both the mean concentrations and TEQ values over the seven years ($p = 0.937$ and 0.064, respectively; Table 1 and Fig. S1†). On the other hand, the TEQ ratios of PCDDs/PCDFs showed an upward trend (Fig. S2†), which was consistent with that in the rice hulls, although the ratio variations were less comparable (from 1 : 9 in 2005 to 7 : 3 in 2009 in the rice hulls).[5] However, the concentration ratios of PCDDs/PCDFs tended to be lower over the years (Fig. 1). The profiles of PCDDs/PCDFs were considered to distinguish a potential sink (enriched in PCDD congeners with 6–8 chlorine atoms (D6–D8)) or source of PCDD/Fs (enriched in PCDFs) derived from industrial and combustion activities in a certain area.[28] The decreased ratios of PCDDs/PCDFs in the present study suggested that the profile of PCDD/Fs in soils has tended to change from sinks to sources over the years, which might enhance the decrease of lighter congeners from the soil during the air–soil exchange. This was probably due to the decrease of open-burning combustion activities and marked decline of PCDD/F concentrations in the local atmosphere.[5] In addition, the mean concentrations of tetra- and penta-chlorinated congeners, particularly for 2,3,7,8-tetra CDF (2,3,7,8-TeCDF) and 2,3,4,7,8-penta CDF (2,3,4,7,8-PeCDF), exhibited a decreasing trend over the years (Fig. S4†). Nevertheless, as the dominant congeners of PCDD/Fs, OCDD generally remained at a constant level, while OCDF, 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,6,7,8-HpCDD tended to be on a steady rise during the studied period. In consequence, the congener profiles showed that the proportions of lower chlorinated congeners (*e.g.*, 2,3,7,8-TeCDD and 2,3,7,8-TeCDF) in $\sum$PCDD/Fs decreased over the years.

Concerning the PBDEs, relatively higher mean concentrations were observed in the soils in 2005 and 2007. After 2007, the mean levels declined as shown in Table 1. However, there was no significant difference observed between the concentrations in each year ($p = 0.889$). The congener patterns showed that the main BDE congeners (*e.g.*, BDE-47, -99, and -153) tended to be at lower levels after 2007. Especially for BDE-209, the concentrations accounted for a large proportion of the $\sum$PBDEs (75% on average; Fig. 1) and slightly declined during the sampling period. In spite of that, the relative distribution of BDE congeners suggested that the percentages of lighter congeners in the $\sum_{13}$PBDEs decreased, *e.g.*, the proportion of BDE-28 decreased from 9% in 2005 to 2% in 2011, while that of BDE-183 increased from 2 to 20% of the $\sum_{13}$PBDEs. This trend was similar to those of PCBs and PCDD/Fs. It was notable that the percentage of BDE-209 exhibited a decreasing trend, which was also similar to that of OCDD.

The general distributions of PCBs, PCDD/Fs and PBDEs over time suggested that the lighter congeners were more easily eliminated from soil than the heavier ones. The reason could be due to (i) the long-term air–soil exchange which enhanced the reduction of the lighter congeners in soil by net volatilization and increased the heavier ones by dry and wet deposition;[11,29] (ii) the fact that biodegradation and other processes (bioavailability, biotransformation, *etc.*) will be more pronounced for the less chlorinated compounds.[29,30] Considering that brominated flame retardants (BFRs) are incorporated into electronic equipment and devices, the centralized dismantling action by local government could directly reduce the indiscriminate emission of PBDEs during E-waste dismantling activities. However, large amounts of E-waste were still imported for centralized disassembly, which might continuously discharge some PBDEs into the surrounding environment. The discrepancies between the trend of heavier congeners of PBDEs and PCBs (or PCDD/Fs) might suggest that the enhanced regulations in 2005 exerted some influence on PBDE distribution in soils in recent years.

