ATMOSPHERIC OCCURRENCE AND GAS-PARTICLE PARTITIONING OF PBDES IN AN INDUSTRIALISED, URBAN AND SUBURBAN AREA OF THESSALONIKI, NORTHERN GREECE

BESIS A., BOTSAROPOULOU E., VOUTSA D. and SAMARA C.

Environmental Pollution Control Laboratory, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124 Thessaloniki Greece
E-mail: tbesis@gmail.com

ABSTRACT

Ambient concentrations and gas/particle partitioning of Polybrominated Diphenyl Ethers (PBDEs) were investigated in a industrial, a traffic and a background site in the urban agglomeration of Thessaloniki, northern Greece. Atmospheric (gas+particle) concentrations of $\sum_{12}$PBDE at industrial site were higher than those observed at urban-traffic and urban-background sites. In industrial site, mean gas-phase $\sum_{12}$PBDE concentrations were 14.4 and 21.2 pg m^{-3} and particle-phase PBDE concentrations were 28.7 and 23.7 pg m^{-3}, for the cold and warm season, respectively. Mean gas-phase concentrations of $\sum_{12}$PBDE at the traffic site were 7.2 pg m^{-3} in the cold season and 11.2 pg m^{-3} in the warm season and particle-phase PBDE concentrations were 19.5 and 17.5 pg m^{-3}, for the cold and warm season, respectively. The corresponding levels at the urban-background site were lower, 4.7 and 6.3 pg m^{-3} in gas-phase and 3.9 and 3.1 pg m^{-3} in particle-phase, for the cold and warm season, respectively. At three sampling sites, the total (g+p) mean concentrations of $\sum_{12}$PBDEs were relatively higher in the warm season. The partition coefficient of PBDEs between the gas and particle phases (K_p) was well correlated with the subcooled liquid vapor pressure ($P°_L$) for all samples.

Keywords: Polybrominated Diphenyl Ethers; Gas phase; Particulate phase; Seasonal variation; Intake; Human Exposure; Greece.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been extensively used as flame retardants in various consumer products such as plastics, textiles, television sets, synthetic building materials, cars and computers (Besis and Samara 2012; Mandalakis *et al*., 2009). 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. There are three major commercial formulations used in the market: Penta-BDE, Octa-BDE, and Deca-BDE (La Guardia *et al*., 2006). PBDE pollution has become the subject of much concern and public outcry that require urgent attention. Due to their high environmental persistence, long-range transport potential, bioaccumulation tendency and toxicity of many congeners, the European Commission prohibited the manufacture and usage of PBDEs.

It is notable that the gas/particle partitioning of the PBDEs, and other POPs, is an important process influencing their environmental fate and mobility. Understanding the mechanisms that influence the gas/particle partitioning of the PBDEs would thus provide useful insight to better understand environmental fate processes, such as deposition, degradation, and atmospheric transport (Xiao *et al*., 2012). Lower brominated congeners are expected to be in the gas phase at a given temperature, whereas higher brominated PBDEs have a greater proportion in the particle phase (Mandalakis *et al*., 2009). Particle-bound PBDEs are mainly associated with the finest particles (<0.49 μm Besis *et al*., 2015; <0.57 μm Mandalakis *et al*., 2009). The predominance of PBDEs in fine particles has significant implications for their atmospheric fate since the scavenging mechanisms causing removal of suspended particulate matter from the

atmosphere (wet and dry deposition) are less efficient for smaller particles and, as consequence, fine aerosols are characterized by long residence times.

The main objective of the present study was to measure particle- and gas-phase concentrations of PBDEs in the urban environment, it's seasonal variation, and the exposure of population via inhalation of PBDE-contaminated air.

2. Materials and methods

2.1. Sample collection

Thessaloniki (40°62´N, 22°95´E) is the second most populated Greek city with approximately 16,000 inhabitants km^{-2} located in the innermost part of Thermaikos Gulf in northern Greece. Thessaloniki is a city historically suffering from high concentrations of airborne particles.

Sampling of PBDEs in the gas and particle phase of the atmosphere was carried out in Thessaloniki during the cold and the warm period of the year 2011 (industrial) and 2013 (urban-traffic and urban-background). Totally, 20 PBDE samples were collected during the sampling programs conducted at the three sites. The sampling system was situated on the roof (~3.0 m above ground level) of the air quality monitoring stations of the Municipality of Thessaloniki located at the sampling sites. Sampling was carried out using a medium-volume air sampler (Graseby Andersen, model PS-1) operated at a constant flow rate of 0.27 m^3 min^{-1}. No substantial drop (<5%) in flow rate was observed at the end of each sampling. The sampling period was 48 hours and the sampling volume was approximately 768 m^3. After sampling, loaded filters and PUFs were collected, resealed in the glass jars, and stored at -20 °C until extraction and analysis.

