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Atmospheric occurrence and gas-particle partitioning of PBDEs at industrial, urban and suburban sites of Thessaloniki, northern Greece: Implications for human health☆

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ABSTRACT

Air samples were collected during the cold and the warm period of the year 2012 and 2013 at three sites in the major Thessaloniki area, northern Greece (urban-industrial, urban-traffic and urban-background) in order to evaluate the occurrence, profiles, seasonal variation and gas/particle partitioning of polybrominated diphenyl ethers (PBDEs). The mean total concentrations of particle phase $\sum_{12}$PBDE in the cold season were 28.7, 19.5 and 3.87 pg m^{-3} at the industrial, urban-traffic and urban-background site, respectively, dropping slightly in the warm season (23.7, 17.5 and 3.14 pg m^{-3}), respectively. The corresponding levels of gas-phase $\sum_{12}$PBDE were 14.4, 7.15 and 4.73 pg m^{-3} in the cold season and 21.2, 11.1 and 6.27 pg m^{-3} in the warm season, respectively. In all samples, BDE-47 and BDE-99 were the dominant congeners. Absorption of PBDEs in the organic matter of particles appeared to drive their gas/particle partitioning, particularly in the cold season. The estimated average outdoor workday inhalation exposure to $\sum_{12}$PBDE in the cold and the warm period followed the order: industrial site (288 and 299 pg day^{-1}) > urban-traffic site (178 and 191 pg day^{-1}) > urban-background site (58 and 63 pg day^{-1}). The exposures to BDE-47, BDE-99, BDE-153 and $\sum_{3}$PBDE via inhalation, for children outdoor worker and seniors were several orders of magnitude lower than their corresponding oral RfD values.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are organic compounds with variable number and position of bromine atoms (2–10) in the diphenyl ether skeleton that have been extensively used as flame retardants in various consumer products such as plastics, textiles, television sets, synthetic building materials, cars and computers (Mandalakis et al., 2008a,b; Besis and Samara, 2012). Additive PBDEs are mixed into plastics and foams, but do not form chemical bonds, thus it makes them much more likely to release out of goods and products (Sjödin et al., 2003).

There are three major commercial formulations used in the market: Penta-BDE, Octa-BDE, and Deca-BDE (La Guardia et al., 2006). Due to the high environmental persistence, long-range transport potential, bioaccumulation tendency and toxicity of many of the 209 PBDE congeners, the manufacture and usage of Penta- and Octa-BDE mixtures was prohibited in the European Union (EC, 2003), while these formulations were voluntarily withdrawn in several US states and Japan. Lately, the use of Deca-BDE was also prohibited in Europe (ECJ, 2008; Besis and Samara, 2012). In 2009, PBDEs were added to the list of persistent organic pollutants (POPs) under the Stockholm convention (UNEP/POPS/COP.4/17, 2009).

Due to their toxicity, exposure to PBDEs has become the subject of much concern worldwide (D'Silva, 2004). Of the three technical mixtures, Penta-BDE has been found to induce the highest toxicity (Darnerud et al., 2001). The structural similarity of PBDEs and thyroid hormone causes disruption of the body's thyroid hormone balance by depressing levels of the T3 and T4 hormones (Hooper and McDonald, 2000; Kuriyama et al., 2007; Tseng et al., 2008; Meeker et al., 2009; Chevrier et al., 2010; Shy et al., 2012). As endocrine disruptors, PBDEs interfere with sexual development (Lilienthal et al., 2006; Chao et al., 2010) and are responsible for problems in reproduction system (Chao et al., 2010; Harley et al., 2010; Main et al., 2007). PBDEs can be classified as developmental neurotoxicants (Chao et al., 2011; Gascon et al., 2012; Costa and Giordano, 2007; Herbstman et al., 2010) and can trigger

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problems on liver and kidney morphology (Albina et al., 2010; Alonso et al., 2010; Costa et al., 2008). The most sensitive populations are pregnant women, developing fetuses, and infants that, besides their high vulnerability to adverse health effects, are regularly more frequently exposed to environmental contaminants than adults via many potential pathways (McDonald, 2002; Besis and Samara, 2012).

Similarly to other semi-volatile organic compounds, in the environmentally relevant temperature range, ambient air PBDEs are partitioning between the gaseous and the particulate phase with the lower molecular weight and more volatile PBDEs existing mainly the gas phase, whereas the higher brominated congeners being associated with the particle phase (Chen et al., 2006; Cetin and Odabasi, 2008; Cincinelli et al., 2014; He et al., 2014; Mandalakis et al., 2009; Shoeib et al., 2004; Ter Schure et al., 2004; Harner and Shoeib, 2002; Ter Schure and Larsson, 2002). The gas-particle partitioning of PBDEs is an important process influencing their environmental fate such as degradation, deposition and atmospheric transport (Xiao et al., 2012; Chen et al., 2006). Particle-bound PBDEs are mainly associated with the finest particles (<0.49 μm Besis et al., 2015; <0.57 μm Mandalakis et al., 2009). This association has significant implications for their atmospheric fate since fine particles are less efficiently removed from the atmosphere by wet and dry deposition and, as a consequence, are characterized by long residence times.

