

We would like to thank the reviewers for their thoughtful reading, comments and questions, which considerably helped to improve this manuscript. We have addressed all comments below and have indicated the corresponding modifications in the revised version of the manuscript.

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,  $K_p$ , values with those determined by three predictive models, the KOA model, a steady state model proposed in literature, and a regression model based on the quantitative structure-property relationship (QSPR) also proposed by other investigators. The apparent halving times ( $t_{1/2}$ ) 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  $\mu_{measured}$ .

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 ( $P_L$ )-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 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).“*

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  $f_{OM}$  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  $0.39 \pm 0.19$ .“*

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).  $\hat{A}$  '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).

$\hat{A}$  '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 gas and particle-phase concentrations of BDE209 provided in Table S5 (0.513 and 0.257  $\mu\text{g m}^{-3}$ , respectively) seem to be in discrepancy with the average measured particulate fraction ( $f_{\text{measured}}$ ) 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.

$\hat{A}$  'c P.7, L. 10: Melymuk et al., 2016b is not in the reference list.

We do not anymore cite this article.

$\hat{A}$  '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

âˆA ´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).

âˆA ´c P.8. L.21:  $p > 0.05$  shall be  $p < 0.05$  here.

Now corrected.

âˆA ´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. „*

âˆA ´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

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

Changed accordingly.

âA´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  $\ln C_{p,i}$  and  $1/T$ .

This is now included (Table S5).

âA´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 âA´c P.10. L. 12: Please change “seasonal” to “temporal”.

Changed accordingly.

âA´c It would be interesting if the authors showed and discussed the logKp-logPL<sub>10</sub> 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

âA´c The statement “ $C_{0,i}$  is the theoretical concentrations of individual PBDE measured at  $t_0$  (i.e. the end date of PBDE production)” is not clear. The authors have to further explain if and how they estimated the  $\ln C_{0,i}$  data used in Eq. (8) and if these data are representative for Central Europe.

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

âA´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.

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

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 âA´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”.



*The manuscript now includes: “ The PBDE concentrations presented here were blank corrected by subtracting the average of the field blanks on an annual basis, separately for GFFs and PUFs.”*

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  $\mu\text{m}$  and the QFF has a pore size of 2.2  $\mu\text{m}$ , 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  $\text{m}^3/\text{h}$ , 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  $\mu\text{m}$ . 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<sub>10</sub> 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 subtracted, which was inappropriate. We have now updated the calculation by firstly performing field blank subtraction 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  $C_g$  or  $C_p$  or  $C_{tot}$  would be linearly correlated with  $1/T$  or any other meteorological parameters? Thermodynamically speaking, there should be a linear relationship between natural-log transformed  $C_g$  ( $\ln C_g$ ) 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  $C_g$  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  $\ln C$  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  $\ln C$  vs.  $1/T$ .

P. 9 Line 3-5 The authors suggests that there are other processes which controls  $C_g$  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  $\ln C_g$  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  $h_{mix}$  in Table S5) shows strong correlations with  $C_p$  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  $f_{OM}$  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  $f_{OM}$  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  $0.39 \pm 0.19$ .“*

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 KOA 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 related 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 collected, 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  $\mu\text{m}$ , which is quite high. For example, IADN employs QFF with a cutoff of 0.3  $\mu\text{m}$ . It's quite plausible that fine particles slip through the filter and end up 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  $\mu\text{m}$  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<sub>10</sub> 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 subtraction was performed, which was inappropriate. We have now updated the calculation by firstly performing field blank subtraction 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 K<sub>p</sub> would be smaller than expected. In this scenario, rather than the Koa based model overestimating the K<sub>p</sub>, it's the measured K<sub>p</sub> 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 measured K<sub>p</sub>'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 preferred 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.  $<1 \mu m$ , 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 m<sup>3</sup> is a representative number. In line 11, the authors report that the sampling volume ranged from 4015 m<sup>3</sup> to 5864 m<sup>3</sup> for samples collected in 2015. The average is closer to 5000 m<sup>3</sup>.

The fictive volume of 5264 m<sup>3</sup> is a representative number as it is the average of all volumes for single samples (the median is 5344 m<sup>3</sup>). Volumes lower than 5000 m<sup>3</sup> 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.

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

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**Abstract.** This study presents multi-year monitoring data on atmospheric polybrominated diphenyl ethers (PBDEs) in Central Europe. Air was sampled on a weekly basis at a background site in the central Czech Republic from 2011 to 2014 (N=114).  $\Sigma_8$ PBDEs (without BDE209) total (gas and particulate) concentrations ranged from 0.084 to 6.08 pg m<sup>-3</sup>, while BDE209 was at 0.05-5.01 pg m<sup>-3</sup>. BDE47, BDE99 and BDE183 were the major contributors to  $\Sigma_8$ PBDEs.

Overall, the atmospheric concentrations of individual PBDEs were controlled by primary emissions, deposition processes and long-range atmospheric transport. Regarding gas-particle partitioning, with the exception of BDE28 (gaseous) and BDE209 (particulate), all congeners were consistently detected in both phases and clear seasonal variations were observed. For example, while the average measured particulate fraction ( $\theta_{\text{measured}}$ ) of BDE47 was 0.53 in winter, this was only 0.01 in summer. Similarly, for BDE99,  $\theta_{\text{measured}}$  was 0.89 in winter, while it was only 0.12 in summer. The observed gas-particle partitioning coefficient ( $K_p$ , in m<sup>3</sup>  $\mu\text{g}^{-1}$ ) was compared with three model predictions, assuming equilibrium or steady-state. None of the models could provide a satisfactory prediction of the partitioning, suggesting the need for a universally applicable model.

20 Statistically significant decreases of the atmospheric concentrations during 2011-2014 were found for BDE100, 99, 153 and 209. Estimated apparent atmospheric halving times for these congeners were ranging from 2.8 (BDE209) to 4.8 (BDE153) years. **The results indicated that photolytic debromination to lower brominated congeners may significantly influence PBDE concentration levels and patterns in the atmosphere.**

## 1 Introduction

25 Since the late 1960s, flame retardants such as polybrominated diphenyl ethers (PBDEs) have been used in large quantities in various consumer products. Such products include: plastics, textiles, electronics and cars (Besis and Samara, 2012). Three main commercial formulations were produced: Penta-BDE, Octa-BDE and Deca-BDE. The major congeners in each formulation were BDE99 and BDE47 for the Penta mixture, BDE183 for the Octa mixture and BDE209 for the Deca mixture (La Guardia et al., 2006). The Deca mixture has been the most widely used, accounting approximately for 83% of the total



PBDEs production worldwide (Besis and Samara, 2012). PBDEs are widespread contaminants as they are persistent, bioaccumulative, toxic and prone to long-range atmospheric transport (LRAT). Therefore, the use and marketing of all PBDE technical mixtures was banned in the European Union by 2008 (Besis and Samara, 2012). These mixtures have been included in the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP, 2009).

5 Similar to other semi-volatile organic compounds (SOCs), once PBDEs enter the air, they partition between the gaseous and the particulate phase. This partitioning is controlled by the physicochemical properties of PBDEs, meteorological parameters (i.e. temperature and relative humidity) and the abundance and composition of suspended particulate matter (Lohmann and Lammel, 2004; Pankow, 1987). This partitioning will significantly affect their removal pathways (i.e. wet and dry deposition, photolysis, reaction with OH radicals) which are different for gases and particles (Wania et al., 1998) and therefore their  
10 mobility and their potential for LRAT (Bidleman et al., 1986). Knowledge about this partitioning is deficient, but is crucial to predict the environmental fate of PBDEs. It is expected, due to their physico-chemical properties, that lower brominated congeners such as BDE-28 are mainly present in the gaseous phase while higher brominated congeners such as BDE-209 are >99% present in the particulate phase (Harner and Shoeib, 2002; ter Schure et al., 2004). However, results from individual studies are contradictory on a global scale. For example, some studies have found that the particulate fraction of PBDEs was  
15 small for most PBDEs investigated (e.g. <20%, Iacovidou et al., 2009). But other studies reported that the particulate fraction significantly increased with increasing degree of bromination for the same temperature (Davie-Martin et al., 2016; Möller et al., 2011; Strandberg et al., 2001; Su et al., 2009). Recently, Li and co-workers developed a new gas-particle partitioning theoretical model for PBDEs based on the assumption that the equilibrium between both phases is not reached due to disturbances caused by wet and dry deposition (Li et al., 2015), but the universal applicability of this model still remains to be  
20 shown (Besis et al., 2017).

About a decade after the European ban on PBDEs, it is still unclear whether global atmospheric concentrations are significantly declining or not. This is due to the limited amount of ambient air monitoring data, particularly in Central Europe. In order to understand whether primary or secondary sources are controlling the atmospheric concentrations of PBDEs, and hence to guide future control strategies, more data are needed to fill this gap.

25 The aim of this study is to provide multi-year monitoring data on atmospheric PBDEs at a background site in Central Europe and to assess whether the PBDEs atmospheric concentrations are significantly decreasing or not in the time span of four years. In particular, the seasonal and semi-long-term variations as well as the gas-particle partitioning of PBDEs were investigated.

## 2 Methodology

### 2.1 Air sampling

30 Air was sampled at the Košetice observatory (49°34'24''N, 15°04'49''E), which is an established background site of the European Monitoring and Evaluation Programme (EMEP) network (Holoubek et al., 2007). The site is located, in an agricultural region, centrally in the Czech Republic. From January 2011 to December 2014, a high-volume air sampler (Digitel

DH77 with PM<sub>10</sub> pre-separator) was used to collect weekly air samples. The sampler addressed the inhalable size fraction, PM<sub>10</sub>. PBDEs are mostly sorbed to fine and sub-micrometer sized particles (Okonski et al., 2014; Besis et al., 2017). The sample volume was 5264 m<sup>3</sup> on average ( $\approx 31.3 \text{ m}^3 \text{ h}^{-1}$ , 7-day sampling duration). Particles were collected on quartz fiber filters (QFFs, QM-A, 150 mm, Whatman, UK) and gas-phase on polyurethane foam (PUF, two in series, T3037, 110 x 50 mm, 0.030 g cm<sup>-3</sup>, Molitan a.s., Czech Republic). PUFs were pre-cleaned via Soxhlet extraction with acetone and dichloromethane for 8 h each. PBDEs analysis was performed on all weekly samples in 2011 and on half of the available weekly samples for the remaining years (Table S1 in the Supplement). Several problems (e.g. sudden change in the flow rate, electrical power shutdown) occurred during the collection and the corresponding 13 samples were discarded for further analysis (Table S1). After sampling, all filters and PUFs were wrapped in aluminium foil, sealed in plastic bags and stored at -18°C until analysis.

10

## 2.2 Sample preparation and analysis

Samples were extracted with dichloromethane by means of an automated extraction system (Büchi B-811, Switzerland). Mass-labelled internal standards (<sup>13</sup>C labelled BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209, Wellington Laboratories, Canada, LGC, UK) were added to each sample prior to extraction. The clean-up and fractionation differed between samples collected prior and those after 2013. Samples from 2011 – 2012 were prepared as follows: the concentrated extracts underwent clean-up using a sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) modified silica column, eluted with 40 mL DCM/*n*-hexane mixture (1:1). Fractionation was achieved in a disposable Pasteur pipette micro column containing (from bottom to top): 50 mg silica, 70 mg charcoal/silica (1:40) and 50 mg of silica (Darco G60 charcoal). The column was prewashed with 5 mL of toluene, followed by 5 mL of DCM/cyclohexane mixture (30%), then the sample was loaded and eluted with 9 mL DCM/cyclohexane mixture (30%) in fraction 1 and 40 mL of toluene in fraction 2. The first fraction was used for PBDE analysis and was concentrated to the final volume of 50  $\mu\text{L}$  and then transferred into an insert in a vial. Samples from 2013 – 2014 were prepared as follows: the clean-up column was achieved using a multi-layer silica column (KOH silica, H<sub>2</sub>SO<sub>4</sub> silica, Na<sub>2</sub>SO<sub>4</sub>, prewashed with *n*-hexane), analytes were eluted with 120 mL of *n*-hexane. Fractionation was performed on a carbon column packed with 50 mg of AX-21 active carbon dispersed on 1 g of Celite 545. After elution with 18 mL of a mixture of cyclohexane-DCM-methanol (2:2:1, v/v) (fraction 1, part of ortho PBDEs) and 6.5 mL of toluene (fraction2 non-ortho PBDEs), fraction 3 eluted with 80 mL of toluene applied on a column with reverse flow was collected. After instrumental analyses of other organic compounds, fraction 1 and 2 were combined, transferred to an insert in a vial, spiked with recovery standard (<sup>13</sup>C BDE-77 and 138) and analysed for PBDEs.

Nine PBDEs (BDE-28, BDE-47, BDE-100, BDE-99, BDE-85, BDE-154, BDE-153, BDE-183 and BDE-209) were analysed using high resolution on an Agilent 7890A GC (Agilent, USA) equipped with a 15 m  $\times$  0.25 mm  $\times$  0.10  $\mu\text{m}$  DB-5 column (Agilent, J&W, USA) (samples from 2011) or a 15 m  $\times$  0.25 mm  $\times$  0.10  $\mu\text{m}$  RTX-1614 column (Restek, USA) (samples since 2012 onwards) coupled to an AutoSpec Premier MS (Waters, Micromass, UK). The MS was operated in EI+ at the resolution of >10000. The temperature programme was 80°C (1 min hold), then 20°C min<sup>-1</sup> to 250°C, followed by 1.5°C min<sup>-1</sup> to 260°C

and 25°C min<sup>-1</sup> to 320°C (4.5 min hold). The injection volume was 3 µL in splitless mode at 280°C, with He used as a carrier gas at constant flow of 1 mL min<sup>-1</sup>. The instrumental limits of quantification (iLOQs) were determined from calibration curves or from individual sample chromatograms corresponding to a signal-to-noise ratio > 9.

