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Polybrominated diphenyl ethers in farmland soils: Source characterization, deposition contribution and apportionment

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HIGHLIGHTS

• PMF was performed for identifying activity-linked PBDE sources.
• PBDE congener profiles of recycling activities were measured for data accumulation.
• Sources of PBDE contamination in farmland soil were revealed and initially verified.

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs), a group of persistent organic pollutants (POPs), are caused for concern recently due to their adverse health effects and environmental ubiquity. In this study, atmospheric and soil PBDE levels in Taizhou, one of the largest WEEE dismantling areas in the world, were measured, ranging from 884 to 2791 pg m^{-3} with an average of 1968 pg m^{-3} for atmosphere and 2.96 to 200 ng g^{-1} dry weight (dw) with the mean of 65.2 ng g^{-1} dw for farmland soils, respectively. The close connection between soil PBDE accumulation and atmospheric deposition was also revealed by the estimation of the annual PBDE deposition flux (3.1 ± 0.9 mg m^{-2} a^{-1}) and the similarity between deposited congener pattern and soil congener profile. Positive matrix factorization (PMF) was conducted to extract possible sources of farmland soil PBDEs and to calculate their contributions. Based on the measured source profiles of PBDE-related activities, five sources were identified representing WEEE dumping, WEEE dismantling, WEEE open burning, residential waste dismantling, and residential waste open burning. WEEE-related recycling activities contributed primary percentage (52%) to farmland soil PBDE concentration, and open burning was an important pathway for PBDEs entering the environment.

1. Introduction

Polybrominated diphenyl ethers (PBDEs), a class of widely used brominated flame retardants (BFRs) in electronic devices (e.g. printed circuit boards, internal plastic parts and plastic outer casings of electronic devices such as personal computers, household appliances, TV cabinets and wire insulation) (Morf et al., 2005; Zhang et al., 2012) and residential products (e.g. building materials, furniture, household textiles and packaging materials containing polyurethane foam) (Gullett et al., 2009; Persistent Organic Pollutants Review Committee, 2006), have triggered an increasing research interest in recent years due to possible detrimental effects on human beings and wildlife like hepatic, endocrine and neurodevelopmental toxicology (Costa et al., 2008; Darnerud, 2003; Wu et al., 2007). According to the degrees of bromination of predominate congeners, three commercial PBDE mixtures (C-PBDEs) were historically produced and consumed (Persistent Organic Pollutants Review Committee, 2006, 2007; Sepúlveda et al., 2010). Since 1970, around 180,000 metric tons of OctaBDE and over 600,000 metric tons of DecaBDE were globally consumed, in the form of additives to high-impact polystyrene that was used in electrical and electronic equipment, and 100,000 metric tons of C-PentaBDE was consumed, to improve fire resistance of polyurethane foam (PUF) used in household products (Persistent Organic Pollutants Review Committee, 2006, 2007; Sepúlveda et al., 2010). After the electronic or residential products fell into disuse and were sent for recycle activities (including disposal, uncontrolled dumping, dismantling, shredding and combustion), the contained PBDEs were released into the environment (Sepúlveda et al., 2010). Thus, many extremely high levels of PBDEs in both atmosphere and soil have been reported in the recycling sites or nearby (Cai and Jiang, 2006; Han et al., 2009).

As additive flame retardants, PBDE congeners are not chemically-bonded to product polymers, resulting in their easy release during

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recycling (Rahman et al., 2001). In this sense, each recycling activity from its scattered individual sites can be deemed as a "source" contributing to the ambient PBDE pollution. The released PBDE molecules, aggregating in both gaseous or particulate phase (Hayakawa et al., 2004), were easily prone to disperse by gaseous transporting and particles carrying from the recycling site to surrounding places, then accumulated in soils far from the sources by dry/wet deposition (Cetin and Odabasi, 2007; Luo et al., 2009; Sepúlveda et al., 2010; ter Schure et al., 2004), which enlarges the scope of pollution. The dispersion and deposition of PBDEs have been described by some studies, e.g. gaseous and particulate deposition flux (Cetin and Odabasi, 2007; Moon et al., 2007; Su et al., 2007; ter Schure et al., 2004), revealing the impact of atmospheric PBDEs on pollution at a "receptor" site. Therefore, eliciting the source–receptor relationship is pertinent in understanding the occurrence of PBDEs in those areas far from the recycling sites (e.g. farmlands where no recycling activities happened). To reach this target, efforts should be taken for depicting characteristics of PBDE sources, quantitatively identifying of possible sources, and estimating of corresponding contributions to the target receptor.

