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

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MS Type: Research article

General comments on the authors' response and the revised manuscript

The revised manuscript is substantially improved, however needs further perfections before it can be accepted for publication in acp.

The authors' response (in green) was reasonable to most of my comments, although some issues remain unsolved (see below in red). In addition, there are several other issues raised that need to be addressed (see Additional comments on manuscript v.3).

Comments on the original manuscript needing further attention

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

We refrained from exploring $\log K_p = f(\log p_L)$ as the temperature dependence of vapour pressure is also reflected in the $\log K_p = f(\log K_{oa})$ plots (see e.g. Pankow and Bidleman, 1992; Cetin and Odabasi 2008; Lammel et al., 2010). Previously, it was common to test another vapour pressure based model i.e., the Junge-Pankow adsorption model (Pankow 1987). Such a model, implicitly assuming that adsorption is dominating gas-particle partitioning of the substances under study, is generally not promising for hydrophobic substances, which gas-particle partitioning is expected to be dominated by absorption in particulate organic matter (Finizio et al., 1997; Lohmann and Lammel, 2004; Goss and Schwarzenbach, 2001). The Junge-Pankow model has nevertheless been tested for PBDEs (Chen et al., 2006) including on another set of aerosol samples we collected and analysed (Besis et al., 2017). These results had confirmed the deficiency of this model and the perception that adsorption is not a significant process for PBDE gas-particle partitioning. Therefore, we prefer to not include this model in the discussion on gas-particle partitioning.

I agree that adsorption is less significant than absorption, nevertheless, the Junge-Pankow adsorption model was found to predict better than the KOA model the $\theta_{measured}$ in the warm season for the moderately brominated congeners DBE-49, -71, -47, and -66 (Besis et al., 2016).

The exclusion of BDE209 from all g/p partitioning models needs explanation.

Two of the presented models used KOA as one of the critical parameter. To the best of our knowledge, given the analytical issues with BDE209, there are no measured KOA as a function of temperature for this compound available. For all remaining BDEs, we have used measured KOA relationships. It is therefore evident that an estimation of KOA as a function of the temperature will be associated with higher uncertainties than the measured values. Moreover, there are higher uncertainties with the reported measured particulate fraction for BDE209, we therefore preferred to exclude this compound from the G/P modelling.

The manuscript now includes (at the beginning of the section on G/P modelling): „BDE209 was not considered in the different modelling approaches for two main reasons. Firstly, higher uncertainties are associated with the measured particulate fractions for this compound (see Section 3.1). Secondly, two of the tested models are based on K_{OA} and the temperature dependence of this parameter is not available (never determined). “

Yang et al., 2018 provides KOA values and their temperature dependence for all 209 PBDE congeners. I would suggest the authors considering this recent publication and include BDE in their g/p partitioning modeling.

P.5. L. 27: the measured f_{OM} value for this site shall be provided.

We have used f_{OM} values provided by the Czech Hydrometeorological Institute which were measured every sixth day at the sampling site.

The manuscript now includes: „The f_{OM} were derived from the atmospheric concentrations of organic carbon (a conversion factor of 1.8 was used) which was determined every sixth day and were ranging from 0.07 to 0.98 with an average value of 0.39 ± 0.19 .“

Summary statistics for the f_{OM} are now provided. However it is not clear which value was used in the modelling of gas-particle partitioning, the average over the 4-year study or the corresponding weekly average?

Also, please check the value of 0.98, it seems to be very high even for PM from a background site.

Finally, please, correct the “The f_{OM} were derived from...” to “The f_{OM} values were calculated from ...”.

P.7, L. 5: The average gas- and particle-phase concentrations of BDE209 provided in Table S5 (0.513 and 0.257 pg 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.

Indeed, these two datasets are in discrepancy, but correct. The average gaseous concentration of BDE209 was biased by few outliers (characterised by the high SD). The seasonal mean particulate mass fraction (FigureS3) was derived from the particulate mass fractions of individual samples. No changes made.

Please, expand axis Y of Figure S3 so as the full SD is shown. In my opinion, in data sets with very large SD the mean value is more representative than the average.

P.7, L. 9, 15, 16, 18: Basis and Samara, 2012 is not in the reference list. Actually, Basis and Samara 2012 is not dealing with the g/p partitioning of PBDEs. Perhaps the authors wanted to cite Basis 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).

Actually this section is not dealing with gas-particle partitioning and we consider that the information reviewed by Basis and Samara (2012) is relevant to support the points made with regard to the congener profiles. No changes made.

I am afraid that my comment was misunderstood. In this section, PBDE concentration levels found in this study are compared with those found in other European locations. Basis and Samara (2012) is a review article compiling literature data from all over the world and should be cited. I also suggested Basis et al. (2016) since it provides more recent data for European sites not included in the review.

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 investigation of seasonality on PBDEs atmospheric concentrations is now included in the Section 3.6.

I cannot see where the seasonal variations on PBDEs atmospheric concentrations are presented, either in the manuscript, or in the Supplementary Material. in Section 3.6, there is only a paragraph in P.13 *“The seasonal variations presented here are in contradiction with many previous studies which reported higher concentrations of most PBDEs in summer compared to winter..... enhance the revolatilisation from surfaces”*. Please, correct this deficiency.