### 2.3 QA-QC

5 Eleven field blanks and eleven laboratory blanks were analysed as per samples. Except for BDE-209, blank levels of individual analytes were below detection or otherwise low (on average <5% of sample mass for detected compounds), suggesting minor contamination during sampling, transport and analysis. In the case of BDE-209, high blank levels were found in some cases (on average 10.1% and 35.1% of sample mass for GFF and PUF, respectively). The higher blanks are probably caused by elevated background concentrations of BDE-209, this may be related to the microabrasion of particles from plastic material  
10 containing BDE-209 (Webster et al., 2009). The PBDE concentrations presented here were blank corrected by subtracting the average of the field blanks **on an annual basis**, separately for GFFs and PUFs. The PBDEs were quantified using isotope dilution and thus recovery-adjusted. Mean PBDE recoveries (± standard deviation) ranged from 60.9% for BDE183 to 149.9% for BDE209 with an average value of 92.7%. Limits of quantifications (LOQs) were determined as the maximum of the iLOQs and the average of the field blanks plus three times their standard deviations. LOQs ranged from 2.09E-05 to 1.04 pg m<sup>-3</sup>  
15 (Table S2). **The different methods of 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.**

### 2.4 Modelling of gas-particle partitioning

Partitioning of organic compounds such as PBDEs between the gas and particle phases is often described using the gas-particle partition coefficient,  $K_p$  (in m<sup>3</sup> µg<sup>-1</sup>) defined by Harner and Bidleman (1998) as:

$$20 \quad K_p = (C_p / C_{TSP}) / C_g \quad (1)$$

where  $C_p$  and  $C_g$  are the concentrations of individual PBDEs (in pg m<sup>-3</sup>) in the particulate and gaseous phases, respectively and  $C_{TSP}$  is the concentration of the total suspended particles (TSP) in the air (in µg m<sup>-3</sup>).

Accurate knowledge of  $K_p$  is crucial for modelling the fate of PBDEs in the environment. In this study, we compared the experimental  $K_p$  values with those determined by three predictive models. For comparison, we considered only cases where  
25 individual PBDEs were detected in both the gas and the particle phase. The first approach, also known as the  $K_{OA}$  model, predicts  $K_p$  based on the octanol-air partition coefficient ( $K_{OA}$ ). It implicitly assumes that equilibrium has been reached between the two phases and that absorption into particulate organic matter (OM) of the particles determines the distribution process, while other types of molecular interaction (i.e. adsorption to minerals or soot) are neglected (Harner and Bidleman, 1998a). Then, assuming that the activity coefficient of the absorbing compound and its molecular weight is the same in octanol and  
30 organic matter,  $K_p$  can be defined as (Harner and Bidleman, 1998b):

$$\log K_{p, \text{abs}} = \log K_{OA} + \log f_{OM} - 11.91 \quad (2)$$

where the subscript e,abs in  $K_p$  highlights the equilibrium assumption of this approach and the fact that it considers only absorptive contributions and  $f_{OM}$  is the fraction of organic matter phase on particles.

The second approach used is the steady state model proposed by Li et al., (2015) in which  $K_p$  is defined as:

$$\log K_{ps, ss} = \log K_{pe, abs} + \log \alpha \quad (3)$$

5 where  $\log \alpha$  represents the non-equilibrium term due to disturbances from wet and dry deposition of particles and is defined as:

$$\log \alpha = -\log(1 + G/C) \quad (4)$$

$$\text{where } C = 5 \text{ and } G = 2.09 \times 10^{-10} f_{om} K_{OA} \quad (5)$$

Finally, the last approach is based on a quantitative structure-property relationship (QSPR) model recently proposed by Wei  
10 et al., (2017). To fit this regression model, several properties were calculated quantum mechanically for each PBDE molecule in the gas phase. The regression fitting was done for a dataset where temperature varied between 10 and 32 °C. This model also implicitly assumes that equilibrium exists between PBDEs in the gas and particle phase. In this approach,  $\log K_p$  is defined as:

$$\log K_{pe, QSPR} = 0.026 V - 0.030 T - 0.858 qC^- + 3.864 qH^+ + 0.002 \quad (6)$$

15 where  $V$  is the molecular volume,  $T$  is the ambient temperature,  $qC^-$  is the most negative charge on a carbon atom and  $qH^+$  is the most positive charge on a hydrogen atom (Wei et al; 2017). These were Mulliken charges calculated with density functional theory at the B3LYP/6-31G(d,p) level.

Equations (1-6), can be used to predict the particulate fractions ( $\theta_{pr}$ ) using:

$$\theta_{pr} = K_p C_{TSP} / (1 + K_p C_{TSP}) \quad (7)$$

20 Given that most PBDEs are sorbed to fine particles (Okonski et al., 2014), the concentration of particles smaller than 10  $\mu\text{m}$  ( $\text{PM}_{10}$ ) instead of  $C_{TSP}$  and the measured  $f_{OM}$  at this site were used (data provided by the Czech Hydrometeorological Institute, <http://www.chmi.cz>). 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 ranged from 0.07 to 0.98 with an average value of  $0.39 \pm 0.19$ . The temperature dependence of  $K_{OA}$  for all PBDEs, except BDE209, was determined from published relationships, based on direct  
25 measurements (Harner and Shoeib, 2002).

## 2.5 Meteorological data and air mass origin

Continuous meteorological data, 2-m agl temperature, relative humidity (RH), 2-m agl wind speed and direction were provided by the observatory (Czech Hydrometeorological Institute).

The influence of LRAT was assessed by evaluating the backward trajectories of specific samples. The Lagrangian particle  
30 dispersion model FLEXPART (Stohl et al., 2005) was used to identify air mass origins of the ten samples showing the highest and the lowest PBDE concentrations from our dataset. The meteorological data (0.5° and 3 hours resolution, 91/137 vertical levels) were retrieved from the ECMWF database (<http://www.ecmwf.int>). For every weekly sample investigated, 100,000 particles were released between 0 and 200 m agl and were followed 5 days backward in time. Additional details can be found elsewhere (Mulder et al., 2015).

### 3 Results

#### 3.1 Breakthrough and sampling artefacts

Breakthrough is an issue of concern as relatively high sample volumes (i.e.  $>1000\text{ m}^3$ ) are usually used to quantify trace contaminants such as PBDEs. Breakthrough of gas-phase PBDEs was evaluated by quantifying separately each of the two PUFs placed in series for all the weekly air samples collected in 2012 ( $N = 26$ , sampled volume =  $4015\text{--}5864\text{ m}^3$ ). This covered a large range of meteorological conditions and the results are considered applicable to the other years. The results of the breakthrough experiments are summarized in Table S5 and Figure S1. On average, less than 6% of individual PBDEs was found on the lower PUF, except for BDE183 and BDE209 (Table S5). In the cases of BDE183 and BDE209, on average 24.6% and 82.0% were found on the lower PUF, respectively. Given that these compounds are not volatile (i.e. vapor pressure of  $3.30 \cdot 10^{-6}$  and  $1.43 \cdot 10^{-8}$  Pa, respectively, (Yue and Li, 2013)), it is unlikely that the high fractions found on the lower PUFs would be caused by breakthrough. Instead, this could have been caused by sampling artefacts or by contamination. Blowoff, which is the loss of SOCs from the filter by evaporation, can disproportionately increase the SOC PUF masses (Melymuk et al., 2014). This effect has already been reported for PBDEs (Allen et al., 2007; Besis and Samara, 2012). However, despite the large volume collected which could enhance this sampling artefact, we consider it unlikely. This process should affect all PBDEs in the same manner but in many cases, only BDE209 was found only in the lower PUF (Table S5). Similarly, a physical breakthrough of fine particles is possible, but this could not explain the fact that 100% of BDE183 or BDE209 were found on the lower PUF. We suggest that the unexpected amounts found in the lower PUFs for these two congeners are the result of contamination from sampling or sample preparation. Indeed, it is unclear whether some flame retardants (likely the Deca mixture) have been used in some electronic and plastic parts present within the air sampler or even within the PUF itself, which was characterized by high field blank levels for BDE209 (see Sect. 2.3). Contamination within the laboratory (i.e. microabrasion of particles from plastic material containing BDE209) is also possible. We should keep in mind that the analysis of BDE209 is more challenging (Law et al., 2008). 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, with the exception of BDE209.

#### 3.2 PBDE concentration levels

Except for BDE85, all congeners were detected in  $>89\%$  of the samples (Table S6), this highlights their persistency in the environment. In this study, the total (gas and particles) concentrations of  $\Sigma_8\text{PBDEs}$  (all congeners except BDE209) ranged from  $0.0843$  to  $6.08\text{ pg m}^{-3}$  with an average value of  $0.524\text{ pg m}^{-3}$ . BDE209 had a lower average concentration of  $0.457\text{ pg m}^{-3}$  (ranging from  $<\text{LOQ}$  to  $4.72\text{ pg m}^{-3}$ ) (Table S6). The PBDE concentrations reported here were similar to those observed for other European background or remote sites (Besis et al., 2017; Degrendele et al., 2016; Iacovidou et al., 2009), which are

usually lower than  $5 \text{ pg m}^{-3}$  (Lee et al., 2004). These background levels are lower than those previously reported for urban sites (Moeckel et al., 2010; Okonski et al., 2014; Salamova and Hites, 2011).

Besides BDE209, which on average contributed to 46.6% of all PBDEs measured, BDE47, 99 and 183 showed the highest concentrations. On average these accounted for 32.5%, 25.2% and 14.6% of  $\Sigma_8$ PBDEs, respectively. As observed in Figure S2, the PBDE profile differed between the two atmospheric phases with the light congeners having a larger contribution to  $\Sigma_8$ PBDEs in the gaseous phase compared to the particulate phase. This PBDE profile, with BDE209 being the prevalent congener, is typical for European environments (Besis et al., 2017; Besis and Samara, 2012; Okonski et al., 2014). This contrasts with North America where BDE47 and BDE99 usually dominate the BDE levels (Besis and Samara, 2012; Liu et al., 2016; Ma et al., 2013; Shunthirasingham et al., 2018). Given that the technical Deca mixture represents 83% of the global PBDEs market (in 2001; Besis and Samara, 2012), these distributions suggest that either lower congeners are more prone to volatilisation from products or from other environmental media compared to the higher brominated congeners or that photolytic degradation of BDE209 to lower brominated BDEs is occurring (Luo et al., 2014). Indeed, an increase of lower brominated congeners (Hexa-through Nona) was observed under photolysis of BDE209 in solvents, sediments, soils and sands (Eriksson et al., 2004; Söderström et al., 2004). However, photolysis is not specific to BDE209, but relevant for all congeners, such as e.g., BDE99 (formation of BDE47; Fang et al., 2008; Sanchez-Prado et al., 2005).

### 3.3 Gas-particle partitioning in air samples

Results of PBDE gas-particle partitioning from individual studies at a global scale are contradictory. For example, some studies have found that most PBDEs have small particulate fractions (Besis et al., 2017; Iacovidou et al., 2009; Mandalakis et al., 2009; Mulder et al., 2015) while other studies found that, for a specific temperature, the particulate fraction significantly increased with increasing degree of bromination (Chen et al., 2006; Davie-Martin et al., 2016; Möller et al., 2011; Strandberg et al., 2001). In this study, with the exception of BDE28 and BDE209, which were detected in about half of the samples only in one phase (Table S6), the remaining congeners were significantly detected in both phases. The particulate fraction ( $\theta_{\text{measured}}$ ) significantly increased with the degree of bromination (Figure S3). For example, for BDE28, the average  $\theta_{\text{measured}}$  was 0.11, while it was 0.24 for BDE47, 0.49 for BDE99, 0.62 for BDE154 and 0.72 for BDE183 (Figure S3). This is consistent with previous studies (Davie-Martin et al., 2016; Strandberg et al., 2001). However, it is important to note that large seasonal variations were observed (Figures 1 and S3). Indeed, while  $\theta_{\text{measured}}$  of BDE47 was on average 0.53 in winter, this was only 0.01 in summer. Similarly, for BDE99,  $\theta_{\text{measured}}$  was 0.89 and 0.12 in winter and summer, respectively. Statistically significant ( $p < 0.05$ ) correlations between  $\theta_{\text{measured}}$  or  $\log K_p$  and  $1/T$  was found for all individual congeners investigated, except BDE209 (Table S7). This important influence of ambient temperature on the gas-particle partitioning of PBDEs have been previously reported but to a lower extent than in the present study (Davie-Martin et al., 2016; Su et al., 2009). This finding suggests that the influence of ambient temperature on the gas-particle partitioning must be taken into account when both considering the LRAT potential of PBDEs or developing environmental models (independent of spatial scale).

In the case of BDE209, the reported particulate fractions may be associated with uncertainties (see Sect. 3.1). This congener was found in about half of the samples only in the particulate phase and the average  $\theta_{\text{measured}}$  was 0.72. The influence of ambient temperature on  $\theta_{\text{measured}}$  or  $\log K_p$  of BDE209 was different than for the other congeners (Table S7). Previously reported particulate fractions for this compound ranged between extreme values (i.e.  $\theta = 0-1$ ) (Cetin and Odabasi, 2007), though some studies reported it mainly in the particulate phase (Cetin and Odabasi, 2008; Li et al., 2016; Ma et al., 2013; Strandberg et al., 2001; Su et al., 2009), and others mainly in the gas phase (Agrell et al., 2004; and references within Li et al., 2016). Li et al., (2016) recently reported on BDE209 levels found on a global scale and also noted the large range of particulate fractions found.

### 10 3.4 Modelling of gas-particle partitioning

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).

