FINGERPRINTS of CHLORINATED, BROMINATED AND MIXED HALOGENATED DIOXINS AT TWO E-WASTE RECYCLING SITES IN GUIYU/CHINA

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Abstract

This study describes the fingerprints of chlorinated, brominated and brominated-chlorinated dibenzofurans and dibenzodioxins at two e-waste open burning/smouldering sites in Guiyu, China. The total concentrations of PXDD/PXDF in the soils were in ppm range. The total furan (PXDF) to dioxin (PXDD) ratios were around 100 revealing that PBDEs[A] as direct furan precursors were responsible for the formation of most of the dioxin-like compounds at the sites. The high levels of mixed chlorinated-brominated dibenzofurans and dibenzodioxins present as main contaminants at the open burning site reveal a significant bromine-chlorine exchange in PBDE[A]/PBDF most probably from PVC and chlorine containing additives (e-g. chlorinated paraffins, tetrachlorobisphenol A, etc.). The comparable concentrations of halogenated PXDF and precursor PBDEs at both sites indicate that a significant share of PBDEs was converted into PBDF/PXDF. When considering that several thousand tons of PBDE[A] are present in the 20 to 50 million tons of e-waste reaching the waste recycling sector every year, and that developing countries process a significant amount of e-waste utilizing rudimentary thermal processes, the load of halogenated PXDD/PXDF formed and released can be expected on the scale of tons and therefore possibly higher than all current inventoried PCDD/PCDF sources combined.

Introduction

About 50-80% of electronic waste (e-waste) from industrialized countries ends up in China, India, Pakistan, Philippines, Vietnam and other Southeast Asian countries[1, 2] for cheap recycling due to the low labour costs and less stringent environmental regulations in these countries[2]. Recycling of e-waste has been undertaken for 10-20 years in these countries. China and several other countries recently restricted the import of e-waste and are tackling this type of harmful e-waste recycling[12].

The particular concern with e-waste is the wide range of toxic compounds including brominated flame retardants (BFRs) such as polybrominated diphenylethers (PBDE, recently listed as POPs in the Stockholm Convention[A]), polychlorinated biphenyls (PCBs), as well as a broad range of toxic heavy metals[;3]. Its recycling has produced contaminated mega-sites with a multitude of contaminants[4-7]. An example of such a site is Guiyu city located in the Chaoyang District in Southeast China, with a total area of 52 km^2 and a population of 150,000. It is a rice-growing region and its industry has been dominated by e-waste recycling since the early 1990s. The soil in this area has been found to be highly contaminated with heavy metals, PBDE[A] and other BFRs, PCBs, brominated and brominated-chlorinated dibenzodioxins and dibenzofurans (PXDD/PXDF) and other toxic compounds[4-7]. Similarly, the drinking water of Guiyu city has been identified unfit for consumption and it is partly imported[,2,5].

A common form of e-waste treatment is to use open burning as a "cleaning step" for removing plastics from cables and other parts of dismantled e-waste. Open burning is also used for final disposal of residues. In Dioxin 2008 we reported high levels of PXDD/PXDF and dioxin-like toxicity in soil samples from areas where e-waste was burned in the open in Guiyu[6]. In this paper we describe the fingerprint of brominated and brominated-chlorinated and chlorinated PXDD/PXDF and discuss formation pathways and likely precursors.

[A] Components of commercial PentaBDE (TetraBDE and PentaBDE) and components of commercial OctaBDE (HexaBDE and HeptaBDE) were listed as POPs in Annex A of the Stockholm Convention at the 4th Conference of the Parties (Geneva 05/2009).

