SEASONAL AND SPATIAL VARIABILITY OF POPS ON SIZE-SPECIFIC PARTICLES AND THEIR GAS/PARTICLE PARTITIONING

Okonski K[1]*, Degrendele C[1], Landlova L[1], Kukucka P[1], Becanova J[1], Klanova J[1]

[1]Research Centre for Toxic Compounds in the Environment (RECETOX), Faculty of Science, Masaryk University, Kamenice 3/126, 62500 Brno, Czech Republic

1. Introduction

A presence of the particulate matter in ambient air (especially of the particles with less than 10 µm in the diameter) has a negative impact on human health as it can induce various respiratory diseases[1,2]. The fine and ultrafine particles are of a special concern as they can penetrate the lungs to the greatest extent and even enter the blood stream[3]. Another factor that has to be considered when assessing the human respiratory risks are persistent chemicals that are associated with the atmospheric particles and represent additional risk when released in human bodies[4]. Size-specific distribution of these chemicals is an important parameter determining their behavior, fate and effects[5]. Size-specific partitioning of organic chemicals between various fractions of the atmospheric particles has been previously studied for polyaromatic hydrocarbons and it has been demonstrated that they are mostly associated with the fine and ultrafine fraction[6,7,8]. However, there is not much known about other groups of compounds, especially emerging pollutants[9]. As such distribution affects the fate of compounds not only from the toxicological point of view but also from the point of the long-range transport of pollutants to the pristine environments, such as the Arctic, new data are needed.

This study reports on seasonal and spatial variability of size-specific particle-gas partitioning behavior of emerging (brominated) pollutants.

2. Materials and methods

2.1 Air sampling

Samples were collected for the period of one year (October 2009 - October 2010) using a high volume air sampler equipped with a six-stage (< 0,49 µm; 0,49-0,95; 0,95-1,5; 1,5-3,0; 3,0-7,2; 7,2-10 µm) cascade impactor collecting particulate phase and polyurethane foam (PUF) plugs collecting the gas phase. For the stages in the impactor quartz filters were used. Air samples were taken from Brno city centre, representing urban site (~385 000 inhibitants, south-east part of the Czech Republic, sampler were set at Kotlarska street, characterised by a heavy taffic) and villiage Telnice, Czech Republic, representing rural site (~1300 inhibitants, approximately 13 km south-east of Brno city centre, no industrial activity).

2.2 Methods and materials

Filters were extracted using dichloromethane (DCM) by means of Büchi B-811 automated extraction system. Polyurethane foams were extracted in Soxhlet extractor. Before extraction, labelled ^{13}C recovery surrogate standards were added (BDE 28, 47, 66, 85, 99, 100, 153,154, 183, 209). Clean-up was performed with H_2SO_4 modified silica gel column, elution with DCM: n-hexane (1:1, v/v). The extracts were reduced in volume by gentle stream of nitrogen. Solvent was changed for nonane. Syringe standards ^{13}C BDE-77 and ^{13}C BDE-138 were added (i.e. standards added to quantify surrogate standards). The final volume was 50 µl. Samples were analysed using GC-EI-HRMS (Agilent 7890A GC coupled to Micromass AutoSpec Premier mass spectrometer).

3. Results and discussion

The highest amount of particles was observed in winter (Fig.1) which can be explained by extensive usage of heating during colder months. Particle-sized mass distribution was characterized by enrichment with particles of the smallest diameter and bimodal distribution with second maximum at the coarse fraction (3,0 -7,2 µm).