Based on the known compositions (congener profiles) of C-PBDE mixtures, some multivariate statistic methods, including principal component analysis (PCA) (Luo et al., 2009), positive matrix factorization (PMF) (Zou, 2011; Zou et al., 2013) and factor analysis (FA) (Jiang et al., 2011), have been employed to quantify the relative contributions of individual C-PBDE mixtures to a specific receptor site (consumption profile-linked apportionment). Nevertheless, it is insufficient because only consumption profiles but no specific activities, such as PBDE usage/consumption scenarios (e.g. in electronic or in household equipment) (Prevedouros et al., 2004) and disposal operations (e.g. dumping, dismantling and combustion) (Wang et al., 2010a) were described. The information on activity is helpful to inventory PBDE emissions (Prevedouros et al., 2004), and further to supervise and control PBDE release in the practices of environmental management (Wang et al., 2010a) because only specific activities can be regulated. Therefore, an activity-linked apportionment dealing with how people treat those PBDE-added materials is expected. A receptor model, PMF, is competent to quantitatively identify possible sources and contributions for pollutants from ambient measurement data without requiring prior knowledge of measured source profiles (Hopke, 2003), and its non-negative constrains ensured the solutions to be meaningful and explicable (Paatero, 1997; Paatero and Tapper, 1994), making it an ideal method for the activity-linked apportionment of selected POPs. In some recent works, PMF model was widely employed in the apportionment of activity-linked POP sources in sediment (Bzdusek et al., 2006; Tian et al., 2013; Zou et al., 2013) and atmosphere (Ma et al., 2010; Okuda et al., 2010), but few were conducted in soil. The transplant of PMF method to soil POP case is reasonable since PMF had been successfully applied in the source apportionment on heavy metal-contaminated soils by the pioneer work of Vaccaro et al. (2007). However, the activity-linked source apportionment of PBDEs is hard to achieve, mostly owing to the lack of adequate PBDE emission characteristics in different activities, which makes it impossible for identifying and explaining the extracted possible sources. Notwithstanding the exactly measured source profiles are not required known prior to source apportionment in PMF model, some basic characteristic of real profiles is still needed to match the extracted factors with reasonable real sources (Paatero, 1997; Hopke, 2003). Up to now, only a few researchers focused on emission behaviors of PBDEs from various sources (e.g. Wang et al., 2010a, 2011), and the dataset of emission characteristics still needs to be enriched and accumulated.

In this study, the connection between soil PBDE accumulation and atmospheric deposition was revealed by estimating the atmospheric deposition flux based on the atmospheric measurements. PMF model was performed to extract possible sources that affected the soil PBDE level and calculate their contributions. In addition, soil PBDE congener patterns adjacent to recycling sites were measured, representing the source profiles of different PBDE emission activities, which were referred to confirm the PMF-extracted results, in order to provide a better understanding of PBDE contamination sources, and also contribute useful information for further studies on the short-run fate and regional transport of PBDEs.

2. Method and materials

2.1. Study area

Taizhou, a less developed city in Eastern China, has become one of the largest waste electrical and electronic equipment (WEEE) dismantling areas in the world since the 1980s. Over 2.2 million metric tons of WEEE was shipped here either legally or illegally every year (Chi et al., 2011). And around 56% of the local people were engaged in WEEE recycling operations during 2008 (H. Wang et al., 2011). In addition to regular WEEE recycling protocol such as sweeping, dumping, heating, acid bathing, and metal melting in large-scale dismantling facilities (Wong et al., 2007), a big amount of WEEE have been disposed informally and primitively by the local residents in their back yards, such as manually dismantling and open incinerating (Cai and Jiang, 2006; Chi et al., 2011). These activities may scatter PBDEs to surrounding area such as agricultural field and cause heavy pollution.

2.2. Sample collection

In this study, the soil adjacent to the major PBDE sources (Table 1) was sampled and measured to represent the PBDE source profiles in the typical PBDE treatment activities. Since the activities distribute across the whole study area, each source profile was represented as the mean

Table 1
List of measured PBDE source profiles.

Source	Description	No. of sample sites
WEEE dumping	The soils adjacent to the dumping and disposal sites of waste electrical and electronic equipment (WEEE). Abandoned electronic household appliances and personal computers were stored. The dumping sites were exposed to sunlight and precipitation, but no combustion happened around.	5
WEEE dismantling	The soils adjacent to the manual dismantling sites of WEEE. Mechanical dismantling and shredding, as well as chemical acid bathing, were employed in these sites.	4
WEEE open burning	The soils adjacent to the combustion sites of WEEE. WEEE were imposed thermal or inadequate metallurgical treatment in open piles for extraction of gold and copper. Thick black smoke plumes above the open burning sites were observed.	3
Residential waste dismantling	The soils adjacent to the manual dismantling sites of residential wastes. Polyurethane foam-based furniture and building materials were manually dismembered in these sites.	4
Residential waste open burning	The soils adjacent to the combustion sites of residential wastes. The sites located beside village houses and near the road. Disused polyurethane foam-based furniture and building materials were openly incinerated for reducing quantity.	3