E-WASTE RECYCLING HEAVILY CONTAMINATES A CHINESE CITY WITH CHLORINATED, BROMINATED AND MIXED HALOGENATED DIOXINS

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Introduction

About 50-80% of electronic waste (e-waste) from industrialized countries ends up in China, India, Pakistan, Vietnam and the Philippines[1, 2] for cheap recycling due to the low labour costs and less stringent environmental regulations in these countries[2]. Recycling of this material has been undertaken for 10-20 years in these countries. E-waste contains a whole range of toxic compounds including polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs) as well as a broad range of toxic heavy metals;[3]. Its low tech recycling has produced contaminated mega-sites with a multitude of contaminants[4, 5]. An example of such a site is Guiyu city. This city is 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, polybrominated diphenylethers (PBDEs) and other BFRs, PCBs and other toxic compounds[4, 5]. Similarly, the drinking water of Guiyu city has been identified unfit for consumption and drinking water is partly imported[,2,5].

In the low tech e-waste treatment, open burning is carried out 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. Since e-waste contains considerable amount of bromine (mainly from BFRs) and chlorine (mainly from PVC, plasticizers like chlorinated paraffins or PCB), a mixture of chlorinated, brominated and mixed halogenated compounds is formed from thermal treatment of this waste[6]. Hence, unintentionally formed POPs like PCDD/F and PAHs are formed and emitted to air[7], soil[5,8,9] and water in addition to the release of toxicants incorporated in the e-waste (heavy metals BFRs etc[3,4]. These releases ultimately provide pathways for human exposure as demonstrated e.g. for PCDD/F[10]. The present study presents data on PCDD/F, PBDD/F and mixed halogenated PXDD/F in soils impacted from different open burning sites in Guiyu. In addition total dioxin-like toxicity in these samples was screened with the DR CALUX assay. The relevance of these compounds with respect to the necessity of remediation measures is evaluated.

Materials and methods

Soil samples (0-10cm soil layer) were collected from four different open burning locations in Guiyu 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_5ClxDD/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 30m 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.
The DR-CALUX assay utilizes a rat hepatoma cell line with a luciferase reporter gene controlled by AhR (BDS, Amsterdam, Netherlands) [11]. Analytical details are reported elsewhere[12].

Results and discussion

Soils were sampled in four different open burning locations in Guiyu. On site A, circuit boards were smouldered for metal recovery. At site B, mainly clothes and other household waste were burned. Soil C and D were collected at two large e-waste burning sites where open burning of all types of e-waste, including wires, plastic residues, bags, circuit boards, etc. was carried out.
High PCDD/F concentration were detected in soil from all four locations (Figure 1 and 2), ranging from 213 ng TEQ/kg to 13,900 ng TEQ/kg. The TEQ of soil C (13,900 ng TEQ/kg) and D (13,300 ng TEQ/kg) exceeded international limits where remediation is required even for industrial sites (Table 1). Samples A (627 ng/kg TEQ) and B (213 ng/kg TEQ) contained lower PCDD/F concentrations which were comparable to contamination identified previously at an acid leaching site in Guiyu[8]. However, the PCDD/F concentrations of these soils are still considerably above the German limit for specific agricultural use (5-40 ng/kg TEQ) or play grounds (100 ng/kg TEQ) (table 1). PCBs contributed less than 10% to the total TEQ at all four locations in contrast to another Chinese e-waste city (Taizhou) where PCB were the main TEQ contributor due to recycling of transformers in this city[9].

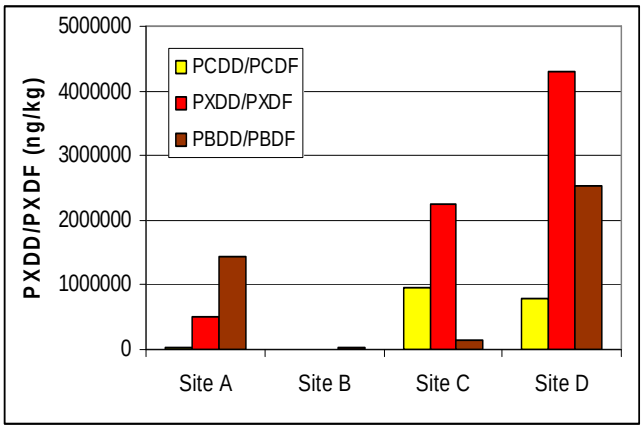

Figure 1: Sum of tetra to octa PCDD/F, PBDDF and PXDD/F in the soil samples from open burning sites in Guiyu (A circuit boards, B: clothes/waste C and D e-waste burning)

PBDD/F were also detected in all soil samples. For site A, B and D the total PBDD/F (tetra to octa) soil concentration exceeded the total PCDD/F concentration by 45, 1.1 and 5 times respectively (on mass basis) while for site C the PBDD/Fs concentration was approximately 15% of the respective PCDD/F levels at this site (Figure 1). PBDFs dominated the profiles in soils A, B and D with a PBDF:PBDD ratio between 28 to 193 indicating that they were formed from PBDE. In contrast, the PBDF:PBDD ratio from soil C was 0.84, indicating different formation conditions[6].
Regarding mixed brominated-chlorinated PXDD/Fs the total homologues analysed (Br_1Cl_xDD/F to Br_4Cl_xDD/F) exceeded the total concentration of PBDD/Fs and PCDD/Fs at both e-waste burning sites (C and D) and also at site B (Figure 2). The concentration of PXDD/F were lower than PBDD/F only for the area where printed circuit boards were smouldered (Figure 2). The Br_5Cl_xDD/F to Br_7Cl_1DD/F, which are normally not detected in incineration processes[6] were not determined and all homologue groups were quantified using the $^{13}C_{12}$-2,3,7,8-TBDF standard with mass correction factors for quantification. This method can be considered semi-quantitative and both factors underestimate the total concentration to some extent. Hence, the actual total concentration of PXDD/F are likely higher then the calculated concentrations[A].

