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Interplay of metals and bromine with dioxin-related compounds concentrated in e-waste open burning soil from Agbogbloshie in Accra, Ghana

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ABSTRACT

Open burning of electronic waste (e-waste) releases various metals and organohalogen compounds in the environment. Here we investigated the interplay of metals (Cu, Pb, Zn, Fe, Co, and Sr) and bromine (Br) in the formation of dioxin-related compounds (DRCs), including polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (DL-PCBs), as well as non-regulated DRCs such as polybrominated dibenzo-p-dioxins/furans (PBDD/Fs) and their monobrominated PCDD/Fs in soils sampled from open burning e-waste sites at Agbogbloshie in Accra, Ghana. The predominant DRCs were PBDFs, PCDFs, PCDDs, and DL-PCBs. Statistical analyzes, X-ray absorption spectroscopy, and the PCDF/PCDD ratio suggested possible formation paths of PCDD/Fs and DL-PCBs by catalytic behaviors of copper chlorides (CuCl, $CuCl_2$, and $Cu_2(OH)_3Cl$) and thermal breakdown of polyvinyl chloride. Predominant formation of brominated furans may be derived from electron transfer from intermediates of PBDE to copper, Cu(II) → Cu(I). Lead chloride also contributed to generate DRCs and may become highly bioaccessible through the open burning of e-waste. The main zinc species ($ZnCl_2$ and ZnS) suggested a possible relationship to generate DRCs and specific zinc source such as tire burning. Cu, Pb, Zn, and Br contained in various e-wastes, wires/cables, plastics, and tires strongly influenced generation of many DRCs.

1. Introduction

Although open burning facilitates the easy recovery of precious metals from electronic waste (e-waste) and reduces the waste mass, both toxic heavy metals and organohalogen compounds (OHCs) are released to the surrounding environment (Wong et al., 2007). Residual soil has been shown to be severely contaminated by toxic metals (including Pb, Cu, and Zn) (Wong et al., 2007) and dioxin-related compounds (DRCs) (Tue et al., 2013), including polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs) (Leung et al., 2007; Zennegg et al., 2009; Wong et al., 2007) and dioxin-like polychlorinated biphenyls (DL-PCBs), (Wong et al., 2007) as well as non-regulated DRCs such as polybrominated dibenzo-*p*-dioxins/furans (PBDD/Fs) (Zennegg et al., 2009) and their mixed brominated/chlorinated homologues (PXDD/Fs) (Zennegg et al., 2009) subsequent to open burning activities. The possible pathway for the generation of DRCs was proposed to be the burning of plastic products containing polyvinyl chloride (PVC) (Leung et al., 2007; Tue et al., 2013; Sepúlved et al., 2010; Wong et al., 2007) and brominated flame retardants (BFRs) (Weber and Kuch, 2003; Sepúlved et al., 2010; Tue et al., 2013; Weber and). Particularly, copper electrical wiring coated with PVC containing chlorine may contribute to the formation of PCDD/Fs through the thermochemical catalytic role of copper (Sepúlved et al., 2010; Wong et al., 2007). In Europe, similar open burning of cables for the

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reclamation of metals was carried out frequently in the 1980s (Quaß et al., 2004). Therefore, contamination by PCDD/Fs has been reported since early times (Van Wijnen et al., 1992). Field studies using samples from these metal reclamation sites have also hypothesized the catalytic roles of copper to generate PCDD/Fs and PCBs (Harnly et al., 1995; Huang et al., 1992; Nie et al., 2012; Van Wijnen et al., 1992).

Several laboratory-scale studies have simulated the burning of plastics and e-wastes. Researchers reported the generation of DRCs by thermal decomposition and the combustion of PVC (PCDD/Fs as the target analyte) (Cheng and Liang, 2000; McNeill et al., 1998; Theisen et al., 1989; Wang et al., 2002), BFRs [PXDD/Fs (Söderström and Marklund., 2002) and various decomposition products (Barontini et al., 2005)], wires/cables (PCDD/Fs) (Gullett et al., 2007), and circuit boards [PCDD/Fs (Duan et al., 2011; Gullett et al., 2007), PBDD/Fs (Duan et al., 2011; Lai et al., 2007), and various decomposition products (Barontini et al., 2005)]. The catalytic pyrolysis of PVC was observed by the addition of metal chlorides such as $CuCl_2$ and $ZnCl_2$ (Cheng and Liang, 2000). The formation of PCDD/Fs was promoted by the combustion of PVC with copper chloride (Wang et al., 2002). Despite the existence of various laboratory studies, the field studies focusing on the formation mechanisms of DRCs are few in number (Liu et al., 2013). If number of the soil from open burning sites increased, the correlation result could be used to discuss the influence of metals on the formation of DRCs by open burning.