Although several studies have reported the levels of PBDEs in the ambient air (Su et al., 2009; Cetin and Odabasi, 2008; Hoh and Hites, 2005; Harner et al., 2006; Agrell et al., 2004; Jaward et al., 2004; Hayakawa et al., 2004; Lee et al., 2004; Li et al., 2009; Iacovidou et al., 2009; Birgul et al., 2012; Martellini et al., 2012; Lammel et al., 2015; Yu et al., 2015), only few studies have investigated the mechanisms that influence their gas/particle partitioning (Chen et al., 2006; Cetin and Odabasi, 2008; Mandalakis et al., 2009; Shoeib et al., 2004; Cincinelli et al., 2014; He et al., 2014). Although indoor air/dust PBDE concentrations are in general higher than outdoor levels since they have been extensively used in indoor applications the health effects arising from the inhalation of PBDEs in urban areas are of greatest concern (Besis and Samara, 2012).

The present study aimed at the assessment of the spatial and seasonal variations of particle- and gas-phase concentrations of PBDEs in the urban atmosphere, the investigation of the mechanisms driving their gas-particle partitioning, and the estimation of population exposure via inhalation of PBDE-contaminated air.

2. Materials and methods

2.1. Area description

Thessaloniki (40°62′N, 22°95′E) is the second largest Greek city with approximately 16,000 inhabitants per km^2 located in the innermost part of Thermaikos Gulf in northern Greece. The city has been historically encountered air-quality problems with PM_{10} concentrations constantly exceeding the European limits (Samara et al., 2013; Voutsa et al., 2014). Oil refining, cement/lime production, scrap metal incineration, steel manufacturing, and electrolytic MnO_2 production are the major industrial sources located to the north and northwest (Samara et al., 2013; Voutsa et al., 2015). The climate is temperate Mediterranean with mean monthly temperatures 4–28 °C and relative humidity 47–80%. The predominant winds are weak (1–3 m s^{-1}) originating mostly from SSW and NNW, while calms (wind speed <0.5 ms^{-1}) are frequently occurring. Major factors that affect the transport and dilution of air pollutants are the seasonal and diurnal variations of mixing height and the local circulating system of sea/land breezes developed mainly in the warm period and transient months (Flocas et al., 2009).

2.2. Sample collection

Sampling of gas- and particle-phase PBDEs was carried out during the cold and the warm period of the year, in 2012 at the industrial site, and in 2013 at the urban-traffic and the urban-background site. The sampling system was situated on the roof (~3.0 m above ground level) of air quality monitoring stations located at the three sampling sites. In total, twenty 48-h samplings were conducted (4 at the industrial site, 8 at the urban-traffic site, and 8 at the urban-background site). Sampling details and meteorological conditions during sampling are presented in Fig. 1 and summarized in Table S1.

Sampling was carried out using a medium-volume air sampler (Graseby Andersen, model PS-1) operated at constant flow rate (0.27 m^3 min^{-1}). The air was drawn through a quartz fiber filter (QFF) to collect particles and then through two polyurethane foam (PUF) plugs (height 8 cm, diameter 7 cm) to collect gas-phase compounds. The sampled air volume was approximately 768 m^3. No substantial drop (<5%) in flow rate was observed at the end of each sampling.

Preceding sampling, quartz filters were cleaned by “baking” at 450 °C for 5 h, wrapped in aluminum foil and sealed in polyethylene zip bags. PUF plugs were washed with a water/detergent solution, rinsed with tap water, Milli-Q water, acetone, and then extracted with dichloromethane/hexane (1:1) in an ultrasonic bath. The extracted plugs were dried in a vacuum desiccator and sealed in clean amber glass jars. Unloaded and loaded filters were weighed in a KERN 870 semi-microbalance (resolution 10 μg) after 48-h conditioning at 20 ± 0.5 °C and 50 ± 5% RH. After sampling, loaded filters and PUFs were collected, resealed in the glass jars, and stored at −20 °C until extraction.

2.3. Analytical procedure

Each PUF plug and QFF were spiked with $^{13}C_{12}$-labeled surrogate standards (^{13}C-BDE 15, 28, 47, 99, 153, 154, 183; 204, 207 and 209; Cambridge Isotope Laboratories Inc., Andover, MA USA) to monitor analytical recovery and extracted with 50 mL dichloromethane/hexane (1:1) in a microwave extraction unit (CEM MARSX, Model 907600, CEM Corp.). PBDEs were analyzed in an Agilent 6890N gas chromatograph interfaced with an Agilent 5973K mass spectrometer. Details regarding the analytical procedure were included in our previous work (Besis et al., 2015) and in Supplementary material (S.1).

A total of 12 BDE congeners (BDE-15, 17, 28, 49 + 71, 47, 66, 100, 99, 154, 153 and 183) were regularly detected in samples. Due to the erratic concentration of BDE-209, this congener was removed from further analysis. Identification of the different congeners was based on comparison of their MS data and retention times with those of authentic reference standards and those reported in the literature.

2.4. Quality control and assurance

The whole sample preparation procedure was conducted under reduced light conditions and all glassware was wrapped in aluminum foil to prevent any possible photolysis of PBDE analytes. The recovery efficiency of the method was evaluated by analysing QFFs and PUFs spiked with a mixture of PBDEs. Most of PBDE congeners provided high recoveries with mean values ranging between 71 and 111%. Both collection media, QFFs and PUFs, exhibited similarly high recoveries of surrogate standards. The average recoveries calculated for $^{13}C_{12}$-labeled (^{13}C-BDE 15, 28, 47,