Materials and methods

Soil samples (0-10cm soil layer) were collected from two open e-waste smouldering/burning locations in Guiyu, China between June and December 2004. At each location, one composite sample was collected. Composites consisted of five soil samples collected at the four corners and the center in an area of about 10×10 m^2 within the respective location. Samples were air dried at room temperature, sieved through 2 mm and stored at 4ºC before analysis. PCDD/Fs were analysed according to USEPA Method 1613B. PBDD/Fs and brominated-chlorinated PXDD/Fs were analysed at the Swiss Federal Laboratories for Materials Testing and Research (Empa, Dübendorf, Switzerland). PBDDs were quantified using internal $^{13}C_{12}$-PBDD/F (CIL EDF-5071). Response factors to lower brominated PBDD/F were determined by using available native congeners. Response factors for tetra- to heptabromo congeners were determined by the use of a corresponding mixture of native higher brominated congeners (CIL EDF-2046). For mixed halogenated PXDDs, all homologues except Br_5Cl_xDD/Fs to Br_7Cl_1DD/Fs. PXDD/Fs were determined; quantification was carried out using $^{13}C_{12}$-2,3,7,8-TetraBDF as internal standard. The GC-MS analyses were carried out using a 30 m RTX-5-Sil MS column (0.25 mm diameter, 0.10 µm film thickness) at a helium gas pressure of 15 psi. The resolution of the MS was set to 9’000.

Results and discussion

The composite soil samples from both e-waste smouldering/burning sites were highly contaminated with the whole range of chlorinated, brominated and brominated-chlorinated PXDF and PXDD with differences in the finger print (Figure 1a/b and 2a/b).

At site 1 printed circuit boards were smouldering for metal recovery. The composite sample from this location was dominated by polybrominated PBDF with contamination levels of 1,400,000 ng/kg for TetraBDF to OBDF (Figure 1a). The homologue pattern of the brominated PBDF showed a decrease from OBDF (380,000 ng/kg) to HeptaBDF (140,000 ng/kg) and HexaBDF (104,000 ng/g) and then a significant increase with high concentrations of PentaBDF, TetraBDF and TriBDF in comparable concentrations (350,000 to 420,000 ng/kg) and low concentrations of DiBDF and MonoBDF (Figure 1a).

This indicates that PBDFs were mainly formed from commercial DecaBDE (containing mainly DecaBDE and some NonaBDE) and PentaBDE (consisting largely of 2, 2’,4, 4’-TetraBDE (#47) and 2, 2’,4,,4’,5- and 2, 2’,4,,4’,6-PentaBDEs (#99 and #100)) mixture commercially used as BFR on Printed Circuit Boards and that commercial OctaBDE did not play a significant role at this site. This is confirmed by the detection of high concentrations of brominated diphenylether ((total PBDE 36,200,000 ng/kg) in the soil sample with mainly DecaBDE (22,200 ng/g) and in lower concentrations Penta- and TetraBDE (3,370,000 and 3,510,000 ng/kg) with minor contribution of Hepta- and OctaBDE (1370,000 and 1,070,000 ng/kg).

Brominated-chlorinated PXDF were found in lower concentrations compared to the purely brominated congeners (Figure 1a). Within the same degree of halogenation the concentrations of homologues sharply decreased with successive degree of chlorination. Therefore in the smouldering process a minor substitution of bromine/hydrogen in the PBDF (PBDE) by chlorine took place during the thermal treatment indicating that significant chlorine sources were not prominently present in the smoulder process of the printed circuit boards.

Brominated and brominated-chlorinated dibenzodioxins (PXDD) were minor contaminants at this site with a halogenated Furan/Dioxin ratio of around 80 (Figure 1a and 1b). This is an extremely high ratio only found as impurities in halogenated dibenzofuran precursors (e.g. PBDE[A] or PCB) or processes with main impact of these type of dibenzofuran precursors. This further demonstrates that other formation pathways (than the formation from PBDE) did not play a significant role at this site especially that brominated flame retardants that act as PBDD precursor (e.g. brominated phenols or Tetrabromobisphenol A) had no relevance.

