PCDD/Fs in Air and Soil around an E-waste Dismantling Area with Open Burning of Insulated Wires in South China

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Abstract Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in ambient air and farmland soil sampled in 2006 around an e-waste dismantling area with open burning of insulated wires in Longtang in south China were investigated. The total toxic equivalent concentrations of PCDD/Fs were 3.2–31.7 pg/m^3 in air and 5.8 12.4 ng/kg in farmland soil at an e-waste site and 0.063–0.091 pg/m^3 in air at a background site. PCDD/Fs in the air at the e-waste site were characterized with dominant 1,2,3,4,6,7,8-HpCDF and OCDF and higher concentrations of furans than dioxins, suggesting open burning of insulated wires was likely to be the main source of PCDD/Fs. Compared with the results in this study, the level of PCDD/F tended to lessen with the average TEQ concentration decreasing by 41 % and the pattern changed to be dominated by OCDD in the air of Longtang in 2010 when insulated wires were openly burned in only a small scale. Our results indicate that the lower chlorinated congeners with higher vapor pressures have enhanced atmospheric transport tendencies.

Keywords E-waste · PCDD/Fs · Open burning of insulated wires · Air · Soil

Rudimentary recycling of electronic wastes (e-waste) can release a large quantity of toxic chemicals, and each type of e-waste releases specific pollutants, such as brominated organic contaminants and heavy metals from printed circuit boards, polychlorinated biphenyls (PCBs) from transformers, and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) from insulated wires. Thus, improper recycling of these wastes poses potentially harmful effects to the local environment (Ni et al. 2010; Chan and Wong 2013; Man et al. 2013). Rudimentary ways including manual disassembling, roasting, acid leaching, and open burning were applied to the various sorts of e-waste materials, including electric motors, electrical equipment enclosures, printed circuit boards, and electric wires, etc. Open burning of scrap wires releases large quantities of PCDD/Fs, yet it occurs widely in some underdeveloped regions and was considered to be one of the main sources in China (Zhu et al. 2008; Zheng et al. 2008).

The average emissions of PCDD/Fs from simulated open burning of insulated wires were 11,900 ng WHO_{98}-toxic equivalency (TEQ)/kg (Gullett et al. 2007). Industrial scrap metal recycling from waste enameled wires emitted 11.3 ng WHO_{2005}-TEQ/m^3 and 2.6 ng WHO_{2005}-TEQ/g of PCDD/Fs in flue gas and residual ash, respectively (Nie et al. 2012). PCDD/Fs were also determined in some laboratory tests of polyvinyl chloride (PVC) pyrolysis (Yasuhara et al. 2006; Conesa et al. 2013). In these studies, fuel and oxygen were provided in order to improve combustion and obtain higher temperatures in laboratory tests. PCDD/F emissions can be affected by the conditions of combustion, and can redistribute between environmental components such as gas-particles or air–soil, and be transformed following release from the source. It is important to characterize the footprint of PCDD/Fs around sites of open burning of insulated wires, yet field data are very few.

Longtang is a town located in Qingyuan city, Guangdong province. It is about 70 km north of Guangzhou, the largest city in south China. It has a nearly 30-year history

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of recycling of e-waste, and it is famous for reclaiming waste metals such as copper and aluminum from e-waste, mainly scrap wires and waste electric motors. Open burning had been widely applied to waste wires in hills in Longtang before 2008. With the environmental regulations having been strengthened, open burning of waste wires gradually disappeared, and automatic stripping machines have gradually replaced the rudimentary method.

The local environment has been getting public attention. High levels of halogenated flame retardants were found in the atmosphere and soil of the e-waste recycling region (Chen et al. 2011; Tian et al. 2011a, b). In comparison with Guiyu (another e-waste contaminated site) in China, lower concentrations of PBDEs and higher concentrations of PCBs were observed at Longtang in both soil and plants, suggesting different e-waste types (Wang et al. 2011). At Longtang, PCDD/Fs were found at high levels in soil sampled in 2009, after large-scale open burning of wires occurred (Hu et al. 2013), and in air sampled between 2009 and 2010 when waste wires were scarcely burned and recycled by wire-stripping machines (Xiao et al. 2014). However, very few field data of PCDD/F emissions from large-scale open burning of wires were reported.

This study characterized the PCDD/F emissions from the open burning of e-wastes by determining the levels and congener profiles of PCDD/Fs in air in the town of Longtang. The levels and profiles for Longtang air were compared to values in soil and background air to evaluate the transfer and fate of PCDD/Fs.

