



The impact of polybrominated diphenyl ether prohibition: A case study on the atmospheric levels in China, Japan and South Korea



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ABSTRACT

The atmosphere is an important medium which could directly reflect the changes of pollutant sources. Worldwide, the commercial products of polybrominated diphenyl ethers (PBDEs) have been officially restricted and subsequently prohibited. For the purpose of evaluating their concentration after prohibition, passive air samplers (PASs) were therefore deployed again across the East Asia during two periods in 2008 after the initial deployment 4 years ago. When compared with the data in 2004, the atmospheric concentrations of PBDEs have declined significantly. Spatially, the PBDE level in China was still the highest, with a mean value of 15.4 pg m^{-3} , and in Japan was the lowest ($2.47 \pm 1.12 \text{ pg m}^{-3}$) in the East Asia. Moreover, the relatively high concentrations were observed at sites where there are electronic or e-waste recycling industries, and this is particularly true in China, suggesting that illegally imported e-waste is still a typical source of PBDEs in this region.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are extensively used as flame retardants in electronics, paints, textiles and furnishings. The annual worldwide consumption of commercial PBDE products, mainly including penta-, octa-, and deca-BDE, increased to approximately 67,000 tons in 2001 (de Wit, 2002). As one of classical persistent organic pollutants (POPs), PBDEs have been characterized by their negatively environmental properties such as persistence, toxicity and bioaccumulation; therefore regulations have been issued in several countries in order to restrict, or even ban the use of them (Król et al., 2012; Wang et al., 2007). For instance, in 2004 the European Union forbids the use of penta- and octa-BDEs. Individual states within the United States of America also

legislated to prohibit its use during the period from 2006 to 2008 (Betts, 2008; Chaemfa et al., 2009b). In East Asia, the use of these mixtures has been discouraged from 1998 onwards in Japan on a voluntary basis (Liu et al., 2013), but in China, usage has been officially restricted since 2008 (Hu et al., 2010).

The atmosphere reflects ongoing emissions of pollutants and responds more rapidly than other environmental media (Wang et al., 2010). The regional atmospheric monitoring of POPs has been performed to identify the sources, to recognize the transport and to understand the temporal trend (Liu et al., 2013). Passive air samplers (PASs) have been frequently used to support national (Liu et al., 2009), regional (Jaward et al., 2004), as well as global (Poza et al., 2006) monitoring programs, due to its simplicity, reliability, cost-effectiveness and friendly operation (Shoeib and Harner, 2002). As for PBDEs, changes in the emission amount can be directly observed with the aid of PAS, though comparing the atmospheric PBDE concentrations at different periods in the

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same region. For instance, a recent study (Schuster et al., 2010) reported a decline in PBDE levels during 2000–2008 at background sites in the UK and Norway.

The East Asia covers a large area from the tropics to the polar regions of Siberia (Pochanart et al., 2004). This region is one of the most populated areas in the world with nearly one quarter of the world's population and is one of the most successful world economic development zones (Mason, 2003). Rapid population and economic growth have characterized the entire region in the past few decades, and hence increasing emissions of various pollutants (Lee et al., 2011; Tan et al., 2011), particularly the PBDEs which was caused by the rapidly increasing production of assorted e-wastes (Jaward et al., 2005; Li et al., 2001; Li et al., 2011a; Zhang and Tao, 2009). For example, several studies have found that BDE-47 and -99 (major components of the commercial penta-BDEs) were the most abundant congeners in gas phase of the atmosphere over East Asia (Chen et al., 2006; Jaward et al., 2005), although this penta-BDE had been limited to be used (Hites, 2004). The reason for this might lie in the fact that these two commercial PBDE mixtures possess lower molecular weight and $\log K_{OA}$, hence are easy to volatilize into the atmosphere (Li et al., 2011a). Additionally, it is possibly caused by numerous consumer electronic products which generally include these two congeners (Rahman et al., 2001), e.g. electrical appliances and electronic devices. This is consistent with the findings from several recent studies, which show that imported e-waste created a “new” source of PBDEs in developing countries in Asia, typically in China (Han et al., 2009; Leung et al., 2006; Wang et al., 2007). From 2004 onwards, our group has employed polyurethane foam (PUF) disk PASs in collecting a range of POPs in East Asia, including PBDEs (Jaward et al., 2005). In this study, we reported the usage of PASs in 2008 after prohibition on PBDEs for the purpose of updating the atmospheric PBDE concentrations over the same region measured in 2004, 4 years after the first measurement.

