Once more, we would like to sincerely thank the reviewers for their precious comments, which, again, improved this manuscript. We have addressed every point below and have indicated the corresponding modifications in a revised version of the manuscript.

Second review for manuscript titled "Are atmospheric PBDE levels declining in Central Europe? Examination of the seasonal variations, gas-particle partitioning and implications for long-range atmospheric transport" by Degrendele et al. (acp-2018-144)
The authors have taken into account all reviewers' questions and comments and have significantly improved the manuscript by providing more information regarding blanks and QA/QC procedures and corrected errors. I think the manuscript can be accepted for publication after the following minor issues are addressed:

P. 1, Line 20, line 28 and elsewhere in the text: Suggest that whenever the authors refer to the PBDE congeners, list the congener numbers from lowest to the highest. It is very strange to give "…found for BDE 100, 99, 153 and 209", why not "…found for BDE 99, 100, 153 and 209"? Also, line 28, "…BDE99 and BDE 47", why not "BDE 47 and 99"? It makes it easier to read.
Thanks, now corrected accordingly.

p. 5 line 22 where did the conversion factor of 1.8 come from? What unit were the atmospheric concentrations of organic carbon given in?
Usually, a conversion factor of 1.4 has been commonly used in aerosol studies. However, we have decided to use 1.8, based on a previous study measuring OC and OM at different US national parks in which the authors suggested that the value of 1.4 was too low for atmosheric research.
The manuscript now reads: „The f_{OM} were calculated from the atmospheric concentrations of organic carbon (available in $\mu g\ m^{-3}$, a conversion factor from organic carbon to OM of 1.8 was used, El-Zanan et al., 2005) which were determined every sixth day. The corresponding weekly averages were used and ranged from 0.07 to 0.98 with an average value of 0.39 ± 0.19.."

p. 6 I presume that the vapor pressures given are at 25 °C. Please state this in the text.
Done accordingly.

Table S8 Should change to Spearman Correlation results.
Done accordingly.

p. 11, line 9 Please specify that the ABL is given as hmix in Table S9.
Thanks, we have now replaced hmix by ABL height in Table S9.

p. 12, last line "Atmospheric boundary layer" was the term used earlier. Better use the same term to be consistent.
Thanks, now corrected accordingly.

P. 20 Figure 1 The blue bars are too light and difficult to read. Please make them darker.
Thanks, now corrected accordingly.

p. 23 Figure 4 I am wondering why the authors did not choose to show BDE 100 and 153, which show statistically significant trends, in this figure instead of BDE 47 and 183 that have no statistically significant trends.

In this Figure 4 as well as in Figure 1, we have chosen to focus on the compounds showing the highest concentrations (i.e. > 80% of Σ_9PBDEs), while the remaining BDEs are presented in Figure S11. Presenting only compounds that show a significant decrease in 2011-2014 in the manuscript could be misleading for the readers.

Minor:
P. 1, Line 29 Usually "accounting for approximately…"
Done accodingly.
P. 3 Line 4 "gas-phase chemicals on …"
Done accodingly.
p. 3 Line 8 "…discarded without further analysis…"
Done accodingly.
p. 5 line 27 spell out above ground level (a.g.l.)
Done accodingly.
p. 5 line 3 and elsewhere : Li et al. <no comma> (2015)
Done accodingly.
p. 7 last line: should read "…LRAT potential of PBDEs and for developing…"
Done accodingly.
p. 10, line 11 …the precipitation rate were found for all PBDEs…
Done accodingly.
p. 11, line 22 missing space between "gaseous" and "concentrations"
Done accodingly.
p. 11, line 26 "On the other hand,…"
Done accodingly.
Table S3 Sample preparation, not Sampling preparation.
Changed accodingly.

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 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 Kp = f(log pL) as the temperature dependence of vapour pressure is also reflected in the log Kp = f(log Koa) 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 gasparticle partitioning.