Materials and Methods

In Longtang (Qingcheng district, Qingyuan city, Guangdong province, China), large quantities of e-waste (about 700,000 metric tons, mainly insulated wires and electric motors) were processed yearly using primitive methods (e.g. open burning and manual disassembling). There were about 1000 plants recycling e-waste in Longtang, and many employers used their houses as workshops in the town. Among the e-waste, thin cables were burned openly to recycle copper in hills and even in workshops' courtyards, for most employers, driven by profits, preferred not to invest in automatic stripping machines, and it was difficult for workers to dismantle thin cables manually. Many scattered open burning sites were present in the hills and courtyards of the town. A short-term sampling scheme was conducted in fine and calm days in January, 2006. A map of sampling location was shown in Fig. 1. Air was sampled in the e-waste recycling area in Longtang (hereinafter e-waste air). The e-waste air sampling site was about 200 m far from the nearest courtyard open burning site and 1500 m far from the nearest hill open burning site. Air was
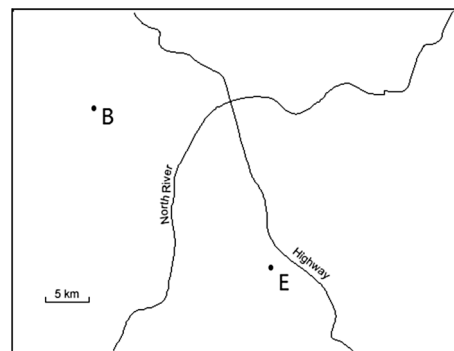

Fig. 1 Sampling locations in Qinyuan (E, e-waste site, B, background site)

also sampled in an adjacent rural town approximately 22 km northwest of the e-waste site (hereinafter background air). No smoke plume was sampled during the sampling period. High-volume air samplers were used with glass fiber filter (GFF) and polyurethane foam (PUF) systems and operated at a flow rate of 1.05 m^3/min. Calibrations were made before and after each sampling. Surface farmland soils (0–5 cm in depth) were collected using a stainless steel sampler in the e-waste recycling area. Each soil sample was a composite of five sub-samples collected from an area of about 4 m^2.

The detailed analytical method was reported elsewhere (Ren et al. 2006). Briefly, samples were spiked with ^{13}C-labeled surrogate standards [Cambridge Isotope Laboratories, Inc (CIL), Andover, MA, USA] prior to the 24-h Soxhlet extraction with toluene. Sample cleanup was accomplished successively according to the following steps: (1) Sample extracts were pre-cleaned with 40 % H_2SO_4/silica gel (70–230 mesh, Merck, Germany) in hexane (Merck, Germany, pesticide quality grade), stirred for 2 h. The entire content of the flask was filtered through a funnel with glass wool covered with Na_2SO_4. Hexane was used to rinse the flask and the slurry. (2) The filtrates were further cleaned on a multi-layer silica gel column, eluted successively with hexane (to be discarded) and 3 % dichloromethane (Merck, Germany, pesticide quality grade)/hexane. (3) Eventually, the latter fraction was cleaned on a basic alumina (Merck, Germany) column, eluted sequentially with hexane (to be discarded), 2 % dichloromethane/hexane (to be discarded) and 50 % dichloromethane/hexane. Finally, injection standards (1,2,3,4-TeCDD and 1,2,3,7,8,9-HxCDD, ^{13}C$_{12}$-labled, CIL, Andover, MA, USA) were added into the extracts. Identification and quantification were performed with gas chromatograph (Trace GC 2000, Milan, Italy) coupled with high resolution mass spectrometry (Finnigan MAT 95 XP, Breman, Germany). Quality assurance and quality control were conducted with the method blank. There were no detectable PCDD/Fs, and the recoveries of all the labeled compounds were about 70 %–110 %.