3.3 Overall comparison over a longer temporal scale

Previously reported results involving the distribution of PCBs, PCDD/Fs and PBDEs in the Taizhou area were combined with our data. For PCBs and PBDEs, although the sum concentrations might not concern the same congeners in those studies, the main congeners were commonly investigated, such as the indicator PCBs and the signature congeners in commercial PBDEs products (*i.e.*, BDE-47, -99, -153, -183 and -209). They generally account for large proportions of the total concentrations and therefore could reflect the overall contamination in the soil. Concerning the TEQ values, we also calculated the TEQ values based on the WHO-TEF$_{1998}$; the results showed relatively small difference from those TEQs based on the WHO-TEF$_{2005}$ (<15%). Therefore, even though WHO-TEF$_{1998}$ was employed in some previous studies, it could be assumed that the overall levels of total TEQs in the soil samples would not be obviously affected. For PCBs, the concentrations and TEQ values exhibited remarkably declining trends from 1993 to 2011, and the levels in 2011 were approximately two orders of magnitude lower than those in the 1990s (Fig. 2). Furthermore, most PCB congeners, such as CB-28, -52, -118 and -126, showed a downward trend over the past ten years (Fig. S6†). For PCDD/Fs, the concentrations have been at a constant level since 2003 (Fig. 3), which implied that PCDD/F levels in soils might be less affected by the local environmental legislation introduced in 2005. The overall congener tendencies were consistent with our presented observation, *e.g.*, the concentrations of 2,3,7,8-TeCDD and 2,3,7,8-TeCDF tended to be lower, while OCDF contributed to a higher degree more recently (Fig. S7†). For PBDEs, relatively high levels were observed by Yang *et al.*[52,53] in 2006 (Fig. 4). Then the levels tended to be lower in the following years, which is in accordance with the present study. Regarding the congener trends, the lighter congeners (*e.g.*, BDE-28, -47 and -99) showed visibly declining trends, while the heavier ones, such as BDE-153, -154 and -209, had only a slight downward trend over the years (Fig. S8†).

The temporal trends of POPs in rice hulls from our previous work showed a remarkable decline for PCBs, PCDD/Fs and PBDEs during the period 2005–2009,[5] which is inconsistent with the soil data in this present study. Several reasons could explain the discrepancies. As previously stated, POP levels in rice hulls are closely related to the air contamination and the decreasing trend is probably a reflection of the improvement of air quality in the local area since 2005.[5] However, the half-life of POPs in soil is generally much longer than that in air,[11,58] which makes

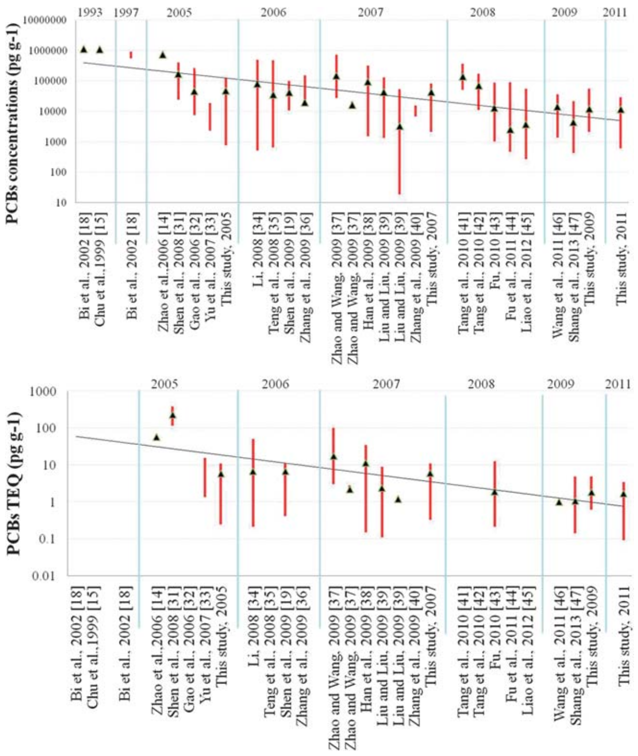

Fig. 2 The temporal trend of PCB concentrations and TEQ values in Taizhou soils over the years. The red line represents the concentration (and TEQ) range of PCBs reported in the references, the black triangle represents the mean concentration (and TEQ) value.

