Referre #1:

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. MSType: 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 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, Kp, 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 (_ 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 _measured.
The breakthrough analysis we had applied was based on raw data, which were not field blank corrected (this was done on the sum of the PUFs after the breakthrough analysis). This was inappropriate and we apologize for this mistake. Upon appropriate field blank correction, we obtain similar results for most congeners, but with much lower detection frequencies in the downstream (second) PUF. The interpretation of the highest masses of BDE183 and BDE209 on the lower PUFs have been updated taking into account the considerations of all reviewers (See updated Section 3.1). As mentioned in the manuscript, we consider the sampling configuration to be adequate to trap efficiently all PBDEs in the gaseous phase except BDE209.

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.

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 prefered 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). "

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.
All specific comments have been answered consequently and the corresponding parts of the manuscript were modified.

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 by "semi-longterm variations".
We have now included the analysis of seasonal variations in the manuscript and have also added semi-long term variations to the title.

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.
We are sorry about the confusion. Indeed, a different procedure was used for samples collected prior 2013 and those collected after.
The manuscript now includes : „"The clean up and fractionation method differed between samples collected prior and those after 2013"

2.3 Modelling of gas-particle partitioning
P.5. L. 27: the measured fOM 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. "

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.

See previous answer (exclusion of BDE209)

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 gasphase concentrations, respectively). ǎA ´c 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?

See previous answer (amounts in the 2nd PUF).

ǎA ´c 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.

We apologize for that. The reference list has been corrected and updated.

3.2 PBDE concentration levels
P.7, L. 5: The average gasand 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 (_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.

P.7, L. 7: Degrendele et al., 2016 cited here is missing from the reference list. Please, provide it.

We apologize about that. Now added.

Besis et al., 2017 could also be cited at this point as providing PBDEs concentrations at background sites in Europe.

This has now been added.

ǎA ´c P.7, L. 10: Melymuk et al., 2016b is not in the reference list.

We do not anymore cite this article.

ǎA ´c 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).

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

3.3 Factors affecting the inter sample variations
ă˘A ´c 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.
We apologize for that error and have now corrected. Moreover, BDE66 has now been removed from this manuscript (see following comment by Reviewer 2).

ă˘A ´c P.8. L.21: p>0.05 shall be p<0.05 here.
Now corrected.

ă˘A ´c 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.
An investigation of Clausius-Clapeyron equation is now included. However, given the important seasonality in the measured particulate fraction of most PBDEs investigated, we do not consider that this is relevant.
The manuscript now includes:"An examination of the temperature dependence of the PBDEs gaseous concentrations using the Clausius-Clapeyron equation (see Supplement) was done and results are presented in Table S10. Significant correlations were found between the natural logarithm of partial pressure versus the inverse of ambient temperature for all PBDEs, except BDE28 and BDE209. This suggests that the gas-phase concentrations of these two congeners are not controlled by temperature dependent sources. This lack of temperature dependence has been previously attributed to long-range atmospheric transport (Hoff et al., 1998; Wania and Haugen, 1998). However, at least for BDE28, we suggest that the photolytic debromination of higher brominated congeners (Bezares-Cruz et al., 2004; Wei et al., 2013) may also play a role. In case of the remaining congeners, the strong influence of ambient temperature on the gaseous concentrations of PBDEs, characterized by the high slopes in Table S10, has been often interpreted by previous studies (Cetin and Odabasi, 2008; Davie-Martin et al., 2016) as a demonstration that PBDE gaseous concentrations are controlled by revolatilisation from surfaces (soils or waters). However, given the large influence of ambient temperature on $\theta_{measured}$ (see Section 3.4), it is uncertain that the gas-phase concentrations of PBDEs are controlled by air-surface exchange rather than by revolatilisation from the particles. 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. $\theta_{measured} < 0.2$), regardless of the ambient temperature. „

ă˘A ´c 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."
This statement is not anymore included in the manuscript.