In addition, the chemical forms of metals in residual soil after open burning could clarify the thermochemical interactions of target metals with other elements. X-ray absorption fine structure (XAFS) technique was applied to the residual samples derived from various thermal processes. These X-ray spectroscopic studies revealed the chemical speciation of copper (Takaoka et al., 2005a, 2005b; Wei et al., 2001), lead (Fujimori et al., 2013a; Funatsuki et al., 2012; Shah et al., 2009; Struis et al., 2009), and zinc (Takaoka et al., 2005c; Shoji et al., 2002; Struis et al., 2004; Fujimori et al., 2011) in various residual samples. Takaoka et al. (2005b) reported a positive relationship between the content of copper chloride hydroxide ($CuCl_2 \cdot 3Cu(OH)_2$) and an increasing ratio of PCBs and chlorobenzenes in the municipal solid waste incineration (MSWI) fly ash. However, there was no report combined chemical forms of heavy metals with concentrations of DRCs using same field samples at e-waste open burning site.

In the current study, we investigated the interplay between metals (Cu, Pb, Zn, Fe, Co, and Sr) and bromine (Br) with DRCs in soil sampled from e-waste open burning sites from Agbogbloshie in Accra, Ghana. By extending the dataset through measuring the concentrations of various DRCs such as PCDD/Fs, DL-PCBs, PBDD/Fs, and monobrominated polychlorinated dibenzo-*p*-dioxins/furans (MoB-PCDD/Fs), we attempted to understand the formation mechanisms of the DRCs by a combined approach of statistical analyzes and XAFS technique. Interrelationships and the grouping of parameters were assessed by Pearson's correlation analysis, principal component analysis, and hierarchical clustering. We identified chemical forms of Cu, Pb, and Zn in representative soils from open burning sites using X-ray absorption near-edge structure (XANES) spectroscopy.

2. Materials and method

2.1. Sampling of soil/ash mixtures from e-waste open burning sites

Ten soil/ash mixtures (E1–E10) were collected from the Agbogbloshie market in August 2010. The site detail was described in supplementary section. During our sampling campaign, we observed that the burning of e-waste occurred mainly in two locations (Fig. S1). The soil/ash mixture samples (0–2 cm depth) were collected using a stainless steel auger. Five subsamples within 1 m^2 were sampled at each point to form one composite soil/ash mixture. To minimize chemical change after sampling, the samples were stored in a freezer in the laboratory of the Council for Scientific and Industrial Research (CSIR), Water Research Institute in Accra, following which samples were transported to Japan by air preserved through freezing using gel ice. Subsequently, the samples were registered to the Environmental Specimen Bank (es-Bank) at the Ehime University and stored at −25 °C.

2.2. Measurement of DRCs

DL-PCBs, PCDD/Fs, PBDD/Fs, and MoB-PCDD/Fs were identified and quantified by gas chromatography/high resolution mass spectrometry (GC-HRMS) using the isotope dilution method operating in electron impact (EI) ionization with the corresponding $^{13}C_{12}$-labeled congeners (see supplementary section for details on the pretreatment and instruments). The calculation of the limits of detection followed the Japanese Industrial Standards for measurements of PCDD/Fs and DL-PCBs (Japanese Industrial Standard, 2005). Quality assurance and quality control for our analytical methods have been confirmed by an intercalibration study on DRCs and PBDEs using an air-dried sediment sample (Takahashi et al., 2006). Toxic equivalents (TEQs) for PCDD/Fs and DL-PCBs were calculated using the World Health Organization toxic equivalency factors (WHO-TEFs), whereas TEQs for PBDD/Fs and MoB-PCDD/Fs were estimated based on WHO-TEFs of similarly substituted PCDD/Fs as the WHO and United Nations environmental program recommend the use of similar interim TEFs for brominated/chlorinated congeners in human health risk assessment (van den Berg et al., 2013).

2.3. X-ray absorption spectroscopy

All XAFS measurements were conducted in the synchrotron light source beamlines in the Photon Factory, Tsukuba, Japan. The K-edge XAFS spectra of Cu, Zn, and the L_3-edge of Pb were measured using hard X-ray beamlines BL9C and 12C employing a Si (111) double crystal monochrometer. The XANES spectra of reference materials were measured by the transmission mode, whereas the soil/ash mixture samples were measured by the fluorescence mode using Lytle detector. Details of XAFS measurement was appeared in supplementary section.

We conducted a linear combination fit (LCF) of the XANES spectrum to determine the major species using REX 2000 ver 2.5.5 software (Rigaku, Japan). The residual value, *R* value $= \Sigma(\mathrm{XANES_{measd}} - \mathrm{XANES_{calcd}})^2/\Sigma(\mathrm{XANES_{measd}})^2$, was used to evaluate the LCF for the experimental spectra. If the LCF result showed <5% fit, we remove the result from the analysis.

3. Results and discussion

3.1. The pollution levels of toxic metals and DRCs

According to our previous report, we selected seven elements (Fe, Co, Cu, Zn, Br, Sr, and Pb) detected in all soil samples to discuss their interplay with DRCs as shown in Table 1 (Itai et al., 2014). Median concentrations of Cu, Zn, and Pb showed levels of 2,000, 4,200, and 1100 mg/kg, respectively, which were comparable with soil concentrations from similar e-waste open burning sites at Guiyu, China (Wong et al., 2007). Wide ranges in the concentrations of toxic metals and bromine were found: 53–22,000 (Cu), 220–17,000 (Zn), 100–14,000 (Pb), and 18–1500 (Br) mg/kg.

The median concentrations (and TEQ concentrations) of