Are atmospheric PBDE levels declining in Europe? Examination of seasonal variations, gas-particle partitioning and implications for long-range atmospheric transport

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Introduction

Since the late 1960s, flame retardants such as polybrominated diphenyl ethers (PBDEs) have been used in large quantities in various consumer products[1]. PBDEs are widespread contaminants as they are persistent, bioaccumulative, toxic and prone to long-range atmospheric transport (LRAT). All PBDEs technical mixtures were therefore banned in Europe[1].

Once PBDEs enter the air, they partition between gas and particulate phases, depending on their physico-chemical properties, meteorological parameters and abundance and composition of the suspended particulate matter[1]. Knowledge about this partitioning is deficient, but is crucial to predict environmental fate of PBDEs as it will influence their removal pathways from air (e.g. wet and dry deposition), affecting their potential for LRAT.

Only one study reported long-term trends of atmospheric PBDEs at various background sites in UK and Norway using passive devices and a consistent decline in PBDEs levels was only observed at 4 of the 11 sites investigated[2]. It is therefore unclear whether significant decreases of PBDEs levels should be expected for more recent years and for other regions of Europe.

The aim of this study is to provide novel long-term data on atmospheric PBDEs in Europe. In particular, the seasonal and long-term variations as well as the gas-particle partitioning of PBDEs were investigated.

Materials and methods

Air was sampled at a background site located in a mixed agricultural and forested area in the central Czech Republic. From January 2011 to December 2014, a high-volume air sampler was used to collect weekly air samples (N=114). Particles were collected on quartz fiber filters and gas-phase on polyurethane foam.

The samples were extracted with dichloromethane by means of an automated extraction system. Mass-labeled internal standards were spiked on each sample prior to extraction. Samples were cleaned-up using a sulphuric acid modified or a multi-layer silica column. Fractionation was achieved on a column containing activated charcoal or a mixture of charcoal and silica.

Ten PBDEs were analyzed using high resolution on an Agilent 7890A GC coupled to an AutoSpec Premier MS. The MS was operated in EI+ at the resolution of >10000.

Except for BDE209, the field and laboratory blank levels were <LOD or ≈LOD. All PBDE concentrations reported have been blank corrected and recovery-adjusted.

Results and discussion

Σ_9PBDEs (without BDE209) total (gas and particulate) concentrations ranged from 0.088 to 6.08 pg m^{-3} with an average value of 0.54 pg m^{-3}, while BDE209 was at 0.47 pg m^{-3} (0.050-5.01 pg m^{-3}). BDE47, 99 and 183 were the major contributors to Σ_9PBDEs, accounting on average for 36%, 27% and 14%, respectively.

For none of the congeners, a significant seasonal variation of the atmospheric concentrations was observed. This suggests that atmospheric levels are still dominated by primary rather than secondary sources, as re-volatilisation from surfaces would be enhanced by elevated temperatures in summer.

Regarding gas-particle partitioning, except for BDE28 (gaseous) and 209 (particulate), all congeners were consistently detected in both phases and clear seasonal variations were observed (Figure 1). For example, while the average particulate fraction (θ) of BDE47 was 0.52 in winter, this was only 0.01 in summer. Similarly for BDE99, θ was 0.88 in winter, while it was only 0.18 in summer. BDE28 and 209 were detected in only about half of the samples in both phases.