2. Materials and methods

2.1. Air sampling

The PUF disk samplers used in this study have been described previously (Jaward et al., 2005; Liu et al., 2009). PUF disks were pre-cleaned by soxhlet extraction with dichloromethane (DCM) and acetone (ACE) for 48 h, respectively. Then, they were dried in a vacuum desiccator and transferred to the sampling locations in sealed and solvent-cleaned aluminum foil.

PASs were deployed at both selected rural and urban sites in several countries for two consecutive periods in 2008: Spring (March to May) and Fall (August to October). A total of 20, 15, and 10 samplers were deployed in China (1 rural and 19 urban sites), Japan (2 rural, 13 urban), and South Korea (2 rural, 8 urban), respectively. Further details for each sampling site are provided in Table S1. At the urban sites, the samplers were deployed in open areas, 3 m above the ground. In rural areas, the sampling sites were distant from local human activity or significant sources. After the sampling, the PUF disks were retrieved, resealed in their original aluminum foil at the sampling locations, then returned to laboratory and stored at $-20\text{ }^{\circ}\text{C}$ until the extraction.

2.2. Extraction and analysis

In the laboratory at Guangzhou Institute of Geochemistry, China, the disks were soxhlet extracted using DCM for 48 h. Activated copper granules were added in order to remove potential elemental sulfur. Prior to the extraction, each sample was spiked with a mixture of PCB-30, PCB-138 and PCB-209 as recovery standard. The extract was concentrated using rotary evaporation and nitrogen-evaporation. Then a multilayer 8 mm i.d. acid silica column, containing 3 g neutral alumina (3% deactivated), 2 g neutral silica gel (3% deactivated), 3 g 50% (w/w) sulfuric acid silica and a small layer of sodium sulfate (all baked at $450\text{ }^{\circ}\text{C}$ overnight) from bottom to top, was used to purify the samples. Each extract was solvent exchanged with hexane and then blown down under gentle stream of nitrogen to a volume of 25 μL . Internal standard BDE-77 in dodecane was added to the samples before analysis.

The sample extracts were analyzed for PBDE compounds by an Agilent GC7890 (GC-ECNI-LRMS) and a mass spectrometric detector (MSD, Agilent 5975C) with a negative chemical ionization source operating in selected ion mode (SIM). A DB-5MS (30 m \times 0.25 mm i.d., 0.25 μm film thickness) capillary column was used for the determination of PBDE congeners. Samples were injected at $290\text{ }^{\circ}\text{C}$ in splitless mode, using ammonia as a reagent gas. The oven program was $110\text{ }^{\circ}\text{C}$ for 1 min, then ramped to $180\text{ }^{\circ}\text{C}$ at a rate of $8\text{ }^{\circ}\text{C min}^{-1}$ and held for 1 min, to $240\text{ }^{\circ}\text{C}$ at $2\text{ }^{\circ}\text{C min}^{-1}$ for 5 min, to $280\text{ }^{\circ}\text{C}$ at $2\text{ }^{\circ}\text{C min}^{-1}$ for 25 min, and further ramped at $5\text{ }^{\circ}\text{C min}^{-1}$ to $290\text{ }^{\circ}\text{C}$ and held for 13 min. The ions m/z 79 and 81 were monitored for BDE-28, -49, -47, -100, -99, -154, -153 and -183. A total of 32 PBDE congeners including BDE-28, -47, -49, -99, -100, -138, -153, -154 and -183 were regularly detected in the samples using an internal standard method.

2.3. Quality control/Quality assurance

All analytical procedures were monitored using strict quality assurance and control measures. Six field (i.e., samplers sent to/from field sites unopened) and three laboratory blanks consisting of pre-extracted PUF disks were extracted and analyzed using the same procedure as the samples. The reported results were blank corrected using the mean of the field blanks and the method detection limits (MDLs) were derived from the field blanks and quantified as 3 times the standard deviation of the blank concentrations. It is considered as not detected when the chromatograph peaks were lower than 3 times the noise levels. MDLs ranged between 0.06 and 0.14 pg m^{-3} for each congener. Recoveries were between 70% and 107% for all the compounds studied. Reported values are not recovery corrected. Instrument performance was monitored using quality control standards after every eight samples analyzed by the instrument.

3. Results and discussion

3.1. Absorption rate of passive air sampling

The absorption rate is a principal factor of the PASs for estimating or deriving atmospheric concentrations of POPs. Hitherto, there have been few studies on the sampling rate of PBDE congeners (Chaemfa et al., 2009a, 2009b; Hazrati and

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