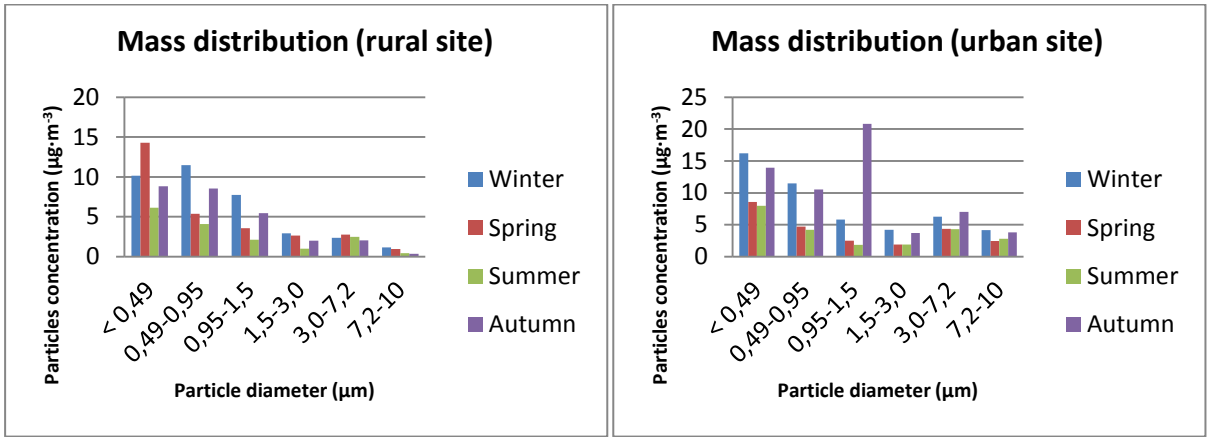

Fig. 1 Particle mass distribution

The ∑PBDEs showed higher affiliation towards particles with smaller diameter, especially during colder months (Fig.2). At the rural site there was a difference between particle size distribution and PBDEs size distribution. Moreover, BDE 209 compared to more volatile congeners was rather uniformly distributed among size-specific particles. Specific congeners of more volatile compounds exhibited size distribution similar to one presented for the sum of brominated compounds in Fig.2.

When it comes to gas/particle partitioning, higher concentrations of PBDEs were found on particles from urban site. Also, heavier congeners were associated more with particulate phase. Lower temperature also influenced phase partitioning i.e. in cold months concentration in the gas phase was depleted (Fig.3 and 4).

BDE 47, 99 and 209 were the most abundant congeners for the whole year. ∑PBDEs air concentrations observed (varying from 0.76 to almost 4 pg·m^{-3}) in the study are comparable with those reported by Agrell et al., 2004 and Wilford et al., 2008 but still lower when compared with other studies available[12,13,14].

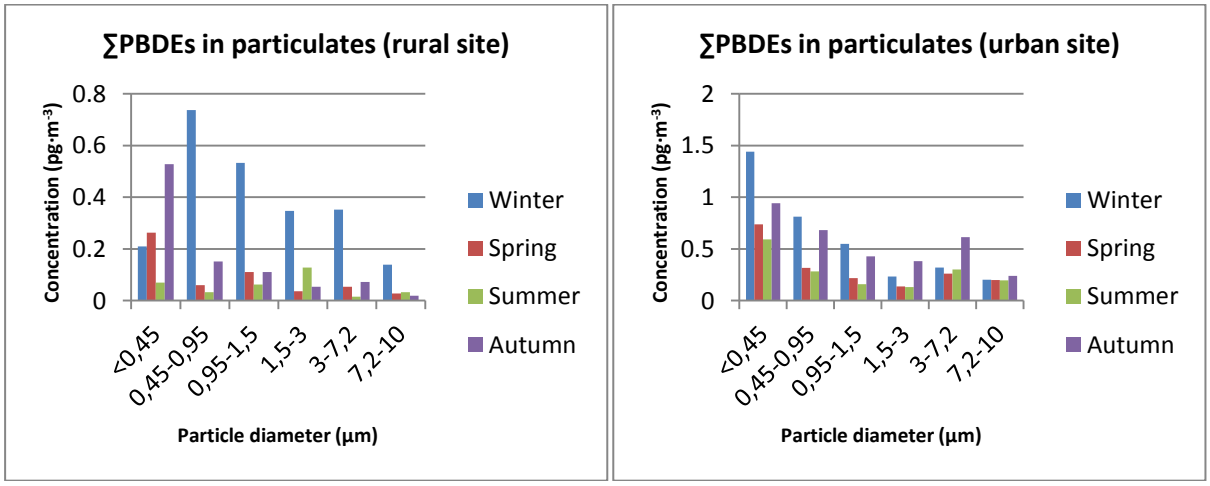

Fig. 2 ∑PBDEs size distribution

Presented results raise concern about human exposure to PBDEs, especially in urban environment, as the majority of brominated compounds were found on fine particles which penetrate lungs to a greater extent. Long range transport potential of these chemical will be influenced. Particles of smaller diameter reside longer in the atmosphere and can be transported over longer distance. Moreover, as compounds react differently, depending on in which phase they are, gas/particle partitioning will also significantly affect their transport in the

atmosphere. Influence of particulate phase on presented results stress the importance of analyzing both gas and particulate fraction.