As presented in Figures 2 and S4, none of the three model approaches successfully predicted  $K_p$  or  $\theta$  for all individual PBDEs considered. The  $K_{OA}$ -model generally captured the overall trend regarding temporal variations of gas-particle partitioning (similar slope as the 1:1 line in Fig 2) but, with the exception of BDE28, consistently overestimated  $K_p$  by 1-2 orders of magnitude. This results in an important overestimation of the particulate fraction as this model predicted that the majority of PBDEs would be mostly present in the particulate phase ( $\theta_{\text{predicted}}$  often  $> 0.9$ , Figure S7). This is in clear disagreement with our observations. Only for BDE28, this model provided satisfactory results. This overestimation of  $K_p$  by the  $K_{OA}$ -model has been also previously reported for different sites in the Mediterranean and China (Besis et al., 2017; Cetin and Odabasi, 2008; Chen et al., 2006).

Similarly to the  $K_{OA}$ -model, the estimations provided by the steady state approach were only acceptable for BDE28. For the other congeners, this model consistently over- and under-predicted  $K_p$  by 1-2 orders of magnitude depending on the compound and season investigated. This model tends to predict that these PBDEs will be within the maximum partition domain (Li et al., 2015) for which  $\log K_p$  is constant with a value of -1.53, regardless of the ambient temperature (Figure 2). This model predicted that the maximum particulate mass fraction for all PBDEs would be  $\approx 0.6$ , given the conditions at the sampling site, which is in disagreement with the observed seasonal variations of this study (discussed above). The only other study testing this model to atmospheric PBDE data did not find an acceptable performance for all PBDEs investigated, though it performed generally better than the  $K_{OA}$ -model (Besis et al., 2017).

The QSPR model generally tends to underestimate  $K_p$  for all compounds studied, except for BDE153 and 183 for which satisfactory predictions were found (Figure 2). For example, for BDE28, this model predicts that at most 7% will be present on particles while in reality, cases with  $>20\%$  on particles were often found for cold temperatures (Figure S4). We note that this regression model has been fitted to data within a limited temperature range (10-32 °C), therefore attempts to extrapolate

outside of this range (in this study, the average weekly temperatures were -6.4 to 23.0 °C) may not be appropriate. However, even within this range, a severe underestimation is seen. We suggest that the complex molecular interactions involved in the partitioning processes cannot be fully captured based on a limited selection of gas phase atomic charges only. For a truly universal regression model, calculations of the interactions between PBDEs and different particle matrices would be required.

5 As we have seen, none of the models are able to predict the partitioning of PBDEs in a satisfactory way. Though, while considering the average conditions for this study, the overall tendency of predicting  $K_p$  or  $\theta$  using the steady state or the QSPR models were higher than those from the  $K_{OA}$ -model (Figure S5), we do not recommend the use of these models given that the very pronounced seasonal variations observed were not captured. Moreover, we would like to reiterate that though in most cases, these two models predicted  $K_p$  within one order of magnitude of the observed value, this can still result in highly

10 inaccurate values of  $\theta$  (Figure S6). Therefore, these models are not ideal when phase-specific removal processes are to be estimated.

Addressing unrealistic implicit assumptions of these models is obviously crucial for the understanding of these discrepancies. The  $K_{OA}$ -model represents absorption in octanol and therefore does not exactly reflect the true process of adsorption on aerosols (a process that must precede any absorption). We highlight a study by Ding et al., (2014) which investigated the adsorption of

15 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

20 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 S7). 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

25 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. Furthermore, octanol is not necessarily the perfect surrogate to describe absorption in particulate OM; better results for prediction of  $\theta$  of PAHs were achieved when absorption in octanol was replaced by absorption in two particulate OM phases, using dimethyl sulfoxide and polyurethane, respectively, as the surrogates in a polyparameter linear free energy relationships model (Shahpoury et al., 2016).

30 Regarding the steady state approach, our results tend to support the conceptual idea behind the model, i.e. that equilibrium between the gaseous and particulate phases is not reached beyond a certain  $\log K_{OA}$  (11.5 suggested by Li et al., (2015)). Indeed, we observed a distinctly different behaviour in the gas-particle partitioning for PBDEs with  $\log K_{OA} < 11$  within the environmental conditions observed (i.e. BDE28) and for all other PBDEs with  $\log K_{OA} > 11$  (Figure 3). Taking into account that the steady state-model considers BDE28 to be within equilibrium (Li et al., 2015) and that the equilibrium  $K_{OA}$ -model



provided satisfactory results only for BDE28, our results tend to suggest that other PBDEs are not within  $K_{OA}$ -predicted equilibrium but instead a different equilibrium or steady state. However, it is evident from Figure 2 that the considerations taken within the steady state model are inadequate to correctly characterize the gas-particle partitioning of PBDEs. Li and co-workers (2015) suggested that this deviation from equilibrium is due to the influence of wet and dry deposition. 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). Though we recognize that wet and dry deposition may increase the relative presence of PBDEs in the gas phase, we do not consider this to be the major mechanism resulting in the steady state of most PBDEs for two reasons.

Firstly, we note that because rain scavenging is more efficient for particles than gases (Wania et al., 1998), samples associated with more intense precipitation are likely to have a lower particulate fraction. This overall trend was observed in this study as statistically significant ( $p < 0.05$ ) correlations between  $\theta_{\text{measured}}$  and the precipitation rate were present for all PBDEs, with only the exception of BDE85 and BDE209 (Table S8). However, the sample with the highest precipitation rate (i.e. 112 mm) had a higher particulate fractions than the following sample which had almost no rain (i.e. 0.4 mm) and this was observed also for other subsequent samples. Therefore, we do not consider wet deposition (nor dry deposition) to be the factor governing the equilibrium (or absence it) of PBDEs. Secondly, this concept should not be exclusive to PBDEs but should also be valid for other SOCs such as benzo(a)pyrene, a high molecular weight polycyclic aromatic hydrocarbon (PAH) with a  $\log K_{OA}$  of 11.6 at 25°C. This compound is generally found only in the particulate phase (Shahpoury et al., 2015) with only limited amount in the gaseous phase. It is therefore unclear why disturbances due to wet and dry deposition should be more pronounced for PBDEs than PAHs. As previously suggested by Cetin and Odabasi, we consider that the higher presence of PBDEs in the gas phase (compared to that expected based on  $K_{OA}$ ), is due to their departure from equilibrium partitioning and that the relaxation to equilibrium is slower for compounds with higher  $\log K_{OA}$  (Cetin and Odabasi, 2008).

To look more widely at processes that could cause departure from the  $K_{OA}$  predicted equilibrium, we should also recognize that there are other factors, beyond the thermodynamic stability of PBDEs in the particle phase, which could also influence the particulate fraction. We cannot assume the lifetime of PBDEs in the particle phase is identical to the lifetime in the gas phase. If the difference between these two lifetimes becomes significant, we would expect a shift from the  $K_{OA}$  predicted equilibrium. Li et al., (2015) considered this idea in terms of dry and wet deposition. We suggest there may also be chemical factors that influence this process. We note a study by Raff and Hites (2007) where gas phase photolysis rate constants are estimated for different BDE congeners. Even amongst congeners with the same number of bromine atoms, significant differences exist in gas phase lifetimes, for example between BDE99 (4 hours) and BDE100 (54 hours).

### 3.5 Factors affecting the inter sample variations

Different parameters can influence the inter sample variation of PBDE atmospheric concentrations. These factors include: advection from urban and industrial sources, the efficiency of removal processes (degradation and deposition) and the

meteorological conditions (e.g. temperature, boundary layer height, precipitation). The results of the Spearman correlation analysis between the gaseous, particulate and total concentrations of individual PBDEs and different meteorological parameters are shown in Table S9.

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). As observed elsewhere (Dien et al., 2015), the particulate concentration of high brominated PBDE (i.e. 100, 99, 154, 153, 183 and 209) were negatively correlated to the precipitation rate. This confirms the significant washout of congeners partitioning mostly to the particulate phase compared to those in the gas-phase (Venier and Hites, 2008), a general trend for lipophilic organic compounds (Ligocki et al., 1985; Shahpoury et al., 2015). The atmospheric boundary layer (ABL) height shows strong correlations with the particulate concentrations of all PBDEs except BDE85, in agreement with a previous study (Dien et al., 2017). The ABL height was also shown to be a primary driver of PBDE concentration's diel variability (Moeckel et al., 2010).

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  $\theta_{\text{measured}}$  (see Section 3.4), it is uncertain that the gaseous 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.  $\theta_{\text{measured}} < 0.2$ ), regardless of the ambient temperature.

On the other side, the particulate concentrations of all individual PBDEs were significantly ( $p < 0.05$ ) higher at colder temperatures (Figure S8), as found for semivolatile organics in general (Bidleman, 1988). Furthermore, this is in agreement with a previous study conducted at a rural and an urban site in the Czech Republic where higher particulate PBDEs concentrations were also found in winter. This was attributed to temperature-induced shifts in gas-particle partitioning (Okonski et al., 2014). The higher degradation in summer and lower ABL height in winter may also support higher particulate PBDEs at cold temperatures. Additionally, Lee et al., (2004) proposed that low ambient air temperatures may cause increased emissions of PBDEs from anthropogenic activities such as combustion.

LRAT represents 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. Air masses mainly

originating from the West, South-West or North-West, i.e. air that has passed through the Atlantic Ocean or the North Sea, were found for 8 of the 10 samples with the lowest PBDE concentrations (Figure S9). In contrast, the samples with  $\Sigma_8$ PBDEs  $> 1 \text{ pg m}^{-3}$  were not associated with air masses from a clear direction but rather by air that stagnated over continental Europe (Figure S10). The fact that the highest PBDE concentrations were observed under advection from different directions suggests that there is a rather homogeneous continental emission source. The high PBDE concentrations observed in these samples is likely due to short and intense emissions of flame retardants, as for example during the incineration of products or waste containing PBDEs.

To conclude this section, the atmospheric concentrations of individual PBDEs were controlled by primary emissions (including combustion and evaporation), deposition processes (rain scavenging) and LRAT while the influence of revolatilisation could not be demonstrated.

### 3.6 Inter-annual and seasonal variations

Several years following the inclusion of the Penta- and Octa-BDE mixtures to the Stockholm Convention, long-term data can be used to assess whether the environmental levels are decreasing as a consequence of primary emissions reduction. The atmosphere is an ideal environmental compartment as it is particularly responsive to changes in primary emissions (Harrad, 2015).

To evaluate whether the atmospheric concentrations of individual PBDEs were significantly declining or not, the following harmonic regression as a function of time was used for this purpose (Liu et al., 2016; Venier et al., 2012):

$$\ln C_i = a_0 + a_1 \sin(zt) + a_2 \cos(zt) + a_3 t \quad (8)$$

Where  $C_i$  is the concentration of individual BDE in a given sample,  $t$  is the date when the sample was collected,  $z=2\pi/365.25$  which fixes the periodicity to one year,  $a_0$  is an intercept that rectifies the units,  $a_1$  and  $a_2$  are harmonic coefficients that describe seasonal variations and  $a_3$  is a first-order rate constant (in  $\text{days}^{-1}$ ). The apparent halving or doubling times ( $\tau_{1/2}$ ) describes the time period it takes to reduce/increase the initial PBDE concentrations to half/twice its value and should not be confused with half-lives related to degradation processes. It was calculated from  $k$  as:

$$\tau_{1/2} = \ln 2/k \quad (9)$$

The regression coefficients  $a_0$ - $a_3$  which were statistically significant ( $p < 0.05$ ) are shown in Table S11.

Unlike a recent study in the North American Great Lakes region (Shunthirasingham et al., 2018), significant ( $p < 0.05$ ) seasonality, characterized by the regression coefficients  $a_1$  and  $a_2$ , were found for all congeners, except BDE85 (Table S11). Indeed, the regression coefficients for BDE28 and BDE209 shows a maximum in spring and a minimum in autumn. On the other hand, higher concentrations in winter and lower in summer were found for most PBDEs (i.e. BDE100, BDE99, BDE154, BDE153 and BDE183) while the opposite seasonal trend was observed for BDE47. For the more brominated congeners (except BDE209), re-volatilisation is insignificant and the effect of atmospheric mixing (depth of the planetary boundary layer) is dominating.

The seasonal variations presented here are in contradiction with many previous studies which reported higher concentrations of most PBDEs in summer compared to winter, with the exception of BDE209 (e.g. Birgul et al., 2012; Cetin and Odabasi, 2008). Another study, based in Japan (Dien et al., 2015) found higher concentrations of lower brominated congeners (BDE47 and BDE99) in warm season while concentrations of the higher brominated congeners which are mainly bound to particles (e.g. BDE183 and BDE209) peaked in winter. The PBDE summer maxima found in the Mediterranean (Birgul et al., 2012; Cetin and Odabasi, 2008) might be related to higher temperatures there, throughout all seasons, which may enhance the revolatilisation from surfaces.

By applying Eq. 9 to all samples, significant decreases at the 95% confidence interval were found for BDE100, BDE99, BDE153 and BDE209 with apparent half-lives of 2.97, 3.81, 4.83 and 2.81 years, respectively (Figure 4 and Table S11) but not for the remaining congeners. Previous research performed on long-term trends of PBDEs in the atmosphere are available mainly for UK and North America. Indeed, at different UK and Norwegian background sites, Schuster et al; (2010) reported significant decreases at four of the eleven sites investigated in 2000-2008 of BDE47, BDE100, BDE99, BDE153 and BDE154 with half-lives of 1.4-4.0 years. At two urban sites in UK, significant decreases were also found for  $\Sigma_9$ PBDEs with half-lives of 2.0-3.4 years (Birgul et al., 2012). 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). Other studies also reported significant decrease of PBDEs at three UK sites in 2000-2010 (Graf et al., 2016) but also in Japan in 2009-2012 (Dien et al., 2015). On the other hand, at a rural site in the UK, no clear and consistent decline in PBDEs concentrations were found (Birgul et al., 2012), while around the American Great Lakes, the PBDE concentrations were decreasing at two urban sites, but were generally unchanged at three remote sites in 2005-2013 (Liu et al., 2016).

