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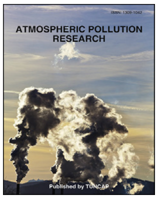

Factors influencing the diurnal atmospheric concentrations and soil-air exchange of PBDEs at an e-waste recycling site in China

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ABSTRACT

Factors influencing the diurnal atmospheric concentrations and soil-air exchange of polybrominated diphenyl ethers (PBDEs) were investigated at an e-waste recycling site in China during winter and summer. Total PBDE concentrations in winter and summer were 11.0–42.4 and 120–431 pg/m^3 in the gaseous phase and 13.3–234 and 69.0–208 pg/m^3 in the particulate phase, respectively. Total PBDE concentrations in the e-waste contaminated and nearby soils were 869 and 611 ng/g in winter and 2130 and 31 ng/g in summer, respectively. Concentrations in the gaseous phase were significantly higher in summer than in winter, but concentrations in the particle phase were comparable between winter and summer. Because of the influence of occasional accidental inputs, no apparent diurnal variations were found for PBDEs in either the particle or gaseous phase. Both temperatures and local emissions affected air concentrations of PBDEs in this area. The estimated directions of soil-air exchange of PBDEs suggest that the e-waste contaminated soil generally acted as a secondary source of several low brominated PBDEs, while the nearby soil acted as a secondary source of BDE28. The diurnal variation of atmospheric concentrations of PBDEs is not strong enough to alter the soil-air exchange direction.

1. Introduction

Soil-air exchange has been considered as an important process controlling the atmospheric concentrations and environmental fates of persistent organic pollutants (POPs) in the terrestrial environment (Cabrerizo et al., 2011; Degrendele et al., 2016). Soil acts as a significant reservoir of atmospheric POPs by acting as a sink during acute discharge periods and a source during subsequent light release periods (Dalla Valle et al., 2005; Harner et al., 1995; Meijer et al., 2003; Schuster et al., 2011). Therefore, in addition to the influence of soil and chemical properties, and environmental parameters such as temperature, humidity or wind speed (Cabrerizo et al., 2011), the magnitude and direction of soil-air exchange of POPs can also change temporally depending on air and soil concentrations affected by production restrictions and emissions controls. Understanding factors that affect the soil-air exchange of POPs is essential for controlling the environmental fate of these chemicals.

E-waste contamination has drawn much attention due to the environmental problems caused by toxic emissions released during crude e-waste recycling activities (Breivik et al., 2016; Cheng et al., 2014; Labunska et al., 2014). Rapid development and increasing personalized demand of electronics have shortened product lifespans, subsequently leading to a major increase in the accumulation of e-waste (Zeng et al., 2016). China is one of the largest recyclers of e-waste, not only because of the largest production and consumption of electronic products, but also the illegal e-waste importation and recycling. Intensive e-waste recycling activities have released many toxins into the environment, such as polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls, and heavy metals (Luo et al., 2011; Zeng et al., 2013; Zhang et al., 2014a). PBDEs, a group of brominated flame retardants, are conventional additives in many electronic products (Chen et al., 2009). Meanwhile, the more toxic polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) can also be formed from PBDEs through fly ash-mediated reactions during thermal processes, such as secondary copper and aluminum smelting processes (Wang et al.,

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2016a, 2016b; Zhang et al., 2016). Commercial penta- and octa-PBDEs have been listed as POPs by the Stockholm Convention and have been banned for more than 6 years in over 170 countries, including China (Abbasi et al., 2015). Despite that the Chinese government has taken various measures to control the emission from the recycling processes, such as formalizing and centralizing e-waste recycling and covering contaminated soil with uncontaminated soil, gradual diffusion of pollutants from the contaminated soils into the air at abandoned recycling sites may still occur. However, there is a lack of research on the re-volatilization of organic pollutants via soil-air exchange from e-waste contaminated sites, especially for PBDEs.

The primary objectives of this study were as follows: (i) to investigate the diurnal variation of the atmospheric PBDE concentrations in Qingyuan, Guangdong Province of China, (ii) to determine the direction of soil-air exchange of PBDEs at an abandoned e-waste recycling area, and (iii) to study the influence of diurnal variation of air concentrations and environmental variables on the soil-air exchange of PBDEs at this area.

2. Materials and methods

2.1. Sampling

Samples were collected at an abandoned e-waste recycling site (Fig. 1) in Qingyuan, Guangdong Province of China [23.57°N, 113.01°E]. This area has the typical monsoon-influenced subtropical climate with a hot, rainy season from March to August and a dry, cool season from September to February. The sampling area is one of the most intensive e-waste recycling regions in China and severely contaminated by crude e-waste recycling activities. According to the laws and regulations of e-waste treatment, a centralized recycling factory has replaced open recycling sites, and these abandoned sites have been covered with ~0.2 m depth uncontaminated soil for over 3 years.

