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 #3

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This paper presents 4 years of air monitoring data of PBDEs (2011-2014) measured at the background site of Košetice observatory in Central Europe. Gas and particle phases of the air samples taken with a high volume air sampler equipped with a PM10 size-exclusion inlet were analyzed separately. The relationship between meteorological conditions and PBDE air concentrations in the particle phase, in the gas phase and total g+p concentrations were examined. Gas-particle partitioning coefficients (Kp) estimated by three models, namely KOA-based model, steady-state model and a quantitative structure-property relationship (QSPR) model proposed by Wei et al. (2017)

were compared with observed Kp. It was found that none of the models provide satisfactory prediction of the gas-particle partitioning observed for PBDEs measured in ambient air and the authors tried to explain why this is the case. Back trajectories were used to examine potential sources of PBDEs in samples with the highest and the lowest PBDE concentrations. Temporal trends of PBDEs measured were assessed using a simple regression method to estimate the first-order halflives which suggest declining trends. The authors suggest that after PBDEs have been regulated under the Stockholm Convention globally, debromination from higher BDE congeners may result in the enrichment of lower brominated congeners which are more persistent and are more mobile than heavier congeners.

This manuscript presents an interesting and valuable air monitoring dataset of PBDE measured in Central Europe. The authors did a fairly thorough analysis of the gas-particle partitioning observed and relationships of air concentrations with meteorological conditions. I found the fact that none of the three theoretical models provide satisfactory g-p partitioning observed interesting and the authors' attempt to explain why this is the case helpful. However, there are a few issues which I'd like to raise to help improve the manuscript and they are given below.

QA/QC:

Blank correction: Were the sample blank corrected using the annual average of the field blanks or the average of all 4 years of blanks? It is recommendable that the samples be blank corrected with the annual average field blank for 2 reasons: 1. The background levels for PBDEs in the lab may vary over time depending on what was being used and exists in the lab (e.g. old cardboard boxes containing PBDEs etc.); and 2. as this is a long-term air monitoring site, it would be problematic in the future if the samples were not blank corrected using annual average field blank, i.e. after collection of a few more years of samples, the LOQs would change. Consistent data management over the long term is important in generating a consistent dataset for the determination of temporal trends of POPs.

Breakthrough and sampling artefacts:

I am in fact not very concern about breakthrough in the PUF resulting in underestimation of the gas phase concentration. In Bidleman and Tysklind (2018, Chemosphere 192: 267-271), it was demonstrated that when PUF2/PUF1≤0.5, the collected fraction exceeds 90 %. Given the case that <20% of the lower congeners were found on PUF2, most of the PBDEs were probably adequately captured by the PUF1+PUF2 sampling train. I'm more concern about the fact that the maximum percentage of BDE 183 and 209 found on PUF2 was 100%, meaning that nothing was found on PUF1 for some samples. It is impossible that there was 100% breakthrough. This looks more like contamination than breakthrough, especially with BDE 209 which usually has high background levels. P. 6 Line 16, how was this underestimation of "up to 4%" determined? For the reasons given for the "breakthrough" of BDE 183 and 209, the fact that there may be blowoff from the filter should affect all congeners rather than just BDE 183 and 209 alone. It is more a sampling artefact than an explanation for the "breakthrough" observed. If it was blowoff from the filter, one should see BDE 183 and 209 more in PUF1 than in PUF2, i.e. it cannot explain the up to 100 % mass found in PUF2. Also, Okonski et al. (2014) found most of the PBDEs on aerosols <0.95 um and the QFF has a pore size of 2.2 um, have the authors considered fine particles physically breaking through the QFF into the PUF below? With the long sampling duration of 7 days and high flow rate of 31.3 m3/h, physical breakthrough of fine particles is possible. Of course, again this does not explain the high percentage mass found on PUF2. Looking at Table S4, when BDE 209 was detectable in gas phase (although it's not very often 41 %), it seems that its gas phase concentrations were higher than its particle phase concentrations which would support this potential artefact. Contamination of the PUF can happen not only inside the air sampler but can also happen in the lab due to micro-abrasion of material present in the lab as well. Have the authors randomly "prove" the precleaned PUFs before deployment to see if they were really "clean" by re-extracting the precleaned PUFs and analyzing the second extract? In any case, I would suggest the authors discuss breakthrough and general sampling artefacts and

contamination separately in section 3.1 rather than lumping all the reasons together to explain the observed "breakthrough" of BDE 183 and 209.