Overall, the results from the present study tend to show that the primary emissions of BDE99, 100, 153 and 209 are declining in Central Europe. The similar rate of declines observed for other European sites (Table S12) indicates that regional scale primary emissions are controlling the trends (Schuster et al., 2010). This is the first study reporting significant decreases only for some of the high brominated congeners but not for the low ones, which have lower first order removal rates (Wei et al., 2013). However, though decreasing trends of some congeners are observed in different locations worldwide, we should keep in mind that PBDEs are still persisting in the environment and that a time lag is needed to clearly see the effect of reduction in primary emissions on background atmospheric concentrations of all PBDEs (Ma et al., 2013).

Interestingly, BDE28 showed an overall increasing trend, although this was statistically significant only at the 90% confidence interval (Figure S11). Similarly, in the Great Lakes area (US), Ma et al., (2013) found that the gaseous concentrations of BDE47 and BDE99 were significantly increasing from 2005 to 2011 at three rural/remote sites with longer doubling times for BDE47 (7-9.4 years) compared to BDE99 (4.3-4.7 years) (Table S12). Taking this into account and considering that BDE28 is a product of the debromination of higher BDE congeners (Vesely et al., 2015; Wei et al., 2013) this is an additional indication that photolytic degradation of higher to lower brominated congeners is occurring in the atmosphere. Results from a modelling

study concluded that 13% of the Penta-BDE occurring in the environment resulted from the degradation of Deca-BDE induced by photolysis (Schenker et al., 2008). The authors argued that once the Penta mixture would be phased out completely, the importance of Deca-BDE as a source of Penta-BDE will increase. Here, we would argue that over the next decades, an increase or a steady state in the atmospheric concentrations of low brominated PBDEs may occur and that the congener profile will likely be dominated by those lighter congeners which are more prone to re-volatilisation (and have a higher persistency) and hence have a higher potential for long-range atmospheric transport. The fact that, in this study, no significant decrease was observed for BDE47 in comparison to BDE99, even though it originates from the same Penta mixture and is known to be a debromination product of BDE99 (Bezares-Cruz et al., 2004), support this hypothesis. However, monitoring air concentrations over longer time span is needed to provide further evidence.

## 10 **4 Conclusions**

This study has shown that the atmospheric PBDE levels are governed by primary emissions, deposition processes and LRAT. One important finding of this study is the seasonal variation of the particulate fraction which was observed for most PBDEs. This has implications for studies using passive sampling design for which the efficiency of particulate collection is still uncertain. Therefore, the interpretation of the seasonal variations of PBDEs from such studies should be done in a cautious manner. Moreover, one should keep in mind that the congener profiles observed in this study differed between the gaseous and the particulate phase; using a sampler collecting only one specific phase would provide a different congener profile.

Additionally, this study has shown that, at the current state of knowledge, none of the available models were able to effectively characterise the gas-particle partitioning of PBDEs. Though some of the tested models provided acceptable predictions for some of the compounds, none were satisfactory for all PBDEs investigated and for the specific conditions at this sampling site. This highlights the need for a gas-particle partitioning scheme for PBDEs that would be universally applicable under a range of atmospheric conditions. This is the minimal criterion to be able to adequately characterize the environmental fate of PBDEs at a global scale.

Finally, the results from this study tend to show that the debromination from high to low brominated congeners, enhanced by photolysis, is also an important process governing PBDE concentrations in the atmosphere. Given that nowadays, all formulations have been phased out, we may expect an enrichment in light congeners in the environment at a global scale. As these compounds are more volatile and have higher persistency than heavier congeners, their secondary formation enhanced by photolysis may be a serious issue of concern. Further studies should confirm whether the atmospheric concentrations of lower brominated PBDEs will increase or be at a steady state within the next decades.

## 30 **Supporting information**

Description of samples collected, results of the breakthrough analysis, summary of individual PBDE concentrations and results of the correlation analyses are provided.

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## References

- 10 Agrell, C., Arnout, F. H., Sveder, J., Bokenstrand, A., Larsson, P. and Zegers, B. N.: Polybrominated diphenyl ethers (PBDES) at a solid waste incineration plant I: Atmospheric concentrations, *Atmos. Environ.*, 38, 5139–5148, doi:10.1016/j.atmosenv.2004.05.024, 2004.
- Allen, J. G., McClean, M. D., Stapleton, H. M., Nelson, J. W. and Webster, T. F.: Personal exposure to Polybrominated Diphenyl Ethers (PBDEs) in residential indoor air, *Environ. Sci. Technol.*, 41, 4574–4579, 2007.
- 15 Besis, A. and Samara, C.: Polybrominated diphenyl ethers (PBDEs) in the indoor and outdoor environments - A review on occurrence and human exposure, *Environ. Pollut.*, 169, 217–229, doi:10.1016/j.envpol.2012.04.009, 2012.
- Besis, A., Botsaropoulou, E., Voutsas, D. and Samara, C.: Particle-size distribution of polybrominated diphenyl ethers (PBDEs) in the urban agglomeration of Thessaloniki, northern Greece, *Atmos. Environ.*, 104, 176–185, doi:10.1016/j.atmosenv.2015.01.019, 2015.
- 20 Besis, A., Lammel, G., Kukučka, P., Samara, C., Sofuoğlu, A., Eleftheriadis, K., Kouvarakis, G., Vassilatou, V. and Voutsas, D.: Polybrominated diphenyl ethers (PBDEs) in background air around the Aegean: implications for phase partitioning and size distribution, *Environ. Sci. Pollut. Res.*, 24, 28102–28120, doi:10.1007/s11356-017-0285-7, 2017.
- Bezares-Cruz, J., Jafvert, C. T. and Hua, I.: Solar photodecomposition of decabromodiphenyl ether: Products and quantum yield, *Environ. Sci. Technol.*, 38, 4149–4156, doi:10.1021/es049608o, 2004.
- 25 Bidleman, T. F.: Atmospheric processes, *Environ. Sci. Technol.*, 22, 361–367, doi:10.1021/es00169a002, 1988.
- Bidleman, T. F. and Tysklind, M.: Breakthrough during air sampling with polyurethane foam: What do PUF 2/PUF 1 ratios mean?, *Chemosphere*, 192, 267–271, doi:10.1016/j.chemosphere.2017.10.152, 2018.
- Birgul, A., Katsoyiannis, A., Gioia, R., Crosse, J., Earnshaw, M., Ratola, N., Jones, K. C., Sweetman, A. J., Man, A. and Lon, C.: Atmospheric polybrominated diphenyl ethers (PBDEs) in the United Kingdom, *Environ. Pollut.*, 169, 105–111, doi:10.1016/j.envpol.2012.05.005, 2012.
- 30 Cetin, B. and Odabasi, M.: Air-water exchange and dry deposition of polybrominated diphenyl ethers at a coastal site in Izmir Bay, Turkey, *Environ. Sci. Technol.*, 41, 785–791, 2007.

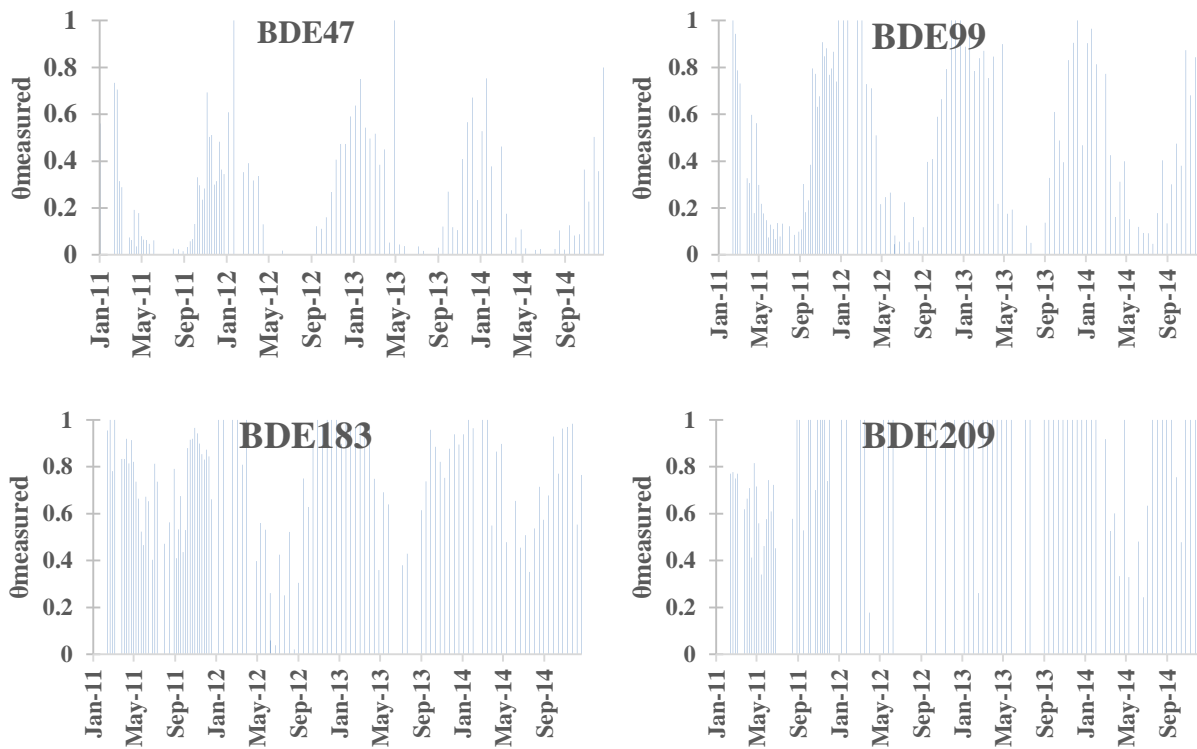
- Cetin, B. and Odabasi, M.: Atmospheric concentrations and phase partitioning of polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey, *Chemosphere*, 71, 1067–78, 2008.
- Chen, L.-G., Mai, B.-X., Bi, X.-H., Chen, S.-J., Wang, X.-M., Ran, Y., Luo, X.-J., Sheng, G.-Y., Fu, J.-M. and Zeng, E. Y.: Concentration levels, compositional profiles, and gas-particle partitioning of polybrominated diphenyl ethers in the atmosphere of an urban city in South China, *Environ. Sci. Technol.*, 40, 1190–1196, doi:10.1021/es052123v, 2006.
- 5 Davie-Martin, C. L., Hageman, K. J., Chin, Y., Nistor, J. B. and Hung, H.: Concentrations, gas-particle distributions, and source indicator analysis of brominated flame retardants in air at Toolik Lake, Arctic Alaska, *Environ. Sci. Process. Impacts*, 18, 1274–1284, doi:10.1039/C6EM00395H, 2016.
- Degrendele, C., Audy, O., Hofman, J., Kučerik, J., Kukučka, P., Mulder, M. D., Příbylová, P., Prokeš, R., Šáňka, M., Schaumann, G. and Lammel, G.: Diurnal Variations of Air-Soil Exchange of Semivolatile Organic Compounds (PAHs, PCBs, OCPs, and PBDEs) in a Central European Receptor Area, *Environ. Sci. Technol.*, 50, 4278–4288, doi:10.1021/acs.est.5b05671, 2016.
- 10 Dien, N. T., Hirai, Y., Miyazaki, T. and Sakai, S.-I.: Factors influencing atmospheric concentrations of polybrominated diphenyl ethers in Japan, *Chemosphere*, 144, 2073–2080, doi:10.1016/j.chemosphere.2015.10.119, 2015.
- 15 Dien, N. T., Hirai, Y. and Sakai, S.-I.: Correlation between atmospheric boundary layer height and polybrominated diphenyl ether concentrations in air, *Environ. Sci. Technol.*, 51, 356–364, doi:10.1021/acs.est.6b03004, 2017.
- Ding, N., Chen, X. and Wu, C.-M. L.: Interactions between polybrominated diphenyl ethers and graphene surface: a DFT and MD investigation, *Environ. Sci. Nano*, 1, 55–63, doi:10.1039/C3EN00037K, 2014.
- Eriksson, J., Green, N., Marsh, G. and Bergman, Å.: Photochemical decomposition of 15 polybrominated diphenyl ether congeners in methanol/water, *Environ. Sci. Technol.*, 38, 3119–3125, doi:10.1021/es049830t, 2004.
- 20 Fang, L., Huang, J., Yu, G. and Wang, L.: Photochemical degradation of six polybrominated diphenyl ether congeners under ultraviolet irradiation in hexane, *Chemosphere*, 71, 258–267, doi:10.1016/j.chemosphere.2007.09.041, 2008.
- Graf, C., Katsoyiannis, A., Jones, K. C. and Sweetman, A. J.: The TOMPs ambient air monitoring network – Continuous data on UK air quality for over 20 years, *Environ. Pollut.*, 217, 42–51, doi:10.1016/j.envpol.2016.01.033, 2016.
- 25 Hafner, W. D. and Hites, R. A.: Effects of Wind and Air Trajectory Directions on Atmospheric Concentrations of Persistent Organic Pollutants near the Great Lakes, *Env. Sci Technol*, 39(20), 7817–7825, doi:10.1021/es0502223, 2005.
- Harner, T. and Bidleman, T. F.: Measurement of octanol-air partition coefficients for polycyclic aromatic hydrocarbons and polychlorinated naphthalenes, *J. Chem. Eng. Data*, 43(1), 40–46, doi:10.1021/je970175x, 1998a.
- Harner, T. and Bidleman, T. F.: Octanol-air partition coefficient for describing particle/gas partitioning of aromatic compounds in urban air, *Environ. Sci. Technol.*, 32, 1494–1502, doi:10.1021/es970890r, 1998b.
- 30 Harner, T. and Shoeib, M.: Measurements of octanol-air partition coefficients (KOA) for polybrominated diphenyl Ethers (PBDEs): Predicting partitioning in the environment, *J. Chem. Eng. Data*, 47, 228–232, doi:10.1021/je010192t, 2002.
- Harrad, S.: A meta-analysis of recent data on UK environmental levels of POP-BFRs in an international context : Temporal trends and an environmental budget, *Emerg. Contam.*, 1, 39–53, doi:10.1016/j.emcon.2015.08.001, 2015.