Composite soil sample No. 2 were collected at a large e-waste burning site where open burning of all types of e-waste, including wires, plastic residues from computers and TVs, circuit boards, etc. was carried out for more then a decade. The CALUX bio-TEQ of the soil from this site showed extremely high dioxin like-toxicity (93,800 ng TEQ/kg)[6]. The instrumental analysis revealed that mainly brominated and brominated-chlorinated dioxins are responsible contaminants with a minor impact from chlorinated PCDD/F (Figure 2a,b). PBDF (2500 ng/g for Tetra- to OctaBDF and total 3940 ng/g)) and brominated-chlorinated PXDF (4,250,000 ng/kg for Tetra- to Octa-PXDF and total 5,150,000 ng/kg) were the predominant contaminants and present in significantly higher concentrations compared to the chlorinated PCDF (800,000 ng/kg for Tetra- to OctaCDF) (Figure 2a).

The halogenated dibenzodioxins were present also at this site in considerably lower concentrations compared to the halogenated dibenzofurans (average furan/dioxin ratio >100; Figure 2a and 2b) demonstrating that PBDE[A] as direct PBDF precursors were responsible for the formation of PBDF and PXDF. PBDEs[A] were also present in high concentrations in the soil (total PBDE 44,400,000 ng/kg) with mainly DecaBDE (31,200,000 ng/kg) and TetraBDE to NonaBDE in about one order of magnitude lower concentrations (1,500,000 to 3,510,000 ng/kg).

The dominating PBDF homologues were Tri- to PentaBDF with lower concentration of Hexa- to OctaBDE (Figure 2a). The high share of brominated-chlorinated PXDF on this site results from the higher impact of chlorination of the PXDF originating from brominated PBDF/PBDE compared to the printed circuit board smouldering site (compare figure 1a and figure 2a). This can be explained by the presence of PVC in the mixed e-waste (wire coating and other PVC plastic parts) or other chlorinated plastic additives (chlorinated paraffins, tetrachlorbisphenol A, etc) and the easy substitution of bromine by chlorine in the thermal reaction of PBDEs[8,9].

As mentioned above the overall ratio of halogenated furans to dioxins was >100. However the ratio of chlorinated PCDF to PCDD was significantly lower (approximately 15). This PCDD/PCDF ratio is still significantly higher compared to waste incineration (normally around 0.4 to 4) but is in the range of the ratio found in the incineration or pyrolysis of PVC (ratio mostly between 7 to 20)[10,11]. This indicates that PVC combustion was mainly responsible for the chlorinated PCDD/PCDF formed at the e-waste smouldering site.

Overall this study is the first comprehensive description of fingerprints of chlorinated, brominated and brominated-chlorinated dibenzodioxins and dibenzofurans at e-waste recycling sites. The study demonstrates that PBDEs[A] are currently the key precursor for dioxin-like compounds in e-waste recycling conducted using burning as performed in Guiyu. Further, the data indicate that PVC plays a relevant role in the formation of PCDD/PCDF and the partial chlorination of PBDF (and PBDE). The comparable ratio of halogenated PXDF and the responsible precursor PBDE[A] at the site indicates that a significant share of PBDEs is converted into dioxin-like and therefore highly toxic compounds.

Considering that several thousand tons of PBDEs[A] are contained in the 20 to 50 million tons of e-waste that enters developing countries around the world (e.g. for China alone the imported amount of PBDE in e-waste was estimated to 35,000 t/year[13]), and that it is recycled utilizing rudimentary thermal processes, the load of halogenated PXDD/PXDF can be expected to be on the scale of tons. This makes e-waste (and other PBDE retarded materials) a source of PXDD/PXDF that is possibly higher than all other current PCDD/PCDF sources combined. As mentioned above, several PBDEs were listed as POPs in the Stockholm Convention[A]. However an exemption was provided for the recycling and final disposal of articles containing the listed PBDEs until 2030. The current study indicates that PBDF/PXDF could be formed in tons scale during rudimentary e-waste recycling from articles containing PBDEs[B]. The current data should serve as a warning that recycling and disposal activities of articles containing PBDEs (e-waste, automotive shredder, foams, upolstery mattresses, textiles etc.) needs to be severely controlled.

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[B] Additionally PBDFs are formed if the PBDE containing plastics are recycled by extrusion, moulding or other thermal treatment steps[8].