I agree that adsorption is less significant that absorption, nevertheless, the Junge-Pankow adsorption model was found to predict better than the KOA model the θmeasured in the warm season for the moderately brominated congeners DBE-49, -71, -47, and -66 (Besis et al., 2016). We now have applied the Junge-Pankow model as suggested (input data. c_J = 17.2 Pa cm and aerosol surface S = 5 x 10^{-5} cm^2 cm^{-3}, measured at the site; Shahpoury et al; 2016 ES&T). The model overpredicts partitioning largely (particulate mass fractions 0.70 (0.33-0.94) for BDE28 and > 0.9 for all other congeners (Figure 1 below).
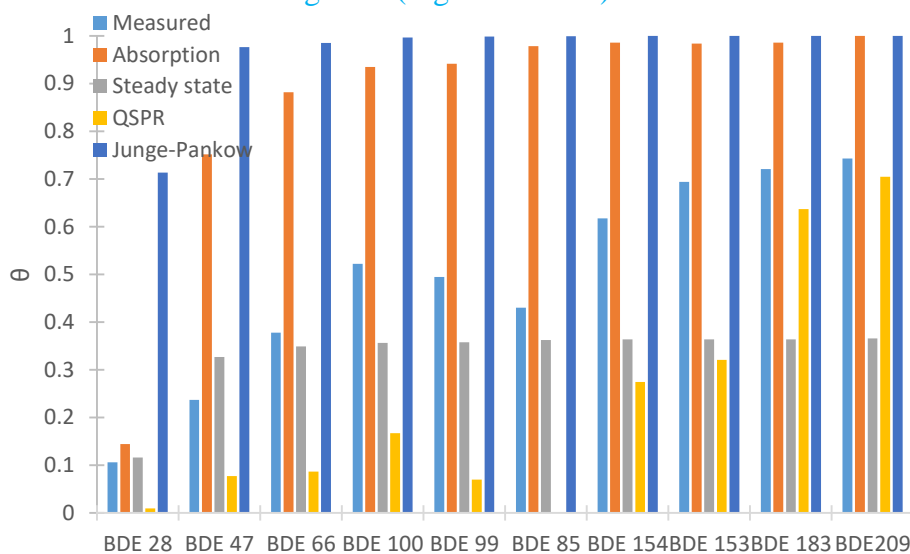

Figure 1: Measured and predicted particulate fraction of all PBDEs investigated for the average conditions at the sampling site.

This result was anticipated, and is similar to previous results (Besis et al., 2017). Such results just confirm the understanding achieved in recent years, that adsorption is less significant than absorption for PBDEs (and other lipophilic semivolatiles), The advancement of understanding gas-particle partitioning is now better phrased in the text (section 2.4).

The manuscript now reads: „K_{OA} model (...) assumes that (...) absorption into particulate organic matter (OM) of the particles determines the distribution process, while other types of molecular interaction (i.e. adsorption to the unspecific surface, to minerals or soot) are negligible (Harner and Bidleman, 1998a).

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 KOA 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.

Thank you very much for indicating this data source. We followed the suggestion and used the $K_{OA}(T)$ estimates of Yang et al., 2018, to predict gas-particle partitioning according to the different models investigated also for BDE209 (Figure 2, below). A large discrepancy to observed values, systematic overestimate of the particulate mass fraction is found for the K_{OA}-model.
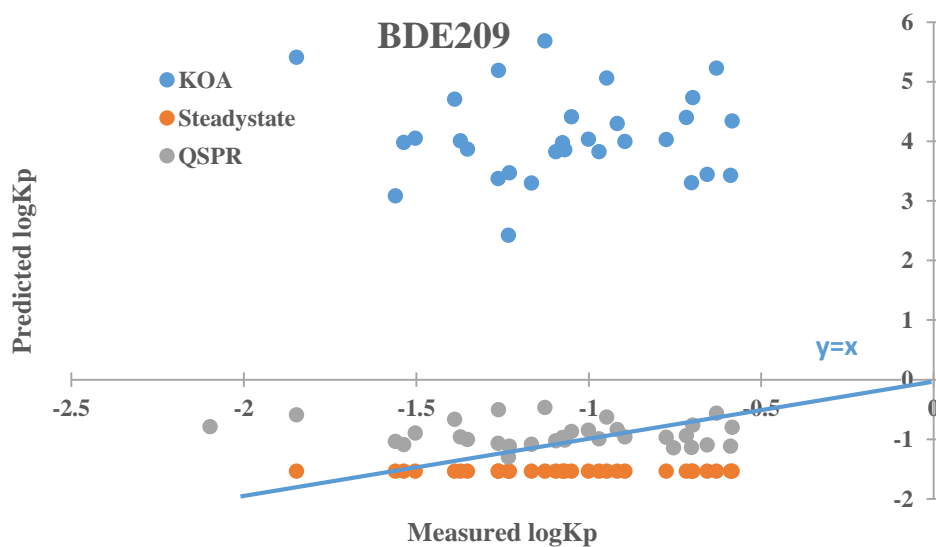