- Hoff, R. M., Brice, K. A. and Halsall, C. J.: Nonlinearity in the slopes of Clausius-Clapeyron plots for SVOCs, *Environ. Sci. Technol.*, 32(12), 1793–1798, 1998.
- Holoubek, I., Klánová, J., Jarkovský, J. and Kohoutek, J.: Trends in background levels of persistent organic pollutants at Kosetice observatory, Czech Republic. Part I. Ambient air and wet deposition 1996-2005., *J. Environ. Monit.*, 9, 557–63, 2007.
- 5 Iacovidou, E., Mandalakis, M. and Stephanou, E. G.: Occurrence and diurnal variation of polychlorinated biphenyls and polybrominated diphenyl ethers in the background atmosphere of Eastern Mediterranean, *Chemosphere*, 77, 1161–1167, doi:10.1016/j.chemosphere.2009.09.043, 2009.
- Law, R. J., Herzke, D., Harrad, S., Morris, S., Bersuder, P. and Allchin, C. R.: Levels and trends of HBCD and BDEs in the European and Asian environments , with some information for other BFRs, *Chemos*, 73, 223–241, 10 doi:10.1016/j.chemosphere.2008.02.066, 2008.
- Lee, R. G. M., Thomas, G. O. and Jones, K. C.: PBDEs in the Atmosphere of Three Locations in Western Europe, *Environ*, 38, 699–706, 2004.
- Li, Y.-F., Qiao, L., Ren, N., Sverko, E., Mackay, D. and Macdonald, R. W.: Decabrominated diphenyl ethers (BDE-209) in Chinese and global air: levels, gas/particle partitioning, and long-range transport: Is long-range transport of BDE-209 really 15 governed by the movement of particles?, *Environ. Sci. Technol.*, 51, 1035–1042, doi:10.1021/acs.est.6b05395, 2016.
- Li, Y. F., Ma, W.-L. and Yang, M.: Prediction of gas/particle partitioning of polybrominated diphenyl ethers (PBDEs) in global air: A theoretical study, *Atmos. Chem. Phys.*, 15, 1669–1681, doi:10.5194/acp-15-1669-2015, 2015.
- Ligocki, M. P., Leuenberger, C. and Pankow, J. F.: Trace organic compounds in rain. III. Particle scavenging of neutral organic compounds, *Atmos. Environ.*, 19, 1619–1626, 1985.
- 20 Liu, L., Salamova, A., Venier, M. and Hites, R. A.: Trends in the levels of halogenated flame retardants in the Great Lakes atmosphere over the period 2005 – 2013, *Environ. Int.*, 92–93, 442–449, doi:10.1016/j.envint.2016.04.025, 2016.
- Luo, P., Ni, H., Bao, L., Li, S. and Zeng, E. Y.: Size distribution of airborne particle-bound polybrominated diphenyl ethers and its implications for dry and wet deposition, *Environ. Sci. Technol.*, 48, 13793–13799, 2014.
- Ma, Y., Salamova, A., Venier, M. and Hites, R. A.: Has the phase-out of PBDEs affected their atmospheric levels? Trends of 25 PBDEs and their replacements in the Great Lakes, *Environ. Sci. Technol.*, 47, 11457–11464, 2013.
- Mandalakis, M., Besis, A. and Stephanou, E. G.: Particle-size distribution and gas/particle partitioning of atmospheric polybrominated diphenyl ethers in urban areas of Greece, *Environ. Pollut.*, 157, 1227–1233, doi:10.1016/j.envpol.2008.12.010, 2009.
- Melymuk, L., Bohlin-Nizzetto, P., Sánka, O., Pozo, K. and Klánová, J.: Current challenges in air sampling of semi-volatile 30 organic contaminants: sampling artifacts and their influence on data comparability, *Environ. Sci. Technol.*, 48, doi:10.1021/es502164r, 2014.
- Moeckel, C., Gasic, B., MacLeod, M., Scheringer, M., Jones, K. C. and Hungerbühler, K.: Estimation of the source strength of polybrominated diphenyl ethers based on their diel variability in air in Zurich, Switzerland., *Environ. Sci. Technol.*, 44, 4225–31, doi:10.1021/es1001049, 2010.

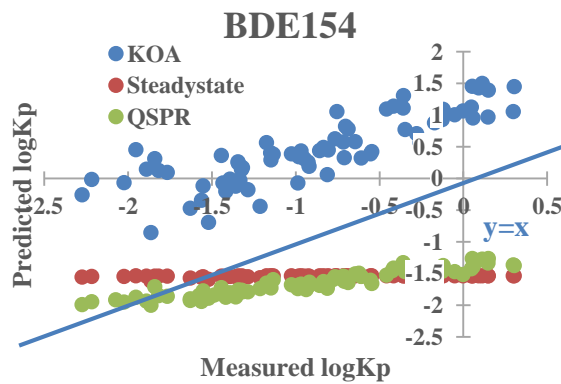
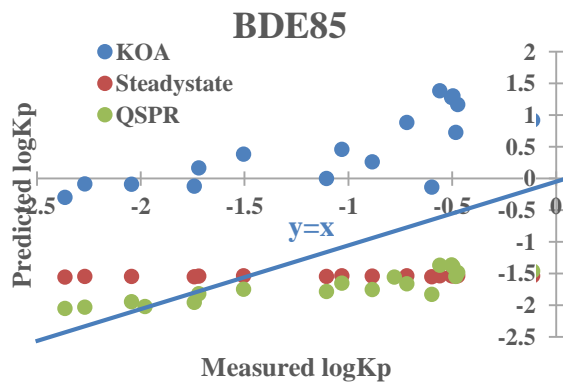
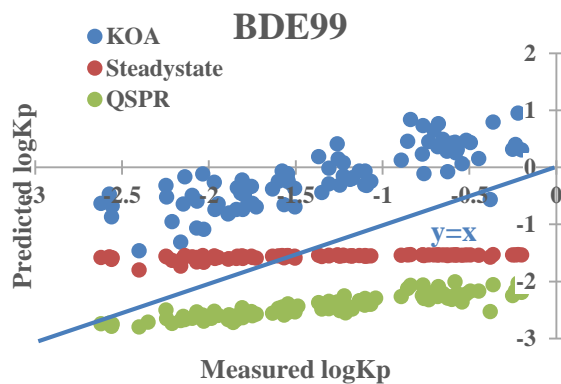
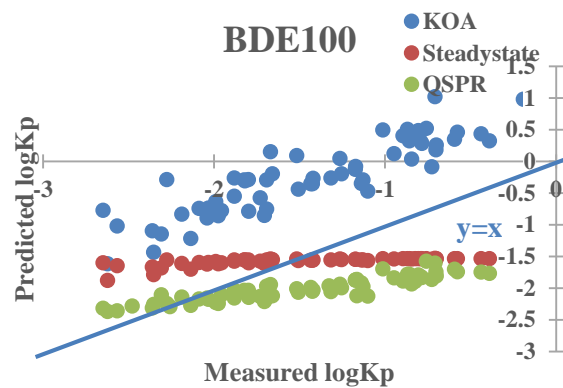
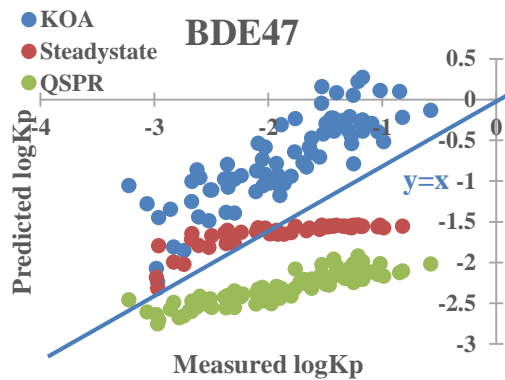
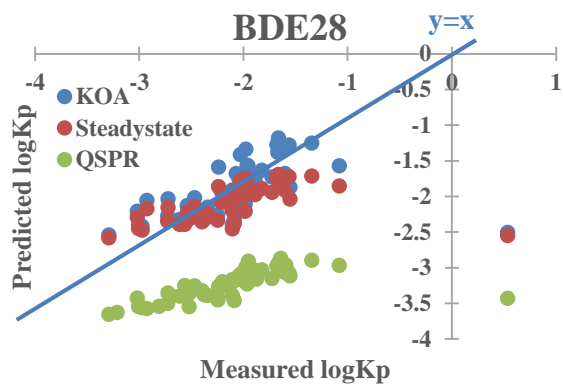


- Möller, A., Xie, Z. Y., Sturm, R. and Ebinghaus, R.: Polybrominated diphenyl ethers (PBDEs) and alternative brominated flame retardants in air and seawater of the European Arctic, *Environ. Pollut.*, 159, 1577–1583, doi:10.1016/j.envpol.2011.02.054, 2011.
- Mulder, M. D., Heil, A., Kukučka, P., Kuta, J., Příbylová, P., Prokeš, R. and Lammel, G.: Long-range atmospheric transport of PAHs, PCBs and PBDEs to the central and eastern Mediterranean and changes of PCB and PBDE congener patterns in summer 2010, *Atmos. Environ.*, 111, 51–59, doi:10.1016/j.atmosenv.2015.03.044, 2015.
- Okonski, K., Degrendele, C., Melymuk, L., Landlová, L., Kukučka, P., Vojta, Š., Jiri, K., Čupr, P. and Klánová, J.: Particle size distribution of halogenated flame retardants and implications for atmospheric deposition and transport, *Environ. Sci. Technol.*, 48, 14426–14434, 2014.
- Raff, J. D. and Hites, R. A.: Deposition versus photochemical removal of PBDEs from lake superior air, *Environ. Sci. Technol.*, 41, 6725–6731, doi:10.1021/es070789e, 2007.
- Salamova, A. and Hites, R. A.: Discontinued and alternative brominated flame retardants in the atmosphere and precipitation from the Great Lakes Basin, *Environ. Sci. Technol.*, 45, 8698–8706, 2011.
- Sanchez-Prado, L., Llompart, M., Lores, M., Garcia-Jares, C. and Cela, R.: Investigation of photodegradation products generated after UV-irradiation of five polybrominated diphenyl ethers using photo solid-phase microextraction, *J. Chromatogr. A*, 1071, 85–92, doi:10.1016/j.chroma.2004.10.065, 2005.
- Schenker, U., Soltermann, F., Scheringer, M. and Hungerbühler, K.: Modeling the environmental fate of polybrominated diphenyl ethers (PBDEs): The importance of photolysis for the formation of lighter PBDEs, *Environ. Sci. Technol.*, 42, 9244–9249, 2008.
- Schuster, J. K., Gioia, R., Breivik, K., Steinnes, E., Scheringer, M. and Jones, K. C.: Trends in European background air reflect reductions in primary emissions of PCBs and PBDEs, *Environ. Sci. Technol.*, 44, 6760–6766, doi:10.1021/es101009x, 2010.
- Shahpoury, P., Lammel, G., Holubová Šmejkalová, A., Klánová, J., Příbylová, P. and Váňa, M.: Polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and chlorinated pesticides in background air in central Europe – investigating parameters affecting wet scavenging of polycyclic aromatic hydrocarbons, *Atmos. Chem. Phys.*, 15, 1795–1805, doi:10.5194/acp-15-1795-2015, 2015.
- Shahpoury, P., Lammel, G., Albinet, A., Sofuoğlu, A., Dumanoglu, Y., Sofuoğlu, S. C., Wagner, Z. and Ždimal, V.: Evaluation of a conceptual model for gas-particle partitioning of polycyclic aromatic hydrocarbons using polyparameter linear free energy relationships, *Environ. Sci. Technol.*, 50, 12312–12319, doi:10.1021/acs.est.6b02158, 2016.
- Shunthirasingham, C., Alexandrou, N., Brice, K. A., Dryfhout-Clark, H., Su, K., Shin, C., Park, R., Pajda, A., Noronha, R. and Hung, H.: Temporal trends of halogenated flame retardants in the atmosphere of the Canadian Great Lakes Basin (2005–2014), *Environ. Sci. Impacts*, 20, 469–479, doi:10.1039/C7EM00549K, 2018.
- Söderström, G., Sellström, U., De Wit, C. A. and Tysklind, M.: Photolytic debromination of decabromodiphenyl ether (BDE 209), *Environ. Sci. Technol.*, 38, 127–132, doi:10.1021/es034682c, 2004.
- Stohl, A., Forster, C., Frank, A., Seibert, P. and Wotawa, G.: Technical note: The Lagrangian particle dispersion model