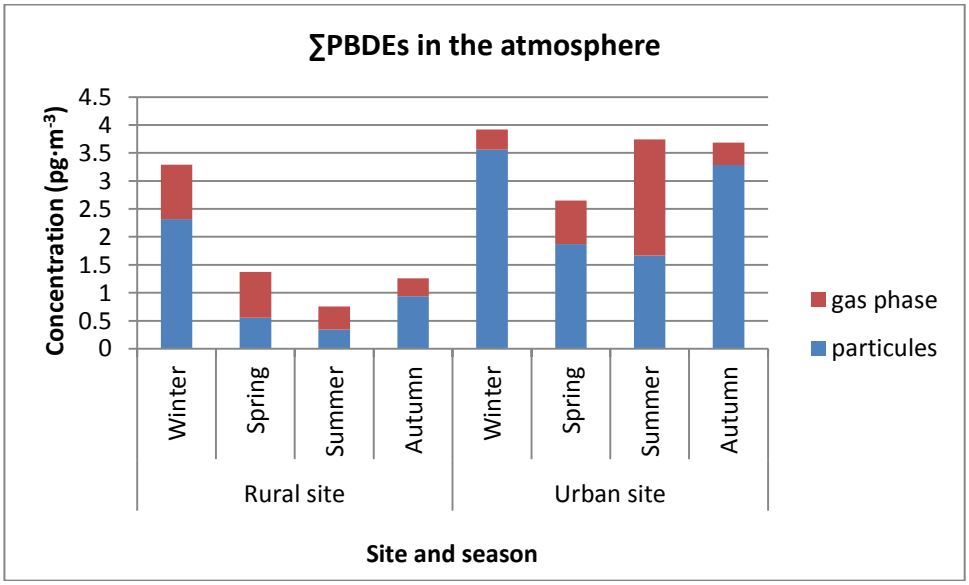

Fig. 3 Seasonal variations of ∑PBDEs in the atmosphere at urban and rural site

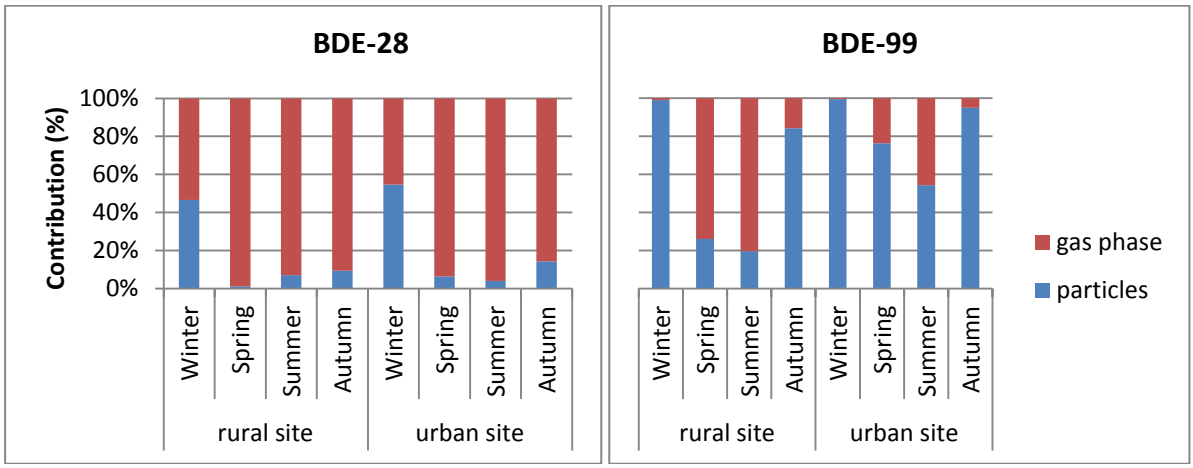

Fig. 4 Gas/particle partitioning of two BDE congeners, BDE-28 and BDE-99

4. Acknowledgements
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5. References:

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