3.2 Gas-particle partitioning in air samples

ã˘A ´c P.9. L. 28: Again seasonality is confused with the correlation with ambient T. Please, correct properly.

Changed accordingly.

ã˘A ´c 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.

This sentence now removed.

The authors could provide the logKp-T relationship as well in addition to the correlation coefficient between _measured and 1/T.

This is now included (Table S5).

ã˘A ´c P.12:

I think that the first reason for non considering that the deviation from equilibrium was 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.

Thank you for the suggestion. We have now changed the order of reasons.

3.5 Modelling of gas-particle partitioning ã˘A ´c P.10. L. 12: Please change "seasonal" to "temporal".

Changed accordingly.

ã˘A´c It would be interesting if the authors showed and discussed the logKp-logPLÎ£ relationship.

Please, see reply above: we refrain from testing gas-particle partitioning of PBDEs on adsorption, as the process is rather determined by absorption.

3.2 Inter-annual variations

ã˘A ´c The statement "C0,i is the theoretical concentrations of individual PBDE measured at t0 (i.e. the end date of PBDE production)" is not clear. The authors have to further explain if and how they estimated the lnC0,i data used in Eq. (8) and if these data are representative for Central Europe.

We have now changed the regression model applied to our dataset, and this term is not included anymore.

ã˘A ´c Is it sure that T units in Eq. (8) are days and not years? Please, confirm.

Yes, T is in days, as we are now also investigating the seasonal variations.

ã˘A ´c It should be clarified that the total (g+p) concentrations were used for Ci in Eq. (8). Why the apparent half-lives were not calculated separately for the two phases?

We have now indicated that total concentrations were used. A derivation of apparent half-lives for individual phases in atmospheric aerosols would be misleading: characteristic times of interphase conversions are much shorter. Hence, there is no ‚live' in one of the phases on the time scale of the study.

Conclusions

Supplementary Material ã˘A ´c 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".

â˘A ´c Table S6: Please change title to: "Results of regression analysis between _measured and the inverse of temperature (K-1) for individual congeners. Numbers in bold indicate cases for which regression coefficients (r2) were statistically significant (p<0.05)" â˘A ´c Table S7: Please change title to: "Results of Pearson correlation analysis between _measured and the precipitation rate for individual PBDEs. Numbers in bold indicate cases for which the correlations were statistically significant (p<0.05)". â˘A ´c Table S8: Please change title to "Apparent half lives (_) of individual PBDEs observed in this study and elsewhere: : :..Â˙z â˘A ´c Figure S3: Please change legend to: "Correlation between the gaseous concentration of individual PBDEs (ln transformed) with the inverse of temperature".

All of these changes now included in the manuscript and Supplement.

Referre #3

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 gasparticle 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.

Indeed, the samples were blank corrected using the annual average of field blanks and not the average of all 4 years of blanks.

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.

We would like to thank the referee for her/his precious comments.

We need to apologize for two mistakes we did. Firstly, it was mentioned that the pore size of the filters used were 2.2 µm. However, this was not the pore size of the filter, which is not indicated by the manufacturer, but this was the cutoff for particle retention in liquid. The same filters are used by US EPA PM_{10} Ambient Air Monitoring and do fulfil the relevant criteria.

Secondly, the breakthrough analysis was previously performed on the raw data. Then the PUFs were summed up, and then the annual mean of field blank concentrations was substracted, which was inappropriate. We have now updated the calculation by firstly performing field blank substraction prior the breakthrough analysis. As pointed out, many of the previously reported concentrations on PUFs were within the blank levels and the detection frequencies are now lower. Still, BDE183 and BDE209 are frequently positively found on the lower PUF. We have now updated this section of the manuscript taking into account all comments from reviewers and discuss breakthrough, sampling artefacts and possible contamination separately (see Section 3.1).

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.

We apologize for that error. We have now updated Table S5 using a Spearman correlation. Moreover, we have now considered the relationship only between lnC and 1/T.

