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Occurrence, composition, source, and regional distribution of halogenated flame retardants and polybrominated dibenzo-*p*-dioxin/dibenzofuran in the soils of Guiyu, China☆

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ABSTRACT

Guiyu, China, is well-known for the crude disposal of electronic waste (EW) and severe persistent organic pollutants (POPs). Therefore, in this study, the occurrence, composition, and source of polybrominated diphenyl ethers (PBDEs), 2,2′,4,4′,5,5′-hexabromobiphenyl (BB153), some novel brominated flame retardants (NBFRs), Dechlorane Plus (DP) and polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/Fs) in farmland soils covering Guiyu were studied. In EW disposal area soils, PBDEs were the most abundant FRs, with concentrations of 13–1014 ng g^{-1}. The primary PBDE sources were technical Penta- and Deca-BDE mixtures in northern and southern Guiyu, respectively. The levels of BB153 were relatively low, possibly because it has been banned in the 1970s. The concentrations of hexabromobenzene (HBB) were 0.048–3.3 ng g^{-1}, while pentabromoethylbenzene (PBEB) was almost not detected in the soils. Two alternatives to commercial PBDEs, decabromodiphenyl ethane (DBDPE) and 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), were the primary NBFRs, with concentrations of 1.8–153 ng g^{-1} and 0.43–15 ng g^{-1}, respectively. DP was another primary FR, with concentrations of 0.57–146 ng g^{-1}. Moreover, syn-DP and anti-DP isomers were not stereoselectively decomposed during the EW disposal process and were therefore present in their original fractions in the soils. The levels of PBDD/Fs in EW disposal area soils were 2.5–17 pg TEQ g^{-1}. 1,2,3,4,6,7,8-HpBDF and OBDF were the dominant congeners, mainly derived from processing, pyrolysis and combustion of BFRs. The regional distribution of pollutants was shown to be related to the disposal manner of EW, with their open thermal disposal tending to release more highly brominated compounds such as BDE209, DBDPE, and 1,2,3,4,6,7,8-HpBDF. Additionally, some riverbank sites were heavily polluted because of nearby point sources, downwind Simapu (SMP) town without EW disposal activity was also contaminated by these pollutants.

1. Introduction

It is well known that the disposal of electronic waste (EW) and consequent persistent organic pollutants (POPs) have been a severe environmental problem. A small town, Guiyu in China, receives 70% of the global EWs for disposal and recycling materials. Due to the high profits from EW disposal, local farming has been abandoned for several decades. However, the manner of disposal for EWs is primitive and crude, this has resulted in severe emission of organic pollutants and heavy metal (BAN and SVTC, 2002).

Brominated flame retardants (BFRs) are commonly added to electronic products to prevent fire. Of these, polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) are the most extensively used BFRs globally. PBDEs, marketed as

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commercial Penta-, Octa- and Deca-BDE technical mixtures, have been produced since the 1970s. PBBs, mainly marketed as Firemaster BP-6 technical mixture, containing up to 56% of 2,2′,4,4′,5,5’-hexabromobiphenyl (BB153), was widely used in the United States in the early 1970s. But commercial Penta-, Octa-BDE and hexabromobiphenyl have been restricted by the Stockholm Convention. Moreover, deca-BDE has been banned for production and use in the European Union and the United States. In recent decades, some novel BFRs (NBFRs), such as hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), and decabromodiphenyl ethane (DBDPE), have been widely employed as alternative FRs. HBB was historically produced by the Velsicol Chemical Corporation and marketed as FR-B by the Nippoh Chemicals Corporation in Japan and Dayang Chemicals Corporation in China. PBEB was produced by the Dead Sea Bromine Group, Ltd. under the trade name FR-105 in the United States during the 1970s and 1980s. BTBPE has been produced by Great Lakes Chemical Corporation and marketed as FF-680 in the United States since the mid-1970s. DBDPE was introduced by Albemarle Corporation in the United States in the mid-1980s, and has been marketed under the trade names Saytex 8010 by Albemarle Corporation, Firemaster 2100 by Chemtura Corporation and FR-1410 by Dead Sea Bromine Group, Ltd. BTBPE and DBDPE are used as alternatives to commercial Octa-BDE (Hoh et al., 2005) and Deca-BDE (Kierkegaard et al., 2004), respectively. Dechlorane Plus (DP), a chlorinated flame retardant, was first manufactured by Hooker Chemical Corporation in the United States in the 1960s, and has been produced by Jiangsu Anpon Electrochemical Company in China since 2003. DP-25, DP-35 and DP-515 are three commercial products of DP, with the same compounds (syn- and anti-DP stereoisomers) but different particle sizes. DP is used as a substitute for Mirex (Hoh et al., 2006). These unregulated FRs are increasingly used in production, but their potential to cause harmful effects is unknown. Polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/Fs) are unintentionally produced chemicals with a similar molecular structure, physicochemical properties and toxicity as polychlorinated dibenzo-*p*-dioxin/dibenzofurans (PCDD/Fs). The pyrolysis and combustion of some BFRs such as PBDEs and HBB have been proved to be important sources of PBDD/Fs (Sakai et al., 2001).