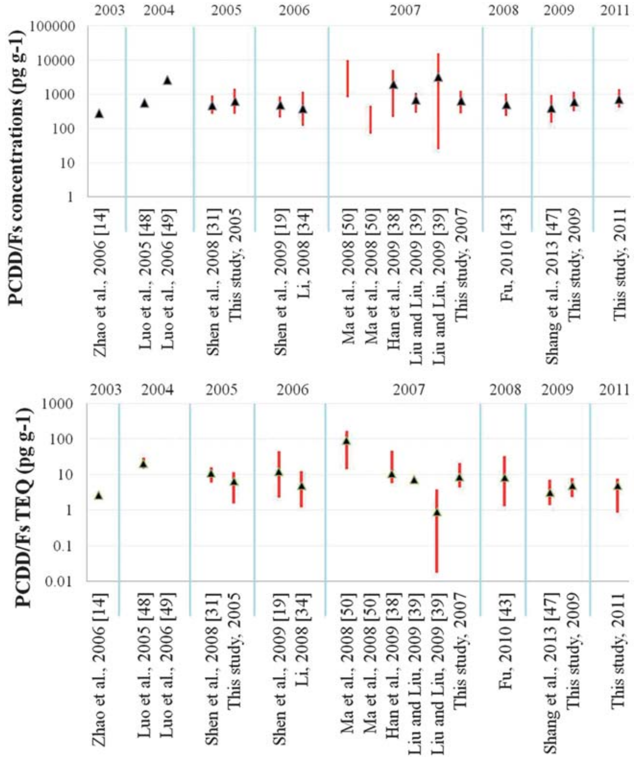

Fig. 3 The temporal trend of PCDD/F concentrations and TEQ values in Taizhou soils over the years.

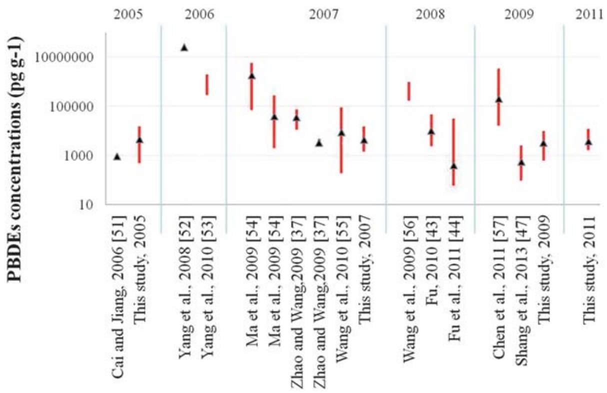

Fig. 4 The temporal trend of PBDE concentrations in Taizhou soils over the years.

the elimination of organic contaminants in soil a longer-term issue. On the other hand, the historical emission of POPs should be taken into account. PCBs have been widely produced and used in the world, and they were banned in the late 20th century. Dismantling activities involving transformers (transformer oil contains abundant PCBs) have been widespread in the Taizhou area in the following years and gradually reduced at the end of the 1990s. It is expected that an apparent decline of PCB levels would be observed subsequently. For PCDD/Fs, the restriction of open-burning activities of E-waste could have reduced the release of PCDD/Fs to the ambient environment since 2005. However, their long half-lives in soil make the natural degradation of PCDD/Fs much longer compared with their degradation in air and a decline of the concentrations in soil might not be apparent for several years. Compared with PCDD/Fs, PBDEs tend to be photolytically degraded and bioaccumulated in both aquatic and terrestrial ecosystems,[59,60] which could enhance their elimination in the field soil. However, even though the E-waste dismantling activities have been strictly regulated since 2005, the import of E-waste for centralized disassembly could still give rise to the discharge of PBDEs into the surroundings. On the other hand, both PCDD/Fs and PBDEs have heavier molecular weights and higher K_{OA} values[58] compared to PCBs. They are more easily sorbed to aerosol particles and could be deposited into the soil through wet and dry deposition.[8,11] Thus, it could be understood why relatively constant levels of PCDD/Fs and only a slight decline of PBDEs were observed in the soil around the E-waste area even after stricter environmental regulations were introduced in 2005.