Figure 2: Comparison of measured and predicted logKp of BDE209. The blue line reprersents the 1:1 line

For congeners with experimental $K_{OA}(T)$ data available (Shoeib and Harner, 2002), we tested on the implied uncertainties of estimated $K_{OA}(T)$. For the highest congener most similar to BDE209, i.e. BDE183, an octaBDE, discrepancies of up to two orders of magnitude are suggested (Figure 3, below). The same deviation from the true K_{OA} value can be expected for BDE209.
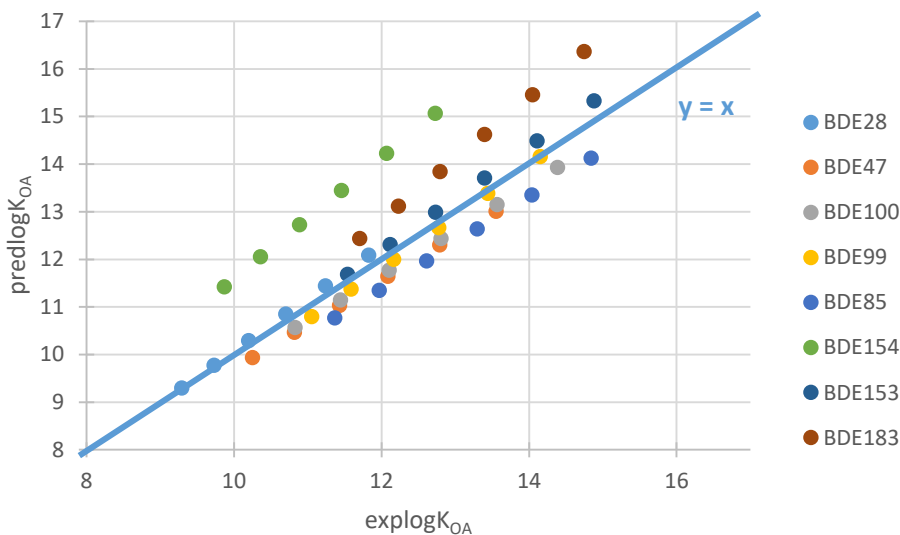
Figure 3: Comparison of logK$_{OA}$ predicted (estimates, (Yang et al., 2018) and measured (exp., Shoeib and Harner, 2002). The results shown are for a temperature range of 253-303 K.

Moreover, the data set of observed BDE209 concentrations in both phases is a particularly small one (32% of the measurements) and is associated with large uncertainties (discussed in section 3.1), and was therefore excluded from this part of the study. Considering this and the large uncertainty of the model input data (K$_{OA}$(T); Fig. 3), we still are not sufficiently confident to include these results in the current article.

P.5. L. 27: the measured fOM value for this site shall be provided.
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 fOM 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 fOM 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?
Thanks. Followed.
The manuscript now reads: „The corresponding weekly averages were used and ranged from 0.07 to 0.98 with an average value of 0.39 ± 0.19.“

Also, please check the value of 0.98, it seems to be very high even for PM from a background site.
We recognize that this value is extremely high for a background site, and this may be due to our choice for the conversion factor of 1.8 from organic carbon to organic matter. For this weekly sample, the f$_{OC}$ was 0.545 (i.e. OC concentration was 3.27 µg/m^3 and PM$_{10}$ concentration was 6 µg/m^3). No changes were done.

Finally, please, correct the "The fOM were derived from…" to "The fOM values were calculated from …".
Done accordingly.