The crude disposal of EW in Guiyu will result in the release of these FRs and PBDD/Fs to the surroundings. Some studies have evaluated the POPs burden in the serum (Bi et al., 2007; Yang et al., 2013), human milk, placenta, and hair (Chan et al., 2007; Zhao et al., 2008) of the residents living in the EW disposal area. Therefore, the occurrences of POPs in the environment have posed adverse effects to human health. As soil is a principal receptor for hydrophobic contaminants, the aim of this study is to explore the levels, compositions, regional distribution and sources of PBDEs, BB153, NBFRs, DP, and PBDD/Fs in farmland soils of Guiyu. The results obtained from this study may be useful for subsequent control of POPs emission and evaluation of the health risk for humans.

2. Materials and methods

2.1. Materials and instruments

^{13}C-labeled standards of BFRs (BFR-LCS, BFR-ISS, BFR-SCS) were supplied by Wellington Laboratories Inc. (Ontario, Canada). ^{13}C-labeled standards of syn-DP, anti-DP and PBDD/Fs (EDF-5408, EDF-5409) were supplied by Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). The detailed information of solvents, acid-base silica gel column, and other materials were described in our previous study (Xu et al., 2015). Active carbon-dispersed silica gel was acquired from Kanto Chemical Co., Inc. (Tokyo, Japan).

Accelerated solvent extractor, rotary vacuum evaporator, and gas chromatography-high resolution mass spectrometry (GC-HRMS) were described in our previous study (Xu et al., 2015). A CHN corder MT-5 elemental analyzer (Yanaco, Kyoto, Japan) was used to measure the total organic carbon (TOC) in soils.

2.2. Study area and soil sampling

The soil samples were acquired by our team in 2009, and were stored in brown glass jars at −20 °C. The information of study area and detailed sampling design were described elsewhere (Xu et al., 2013). A summary of 23 sampling sites is listed in Table 1, and the site map is shown in Fig. 1.

2.3. Analytical method

A total of 20 g of homogeneous soils were spiked with ^{13}C-labeled surrogates (BFR-LCS, syn-DP, anti-DP and EDF-5408) and extracted by ASE with toluene, the extraction condition was 150 °C and 1500 psi, two 7 min-static cycles were performed. For the extract, the procedures of solvent exchange, sulfuric acid treatment, concentration and removal of sulfur were described in our previous study (Xu et al., 2015). Then, the concentrated extract was applied to the acid-base silica gel column. (1) For the analytes excluding BTBPE, DBDPE and DP, the acid-base silica gel column was eluted with 200 mL of *n*-hexane, after which the eluent was concentrated and applied to a 1 g active carbon-dispersed silica gel column. The active carbon-dispersed silica gel column was subsequently eluted with 100 mL of DCM/n-hexane (1/3, v/v) for the BFR fraction, after which it was reversed and eluted with 40 mL of toluene for the PBDD/F fraction. The BFR fraction and PBDD/F fraction eluents were evaporated and spiked with injection internal standards (BFR-ISS and EDF-5409, respectively). (2) For BTBPE, DBDPE and DP analysis, the acid-base silica gel column was eluted with 80 mL of DCM/n-hexane (3/7, v/v), after which the eluent was evaporated and spiked with injection internal standard (BFR-SCS). The final samples were redissolved in 50 μL of decane for analysis.

A GC/HRMS with a DB-5HT column (15 m × 0.25 mm i.d. × 0.10 μm film thickness) was used for separation and quantification. The injection volume was 1 μL, the flow of carrier gas was set at 4.0 mL/min for 1 min after injection, then was maintained at 1.0 mL/min. The temperatures of the GC-HRMS system are shown in Table 2. The HRMS was operated in EI^{+} mode, the ionizing energy, trap current and ion accelerating voltage were 35 eV, 650 μA and 8000 V, respectively. Two isotope ions of each compound were monitored at 10,000 resolution. BDE1, 2, 3, and BDE10 in the BFR standards were not determined because of their volatilization; however, several coeluting congeners were reported as the sums, such as BDE156/169 and 1,2,3,4,7,8/6,7,8-HxBDD. Therefore, the target compounds were 37 PBDE congeners, BB153, HBB, PBEB, BTBPE, DBDPE, syn-DP, anti-DP, and 14 PBDD/F congeners. Most compounds were monitored based on the molecular ions, but the coeluting BB-153 and BDE-154 were monitored based on the fragment ions [M-2Br]$^{+}$ instead of the molecular ions to distinguish BDE154 and ^{13}C-BB153 under 12,000 resolution. Otherwise, the molecular ions of BDE154 and ^{13}C-BB153 require a resolution of 16,000 to distinguish. BTBPE, DBDPE and DP were monitored based on the fragment ions $[M-C_6H_2Br_3O]^+$, $[M-C_7H_2Br_5]^+$ and $[M-C_{13}H_{12}Cl_6]^+$, respectively, because their molecular ions showed low responses.

2.4. Quality assurance/quality control (QA/QC)

The operational blank sample and the parallel sample were included in each batch of eight samples. PBDEs, BB153, NBFRs, DP