4 Conclusions

The levels of PCBs, PCDD/Fs and PBDEs in soils from the Taizhou E-waste area suggested an inconsistent temporal tendency with those in rice hulls after stricter environmental regulations were introduced in 2005. PCB levels showed a decreasing trend over the period 2005–2011, while PCDD/Fs were at a relatively constant level, and PBDE concentrations tended to be slightly lower after 2007, although the decline was not statistically significant. The trends of congeners and their proportions suggested that the less halogenated compounds are more likely to be eliminated from the soils. The results suggested that the enhanced regulations and centralized dismantling action introduced in 2005 might exert a limited influence on the levels and distribution of these three types of POPs in soils in the subsequent several years. Further study is necessary to investigate the long-term effect on POPs of the stricter regulations in Taizhou from 2005.

Acknowledgements

Funding for this study was jointly provided by National Natural Science Foundation of China (21107121, 21277165 and 21107122) and National High Technology Research and Development Program of China (2011AA060604).

Notes and references

1 O. A. Ogunseitan, J. M. Schoenung, J. M. Saphores and A. A. Shapiro, *Science*, 2009, **326**, 670–671.
2 A. Sepúlveda, M. Schluep, F. G. Renaud, M. Streicher, R. Kuehr, C. Hagelüken and A. C. Gerecke, *Environ. Impact Assess. Rev.*, 2010, **30**, 28–41.
3 UNEP DEWA/GRID-Europe, 2005, E-waste, the Hidden Side of IT Equipment's Manufacturing and Use. Chapter 5 Early Warning on Emerging Environmental Threats, www.grid.unep.ch.
4 J. Puckett, L. Byster, S. Westervelt, R. Gutierrez, S. Davis, A. Hussain and M. Dutta, *Silicon Valley Toxics Coalition*, 2002, http://ban.org.
5 J. J. Fu, T. Wang, P. Wang, G. B. Qu, Y. W. Wang, Q. H. Zhang, A. Q. Zhang and G. B. Jiang, *Chemosphere*, 2012, **88**, 330–335.
6 H. G. Ni, H. Zeng, S. Tao and E. Y. Zeng, *Environ. Toxicol. Chem.*, 2010, **29**, 1237–1247.
7 M. H. Wong, S. C. Wu, W. J. Deng, X. Z. Yu, Q. Luo, A. O. Leung, C. S. Wong, W. J. Luksemburg and A. S. Wong, *Environ. Pollut.*, 2007, **149**, 131–140.
8 Y. M. Li, G. B. Jiang, Y. W. Wang, P. Wang and Q. H. Zhang, *Chin. Sci. Bull.*, 2008, **53**, 521–528.
9 J. L. Barber, G. O. Thomas, G. Kerstiens and K. C. Jones, *Environ. Pollut.*, 2004, **128**, 99–138.
10 I. T. Cousins and D. Mackay, *Chemosphere*, 2001, **44**, 643–654.
11 K. C. Jones, *Environ. Sci. Pollut. Res.*, 1994, **1**, 172–177.
12 H. X. Liu, Q. H. Zhang, Z. W. Cai, A. Li, Y. W. Wang and G. B. Jiang, *Anal. Chim. Acta*, 2006, **557**, 314–320.
13 P. Wang, Q. H. Zhang, Y. W. Wang, T. Wang, X. M. Li, L. Ding and G. B. Jiang, *Anal. Chim. Acta*, 2010, **663**, 43–48.
14 X. Zhao, M. Zheng, B. Zhang, Q. Zhang and W. Liu, *Sci. Total Environ.*, 2006, **368**, 744–752.
15 S. Chu, M. Cai and X. Xu, *Sci. Total Environ.*, 1999, **234**, 119–126.
16 H. X. Liu, Q. F. Zhou, Y. W. Wang, Q. H. Zhang, Z. W. Cai and G. B. Jiang, *Environ. Int.*, 2008, **34**, 67–72.
17 A. O. Leung, Z. W. Cai and M. H. Wong, *J. Mater. Cycles Waste Manage.*, 2006, **8**, 21–33.
18 X. H. Bi, S. G. Chu, Q. Y. Meng and X. B. Xu, *Agric., Ecosyst. Environ.*, 2002, **89**, 241–252.