- FLEXPART version 6.2, *Atmos. Chem. Phys.*, 5, 2461–2474, 2005.
- Strandberg, B., Dodder, N. G., Basu, I. and Hites, R. A.: Concentrations and spatial variations of polybrominated diphenyl ethers and other organohalogen compounds in Great Lakes air., *Environ. Sci. Technol.*, 35, 1078–83, 2001.
- Su, Y., Hung, H., Brice, K. A., Su, K., Alexandrou, N., Blanchard, P., Chan, E., Sverko, E. and Fellin, P.: Air concentrations of polybrominated diphenyl ethers (PBDEs) in 2002 – 2004 at a rural site in the Great Lakes, *Atmos. Environ.*, 43, 6230–6237, doi:10.1016/j.atmosenv.2009.08.034, 2009.
- 5 Venier, M. and Hites, R. A.: Atmospheric deposition of PBDEs to the Great Lakes featuring a Monte Carlo analysis of errors, *Environ. Sci. Technol.*, 42, 9058–9064, doi:10.1021/es8008985, 2008.
- Venier, M., Hung, H., Włodzimierz, T. and Hites, R. A.: Temporal Trends of Persistent Organic Pollutants: A Comparison of Different Time Series Models, *Env. Sci Technol*, 46, 3928–3934, doi:10.1021/es204527q, 2012.
- 10 Vesely, M., Vajglova, Z., Kotas, P., Kristal, J., Ponec, R. and Jiricny, V.: Model for photodegradation of polybrominated diphenyl ethers, *Environ. Sci. Pollut. Res.*, 22, 4949–4963, doi:10.1007/s11356-014-3741-7, 2015.
- Wania, F. and Haugen, J.: Temperature dependence of atmospheric concentrations of semivolatile organic compounds, *Environ. Sci. ...*, (97), 1013–1021, doi:10.1021/es970856c, 1998.
- 15 Wania, F., Axelman, J. and Broman, D.: A review of processes involved in the exchange of persistent organic pollutants across the air-sea interface, *Environ. Pollut.*, 102, 3–23, doi:10.1016/s0269-7491(98)00072-4, 1998.
- Webster, F. T., Harrad, S., Millette, J. R., Holbrook, R. D., Davis, J. M., Stapleton, H. M., Allen, J. G. and Mcclean, M. D.: Identifying transfer mechanisms and sources of decabromodiphenyl ether (BDE 209) in indoor environments using environmental forensic microscopy, *Environ. Sci. Technol.*, 43, 3067–3072, 2009.
- 20 Wei, H., Zou, Y., Li, A., Christensen, E. R. and Rockne, K. J.: Photolytic debromination pathway of polybrominated diphenyl ethers in hexane by sunlight, *Environ. Pollut.*, 174, 194–200, doi:10.1016/j.envpol.2012.11.035, 2013.
- Wei, X., Yuan, Q., Serge, B., Xu, T., Ma, G. and Yu, H.: In silico investigation of gas/particle partitioning equilibrium of polybrominated diphenyl ethers (PBDEs), *Chemosphere*, 188, 110–118, doi:10.1016/j.chemosphere.2017.08.146, 2017.
- Yue, C. Y. and Li, L. Y.: Filling the gap: Estimating physicochemical properties of the full array of polybrominated diphenyl ethers (PBDEs), *Environ. Pollut.*, 180, 312–323, doi:10.1016/j.envpol.2013.05.029, 2013.
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**Figure 1: Measured particulate fraction ( $\theta_{\text{measured}}$ ) of selected PBDEs.**



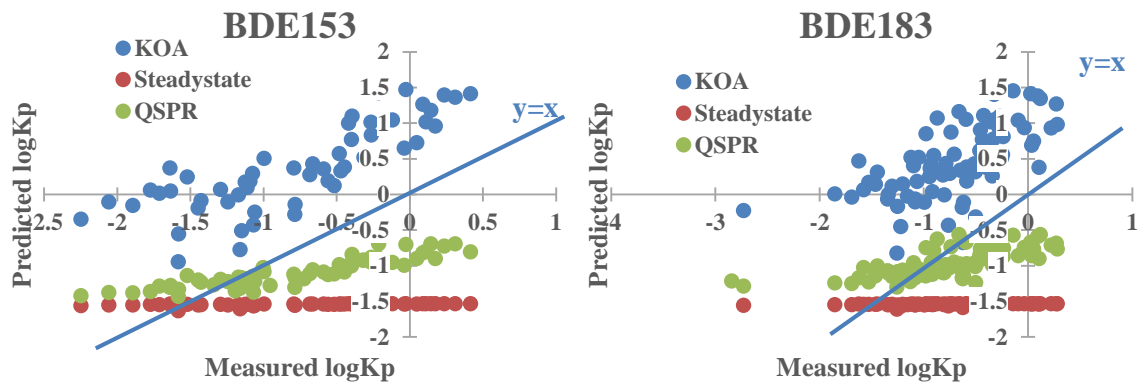
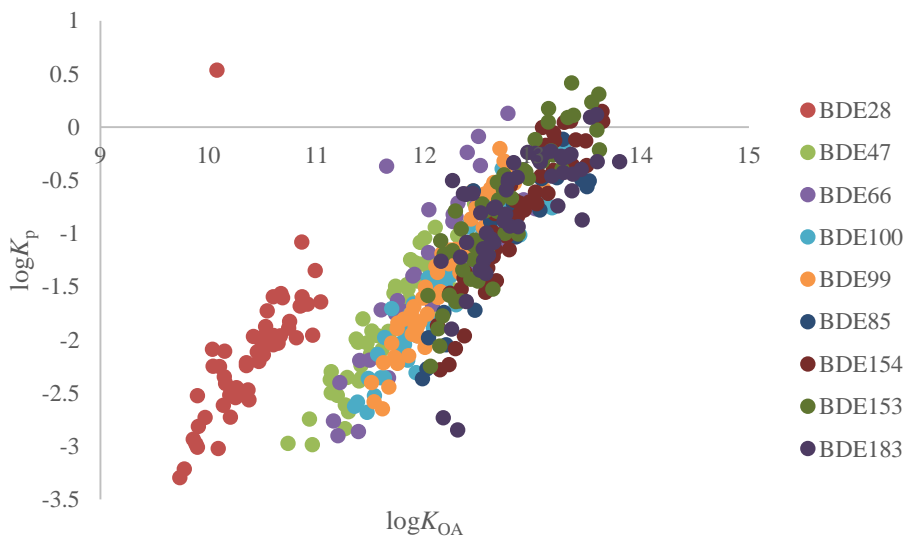


Figure 2: Comparison of measured and predicted  $\log K_p$  of individual PBDEs. The blue lines represent the 1:1 line.



5 Figure 3: Influence of  $\log K_{OA}$  on measured  $\log K_p$  for individual PBDEs

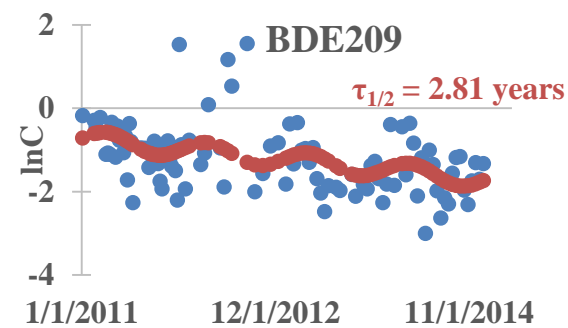
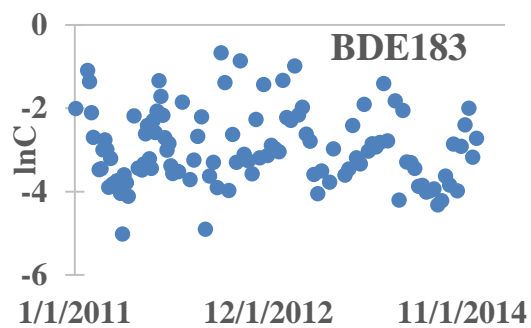
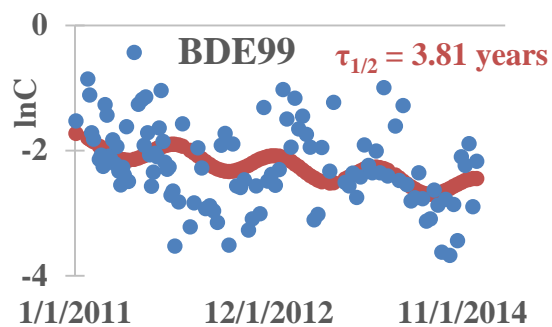
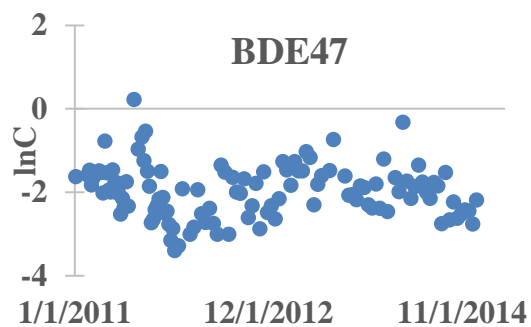


Figure 4: Multi-year trends of the most abundant PBDEs.

## Table of Contents

### List of Tables

Table S1: Additional information about the air sampling performed.....	S2
Table S2: Range of the limit of quantifications determined by the instrument and by the field blank concentrations plus three times their standard deviations. ....	S2
Table S3: Comparison of the change of sampling preparation on the reported PBDE concentrations. ....	S3
Table S4: Comparison of the relative response factors (RRF) of individual PBDEs on different analytical columns.....	S3
Table S5: Results of breakthrough experiments.....	S3
Table S6: Summary of the atmospheric concentrations (in $\text{pg m}^{-3}$ ) and detections (in %) of individual PBDEs found in this study .....	S4
Table S7: Results of regression analysis between $\theta_{\text{measured}}$ and $\log K_p$ and the inverse of temperature ( $\text{K}^{-1}$ ) for individual congeners. ....	S5
Table S8: Results of Pearson correlation analysis between $\theta_{\text{measured}}$ and the precipitation rate for individual PBDEs.....	S5
Table S9: Results of the Spearman correlation analysis ( $r$ ) between the individual concentrations of PBDEs and different meteorological parameters. ....	S5
Table S10: Results of Clausius Clapeyron plots listing slopes (m), constants (b), coefficient of determination ( $r^2$ ) and confidence level (p) for PBDEs.....	S6
Table S11: Results of the harmonic regression applied to the PBDE dataset. ....	S6
Table S12: Apparent half lives ( $\tau_{1/2}$ ) of individual PBDEs observed in this study and elsewhere.....	S7

### List of Figures

Figure S1: Results of the breakthrough experiments for BDE47, BDE99, BDE183 and BDE209 .....	S8
Figure S2: Average contribution of individual BDEs to $\Sigma_8\text{PBDEs}$ .....	S8
Figure S3: Average measured particulate fraction ( $\theta_{\text{measured}}$ ) found in this study .....	S8
Figure S4: Comparison of measured and predicted $\theta$ .....	S9
Figure S5: Comparison of the predicted and measured $\log K_p$ and $\theta$ using the average conditions at the sampling site.....	S10
Figure S6: Schematic of the effect of an over- or under-estimation of $K_p$ by one order of magnitude in terms of $\theta$ .....	S11
Figure S7: Comparison of the measured particulate fractions ( $\theta_{\text{measured}}$ ) of two sets of isomers. ....	S11
Figure S8: Correlation between the gaseous (orange dots) or the particulate (blue dots) concentration of individual PBDEs (ln transformed) with the inverse of temperature. ....	S13
Figure S9: Selected examples of 5 days backward trajectories of samples associated with the lowest PBDE concentrations .....	S13
Figure S10: Selected examples of 5 days backward trajectories of samples associated with the highest PBDE concentrations .....	S14
Figure S11: Multi-years trend of some PBDEs .....	S15

## Temperature dependence of PBDEs

The gas-phase behavior of PBDEs can be described by the Clausius-Clapeyron equation:

$$\ln P = (-\Delta H_v/R)(1/T) + \text{constant} \quad (\text{Eq. S1})$$

where P is partial pressure (Pa), T is temperature (K),  $\Delta H_v$  is enthalpy of vaporization ( $\text{kJ}\cdot\text{mol}^{-1}$ ) and R is the gas constant. The temperature dependence of atmospheric PBDE concentrations was expressed as the linear regressions of the natural logarithm of partial pressure versus the inverse of the temperature:  $\ln P = m/T + b$ , where m and b are constants. (Eq. S2)

Partial pressures of individual compounds were calculated for each sampling event using gas phase concentrations and the ideal gas law.

Table S1: Additional information about the air sampling performed

Year	Sampled volume (min-max)	Number of samples considered	Number of samples excluded	Number of field blanks	Number of laboratory blanks	Time span covered
2011	4512 ; 5863	40	9	3	2	63%
2012	4015 ; 5864	26	1	3	2	42%
2013	3753 ; 5480	23	3	2	3	38%
2014	5236 ; 5597	25	0	3	4	41%

Table S2: Range of the limit of quantifications (LOQs) determined by the instrument (iLOQ) and by the field blank concentrations plus three times their standard deviations ( $\text{LOQ}_{\text{blanks}}$ ). To calculate LOQs in  $\text{pg m}^{-3}$ , the average and representative sample volume ( $V=5264 \text{ m}^3$ ) was used

	iLOQ (min-max)		$\text{LOQ}_{\text{blanks}}$ (min-max)	
	pg/sample	pg/m <sup>3</sup>	pg/sample	pg/m <sup>3</sup>
BDE 28	0.26 - 5486	4.92E-05 - 1.04	0 - 4.84	0 - 9.19E-04
BDE 47	0.11 - 2089	2.09E-05 - 0.40	8.30 - 129.7	1.58E-03 - 2.46E-02
BDE 100	0.18 - 281	3.50E-05 - 0.05	0 - 277	0 - 5.26E-02
BDE 99	0.27 - 1238	5.07E-05 - 0.24	12.5 - 107	2.37E-03 - 2.03E-02
BDE 85	0.25 - 310	4.75E-05 - 0.06	0 - 0	0 - 0
BDE 154	0.26 - 246	4.84E-05 - 0.05	0 - 6.26	0 - 1.19E-03
BDE 153	0.29 - 382	5.57E-05 - 0.07	0 - 0	0 - 0
BDE 183	0.84 - 593	1.59E-04 - 0.11	0 - 32.5	0 - 6.16E-03
BDE 209	3.10 - 5374	5.90E-04 - 1.02	0 - 3031	0 - 5.76E-01



Table S3: Comparison of the change of sampling preparation on the reported PBDE concentrations. Sampling preparation 1 was used for samples from 2011-2012 while the sampling preparation 2 was used for samples from 2013 (see Section 2.2 for further details). For each sampling preparation method, 500 pg of each congener was spiked on four PUFs.