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 (θmeasured) 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.

Done accordingly. We have now expanded the Y-axis to 1.2, such that we can fully see the SD.

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 gasparticle 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.

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. Besis and Samara (2012) is a review article compiling literature data from all over the world and should be cited. I also suggested Besis et al. (2016) since it provides more recent data for European sites not included in the review.

Thanks for clarifying, and sorry for the misunderstanding. We have now added these two references.

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.

This is a misunderstanding. As suggested by reviewer #3, we have now used the opportunity of analyzing the semi-long term trends along with the seasonality using the regression model proposed by Venier et al; (2012). The paragraph preceeding the one mentioned here was presenting these seasonal differences which were statistically significant using the regression model (paragraph in p.13: „Unlike a recent study … ABL height is dominating". No changes were done.

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.

This is a misunderstanding. This comment was related to the seasonality of the measured particulate fraction, which has already been improved in the first revision incorporating the seasonal variations (Figure S3 and related discussion in the manuscript). No changes were done.

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

This is now included (Table S5).

The correct Table is S7. Please unbold the r2 value between θmeas and 1/T for BDE-209 as it not statistically significant.

We apologize for these errors. Table S7 has been changed accordingly.

Additional comments on manuscript v.3

Abstract

☐ Instead of providing only the average θmeasured 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 ≈ spring > summer.

Followed. We have now added a more general description of the seasonal trend of the gas-particle partitioning as well as the standard deviations of the reported particulate fractions for BDE47 and BDE99.

The abstract now reads: „Clear seasonal variations with significantly higher measured particulate fraction (θmeasured) in winter compared to summer was found for all PBDEs except BDE209. For example, while the average θmeasured of BDE47 was 0.53 ± 0.19 in winter, this was only 0.01 ± 0.02 in summer. Similarly, for BDE99, θmeasured was 0.89 ± 0.13 in winter, while it was only 0.12 ± 0.08 in summer."

☐ Photolytic debromination was only assumed, not indicated by the results. Please, rephrase.

Followed.

The abstract now reads: „The results suggest that photolytic debromination … atmosphere"

Equation (5): Please, use capital letters for OA in fom.

Changed accordingly.

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

Changed accordingly.

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

Changed accordingly.

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 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.

We apologize for this error. This has been changed accordingly.

P.7, L.24-33: The authors highlight here the large seasonal variations found for θmeasured 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 (θmeasured) 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)

This is a misunderstanding. Figure 1 shows the complete time series of the experimentally determined particulate mass fraction of the four most abundant PBDE congeners. This is the only figure which shows the time series, while Figure S3 shows seasonally aggregated data. For clarification, we improved the layout. Y-axis expanded in Figure S3, as suggested.

☐ Moreover, the larger seasonal differences found here in comparison to other studies need explanation. Large seasonal differences in θmeas 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, Besis et al. (2016), found θmeas ~25% lower in summer in comparison to winter for a difference in temperature of about 10-15 oC.

The large seasonal differences of the measured particulate fraction of PBDEs found in this study (T is ranging from -6.4 to 23.0 °C for individual samples) are similar to the one reported at the Great Lakes with a similar temperature range (from -9.9 to 23 °C), but higher than those measured in Greece (difference in temperature of 8-13 °C) or in the Arctic (difference in temperature of 18°C).

The manuscript now reads: „The large seasonal differences in the gas-particle partitioning of PBDEs have been previously reported from a rural site in the American Great Lakes area where the differences in the ambient temperatures were similar to this study, about 30 °C (Su et al., 2009). Less seasonal difference in gas-particle partitioning was found in the Arctic or in Greece where the temperature range was lower than 20 °C (Besis et al., 2016; Davie-Martin et al., 2016)"

The following sentence, which conludes on the relevance of the temperature dependence of gas-particle partitioning we removed, as this emphasis is not needed here.

P.8, L.14-15: It is stated that "none of the three model approaches successfully predicted Kp or θ for all individual PBDEs considered". Did the authors examined the seasonality of the predictabilities of the models? As observed in Besis et al. (2016), Θmeasured data were closer to Θpredicted by the KOA model in summertime samples as compared to the wintertime samples.