An investigation of Clausius-Clapeyron equation is now included. However, given the very strong influence of ambient temperature on the measured particulate mass fraction of most PBDE congeners, we do not consider that this is relevant.

The manuscript now includes:"An examination of the temperature dependence of the PBDEs gaseous concentrations using the Clausius-Clapeyron equation (see Supplement) was done and results are presented in Table S10. Significant correlations were found between the natural logarithm of partial pressure versus the inverse of ambient temperature for all PBDEs, except BDE28 and BDE209. This suggests that the gas-phase concentrations of these two congeners are not controlled by temperature dependent sources. This lack of temperature dependence has been previously attributed to long-range atmospheric transport (Hoff et al., 1998; Wania and Haugen, 1998). However, at least for BDE28, we suggest that the photolytic debromination of higher brominated congeners (Bezares-Cruz et al., 2004; Wei et al., 2013) may also play a role. In case of the remaining congeners, the strong influence of ambient temperature on the gaseous concentrations of PBDEs, characterized by the high slopes in Table S10, has been often interpreted by previous studies (Cetin and Odabasi, 2008; Davie-Martin et al., 2016) as a demonstration that PBDE gaseous concentrations are controlled by revolatilisation from surfaces (soils or waters). However, given the large influence of ambient temperature on $\theta_{measured}$ (see Section 3.4), it is uncertain that the gas-phase concentrations of PBDEs are controlled by air-surface exchange rather than by revolatilisation from the particles. 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. $\theta_{measured}$ < 0.2), regardless of the ambient temperature. „

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.

We have now removed the correlation of C with 1/T and focused the discussion on lnC vs. 1/T.

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, see the previous comment on Clausius Clapeyron plots.

Please show the p-values for the regressions in Figure S3.

Now indicated in the caption.

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.

We are sorry about these mistakes which have now been corrected. Please note that BDE66 was removed from this article.

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.

We have used fOM 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."

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.

Thank you for the suggestion.

The manuscript now includes: „However, the term describing this influence in Eq 4 does not consider important characteristics of the site such as meteorological conditions (e.g. precipitation rate, temperature) or aerosol properties (e.g. mass size distribution, PM composition)."

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.

We had apply a pp-LFER model on our data, and the predicted K_p was higher than the one determined by the K_{OA} model. This is, actually, expected as more attractive molecular interactions beyond absorption in organic matter were considered. However, given the uncertainties related to input parameters and the preliminary nature of the model setup, we decided to not include this in the current manuscript. The application of ppLFER for interphase partitioning of PBDE in the atmospheric environment, including gas-particle partitioning is an on-going research of our group (Shahpoury et al; in prep).

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 _BDE153 = 0.6 corresponds to a _BDE154 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?

We thank the reviewer for noticing the mistake in Figure S10; the axes had been mislabelled and have now been corrected.

We had wanted to emphasize the importance of the Br atom in the ortho position (relative to oxygen substituted carbon atom). Not only the 6 and 6' positions fulfill this requirement, but also the 2 and 2' positions. In the case of BDE 154 (2,2',4,4',5,6'-BDE) there are three Br atoms in ortho positions. BDE 47 (2,2',4,4'-BDE) contains two Br atoms in ortho positions, whereas BDE 66 (2,3',4,4'-BDE) only contains one.

We acknowledge that using just the positional labels 6 and 6' could be confusing and unclear for the reader. To address this, we have updated the manuscript to discuss this concept in terms of ortho substituted Br (which should imply the 2, 2', 6 and 6' positions).

