

Interactive comment on “Are atmospheric PBDE levels declining in Central Europe? Examination of the seasonal variations, gas-particle partitioning and implications for long-range atmospheric transport” by Céline Degrendele et al.

Anonymous Referee #1

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MS No.: acp-2018-144 Title: Are atmospheric PBDE levels declining in Central Europe? Examination of the seasonal variations, gas-particle partitioning and implications for long-range atmospheric transport Author(s): Céline Degrendele et al. MS Type: Research article

General comments The manuscript presents four-year monitoring data (2011-2014) on atmospheric polybrominated diphenyl ethers (PBDEs) at the Košetice observatory, in an agricultural region in central Czech Republic. Particle- and gas-phase samples were collected on a weekly basis (7-day sampling duration) using a high-volume air

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sampler with PM10 pre-separator equipped with QFFs and 2 PUF plugs in series. PBDEs analysis was performed on 101 valid weekly samples (31 from 2011, 25 from 2012, 20 from 2013, 25 from 2014). Correlations were examined between the individual concentrations (g, p, g+p) of PBDEs and prevailing meteorological parameters. The g/p partitioning of PBDEs, with the exception of BDE209, was investigated by comparing experimental partition coefficient, K_p , values with those determined by three predictive models, the KOA model, a steady state model proposed in literature, and a regression model based on the quantitative structure-property relationship (QSPR) also proposed by other investigators. The apparent halving times ($\tau_{1/2}$) were calculated to investigate potential declining trends. The LRAT was also assessed by evaluating the backward trajectories of a small number of samples (10) using the Lagrangian particle dispersion model FLEXPART.

The authors have used appropriate methods for sampling/analysis of PBDEs and a thorough QA-QC procedure. The manuscript contains interesting data concerning the g/p partitioning behavior of PBDEs and the semi-longterm trends of their atmospheric levels at a background area of Central Europe.

My major concern is the large and variable amounts found for many PBDEs in the 2nd PUF plug. Since these amounts were included in the gas phase fraction probably resulted to underestimation of the particle fraction θ_{measured} .

Another question is why the subcooled-liquid-vapor pressure (PL)-based model was excluded from the g/p partitioning analysis.

The exclusion of BDE209 from all g/p partitioning models needs explanation. In addition to the above deficiencies, the manuscript needs substantial revision concerning various obscurities, inconsistencies, lacking information data, and missing references in the reference list. Finally, there is much room for language use improvement.

Specific comments Title: The manuscript does not provide information on the seasonal variations of PBDEs levels, therefore “seasonal variations” in the title shall be replaced

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by “semi-longterm variations”.

2.2 Sample preparation and analysis It is obscure here whether the authors used a different preparation procedure for samples collected in 2013 and 2014 than those used for samples from 2011 – 2012. Please, clarify. 2.3 Modelling of gas-particle partitioning P.5. L. 27: the measured fOM value for this site shall be provided. P.5. L. 29-30: The statement “Given the uncertainties while estimating such important physicochemical properties as KOA from other parameters, we did not consider BDE209 in the predictions” needs further clarification. Do the authors mean that the uncertainties for estimating KOA from other parameters is larger for BDE209 than for the lower PBDE congeners? In any case, the exclusion of BDE209 from all g/p partitioning models shall be explained.

3.1 Breakthrough and sampling artefacts In the breakthrough experiments on the 25 samples from 2012, a significant amount of PBDEs was found in the lower PUF plug, particularly for BDE183 and BDE209 (on average 31.9% and 53.6 % of their total gas-phase concentrations, respectively). – Possible contamination of the PUFs from the electronic/plastic parts of the air sampler is considered as one of the reasons. However, in such a case, the contamination level would be the same in each sampling. Did the authors check that? – The authors say that these findings are in agreement with a detailed breakthrough study previously published (Melymuk et al., 2016a), however this reference is not in the reference list. Also, in their explanation for possible volatilisation loss from the filter, they cite Melymuk et al., 2014, which is also missing from the reference list. 3.2 PBDE concentration levels P.7, L. 5: The average gas- and particle-phase concentrations of BDE209 provided in Table S5 (0.513 and 0.257 $\mu\text{g m}^{-3}$, respectively) seem to be in discrepancy with the average measured particulate fraction (θ_{measured}) presented in Figure S6, which ranges between 55-85% in the four seasons. Please, check and correct if needed. P.7, L. 7: Degrendele et al., 2016 cited here is missing from the reference list. Please, provide it. Besis et al., 2017 could also be cited at this point as providing PBDEs concentrations at background sites in Europe.