19 C. Shen, Y. Chen, S. Huang, Z. Wang, C. Yu, M. Qiao, Y. Xu, K. Setty, J. Zhang, Y. Zhu and Q. Lin, *Environ. Int.*, 2009, **35**, 50–55.

20 A. O. Leung, W. J. Luksemburg, A. S. Wong and M. H. Wong, *Environ. Sci. Technol.*, 2007, **41**, 2730–2737.

21 J. J. Jou, K. L. Lin, J. C. Chung and S. L. Liaw, *J. Hazard. Mater.*, 2007, **147**, 1–7.

22 J. Kobayashi, M. Sakai, H. Kajihara and Y. Takahashi, *Environ. Pollut.*, 2008, **156**, 1233–1242.

23 N. Seike, N. Kashiwagi and T. Otani, *Environ. Sci. Technol.*, 2007, **41**, 2210–2215.

24 S. H. Im, K. Kannan, J. P. Giesy, M. Matsuda and T. Wakimoto, *Environ. Sci. Technol.*, 2002, **36**, 3700–3705.

25 K. S. Kim, S. K. Shin, K. S. Kim, B. J. Song and J. G. Kim, *Environ. Int.*, 2008, **34**, 202–209.

26 Y. Luo, X. J. Luo, Z. Lin, S. J. Chen, J. Liu, B. X. Mai and Z. Y. Yang, *Sci. Total Environ.*, 2009, **407**, 105–111.

27 R. J. Law, C. R. Allchin, J. de Boer, A. Covaci, D. Herzke, P. Lepom, S. Morris, J. Tronczynski and C. A. de Wit, *Chemosphere*, 2006, **64**, 187–208.

28 D. M. Wagrowski and R. A. Hites, *Environ. Sci. Technol.*, 2000, **34**, 2952–2958.

29 W. A. Lead, E. Steinnes, J. R. Bacon and K. C. Jones, *Sci. Total Environ.*, 1997, **193**, 229–236.

30 Y. S. Chang, *J. Mol. Microbiol. Biotechnol.*, 2008, **15**, 152–171.

31 C. Shen, S. Huang, Z. Wang, M. Qiao, X. Tang, C. Yu, D. Shi, Y. Zhu, J. Shi, X. Chen, K. Setty and Y. Chen, *Environ. Sci. Technol.*, 2008, **42**, 49–55.

32 J. Gao, Y. Luo, Q. Li, H. Zhang, L. Wu, J. Song, W. Qian, P. Christie and S. Chen, *Environ. Geochem. Health*, 2006, **28**, 79–87.

33 S. Yu, S. Jiang, L. Ju, J. Chai, N. Wu, C. Xu and X. Zhang, *J. Environ. Health*, 2007, **24**, 304–307.

34 Y. M. Li, Doctoral thesis, 2008, (in Chinese).

35 Y. Teng, M. K. Zheng, Y. M. Luo, J. Gao, Z. G. Li and L. H. Wu, *Environ. Sci.*, 2008, **29**, 3477–3482, (in Chinese).

36 X. Zhang, Y. Luo, Y. Teng, Y. Yu, J. Wang, L. Xu and Z. Li, *Soils*, 2009, **41**, 588–593, (in Chinese).

37 G. F. Zhao and Z. J. Wang, PHAHs levels in soil samples from the E-waste disassembly sites and their sources allocation, *Environ. Sci.*, 2009, **6**, 1850–1854, (in Chinese).