The manuscript now includes: „We highlight a study by Ding et al., (2014) which investigated the adsorption of different congeners on graphene (a structure that on a molecular level has similarities to black carbon). It was found that, in addition to the number of bromine atoms, the adsorption energy was also affected by the 3-dimensional structure of the PBDE congener. Specifically, steric interactions between bromine atoms in the ortho position (relative to the oxygen substituted carbon atom) appear to be important. This effect is best illustrated by congeners BDE153 and BDE154, both of which have the same number of bromine atoms. However, BDE154 has three Br atoms in the ortho position; this meant the congener adopted a twisted structure and adsorbed more weakly onto the graphene surface. BDE153 on the other hand, with only two Br atoms in the ortho position, can adopt a planar structure and adsorb more strongly. The consequences of this effect are observed in our results (Figure S10). We also note similar behaviour between BDE99 and BDE100; it appears that congeners with more Br atoms in the ortho position tend to have smaller particulate fractions when compared with other congeners of the same mass. Such effects are not captured by using K_{OA} alone as a predictor (octanol having more degrees of freedom can better accommodate to twisted structures). We speculate these effects could influence the ability of specific BDEs to both adsorb onto and diffuse within the bulk condensed phases of PM."

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.

Thank you for the suggestion. We have now applied one of the method used by Venier et al (2012), which also addresses seasonal variations. See Section 3.5

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).

Thank you for informing us about this interesting article. We have now included these results in the discussion on PBDE long term trends worldwide, as well as in the Table comparing the half-lives of PBDEs.

The manuscript now includes:" Similarly, at two sites around the Canadian Great Lakes, PBDE concentrations were found to decrease slowly, with half lives in the range of 2-16 years and faster decline rates at the site closest to urban areas (Shunthirasingham et al., 2018)."

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

We have now improved the layout of all figures present in the manuscript.

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.
We have now carefully checked 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: : :
Thank you, modified accordingly.

Referee #2:

In this manuscript, the authors present an analysis of PBDEs atmospheric concentrations for samples collected at a background station in Czech Republic over a 4 years period. The authors analyzed seasonality in the data as well as gas-particle partitioning. The dataset is interesting and they can provide some useful insights into the atmospheric concentrations of PBDEs in Europe. The manuscript though needs some work before it can be published.

General comments:
QA/QC: I have some concerns regarding the data that the authors didn't address at all. Samples from 2011-12 were extracted and cleaned using a method significantly different from those from 2013-2014. Also, samples from two different subsets (2011 and 2011-2014) were analyzed using two different instruments, columns and conditions. When datasets are analyzed using different methods, the issue of consistency and comparability needs to be addressed and this is especially important for long term data series. This comments dribbles down also to other QA/QC parameters such as blanks, and limit of detection /quantitation. It's not clear how this issue was dealt with for blanks: how were blanks calculated (e.g. annually or over the 4 years)? It's generally preferred to do it annually since it reflects more accurately lab practices at the time of processing. This dataset is very valuable and provides useful information for scientists and legislators but at the moment it is tainted by this QA/QC problem. The authors need to demonstrate that there is comparability and that their results are not affected by analytical issues.
We apologize for not providing sufficient proof of the comparability between the results obtained from different sampling preparation and/or column. We have now added a table comparing the results of spiked PUFs from the two different sampling preparation methods as well as a table showing the changes of the relative response factors relqted to the different columns used.
The manuscript now includes: "The different sample preparation and/or column used has a minor effect on the overall quality of the data (<12%, Tables S3 and S4). Therefore, the data obtained are directly comparable and suitable to derive long term trends"

The samples were blank corrected using the field blanks generated in individual years, and not the average of the field blanks of 4 years.
The manuscript now includes: " The PBDE concentrations presented here have been blank corrected by subtracting the average of the field blanks on an annual basis, separately for GFFs and PUFs."

Breakthrough: Given the extremely large volumes collects, I am surprised that the breakthrough is so limited. Nevertheless, the breakthrough for BDE209 and BDE183 is a bit unsettling. I agree with the other reviewer in that it's particularly interesting that in certain samples 100% of these two congeners were detected in the second PUF. The authors speculate that this effect

could be due to lab contamination but lab blanks would clearly reflect that and blank subtraction would equalize samples. A relatively simpler explanation that the authors didn't consider in the paper is the filter pore size. Here the filter cutoff is 2.2 um, which is quite high. For example, IADN employs QFF with a cutoff of 0.3 um. It's quite plausible that fine particles slips through the filter and end us in the PUF. This behavior should also be taken into account for the gas-particle partitioning.