2.2. Analytical procedure

PBDEs were analysed in an Agilent 6890N gas chromatograph interfaced with an Agilent 5973K mass spectrometer operating in electron impact ionization (70 eV) and selected ion monitoring (SIM) mode. A DB5-MS capillary column (5% phenyl-methylpolysiloxane, 15 m, 0.25 mm i.d., 0.1 mm film thickness) and ultrahigh purity helium with a flow rate of 1 mL min^{-1} were used. 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. The recovery efficiency of the method was evaluated by the analysis of quartz filters and PUFs spiked with a mixture of PBDEs. Most of PBDE congeners provided high recoveries with mean values ranging between 71 and 111%. All types of samples analyzed in the present study (quartz filters and PUF plugs) exhibited similarly high recoveries of surrogate standards. The average recoveries calculated for $^{13}C_{12}$-labeled (^{13}C-BDE 15, 28, 47, 99, 153, 154 and 183) were 70±6, 94±8, 101±11, 110±8, 91±7, 82±8 and 98±12, respectively.

3. Results and discussion

3.1. Atmospheric concentrations of PBDEs

Among the three sites, the PBDE concentrations (gas plus particle phase) at industrial site were higher than those obtained from urban-traffic and urban-background sites. Total (g+p) concentrations of $\sum_{12}$PBDE at industrial site (43.1 and 44.8 pg m^{-3} for the cold and the warm season, respectively) were significantly higher than those determined at the urban-traffic (26.6 and 28.6 pg m^{-3} for the cold and the warm season, respectively) and urban-background site (8.6 and 9.4 pg m^{-3} for the cold and the warm season, respectively). The $\sum_{12}$PBDE concentrations found at the three sites in Thessaloniki are in close agreement with PBDE concentrations found in urban Athens and the suburbs of Heraklion, Crete (Mandalakis *et al*., 2009) and in general agreement with the levels found at several locations all over the world (Besis and Samara, 2012). Since the most important sources of PBDEs are and the usage of household appliances, building materals, textiles, furniture, and others goods containing flame retardants, higher population density and larger residential area can cause higher ambient concentrations of PBDEs (Wang *et al*., 2012).

At the industrial site, mean gas-phase $\sum_{12}$PBDE concentrations were 14.4 and 21.1 pg m^{-3} and particle-phase PBDE concentrations were 28.7 and 23.7 pg m^{-3}, for the cold and warm season, respectively. Mean gas-phase concentrations of $\sum_{12}$PBDE at the traffic site were 7.2 pg m^{-3} in the

cold season and 11.2 pg m^{-3} in the warm season, and particle-phase PBDE concentrations were 19.5 and 17.5 pg m^{-3}, for the cold and warm season, respectively. The corresponding levels at the urban-background site were lower, 4.7 and 6.3 pg m^{-3} in gas-phase and 3.9 and 3.1 pg m^{-3} in particle-phase, for the cold and warm season, respectively.

At three sampling sites, the total mean concentrations of $\sum_{12}$PBDEs were relatively higher in the warm season. Seasonal differences were statistically significant at the three sampling sites (p<0.05). The dominant congeners in all samples in the present study were BDE-47 and -99.

3.2. Gas-Particle Partitioning

The distribution of semi-volatile organic compounds between the particle and gas phases is commonly described by the particle/gas partition coefficient, K_P (m^3 μg^{-1}) (Mandalakis *et al*., 2009):

$$K_P = F/(A\ TSP) \quad (1)$$

where, F and A are the analyte concentrations (pg m^{-3}) on the quartz filter and on the PUF, respectively, and TSP is the concentration (µg m^{-3}) of suspended particles. Both of the mechanisms driving gas/particle partitioning of SOCs (adsorption onto aerosol surface and absorption into aerosol organic matter) have been proven to lead to a similar linear relationship between log K_P and the logarithm of subcooled liquid vapor pressure (P^o_L Pa) (Pankow, 1994):

$$\log K_P = m \log P^o_L + b \quad (2)$$

In the present study, K_P values were calculated for all PBDE congeners present in both gas and particle phase, and they were subsequently regressed against temperature-corrected vapor. The partition coefficient of PBDEs between the gas and particle phases (K_p) was well correlated with the subcooled liquid vapor pressure ($P°_L$) for all samples (Figure 1).