The air was sampled at an abandoned e-waste open-burning site near a village 9–11 December 2011 and 27–29 June 2012. No e-waste recycling activities were observed within 500 m during the sampling periods. Air samples were collected from 12:00 p.m. at 4-h intervals over 2 days using a high-volume active air sampler at a height of 1.5 m allowed for mixed air to be sampled. The air sample was first passed through a glass fiber filter (GFF, 20.3 × 25.4 cm, prebaked at 450 °C for 4 h) and then a polyurethane foam plug (PUF, 6.5 cm diam. × 7.5 cm, pre-extracted with acetone and dichloromethane) at a flow rate of ~0.3 m^3/min to collect the gas and particle phases separately.

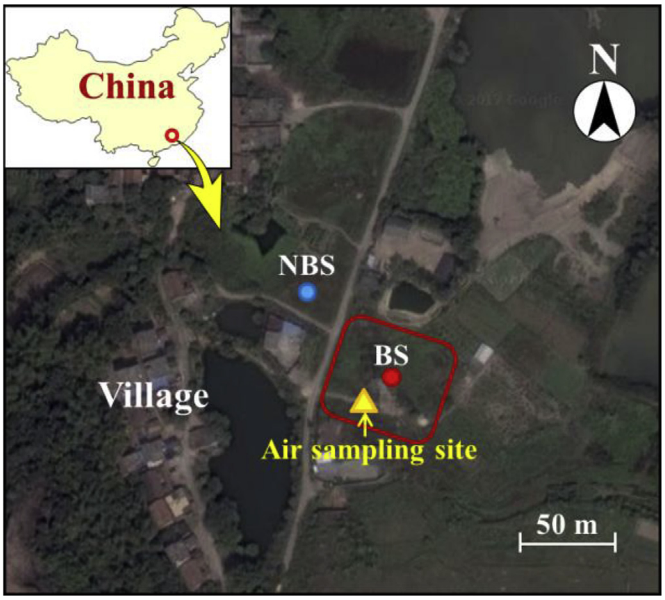

Fig. 1. Sampling site.

Topsoil samples (0–5 cm) were also collected after active air sampling at an abandoned e-waste burning site (BS) and a nearby site (NBS, ~50 m away). Each topsoil sample was a composite of three sub-samples. All samples were wrapped in aluminum foil, put into polyethylene zip-bags, and stored at −20 °C. Meteorological data were monitored simultaneously using a wireless weather station. The wind speed was <3 m/s and no rain event occurred during the sampling periods.

2.2. Sample extraction and analysis

All samples (PUF, GFF, or ~10 g freeze-dried soil) were first spiked with surrogate standards (PCB198 and PCB209), and then Soxhlet extracted with dichloromethane (DCM) and activated copper for 24 h. The extract was solvent-exchanged with hexane and cleaned using a multilayer column containing anhydrous sodium sulfate, 50% (w/w) sulfuric acid-silica gel, neutral silica gel (3% deactivated), and neutral alumina (3% deactivated) from top to bottom with an eluent of 20 mL hexane/DCM (1:1, v/v). After being concentrated to ~50 μL, $^{13}C_{12}$-PCB141 was added as the internal standard.

Agilent GC7890-5975C MSD operated in electron capture negative ionization with a DB5-MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) was used for the determination of 7 BDE congeners (BDEs 28, 47, 99, 100, 153, 154 and 183). Temperatures were set to 150 °C for both the MSD source and quadrupole. BDE209 was not detected in this study because BDE209 was very difficult to evaporate from soil into the air. Total organic carbon (TOC) in the soil sample was detected using a Vario EL-III elemental analyzer.

2.3. QA/QC

A field blank and a procedural blank were analyzed with each batch of 12 samples to identify potential contamination during sampling and analysis. No target compounds were detected in all blanks. The average recoveries of the surrogate PCB198 and PCB209 were 100 ± 7.2% and 101 ± 13% in the air samples and 96.2 ± 6.7% and 111 ± 11% in the soil samples, respectively. The reported results were not corrected for surrogate recovery.

2.4. Calculation of fugacity fraction

Fugacity model (Mackay, 2001) has been commonly used to assess the direction of soil-air exchange of POPs by predicting their soil and air fugacities (Backe et al., 2004; Bidleman and Leone, 2004; Li et al., 2010; Ruzickova et al., 2008). To estimate the equilibrium status, measurements of the chemical's gaseous concentration and its corresponding concentration in surface soil are needed. Fugacity value, which represents the tendency of a chemical to escape from one matrix into another, can be calculated using the fugacity capacity and the concentration in the compartment (Backe et al., 2004; Bidleman and Leone, 2004).

Air (f_a) and soil (f_s) fugacities (Pa) of PBDEs were calculated using the following equations:

$$f_a = C_a \, R \, T \qquad (1)$$

$$f_s = C_s \, R \, T/(0.411 \, \rho_s \, \varphi_{soc} \, K_{oa}) \qquad (2)$$

where C_a and C_s are the concentrations of PBDEs in the air and soil

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