We would like to thank the referee for her/his precious comments.

We need to apologize for two mistakes we did. Firstly, it was mentioned that the pore size of the filters used were 2.2 μm however, this was not the pore size of the filter, which is not indicated by the manufacturer, but this was the cutoff for particle retention in liquid. The same filters are used by the US EPA PM_{10} Ambient Air Monitoring and do fulfil the relevant criteria. Secondly, the breakthrough analysis was previously performed on the raw data. Then the PUFs were summed up, and then the field blank substraction was performed, which was inappropriate. We have now updated the calculation by firstly performing field blank substraction prior the breakthrough analysis. As pointed out, many of the previously reported concentrations on PUFs were within the blank levels and the detection frequencies are now lower. Still, BDE183 and BDE209 are frequently positively found on the lower PUF. We have now updated this section taking into account all comments from reviewers.

Factors affecting inert sample variations: Seasonality was not discussed or introduced before. As reviewer 1 noted, here seasonality is confused with ambient temperature, which is a cause but not an effect. Seasonality should be treated separately from the analysis with met data. The authors can not draw any conclusions on seasonality just based on the 1/T analysis (see page 8 lines 17 and 33, for example) The lack of relationship with most of meteorological parameters excluding temperature, is not surprising nor specific to PBDEs. Hafner and Hites showed that directional terms did not generally improve the regression models (Environ. Sci. Technol. 39, 20, 7817-7825) for most SOCs. The results of the Pearson correlation analysis reported in Table S5 are so scattered that I find hard to draw any solid conclusion on these relationships. For example, why would BDE47 have a negative significant correlation with 1/T and BDE 66 a negative one?

We apologize for that confusion and have now included a discussion on seasonality in the part on semi-long term trends. We have now removed BDE66 from this manuscript and have shortened the discussion on the possible influence of meteorological parameters on the PBDE concentrations.

The manuscript now includes:" No or low influence of wind speed and wind direction on the PBDE concentrations were observed, consistent with previous studies (Besis et al., 2015; Cetin and Odabasi, 2008), but also more generally consistent for POPs (Hafner and Hites, 2005)."

Gas-particle partitioning and modeling: the measured values for the particle fractions are certainly affected by the large filter cutoff, as discussed above. This artifact is certainly playing a significant role in the modeling and consequent interpretation.

It is quite clear that the Koa model does a better job at describing this relationship than the other ones. If the gas phase concentrations were overestimated based on the larger than usual cutoff of the filters, the Kp would be smaller than expected. In this scenario, rather than the Koa based model overestimating the Kp, it's the measured Kp that is underestimated.

The filtration efficiency, though not provided by the manufacturer, is very high even for nano-sized particles ('total filter', commonly used by monitoring networks, such as e.g., the US EPA). Therefore, we expect no significant influence of the filtration efficiency on measureed K_p's.

I find that excluding BDE209 from the modeling is introducing a bias in the analysis and results. The authors should at least clarify why they chose to exclude it.

Two of the presented models used K_{OA} as one of the critical parameter. To the best of our knowledge, given the analytical issues with BDE209, there are no measured K_{OA} as a function of temperature for this compound available. For all remaining BDEs, we have used measured K_{OA} relationships. It is therefore evident that an estimation of K_{OA} as a function of the temperature will be associated with higher uncertainties than the measured values. Moreover, we should keep in mind that there are higher uncertainties associated with the reported measured particulate fractions. We therefore prefered to exclude this compound from this section.

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)."

Inter-annual variations: Seasonality is generally quite strong and its effect should be removed when calculating halving times. As mentioned by reviewer 3, there are a number of regression models that take into account seasonality than can be employed here.

Thank you for the suggestion. We have now used a different regression model to quantify the semi long-term trends apart from the seasonality.