Due to the lack of TEFs[B] for PBDD/F and PXDD/F, an estimation of TEQ is not possible based on their concentrations. However the WHO-IPCS expert group has stated in their re-evaluation of TEF factors that based on mechanistic considerations PBDDs, PBDFs, PXDDs, PXDFs undoubtedly belong to the TEF concept and identified them and some other compound classes for possible future inclusion in the TEF/TEQ concept[13]. A range of PBDD/F and some PXDD/F showed in vivo studies that the 2,3,7,8-substitututed brominated and

[A] In our estimation the total PXDD/PXDF concentration might be 30% to 100% high than the current quantification.
[B] No TEF factors have been assigned yet due to the lack of human exposure data[13].

brominated-chlorinated congeners have similar activities compared to the chlorinated analogues[14,15] but depend on the assay used[15] and even some trihalogenated congeners shown dioxin-like toxicity[15]. Therefore currently[C] the only practical way to determine dioxin-like toxicity in samples with relevant contributions from PBDD/F and/or PXDD/F is the determination of total dioxin-like toxicity using accredited bio-assay methods.
For this study we used the DR CALUX assay to determine total dioxin-like toxicity of the soil samples. To assure that only the toxicity of persistent halogenated aromatics were determined, present PAHs[5] and other less persistent contaminants were removed by sulphuric acid/silica gel treatment. The dioxin-like toxicity for site A, C and D were five to fourteen times higher compared to the PCDD/F derived TEQ (Figure 2). The highest discrepancy was found for circuit board smouldering site A where total PBDD/F were 45 times above total PCDD/F. While for the cloth/waste burning site B with comparable PCDD/F and PXDD/F and PBDD/F concentrations, the bio-TEQ (321 ng TEQ/kg) were only 50% above the instrumental TEQ derived from PCDD/F (213 ng TEQ/kg). These data indicate that the PBDD/F and PXDD/F were responsible for the main dioxin-like toxicity in the three soils where e-waste were burned/thermally treated.

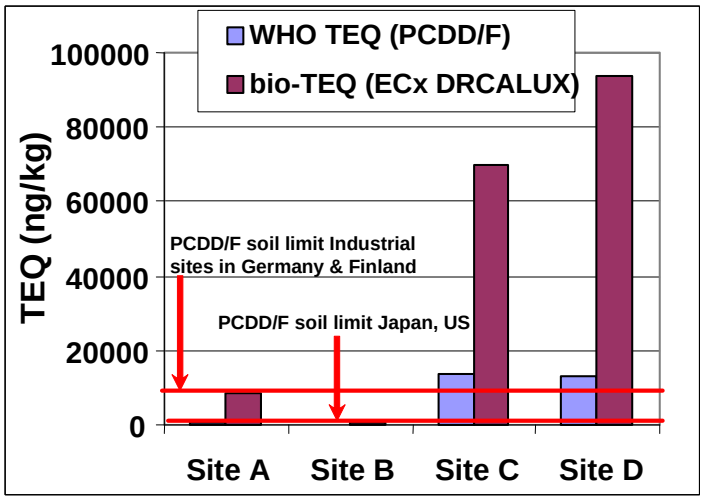

Figure 2: Comparison of WHO TEQ (PCDDs, PCDFs, PCBs) and bio-TEQ (DRCALUX) with soil guidelines for remediation in some countries.

This demonstrates that for thermal recycling activities where significant BFR retarded material is present, the determination of only PCDD/F and PCBs can considerably underestimate the dioxin-like contamination by more than one order of magnitude and that PBDD/F and PXDD/F have to be taken into account. Considering the total measurement efforts for these compound classes and the weak data base of current TEF/TEQ for these compound classes[13], currently only bio-assay based assessments can be considered as a reasonable dioxin-like toxicity evaluation for samples containing relevant concentrations of PBDD/F and PXDD/F.

E-waste recycling villages – contaminated sites calling for remediation concepts

As mentioned already above, the PCDD/F contamination level at both e-waste burning sites were above all soil regulation levels where remediation is required even for industrial areas (Table 1, Figure 2). The total dioxin-like toxicity of 93,811 ng TEQ/kg and 70,009 ng TEQ/kg in the soils at the two e-waste burning sites reveal that open e-waste burning sites are highly contaminated with dioxin and dioxin-like compounds. Furthermore a wide range of other contaminants[3,4,5] make theses areas one of the heaviest polluted site types known. People still work and live on/around these sites without any protective measures; children play without any awareness of the health threats and farmers still grow their rice and vegetables just nearby. This situation calls for an immediate significant improvement of e-waste recycling practices in developing/transition countries. Additionally, appropriate remediation measures need to be evaluated and started.

[C] Due to the approximately 5000 mixed halogenated PXDD/PXDF congeners containing more than 1000 2,3,7,8-substituted congeners, the TEF concept and instrumental analysis come to their limit. Therefore the most practicable way to evaluate samples impacted by brominated-chlorinated PXDD/PXDF will be assessments using accredited bio-assay approaches.

Table 1: PCDD/Fs soil guidelines for remediation measures (pg I-TEQ /g dw)

Country	Agriculture	Residential	Industrial	Soil (in general)
Germany[16]	5-40	Playground 100 1,000	10,000	
The Netherlands[16]	10 dairy farming 1,000	1,000		
Sweden[16]	10	10	250	
Finland[16]	500	500	10,000	
United States[17]		1,000		
Japan (PCDD/Fs+co-PCBs) [18]				1,000 Sediment 150

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