We also evaluated the efficiency of these models for the summer and winter sample subsets (new Figure S5), and it is evident that none of these models successfully captured the particulate fraction for all PBDEs in a specific season (in Figure S5, the individual dots are not scattered around the 1:1 line).

The manuscript now reads: „As presented in Figures 2 and S4, none of the three model approaches successfully predicted K_p or θ for all individual PBDEs considered, which is also the case when considering only winter or summer samples (Figure S5)."

P.8, L.28-30: This sentence is not accurate. Besis 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.

Sorry about this mistake. We have now changed accordingly the text.

The manuscript now reads: „The only other study test of this model on atmospheric PBDE data did not find an acceptable performance for all PBDEs investigated, although, for BDE209 it predicted better than the K_{OA}-model (Besis et al., 2017)"

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

We are not convinced that adding the correlation between Cp of individual PBDEs and precipitation rate (presented in Section 3.3) also in this section would add clarity, but rather would disturb the reader from the original message (i.e. predicting K_p within one order of magnitude is not sufficiently accurate for characterizing phase-specific removal processes). However, we have now provided an example of this phase-specific removal process (i.e. wet scavenging of particles) and made a reference to the previous section.

The manuscript now reads: „Therefore, these models are not ideal when phase-specific removal processes such as the wet scavenging of particles (see Section 3.3) are to be estimated."

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. θmeasured < 0.2), regardless of the ambient temperature" is unclear. In the present study, only BDE-28 has θmeasured < 0.2 regardless of the ambient T, but does not follow the C-C equation.

This is exactly our point. If we would consider all PBDEs, the results would suggest that BDE28 and BDE209 are influenced by LRAT while the other congeners are influenced by revolatilisation from the surfaces. However, given the important seasonal variations of $\theta_{measured}$ for all PBDEs except BDE28 and BDE209, it is not clear whether the influence of ambient temperature on the gaseous concentrations are due to air-surface exchange rather than revolatilisation from the particles. Therefore, the only valid conclusion that can be taken from this study is that the gaseous BDE28 concentrations were controled by LRAT rather than by air surface exchange.

The manuscript now reads: „Following this, we can only conclude from the present study that the gaseous concentrations of BDE28 were not controlled by air-surface exchange."

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 Cp concentrations for PBDEs in winter, but this does not necessarily mean emission from combustion sources. Please, correct this sentence.

This has been changed accordingly.

The manuscript now reads: „In conclusion, the atmospheric concentrations of individual PBDEs were controlled by deposition processes (wet scavenging), meteorological parameters (ABL height, temperature) and LRAT while the influence of revolatilisation could not be demonstrated."

Conclusions
☐ Please, keep only conclusions that are supported by your results.

Followed: We have now removed the sentence that atmospheric PBDE levels were governed by primary emissions, which was not supported by our 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!

Followed: Now more emphasised in the discussion of the main results part of the manuscript, see Section 3.3 and previous comment.

☐ 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.

Misunderstanding: The critique was not on the passive sampling design, but rather on the interpretation of results for semi-volatile organic compounds' levels obtained from such passive devices. In fact, many studies interpreted the summer maxima organics concentrations based

on passive techniques as the proof that their atmospheric concentrations are dominated by air-surface exchange, regardless of the shift in gas-particle partitioning.

The manuscript now reads: „Therefore, the interpretation of the seasonal variations of PBDEs from such studies should be done in a cautious manner, distinguishing whether the increased concentrations are due to gas-particle partitioning shift or to increased secondary emissions.“

☐ Please, give again the names of the "available models".

Changed accordingly.

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/m3. These should be referred as method LOQs. I would suggest the authors providing the iLOQ for each compound in pg/μL.

Followed: We have now provided all iLOQs in pg/ μL.

☐ What is the usefulness of calculating LOQblanks in pg/m3 since field blanks are not subjected to air sampling?

Followed: LOQ_{blanks} now presented n pg/ μL throughout.

☐ 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.

Sure. LOQs were indeed determined as the maximum between iLOQs and LOQ_{blanks}. For clarification, we have now replaced the 0 values for LOQ_{blanks} by ND.