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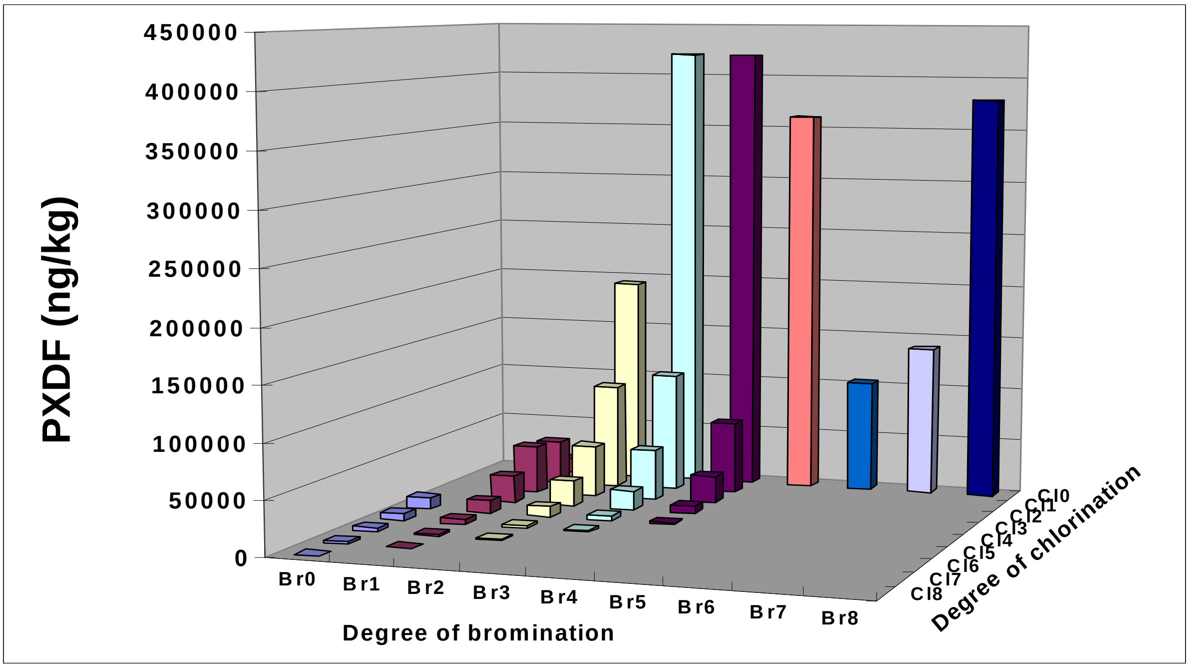

Figure 1a: PCDF, PBDF and PXDF in soil at site 1 (printed circuit board smouldering site) in Guiyu/China