	Average amount (pg) from sampling preparation 1	RSD from sampling preparation 1	Average amount (pg) from sampling preparation 2	RSD from sampling preparation 2	Relative difference (%)
BDE 28	481	13	495	14	-3
BDE 47	495	9	481	8	3
BDE 100	526	11	485	14	8
BDE 99	521	12	502	8	4
BDE 85	465	18	498	22	-7
BDE 154	475	8	520	11	-9
BDE 153	534	14	479	12	10
BDE 183	487	9	499	12	-2
BDE 209	564	16	512	18	9

Table S4: Comparison of the relative response factors (RRF) of individual PBDEs on different analytical columns

	RRF DB5 column	RRF RTX-1614 column	% deviation
BDE 28	0.948	0.964	<b>1.7</b>
BDE 47	1.005	0.932	<b>-7.8</b>
BDE 100	1.022	1.047	<b>2.4</b>
BDE 99	0.956	0.981	<b>2.5</b>
BDE 85	0.692	0.674	<b>-2.7</b>
BDE 154	0.899	0.926	<b>2.9</b>
BDE 153	0.935	0.999	<b>6.4</b>
BDE 183	0.856	0.828	<b>-3.4</b>
BDE 209	1.367	1.221	<b>-12.0</b>

Table S5: Results of breakthrough experiments. Only samples for which analytes were detected in at least one of the PUF plugs were considered.

Compound	Frequency of detection on upper PUF	Frequency of detection on lower PUF	% of gas-phase compound mass found on the lower PUF				
			Min	Max	Average	Standard deviation	Median
BDE 28	100%	11.5%	0.0	86.0	5.2	18.1	0.0
BDE 47	92.6%	11.5%	0.0	19.6	2.0	5.7	0.0
BDE 100	74.1%	3.8%	0.0	22.5	1.1	5.0	0.0
BDE 99	66.7%	0%			0.0		
BDE 85	22.2%	0%			0.0		
BDE 154	70.4%	19.2%	0.0	30.1	4.3	8.3	0.0
BDE 153	63%	11.5%	0.0	48.0	5.4	14.0	0.0
BDE 183	55.6%	26.9%	0.0	100.0	24.6	36.2	0.0
BDE 209	3.7%	19.2%	10.1	100.0	82.0	40.2	100.0

Table S6: Summary of the atmospheric concentrations (in  $\text{pg m}^{-3}$ ) and detections (in %) of individual PBDEs found in this study

		BDE 28	BDE 47	BDE 100	BDE 99	BDE 85	BDE 154	BDE 153	BDE 183	BDE 209	$\Sigma_8$ PBDEs
Gas phase	Detection	97	98	75	90	32	87	66	87	41	100
	Min	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.005
	Max	3.731	1.218	0.185	0.570	0.016	0.040	0.054	0.481	4.721	5.858
	Average	0.051	0.140	0.022	0.071	0.003	0.007	0.007	0.023	0.490	0.299
	SD	0.360	0.153	0.027	0.078	0.003	0.006	0.009	0.066	1.027	0.579
Particulate phase	Detection	51	82	89	99	25	90	82	96	79	99
	Min	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Max	0.036	0.312	0.111	0.424	0.039	0.152	0.142	0.367	0.685	1.380
	Average	0.004	0.043	0.017	0.071	0.006	0.023	0.028	0.059	0.257	0.232
	SD	0.006	0.054	0.020	0.082	0.008	0.029	0.030	0.069	0.142	0.285
Total	Detection	98	100	100	100	40	100	91	99	89	100
	Min	<LOQ	0.034	0.001	0.025	<LOQ	0.003	<LOQ	<LOQ	<LOQ	0.084
	Max	3.731	1.251	0.205	0.650	0.039	0.152	0.142	0.511	4.721	6.079
	Average	0.053	0.173	0.031	0.134	0.006	0.027	0.030	0.078	0.457	0.524
	SD	0.359	0.151	0.028	0.098	0.006	0.027	0.029	0.087	0.710	0.611

Table S7: Results of regression analysis between  $\theta_{\text{measured}}$  and  $\log K_p$  and the inverse of temperature ( $K^{-1}$ ) for individual congeners. Numbers in bold indicate cases for which regression coefficients ( $r^2$ ) were statistically significant ( $p < 0.05$ )

		BDE 28	BDE 47	BDE 100	BDE 99	BDE 85	BDE 154	BDE 153	BDE 183	BDE 209
$\theta_{\text{measured}}$	$r^2$	<b>0.31</b>	<b>0.74</b>	<b>0.55</b>	<b>0.84</b>	<b>0.51</b>	<b>0.76</b>	<b>0.61</b>	<b>0.5</b>	<b>0.06</b>
	slope	1128.62	2353.9	3161.41	3415.06	2919.25	3342.31	2927.09	2062.44	926.44
	intercept	-3.9	-8.12	-10.7	-11.63	-9.92	-11.25	-9.72	-6.6	-2.55
$\log K_p$	$r^2$	<b>0.38</b>	<b>0.79</b>	<b>0.83</b>	<b>0.80</b>	<b>0.78</b>	<b>0.88</b>	<b>0.80</b>	<b>0.48</b>	0.02
	slope	4169.20	6656.07	6715.63	6934.83	6354.32	7596.57	6783.09	4718.46	-516.98
	intercept	-17.08	-25.66	-25.26	-25.92	-23.72	-27.79	-24.75	-17.43	0.74

Table S8: Results of Pearson correlation analysis between  $\theta_{\text{measured}}$  and the precipitation rate for individual PBDEs. Numbers in bold indicate cases for which the correlations were statistically significant ( $p < 0.05$ )

		BDE 28	BDE 47	BDE 66	BDE 100	BDE 99	BDE 85	BDE 154	BDE 153	BDE 183	BDE 209
precipitation rate		<b>0.05</b>	<b>0.11</b>	<b>0.11</b>	<b>0.08</b>	<b>0.15</b>	0.06	<b>0.18</b>	<b>0.14</b>	<b>0.10</b>	0.03
	RH	<b>0.13</b>	<b>0.31</b>	<b>0.32</b>	<b>0.25</b>	<b>0.38</b>	<b>0.30</b>	<b>0.31</b>	<b>0.27</b>	<b>0.16</b>	0.02

Table S9: Results of the Spearman correlation analysis ( $r$ ) between the individual concentrations of PBDEs and different meteorological parameters. Numbers in bold indicates cases significant at the 99% confidence interval

		BDE 28	BDE 47	BDE 100	BDE 99	BDE 85	BDE 154	BDE 153	BDE 183	BDE 209
Ctot	precipitation	-0.11	-0.04	-0.18	<b>-0.33</b>	-0.07	<b>-0.52</b>	<b>-0.51</b>	<b>-0.50</b>	-0.19
	wind direction	<b>-0.26</b>	-0.20	<b>-0.34</b>	<b>-0.38</b>	-0.13	<b>-0.49</b>	<b>-0.50</b>	<b>-0.45</b>	-0.12
	wind speed	<b>-0.42</b>	<b>-0.51</b>	<b>-0.27</b>	<b>-0.32</b>	-0.11	-0.22	-0.17	-0.11	0.07
	RH	-0.07	<b>-0.25</b>	0.08	0.04	0.04	<b>0.35</b>	<b>0.42</b>	<b>0.39</b>	-0.02
	hmix	-0.24	-0.24	<b>-0.42</b>	<b>-0.44</b>	-0.20	<b>-0.60</b>	<b>-0.62</b>	<b>-0.57</b>	-0.11
Cg	precipitation	-0.06	0.17	0.21	0.14	0.33	0.16	0.23	0.04	0.03
	wind direction	-0.22	-0.07	-0.01	0.07	0.23	0.08	0.17	0.21	-0.07
	wind speed	<b>-0.38</b>	<b>-0.42</b>	-0.25	-0.17	-0.24	-0.24	-0.12	0.00	0.16
	RH	-0.18	<b>-0.52</b>	<b>-0.52</b>	<b>-0.53</b>	<b>-0.60</b>	<b>-0.51</b>	<b>-0.42</b>	-0.22	0.15
	hmix	-0.14	0.07	0.13	0.25	<b>0.48</b>	0.21	0.25	0.12	-0.10
Cp	precipitation	<b>-0.35</b>	<b>-0.50</b>	<b>-0.49</b>	<b>-0.52</b>	-0.24	<b>-0.50</b>	<b>-0.49</b>	<b>-0.58</b>	<b>-0.40</b>
	wind direction	-0.33	<b>-0.33</b>	<b>-0.27</b>	<b>-0.36</b>	-0.27	<b>-0.42</b>	<b>-0.42</b>	<b>-0.46</b>	-0.25
	wind speed	0.01	0.04	-0.11	-0.04	0.36	-0.07	-0.05	-0.10	0.02
	RH	<b>0.45</b>	<b>0.48</b>	<b>0.52</b>	<b>0.50</b>	<b>0.60</b>	<b>0.47</b>	<b>0.51</b>	<b>0.45</b>	0.12
	hmix	<b>-0.51</b>	<b>-0.54</b>	<b>-0.57</b>	<b>-0.57</b>	<b>-0.48</b>	<b>-0.54</b>	<b>-0.57</b>	<b>-0.59</b>	<b>-0.31</b>

Table S10: Results of Clausius Clapeyron plots listing slopes (m), constants (b), coefficient of determination ( $r^2$ ) and confidence level (p) for PBDEs. For congeners listed in bold, regression parameters are statistically significant at the 99% confidence interval

	$r^2$	p	N	m	b
BDE 28	0.03	0.08	111	-1747	-24.32
<b>BDE 47</b>	<b>0.43</b>	<b>&lt;0.01</b>	<b>112</b>	<b>-5760</b>	<b>-7.91</b>
<b>BDE 100</b>	<b>0.47</b>	<b>&lt;0.01</b>	<b>85</b>	<b>-7186</b>	<b>-5.08</b>
<b>BDE 99</b>	<b>0.48</b>	<b>&lt;0.01</b>	<b>103</b>	<b>-7078</b>	<b>-4.20</b>
<b>BDE 85</b>	<b>0.61</b>	<b>&lt;0.01</b>	<b>37</b>	<b>-7212</b>	<b>-6.89</b>
<b>BDE 154</b>	<b>0.59</b>	<b>&lt;0.01</b>	<b>99</b>	<b>-7584</b>	<b>-4.88</b>
<b>BDE 153</b>	<b>0.58</b>	<b>&lt;0.01</b>	<b>75</b>	<b>-8308</b>	<b>-2.40</b>
<b>BDE 183</b>	<b>0.19</b>	<b>&lt;0.01</b>	<b>99</b>	<b>-4946</b>	<b>-13.56</b>
BDE 209	0.03	0.28	47	-1951	-21.40

Table S11: Results of the harmonic regression applied to the PBDE dataset. Only the regression coefficients which were statistically significant ( $p < 0.05$ ) are shown

	N	$r^2$	$a_0$	$a_1$	$a_2$	$a_3$
BDE28	112	0.07	<b>-19.53</b>	<b>0.28</b>		
BDE47	114	0.10			<b>-0.25</b>	
BDE100	114	0.13	<b>22.54</b>		<b>0.23</b>	<b>-6.40E-04</b>
BDE99	114	0.16	<b>18.30</b>		<b>0.17</b>	<b>-4.98E-04</b>
BDE85	46	0.15				
BDE154	114	0.35			<b>0.69</b>	
BDE153	104	0.29			<b>0.62</b>	<b>-3.93E-04</b>
BDE183	113	0.22			<b>0.59</b>	
BDE209	101	0.21	<b>26.68</b>	<b>0.21</b>		<b>-6.76E-04</b>

Table S12: Apparent half lives ( $\tau_{1/2}$ ) of individual PBDEs observed in this study and elsewhere. Compounds in bold represent the cases which were statistically significant at the 95% confidence interval and ns indicates cases which were not statistically significant.