38 J. Han, H. Shen, C. Yu, G. Song and B. Ma, *Chin. J. Health Lab. Technol.*, 2009, **19**, 1124–1127, (in Chinese).

39 J. S. Liu and W. P. Liu, *J. Hazard. Mater.*, 2009, **163**, 959–966.

40 J. Zhang, D. Li, H. Wang, X. Tang and Y. Zhu, *Acta Pedol. Sin.*, 2009, **46**, 434–441.

41 X. Tang, C. Shen, D. Shi, S. A. Cheema, M. I. Khan, C. Zhang and Y. Chen, *J. Hazard. Mater.*, 2010, **173**, 653–660.

42 X. Tang, C. Shen, L. Chen, X. Xiao, J. Wu, M. I. Khan, C. Dou and Y. Chen, *J. Soils Sediments*, 2010, **10**, 895–906.

43 J. J. Fu, Doctoral thesis, 2010, (in Chinese).

44 J. J. Fu, Y. W. Wang, A. Q. Zhang, Q. H. Zhang, Z. S. Zhao, T. Wang and G. B. Jiang, *Chemosphere*, 2011, **82**, 648–655.

45 C. Liao, J. Lv, J. Fu, Z. Zhao, F. Liu, Q. Xue and G. Jiang, *Int. J. Environ. Health Res.*, 2012, **22**, 317–330.

46 X. Wang, X. Lou, G. Han, H. Shen and G. Ding, *J. Hyg. Res.*, 2011, **40**, 583–586, 590. (in Chinese).

47 H. T. Shang, P. Wang, T. Wang, Y. W. Wang, H. D. Zhang, J. J. Fu, D. W. Ren, W. H. Chen, Q. H. Zhang and G. B. Jiang, *Environ. Int.*, 2013, **54**, 50–58.

48 Y. M. Luo, Y. Teng, Q. B. Li, L. H. Wu, Z. G. Li and Q. H. Zhang, *Acta Pedol. Sin.*, 2005, **42**, 570–575, (in Chinese).

49 Y. Luo, Y. Teng, Z. Li, Y. Wu, Y. Bu, L. Fang, M. Zheng and Z. Li, *Acta Pedol. Sin.*, 2006, **43**, 563–570, (in Chinese).

50 J. Ma, K. Kannan, J. Cheng, Y. Horii, Q. Wu and W. Wang, *Environ. Sci. Technol.*, 2008, **42**, 8252–8259.

51 Z. W. Cai and G. B. Jiang, *Talanta*, 2006, **70**, 88–90.

52 Z. Z. Yang, X. R. Zhao, Q. Zhao, Z. F. Qin, X. F. Qin, X. B. Xu, Z. X. Jin and C. X. Xu, *Bull. Environ. Contam. Toxicol.*, 2008, **80**, 340–344.

53 Z. Z. Yang, Y. F. Li, Y. X. Hou, H. Y. Liang, Z. F. Qin and S. Fu, *Bull. Environ. Contam. Toxicol.*, 2010, **84**, 260–263.

54 J. Ma, R. Addink, S. Yun, J. Cheng, W. Wang and K. Kannan, *Environ. Sci. Technol.*, 2009, **43**, 7350–7356.

55 X. Wang, F. Wang, J. Jia, Y. Li, Y. Sun, M. Wu, G. Sheng and J. Fu, *China Environ. Sci.*, 2010, **30**, 1664–1669, (in Chinese).

56 H. M. Wang, Y. J. Yu, M. Han, S. W. Yang, Q. Li and Y. Yang, *Bull. Environ. Contam. Toxicol.*, 2009, **83**, 789–793.

57 T. Chen, C. Zhou, Y. J. Mou and B. B. Yu, *J. Ecol. Rural Environ.*, 2011, **27**, 20–24.

58 D. Mackay, *Multimedia Environmental Model: The Fugacity Approach*, Lewis Publishers, Boca Raton, 2nd edn, 2001.

59 Y. H. Shih and C. K. Wang, *J. Hazard. Mater.*, 2009, **165**, 34–38.

60 O. Segev, A. Kushmaro and A. Brenner, *Int. J. Environ. Res. Public Health*, 2009, **6**, 478–491.