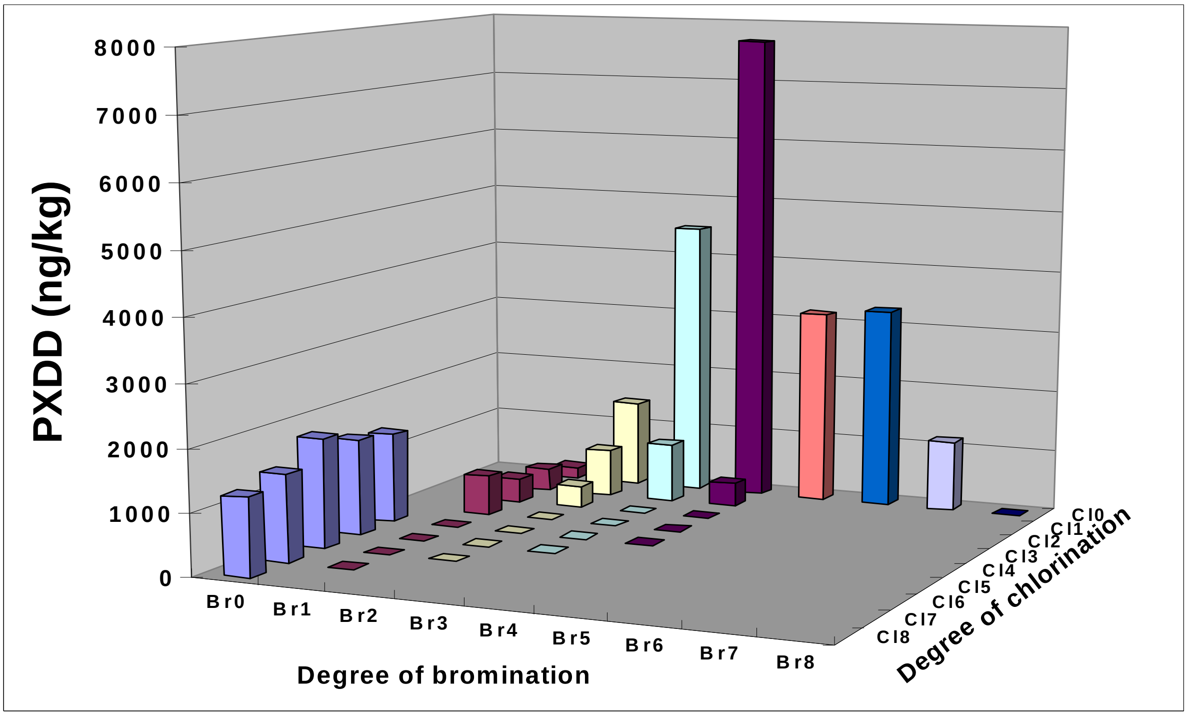

Figure 1b: PCDD, PBDD and PXDD in soil at site 1 (printed circuit board smouldering site) in Guiyu/Guiyu