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– P.7, L. 10: Melymuk et al., 2016b is not in the reference list. – P.7, L. 9, 15, 16, 18: Besis and Samara, 2012 is not in the reference list. Actually, Besis and Samara 2012 is not dealing with the g/p partitioning of PBDEs. Perhaps the authors wanted to cite Besis et al., 2016 (Atmospheric occurrence and gas-particle partitioning of PBDEs at industrial, urban and suburban sites of Thessaloniki, northern Greece: Implications for human health, *Envir. Poll.* 215 (2016) 113-124).

3.3 Factors affecting the inter sample variations – P. 8, L.10-12: The statement “In this study, when considering the total concentrations of individual PBDEs, a significant influence of ambient temperature 10 was suggested only for BDE47 and BDE66 (higher concentrations for higher temperatures) and BDE153, BDE154 and BDE183 (higher concentrations for lower temperatures) (Table S5)” is not true! Table S5 shows negative correlation with $1/T$ (i.e. positive with T) only for BDE47, while positive for BDEs 66, 153, 154, 183. Please, correct properly. – P.8. L.21: $p > 0.05$ shall be $p < 0.05$ here. – Seasonality is confused here with the correlation with ambient T . Unfortunately, seasonal variations of PBDEs levels are not examined in the manuscript. Correlations with ambient T are as expected. Why the authors did not provide Clausius-Clapeyron plots for the gas-phase concentrations? – The statement in P.8. L. 17-18 “Overall, the absence of seasonality in the total concentrations of most PBDEs suggests that their atmospheric levels are still driven by primary sources.” shall be “Overall, the absence of correlation of the total concentrations of most PBDEs with ambient temperature suggests that their atmospheric levels are still driven by primary sources.”

3.2 Gas-particle partitioning in air samples

– P.9. L. 28: Again seasonality is confused with the correlation with ambient T . Please, correct properly. – P.9. L. 30: The finding that the temperature is an important variable affecting the partitioning of PBDEs in the atmosphere is not new, it has been shown in all similar studies. The authors could provide the $\log K_p$ - T relationship as well in addition to the correlation coefficient between θ_{measured} and $1/T$. – P.12: I think that the first reason for non considering that the deviation from equilibrium was

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due to the influence of wet and dry deposition should be the comparison of the particle fraction of PBDEs between samples with high and low precipitation height. I suggest changing the order of reasons.

3.5 Modelling of gas-particle partitioning – P.10. L. 12: Please change “seasonal” to “temporal”. – It would be interesting if the authors showed and discussed the $\log K_p$ - $\log PL$ relationship.

3.2 Inter-annual variations

– The statement “ $C_{0,i}$ is the theoretical concentrations of individual PBDE measured at t_0 (i.e. the end date of PBDE production)” is not clear. The authors have to further explain if and how they estimated the $\ln C_{0,i}$ data used in Eq. (8) and if these data are representative for Central Europe. – Is it sure that T units in Eq. (8) are days and not years? Please, confirm. – It should be clarified that the total (g+p) concentrations were used for C_i in Eq. (8). Why the apparent half-lives were not calculated separately for the two phases?

Conclusions

Supplementary Material – Table S3: For clarity reasons, please change “% of compound mass found on the lower PUF” to “% of gas-phase compound mass found on the lower PUF”. – Table S6: Please change title to: “Results of regression analysis between θ_{measured} and the inverse of temperature (K-1) for individual congeners. Numbers in bold indicate cases for which regression coefficients (r^2) were statistically significant ($p < 0.05$)” – Table S7: Please change title to: “Results of Pearson correlation analysis between θ_{measured} and the precipitation rate for individual PBDEs. Numbers in bold indicate cases for which the correlations were statistically significant ($p < 0.05$)”. – Table S8: Please change title to “Apparent half lives (τ) of individual PBDEs observed in this study and elsewhere.” – Figure S3: Please change legend to: “Correlation between the gaseous concentration of individual PBDEs (ln transformed) with the inverse of temperature”.

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