Results and Discussion

Total concentrations of 17 2,3,7,8-substituted PCDD/Fs ($\sum_{17}$PCDD/Fs) in the e-waste air ranged from 52 to 548 pg/m^3 with an average of 237 pg/m^3. In terms of TEQ, the TEQ in the e-waste air ranged from 3.2 to 31.7 pg WHO$_{2005}$-TEQ/m^3 with an average of 13.6 pg WHO$_{2005}$-TEQ/m^3, much higher than the reported range for global urban/industrial areas (Lohmann and Jones [1998]), suggesting a serious pollution level resulted from the e-waste recycling operations. The total concentrations of PCDD/Fs in e-waste air obtained in the present study were similar to those from other e-waste sites such as Fengjiang in Taizhou (Wen et al. [2011]) and Guiyu (Li et al. [2007]). PCDD/Fs were also reported in the air of Longtang sampled in summer 2009 and winter 2010, and the data in that winter with similar meteorological conditions were used for comparison with those in this study. The PCDD/F level was found to lessen with the average TEQ concentration decreasing by 41 % in winter 2010 (mean 8.0 pg WHO$_{2005}$-TEQ/m^3) when wires were openly burned on a much smaller scale (Xiao et al. [2014]). The decreasing trend of PCDD/F levels from 2006 to 2010 might have been due to the implementation of laws forbidding open burning of waste wires, and the increased use of wire-strapping machines in recent years.

The concentrations of $\sum_{17}$PCDD/Fs in rural background air ranged from 0.063 to 0.091 (mean 0.077) pg WHO$_{2005}$-TEQ/m^3, which were 1–2 orders of magnitude lower than those in e-waste air. There were no large industrial plants in the rural site. The great difference of PCDD/F levels between e-waste air and background air suggests crude e-waste recycling had caused higher pollution levels in the local environment. Waste wires were openly burned in hills where some of PCDD/Fs could deposit and be absorbed onto trees and soil, acting as a large reservoir of PCDD/Fs. Therefore, levels of PCDD/Fs in air will decrease when they diffuse and transport.

Soil is known to be one of the main sinks for airborne PCDD/Fs. Due to their high persistence and slow biodegradation processes, PCDD/Fs can accumulate in soil containing organic matter. Thus, the concentrations of PCDD/Fs in soil can provide information about long-term local contamination from these pollutants. In this study, the concentrations of $\sum_{17}$PCDD/Fs in farmland soils at the e-waste recycling site ranged from 5.8 to 12.4 ng WHO$_{2005}$-TEQ/kg, with an average of 7.1 ng WHO$_{2005}$-TEQ/kg. The total concentrations of PCDD/Fs in farmland soils were comparable to those in rice field soils collected from Guiyu (Leung et al. [2007]). There are no common international guidelines for PCDD/Fs in soils. Some European countries have used the following guidelines for soil classification and remediation (Schulz [1993]): soils containing PCDD/Fs at 5 ng TEQ/kg or lower should be safe for all agricultural purposes; soils with 5–40 ng TEQ/kg are not restricted for cultivation of foodstuffs, but these soils should be avoided for agricultural uses if the levels of PCDD/Fs in foodstuffs are found to be bioconcentrated. According to the guidelines, soils in this study were not highly contaminated, but further systematic surveys of soil and crop contamination should be conducted.

To further characterize PCDD/F emissions from open burning of insulated wires, we examined the congener profiles of 17 2,3,7,8-PCDD/Fs in e-waste air (Fig. 2). The concentration of each individual furan was higher than that of the corresponding dioxin with chlorination substitution at the same positions. The total concentrations of 2,3,7,8-PCDFs ($\sum$PCDFs) were obviously higher than those of dioxins ($\sum$PCDDs). The ratios of $\sum$PCDFs/$\sum$PCDDs ranged from 2 to 13, and increased with increasing concentration of PCDD/Fs. 1,2,3,4,6,7,8-HpCDF and OCDF were major congeners, contributing 23 % ± 0.3 % and 21 % ± 8 % to $\sum_{17}$PCDD/Fs, respectively. These features were very consistent with those of experimental open burning of wires, where the percentages of the major congeners of 1,2,3,4,6,7,8-HpCDF and OCDF and ratios of $\sum$PCDFs/$\sum$PCDDs were 24 % ± 2 %, 15 % ± 3 %, and 2 %–5 %, respectively, for operating in an open burning test facility (Gullett et al. [2007]), and 32 %, 18 % and 15 % for operating in a room (Chen [2011]). PCDD/F emissions from combustion of insulated wires containing PVC were characterized with abundant PCDFs, especially higher chlorination furans, which had been also found in pyrolysis of PVC with copper chloride (Wang et al. [2002]) and combustion of PVC with paper (Yasuhara et al. [2006]). The features are similar to medical waste incinerators, and secondary copper and aluminum smelters, which might contain PVC in feedstock. However, there are differences from several important sources, including municipal solid waste incinerators with major congeners of OCDD, 1234678-HpCDF and 1234678-HpCDD, iron ore sintering and landfills with dominant 2,3,7,8-TCDF, cement kilns with major congeners of higher chlorinated dioxins, diesel-fueled or unleaded gas-fueled vehicles, forest fires, and pentachlorophenol (PCP) chemicals with predominant OCDD (USEPA [2006]).