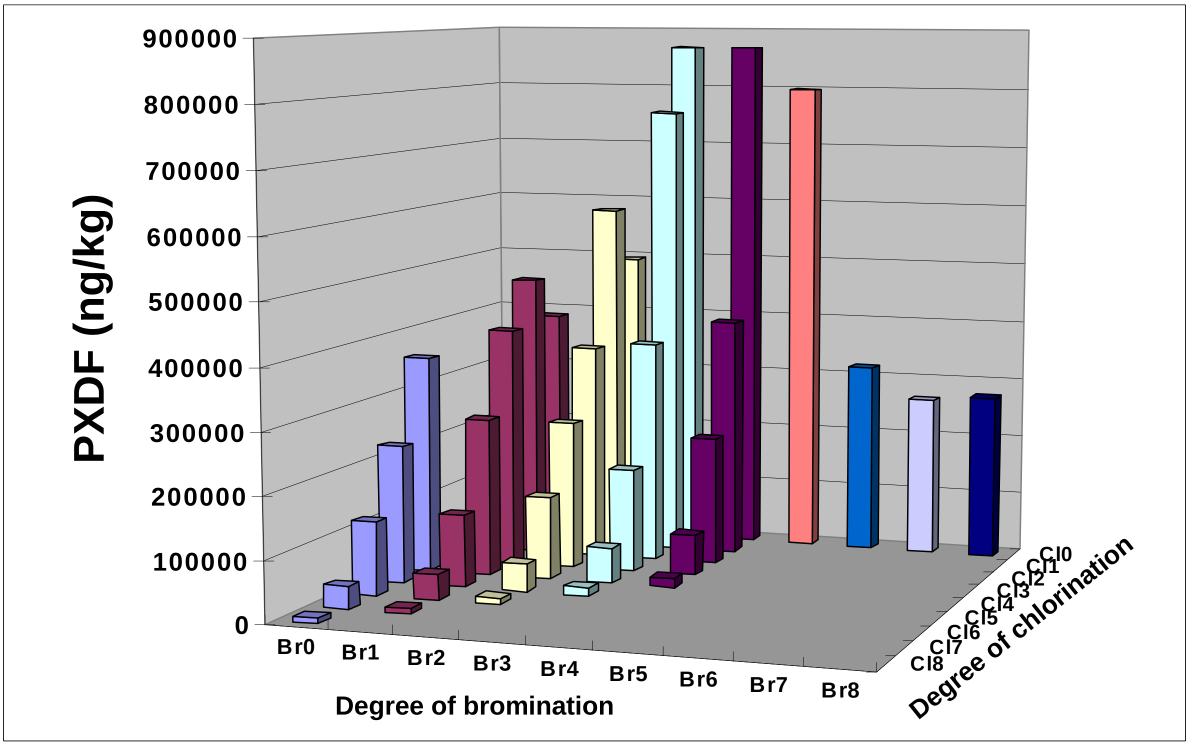

Figure 2a: PCDF, PBDF and PXDF in soil at site 2 (open e-waste burning site) in Guiyu/China

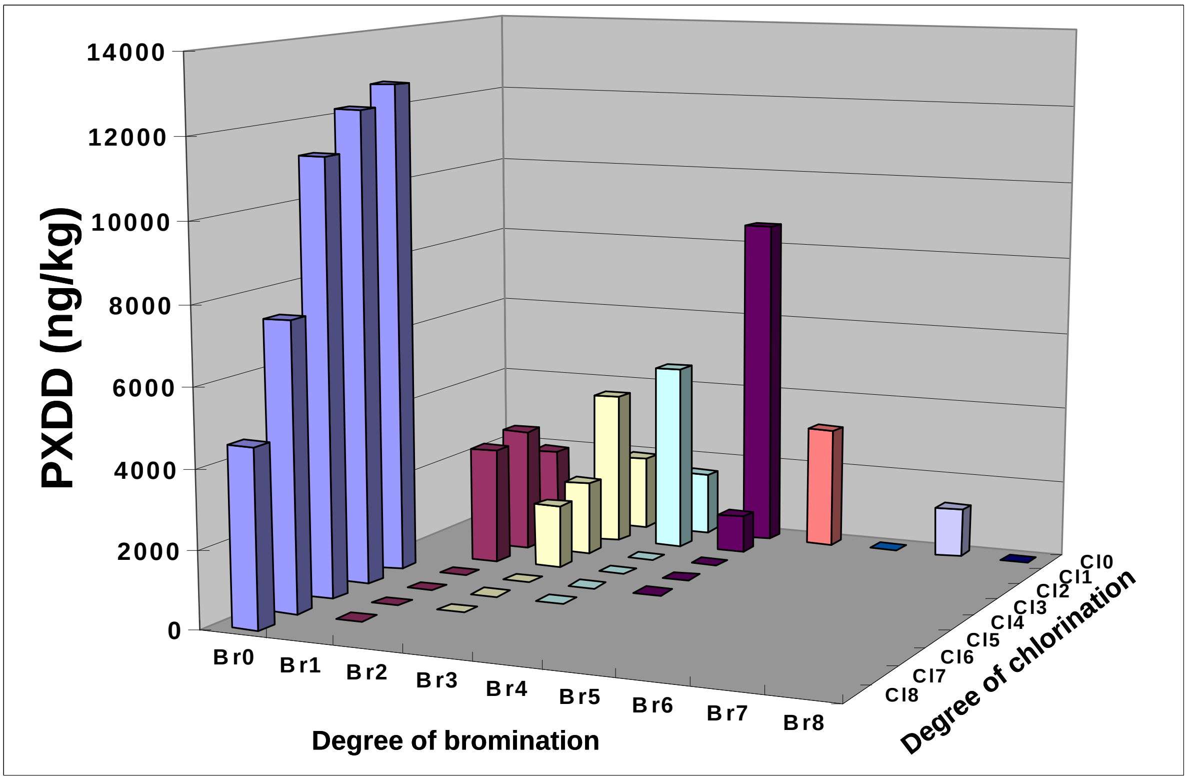

Figure 2b: PCDD, PBDD and PXDD in soil at site 2 (open e-waste burning site) in Guiyu/China