P.9. L. 28: Again seasonality is confused with the correlation with ambient T. Please, correct properly.

Changed accordingly.

I cannot see where the seasonal variations on PBDEs atmospheric concentrations are presented, either in the manuscript, or in the Supplementary Material. in Section 3.6, there is only a paragraph in P.13 *“The seasonal variations presented here are in contradiction with many previous studies which reported higher concentrations of most PBDEs in summer compared to winter..... enhance the revolatilisation from surfaces”*. Please, correct this deficiency.

The authors could provide the logKp-T relationship as well in addition to the correlation coefficient between θ_{measured} and $1/T$.

This is now included (Table S5).

The correct Table is S7. Please unbold the r^2 value between θ_{meas} and $1/T$ for BDE-209 as it not statistically significant.

Additional comments on manuscript v.3

Abstract

- Instead of providing only the average θ_{measured} for winter and summer for 2 PBDEs (without the corresponding SDs), I would suggest to provide a general description of the seasonal trend that for all PBDEs, except maybe BDE-209, seems to be winter > autumn \approx spring > summer.
- Photolytic debromination was only assumed, not indicated by the results. Please, rephrase.

Equation (5): Please, use capital letters for OA in f_{om} .

P.5, L.22: Please correct “The fOM were derived from...” to “The fOM values were calculated from...”.

P.6, L.10: please delete extra parenthesis and commas.

P.6, L.23-24: The statement “Given that Bidleman and Tysklind (2018) demonstrated that when less than 50% is found in the lower PUF plug, the collected gaseous mass fractions should be larger than 90%,...” is not correct. Bidleman and Tysklind (2018) predicted that the collection efficiency of the gas phase exceeds 90% when the PUF2/PUF1 ratio is <0.5 (this means $<33\%$ in the lower PUF). Please, correct this point properly.

P.7, L.24-33: The authors highlight here the large seasonal variations found for θ_{measured} providing related information in Figures 1 and S3. I think that this finding, which is also highlighted in the conclusions section, deserves better discussion.

- Firstly, Fig. 1, that shows measured particulate fraction (θ_{measured}) for 4 PBDEs only on individual dates, is not essential and should be deleted, or replaced by S3 (please, expand axis Y of Figure S3, so as the full seasonal SDs are shown)
- Moreover, the larger seasonal differences found here in comparison to other studies need explanation. Large seasonal differences in θ_{meas} should be expected for large seasonal differences in ambient temperature. What is the seasonal difference of ambient temperature in this study and in the cited studies? For instance, Basis et al. (2016), found θ_{meas}

~25% lower in summer in comparison to winter for a difference in temperature of about 10-15 °C.

P.8, L.14-15: It is stated that “*none of the three model approaches successfully predicted K_p or θ for all individual PBDEs considered*”. Did the authors examined the seasonality of the predictabilities of the models? As observed in Basis et al. (2016), θ_{measured} data were closer to $\theta_{\text{predicted}}$ by the K_{OA} model in summertime samples as compared to the wintertime samples.

P.8, L.28-30: This sentence is not accurate. Basis et al. (2017) found that the steady-state model, when performed at a background site, was superior to predict G/P partitioning of BDE-209, while the KOA model was comparable or slightly better than the steady-state model for BDE-66 and BDE-154.

P.11, L.6: The reverse correlation found in your study between C_p of several PBDE congeners and precipitation shall be commented here.

P.11, L.23-25: The suggestion “*Therefore, we would suggest to focus the interpretation of Clausius Clapeyron equation only for those substances which are mainly in the gas-phase (i.e. $\theta_{\text{measured}} < 0.2$), regardless of the ambient temperature*” is unclear. In the present study, only BDE-28 has $\theta_{\text{measured}} < 0.2$ regardless of the ambient T, but does not follow the C-C equation.

P.12, L.8-9: There is no any evidence in this study that could support the statement that combustion can be concluded as a primary PBDE emission source. The results indicated increased C_p concentrations for PBDEs in winter, but this does not necessarily mean emission from combustion sources. Please, correct this sentence.

Conclusions

- Please, keep only conclusions that are supported by your results.
- Please, note that the important finding of this study, i.e. the seasonal variation of the particulate fraction which was observed for most PBDEs, that is significantly larger than in other studies, was not adequately explained in the manuscript!
- The critique on passive sampling designs is pointless here. I suggest just highlighting the prevalent congeners in each phase that were found in this study.
- Please, give again the names of the “*available models*”.

Supplementary Material

Table S2: I am very confused about the LOQs as reported in this Table.

- I cannot understand the meaning of iLOQs expressed in pg/sample (suppose per filter or PUF plug) or in pg/m^3 . These

should be referred as method LOQs. I would suggest the authors providing the iLOQ for each compound in pg/ μ L.

- What is the usefulness of calculating LOQblanks in pg/m³ since field blanks are not subjected to air sampling?
- Furthermore, the LOQ of a specific measurand in field blanks includes the iLOQ, as a consequence it cannot be zero. Please, correct or clarify Table S2.