Specific Comments:
Page 3 Why is the use of the PM 10 separator never discussed in the manuscript other than at line 6 here? Perhaps I am missing something.

A defined cutoff is operationally preferable, rather than an undefined sampling of PM (limitations of isokinetic sampling etc.). PM_{10} is the most common cutoff in air quality and aerosol research and exposure studies, as it addresses the inhalable size fraction. Moreover, PBDEs as most other SOCs are present mainly on fine particles (i.e. <1 µm, Okonski et al; 2014).

The manuscript now reads: "The sampler addressed the inhalable size fraction, PM_{10}. PBDEs are mostly sorbed to fine and sub-micrometer sized particles (Okonski et al., 2014; Besis et al., 2017)".

Page 3 Bottom half Remove references to PCBs and dioxins since they are not relevant here.
Changed accordingly.

Pages 1-2 The use of term novel here is out of place, I am afraid. The authors didn't clarify what is the novel aspect of this study.
We agree and have now removed the term „novel" from the manuscript.

Page 6, Line 16 How was the 4% underestimation calculated?
This was estimated by assuming that a third PUF would capture 20% of the second PUF and so on. However, we have now removed this estimation and included the reference from the more accurate estimation of Bidleman and Tysklind (2018).

The manuscript now reads: " 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%, we consider the current sampling configuration and sample preparation to be efficient for trapping all gas-phase PBDE congeners addressed, except BDE209."

Page 6, Line 9 The reference to indoor studies is unnecessary since it's unfair to compare the two concentrations.
Removed reference to indoor air accordingly.

Page 7, line 16 Please use more up to date reference for North America (see Liu et al., / Environment International 92– 93 (2016) 442–449 and Ma et al., 2013).
We have now used only the latest available information from North America.

Page 7, line 26 Table S2 I wonder if this volume of 5264 m3 is a representative number. In line 11, the authors report that the sampling volume ranged from 4015 m3 to 5864 m3 for samples collected in 2015. The average is closer to 5000 m3.
The fictive volume of 5264 m^3 is a representative number as it is the average of all volumes for single samples (the median is 5344 m^3). Volumes lower than 5000 m^3 were rare.

Page 9, line 6 Backward air trajectory was not properly introduced and it seems abruptly introduced here.
We have now introduced it.
The manuscript now reads: " LRAT is an important source of POPs such as PBDEs in background environments. The analysis of air mass history, as described in Section 2.5, was performed to identify potential source areas for PBDE in Central Europe."

Page 13, line 11 Add also Liu et al., 2016.
Ok, done

Page 13, lines 20-1 What was n in this partial regression? How was autumn and summer defined? I am quite wary of results involving BDE66 as mentioned above.
We have now removed this part from the manuscript.

Figures in main text: They are quite blurry and hard to read.
We have now improved them.

Figure 2 Define the blue lines in caption.
Ok, done

Figure 3 If trends are significant, include R and p value on plot. If they are not significant, remove the trend line.
We have now updated accordingly this Figure.

Table S4 I am quite surprised about BDE-66 levels. This congener is generally not that abundant in air and it wasn't a major one in commercial formulations. Since it elutes in a region that is quite crowded, I wonder if the peak was mistaken for something else. My hypothesis is reinforced by other places where BDE66 behaves differently than similar congeners (e.g BDE47); for example, in Table S3, the breakthrough behavior of BDE66 is remarkably different from that of BDE47, although admittedly this might have something to do with detection limits.
We recognize that as no internal standard was available for this compound, there are higher uncertainties in congener identification. We have now removed this compound from the manuscript.

Table S8 There is a more recent paper on temporal trends for samples around the Great

Lakes (see Liu et al., / Environment International 92–93 (2016) 442–449) where data for 2005-2013 were used.

Thank you for letting us know about this interesting article. Previous data have now been replaced by these ones.

Figure S12 If trends are significant, include R and p value on plot. If they are not significant, remove the trend line.

We have now updated accordingly this Figure.