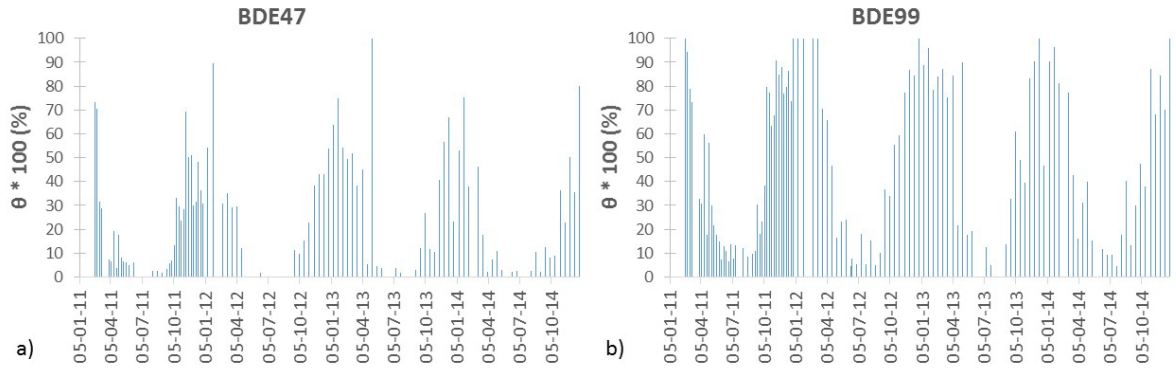

Figure 1: Particulate fractions (θ) of BDE47 (a) and BDE99 (b) in 2011-2014

The observed gas-particle partitioning coefficient (K_p in m^3 μg^{-1}) was compared with model predictions. The K_{OA} model assumes that both phases are in equilibrium and that partitioning is dominated by absorption into particulate organic matter (POM)[3]. A novel extension of the K_{OA} model considers absorption in POM being not in equilibrium due to disturbances of the particulate phase caused by wet and dry deposition (steady state model[4]). Both models generally failed to predict the partitioning mechanisms of PBDEs (Figure 2). While the K_{OA} model generally captured the overall trend (i.e. higher K_p for lower temperature), it consistently overestimates K_p by 0.6-1.7 orders of magnitude for individual congeners. The steady state model generally underestimates K_p by 0.5-1.0 orders of magnitude, accordingly it tends to perform better in summer compared to winter. A poly-parameter linear energy free

relationship, which is promising as it accounts for all kind of molecular interaction at the interface[5], was tested too.

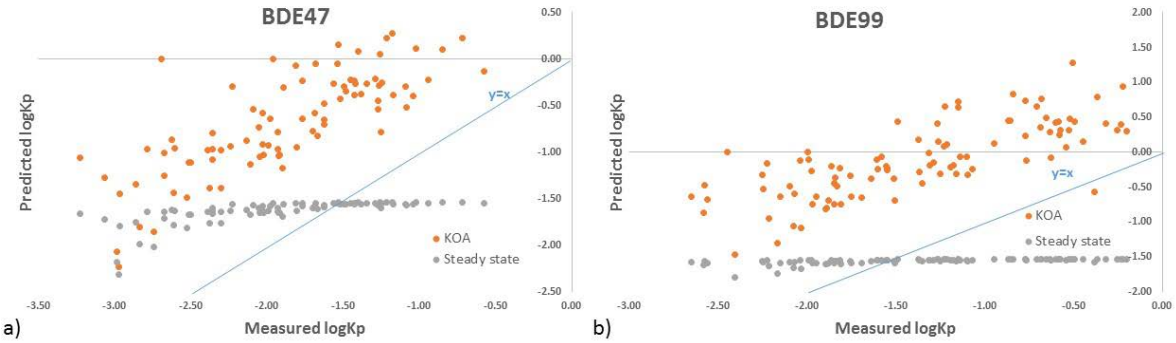

Figure 2: Comparison of predicted and measured $logK_p$ of BDE47 (a) and BDE99 (b)

To determine long-term trends, linear regressions of $lnBDE_i$ against time were analysed. Statistically significant decreases of the atmospheric concentrations during 2011-2014 were found for BDE100, 99, 153 and 209 (Figure 3). Estimated atmospheric half-lives for these congeners were ranging from 2.6 (BDE209) to 4.5 (BDE153) years. Significant increases of BDE28 and 66 were found for autumn and summer, respectively. This suggests the accumulation of persistent products of higher brominated congeners' photolysis in the environment.

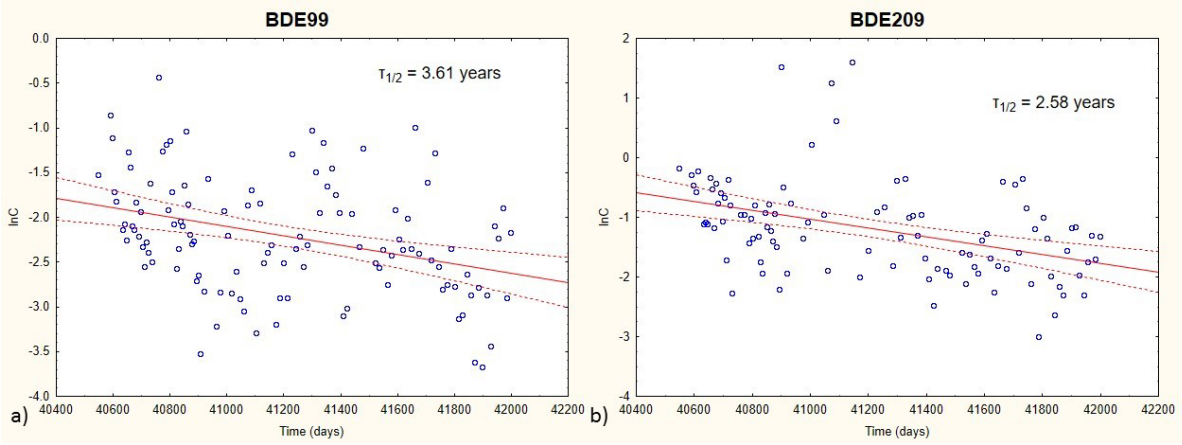

Figure 3: Long-term trends of BDE99 (a) and BDE209 (b)

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