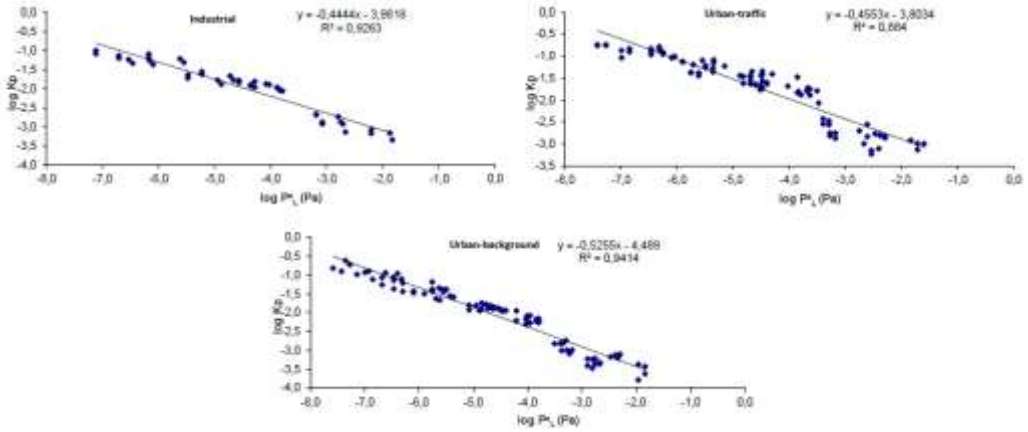

Figure 1: Plots of log Kp versus Log P°L

3.3. Inhalation exposure to PBDEs

The outdoor workday inhalation exposure to PBDEs at the two sites was estimated using the following equation also used by other researchers (Harrad *et al*., 2004):

$$\text{Intake (pg day}^{-1}) = (C_{OP} \cdot F_{OP}) \cdot R_R$$

where, R_R is the average respiration rate, C_O is the concentrations of PBDEs (pg m^{-3}) outdoors, and F_O is the percentage of time spent outdoors. Recently updated mean inhalation rate of 20 m^3 day^{-1} was used (Čupr *et al*., 2013). The average time that a worker spends outdoors was assumed as 8 h day^{-1} (Čupr *et al*., 2013). For all PBDEs, 100% absorption was assumed.

The average outdoor workday inhalation exposure to concentrations of $\sum_{12}$PBDE was found to be 288 and 299 pg day^{-1} at the industrial site and 178 and 191 pg day^{-1} at the urban-traffic site in the

cold and the warm period, respectively, dropping to 57 and 63 pg day^{-1} at the urban-background site.

4. Conclusions

The industrial site exhibited higher PBDE concentrations that the urban-traffic and urban-background sites. Seasonal differences were statistically significant at the three sampling sites (p<0.05). The partition coefficient of PBDEs between the gas and particle phases (K_p) was well correlated with the subcooled liquid vapor pressure ($P°_L$) for all samples. At three sampling sites, the total mean concentrations of $\sum_{12}$PBDEs were relatively higher in the warm season. The average outdoor workday inhalation exposure to concentrations of $\sum_{12}$PBDE was higher at the industrial site than at the urban-traffic site and at the urban-background site.

ACKNOWLEDGEMENTS

This research has been co-financed by the European Union (European Social Fund – ESF) and the Greek Ministry of Education through the Research Funding Program THALES (Project code/Title: MIS 377304/"Bioactivity of airborne particulates in relation with their size, morphology and chemical composition". We thank Dr. Apostolos Kelesis, Municipality of Thessaloniki, for providing meteorological data and on-site support.

REFERENCES

1. Besis, A. and Samara, C. (2012), Polybrominated diphenyl ethers (PBDEs) in the indoor and outdoor environments – a review on occurrence and human exposure. Environmental Pollution 169, 217-229.
2. Besis, A., Botsaropoulou E., Voutsa D. and Samara, C. (2015), Particle-size distribution of polybrominated diphenyl ethers (PBDEs) in the urban agglomeration of Thessaloniki, northern Greece. Atmospheric Environment 104, 176-185.
3. Čupr, P., Flegrová, Z., Franců, J., Landlová, L. and Klánová, J. (2013), Mineralogical, chemical and toxicological characterization of urban air particles. Environment International 54, 26-34.
4. La Guardia, M.J., Hale, R.C. and Harvey, E. (2006), Detailed polybrominated diphenyl ethers (PBDE) congener composition of the widely used Penta-, Octa-, and Deca-PBDE technical flame-retardant mixtures. Environmental Science and Technology 40, 6247-6254.
5. Mandalakis, M., Besis, A. and Stephanou, E.G. (2009), Particle-size distribution and gas/particle partitioning of atmospheric polybrominated diphenyl ethers in urban areas of Greece. Environmental Pollution 157, 1227-1233.
6. Wang, C., Li, W., Chen, J.W., Wang, H.Q.J., L, T.C., Shen, G.F., Shen, H.Z., Huang, Y., Wang, R., Wang, B., Zhang, Y.Y., Tang, J.H., Liu, W.X., Wang, X.L. and Tao, S. (2012), Summer atmospheric polybrominated diphenyl ethers in urban and rural areas of northern China. Environmental Pollution 171, 234-240.
7. Xiao, H., Shen, L., Yushan Su, Y., Barresi, E., DeJong, M., Hung, H., Lei, Y.-D., Wania, F., Reiner, E.J., Sverko, E. and Kang, S.-C. (2012), Atmospheric concentrations of halogenated flame retardants at two remote locations: The Canadian High Arctic and the Tibetan Plateau. Environmental Pollution 161, 154-161.