Waste electrical motors were also dismantled in the area, and the scrap transformers containing PCBs as dielectric fluid could potentially release PCDD/Fs. However, The PCDD/F profiles in e-waste air in this study were very different from those in commercial PCBs with a dominant congener of 2,3,7,8-TCDF, and from those in emissions from a PCB incinerator with a predominant congener of OCDF in the stack ash and with major congeners of
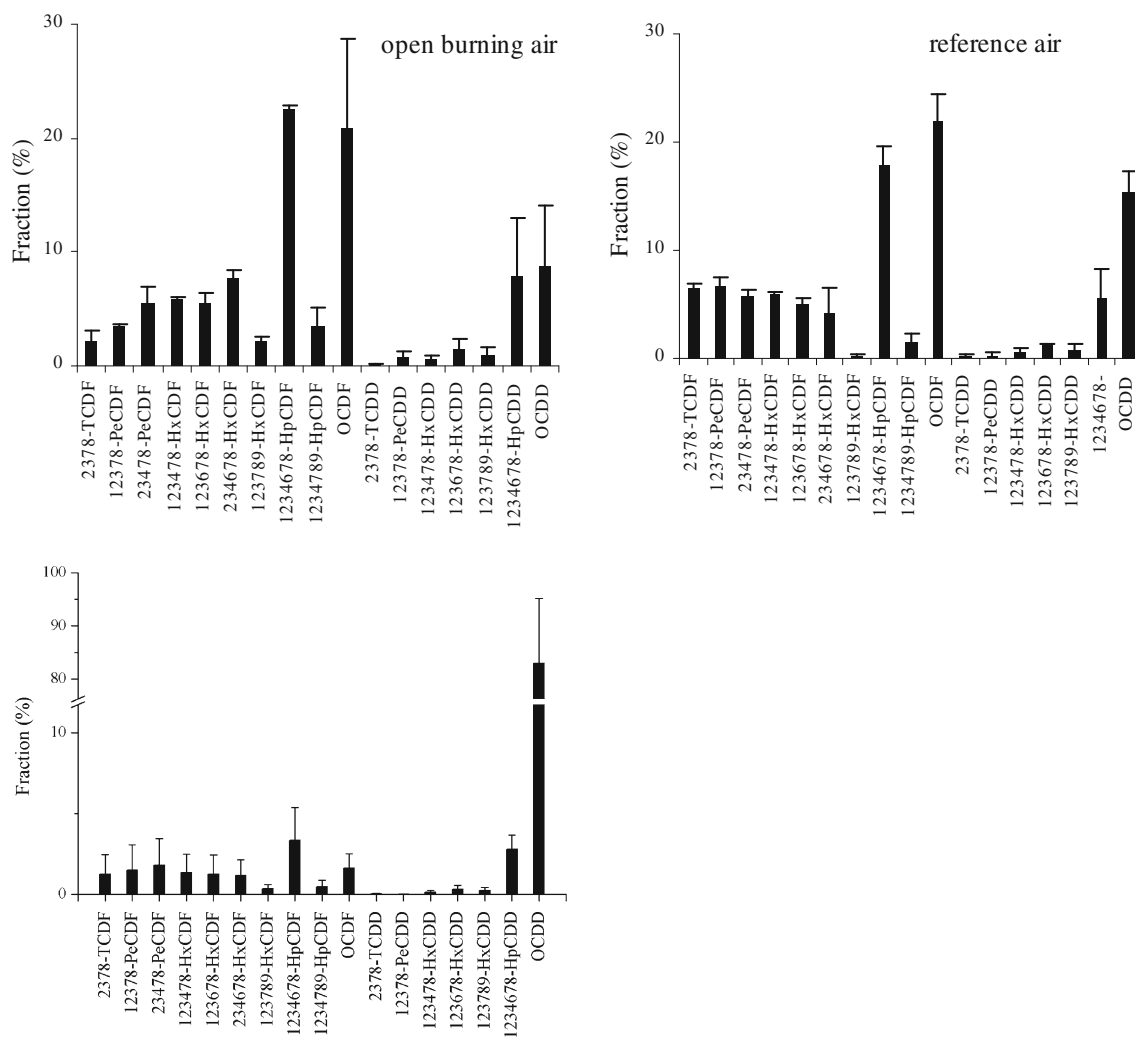
Fig. 2 Congener profiles of PCDD/Fs in air and farmland soils around an e-waste recycling area (*bars* indicate standard deviation)