The analysis of the relationship between air concentrations (g, p, g+p) and meteorological conditions:

Table S5: Pearson correlation (linear relationship) analysis is used here instead of Spearman correlation (monotonic relationship). Is there any reason why Cg or Cp or Ctot would be linearly correlated with 1/T or any other met parameters? Thermodynamically speaking, there should be a linear relationship between natural-log transformed Cg (ln Cg) and 1/T (the Clausius-Clapeyron relationship), which provides information on the relative importance of volatilization from local sources and LRAT (Wania et al. ES&T, 1998, 32: 1013-1021), not Cg and 1/T. This relationship is explored in Figure S3. It is puzzling to try correlating C with 1/T in Table S5. If one only wants to know if C increases or decreases when T or any meteorological parameter increases, then a Spearman correlation should be used here. p. 8 line 29 "…gaseous concentration of all PBDEs…increased with ambient temperature (Table S5, Figure S3)". Figure S3 shows ln C versus 1/T while Table S5 shows C versus 1/T. This is very confusing. I suggest removing the correlation of C with 1/T in this table and focus the discussion on Figure S3 which would also tell the readers how C varies with temperatures. P. 9 Line 3-5 The authors suggests that there are other processes which controls Cg other than air-surface exchange. The authors should also refer to Wania et al. (1998) and point out that the shallow slopes for BDE 28 and 66 between ln Cg and 1/T suggest influence from LRAT which is a good reason for these lighter PBDEs which are relatively more volatile. Please show the p-values for the regressions in Figure S3.

As Referee #1 already pointed out, BDE 66 shows higher concentration for lower temperatures not vice versa. Also it says ABL height (shown as hmix in Table S5) shows strong correlations with Cp except BDE 28 on p. 8 line 8, but in Table S5, it seems that only BDE 85 didn't show a significant relationship, not BDE 28. Please correct.

Application and discussions of g-p partitioning models:

Was the fOM used in the equations the average value of PM10 concentrations (as the caption of Fig. S8 and S9 suggested) or the actual PM10 concentrations measured during each week of sampling? I presume that there is continuous measurement of PM10 at Košetice observatory? If the overall average value for the 4 years was used, please explain why you have not used the corresponding weekly average PM10 which I would suspect to vary quite a lot in different seasons, as well as over the years.

I am surprised that the authors have not pointed out the potential that the interference term from wet and dry deposition in the steady state model may be site specific and depends on the properties of the particles (including size distribution and physical composition). This would have partially explained why measured PBDE g-p partitioning are contradictory at a global scale which they have pointed out on p. 9.

Why didn't the authors try to use the ppLFER-type models proposed by Arp et al. (2008) and Shahpoury et al. (2016) to see if they give a better description of the g-p partitioning observed here? These models also take into account the makeup of the particles which may perform better than the 3 models used here that only consider the phys-chem properties of PBDEs.

p. 11 line 15 Should this sentence read "...6 and/or 6' position, such as for BDE 154" here? For BDE 154 (2,2',4,4',5,6'-BDE), there is only one Br at the 6' position. In the text, it says that the effect of stronger adsorption for the planar structure of BDE 153 as compared to BDE 154 which has a twisted structure is observed in the air monitoring results. If I am reading Figure S10 correctly, it seems that the measured particulate fraction of BDE 153 were lower than that of BDE 154 (e.g. a θBDE153 = 0.6 corresponds to a θBDE154 of 0.6-0.8). This means there is more BDE 154 sorbed to particles than BDE 153 which is opposite to what is stated in the text. Also, it seems that BDE 47 (2,2',4,4'-BDE) and 66 (2,3',4,4'-BDE) shows similar relationship in Figure S10 although none has a Br in the 6 or 6' position. Is there any explanation of this

relationship?

Trend analysis:

As Referee #1 pointed out, there is no analysis on seasonal variations at all. The authors should take the opportunity to analyze for temporal trends to better understand the seasonal variations in concentrations. Why only used a first-order relationship to try to develop time trends? Venier et al. (2012, ES&T, 46: 3928-34) compared 4 methods for deriving time trends for POPs. The authors can consider using any of the 4 methods, which take into consideration seasonal variations, to derive time trends.

The comparison of trends from literature can be updated with new trend information from the Great Lakes reported in Shunthirasingham et al. (2018, ESPI, 20: 469-479).

The figures in the main article look blurry, please re-make them.

Referee #1 noticed that there are missing references in the list. Also, it seems that some references are not typed in correctly, e.g. Davie-Martin et al. (2016) is missing a co-author's name. Please carefully check all references.

Minor: p. 2 line 7 ...once PBDEs enter the air, they would partition between... p. 6 line 1 Suggest to remove the word "Indeed" which is a strange connector for these two sentences. p. 14 line 15, ...the minimal criterion...