2,3,7,8-TCDF, 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,7,8-HxCDF in the bottom ash (Jiang et al. 1997). Waste electrical motors were mainly dismantled by machine cutting and crushing, from which the released concentrations of PCDD/Fs and PCBs would be relatively small. Furthermore, there were no other potential sources such as municipal solid waste incinerators, medical waste incinerators, and household waste burning, etc.

About 1000 family workshops were engaged in dismantling e-waste in Longtang. Waste wires were openly burned to recycle copper without stripping of coat. Some researchers considered that open burning of scrap wires was one of the main sources of PCDD/Fs in China (Zhu et al. 2008; Zheng et al. 2008). The dismantling scale of e-waste in Longtang was one of the largest in world, and waste wires were the major e-waste. In addition, the great difference of PCDD/F levels between 2006 and 2010 were consistent with the discontinuation of open burning of

insulated wires. That is, the obviously higher levels were found when open burning of insulated wires occurred. Therefore, PCDD/Fs in e-waste air might be mainly attributed to be the open burning of electric wires.

A different pattern was found in the air of Longtang sampled in winter 2010 with the dominant OCDD contributing 27 % of $\sum_{17}$PCDD/Fs (Xiao et al. 2014). After 2008, open burning of waste wires was legally forbidden and mostly substituted by mechanical stripping. In addition, some new sources such as industrial thermal wire reclamation in incinerators and ceramic factories appeared in recent years, which might have resulted in the change of PCDD/F patterns.

As shown in Fig. 2, the congener profiles in the background air were similar to those in the e-waste air with 1,2,3,4,6,7,8-HpCDF and OCDF accounting for 18 % ± 2 % and 22 % ± 3 % of $\sum_{17}$PCDD/Fs. Nevertheless, the lower chlorinated congeners (lower-CDD/Fs)

were slightly more abundant in the background air than in the e-waste air. A ratio is defined as the average percentage contribution of the individual congener to total PCDD/Fs in the background air divided by those in the e-waste air. These ratios can partially reflect their potential for atmospheric transport from the source region to the ambient region. It is interesting to note that lower-CDD/Fs such as 2,3,7,8-TeCDF, 1,2,37,8-PeCDF and 2,3,7,8-TeCDD with higher vapor pressures have higher transport tendencies (ratios 1.3–2.7) than the more highly chlorinated DD/Fs, such as hexa-, hepta-CDD/Fs and OCDF. These have lower vapor pressures and lower transport tendencies (ratios 0.3–1.1). This finding suggests that semi-volatile organic compounds with higher vapor pressures present in the gas phase or sorbed onto particles are readily subject to transport in the atmosphere. However, OCDD with the lowest vapor pressure shows a higher ratio of 1.7. A possible reason is that OCDD may have been formed from photochemical synthesis from PCP in air during transport, which was hypothesized according to the global unbalanced mass of PCDD/Fs with deposition of OCDD exceeding emissions and laboratory tests of irradiation of PCP solution by Baker and Hites (2000).

According to the profile in soil (Fig. 2), 1,2,3,4,6,7,8-HpCDF and OCDF were still the important furans. However, the congener pattern in soil was different from that in air. OCDD changed to be dominant, with its average percentage content relative to $\sum_{17}$PCDD/Fs of 83 % in soil. In contrast to the congener pattern in air, which was directly affected by the sources, the pattern in soil was influenced by the different atmospheric transportation, precipitation and transformation abilities of the congeners. Degradation half-life times of PCDD/Fs in soil were suggested to be several decades and photolysis on soil surface was generally restricted to the top 1 mm of the soil, so the influence of degradation might be regarded as negligible (Sinkkonen and Paasivirta 2000). The extremely high percentages of OCDD were likely to be mainly attributed to other origins such as synthesis of OCDD from PCP in air, in surface soil and even in deep soil (Baker and Hites 2000; Liu et al. 2002; Ren et al. 2009; Gu et al. 2011).

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