Reference	This study	Schuster et al; 2010	Birgul et al; 2012			Liu et al; 2013					Shunthirasingham et al; 2018	
Location, type of site	Kosetice, CZ, background site CZ	Background sites UK and NO	London	Manchester UK	HAZ	Chicago	Cleveland	St. Point USA	S.B.D.	Eagle Harbor	Burnt Island CA	Point Petre
Years	2011-2014	2000-2008	2002-2010	2003-2010	2000-2010	2005-2011					2005-2013	2005-2014
	Half-life	Half-life $\pm$ SD	Half-lives (min-max)			Half-life $\pm$ SD					Half-life	
BDE 28											26	15
BDE 47		2.4 $\pm$ 0.2				4.6 $\pm$ 0.4	5.4 $\pm$ 0.7	ns	ns	ns	-23	7.2
<b>BDE 100</b>	<b>2.97 (1.87 ; 7.15)</b>	4.0 $\pm$ 0.4									-17	5.9
<b>BDE 99</b>	<b>3.81 (2.48 ; 8.18)</b>	3.3 $\pm$ 0.3				11 $\pm$ 3	7.6 $\pm$ 1.5	ns	ns	-8.1 $\pm$ 2.8	13	6.6
BDE 85												
BDE 154		3.3 $\pm$ 0.1									1.8	0.95
<b>BDE 153</b>	<b>4.83 (2.57 ; 38.94)</b>	1.4 $\pm$ 0.3									2.5	-5
BDE 183												
<b>BDE 209</b>	<b>2.81 (1.91 ; 5.29)</b>					-15 $\pm$ 7	7.0 $\pm$ 2.0	ns	14 $\pm$ 7	16 $\pm$ 8	5.7	16
$\Sigma$ PBDEs			3.4 (2.2-6.9)	2.0 (1.3-4.6)	2.2-9.0	11 $\pm$ 3	5.6 $\pm$ 0.8	6.3 $\pm$ 1.1	ns	ns	-20	8.4

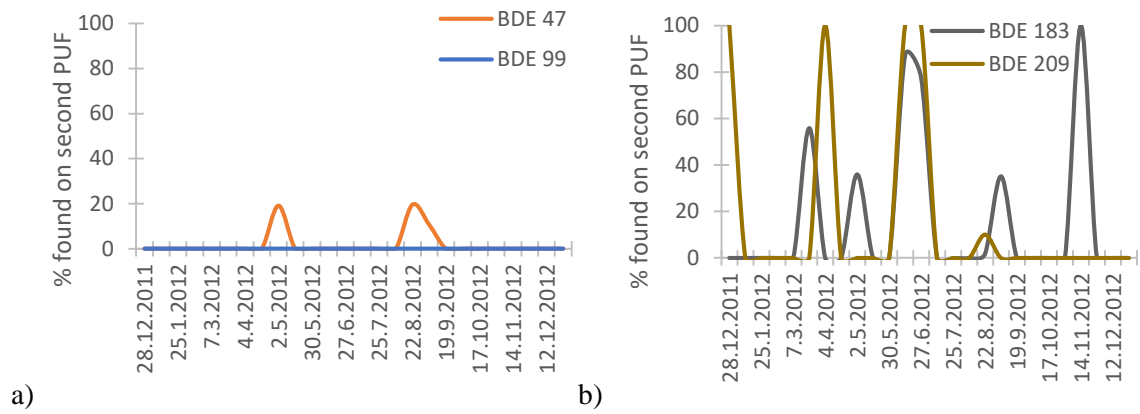


Figure S1: Results of the breakthrough experiments for BDE47, BDE99 (a), BDE183 and BDE209 (b)

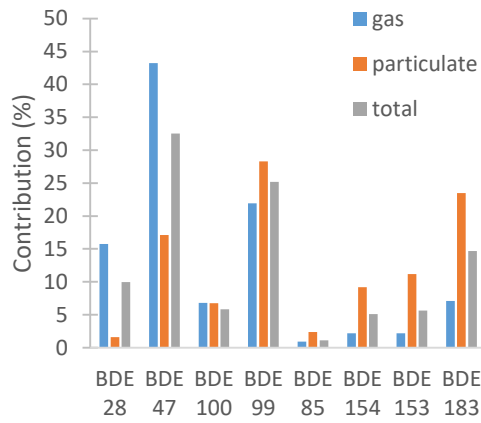


Figure S2: Average contribution of individual BDEs to  $\Sigma_8$ PBDEs

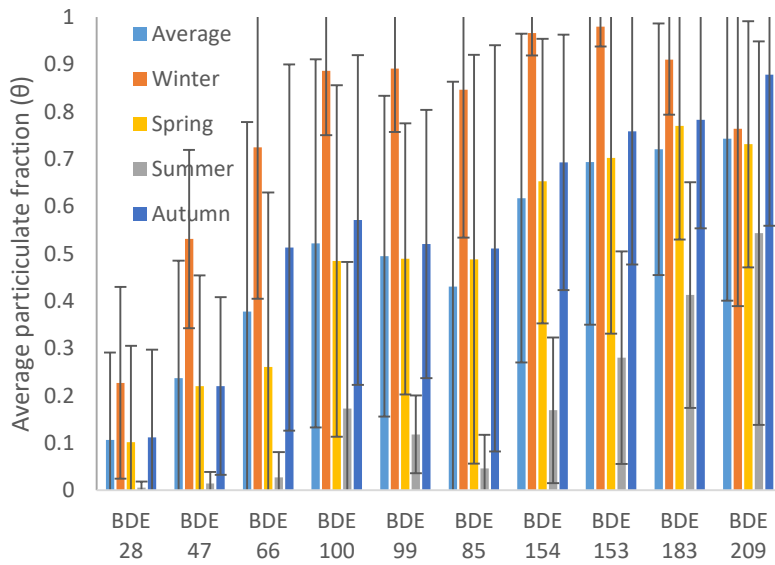


Figure S3: Average measured particulate fraction ( $\theta_{\text{measured}}$ ) found in this study

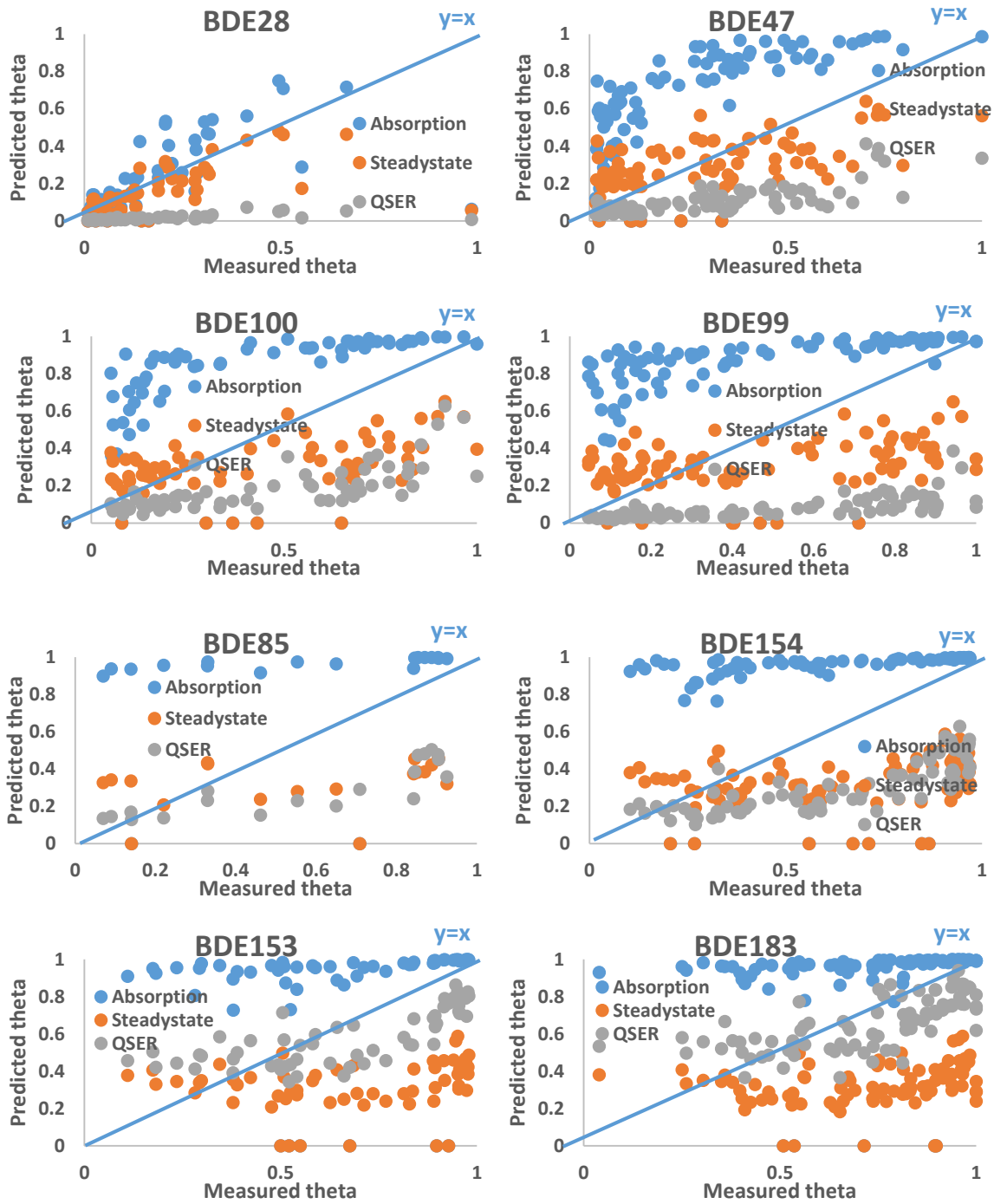
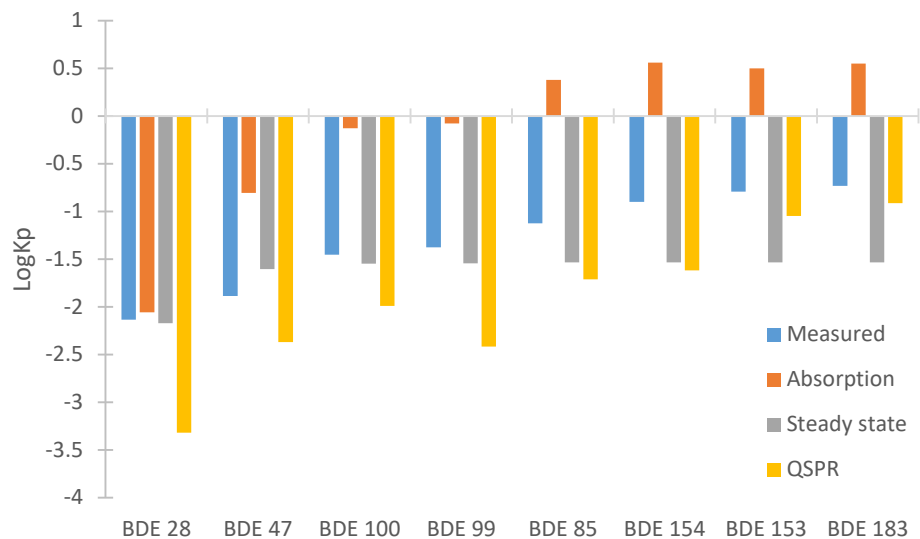
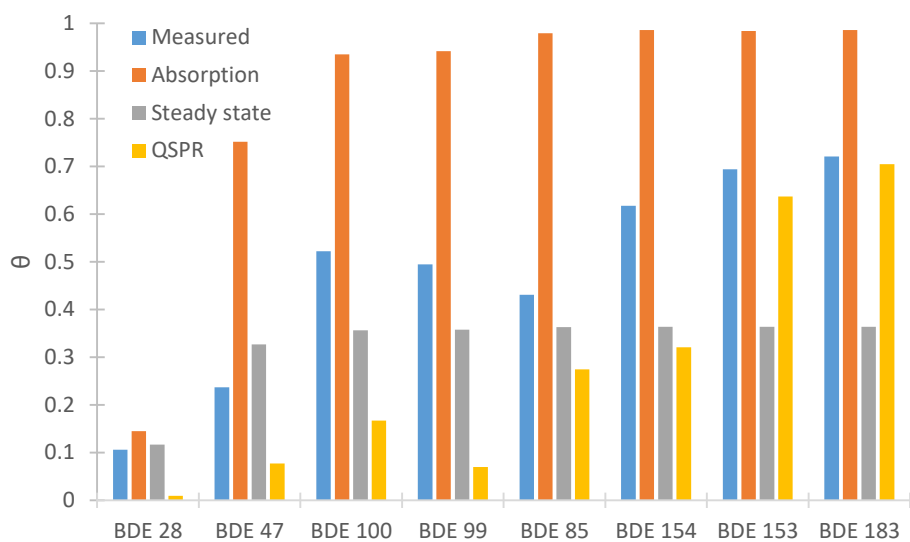


Figure S4: Comparison of measured and predicted  $\theta$



a)



b)

Figure S5: Comparison of the predicted and measured  $\log K_p$  (a) and  $\theta$  (b) using the average conditions at the sampling site (i.e.  $T=281.8$  K,  $PM_{10}=19.6 \mu\text{g}\cdot\text{m}^{-3}$ )



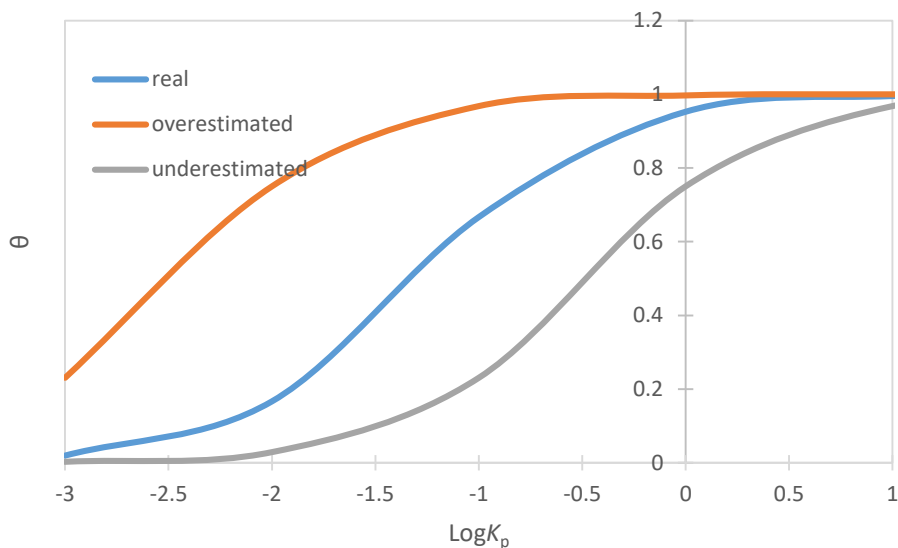


Figure S6: Schematic of the effect of an over- or under-estimation of  $K_p$  by one order of magnitude in terms of  $\theta$ . The average  $PM_{10}$  concentrations ( $19.6 \mu\text{g}\cdot\text{m}^{-3}$ ) at the sampling site during this study was used.

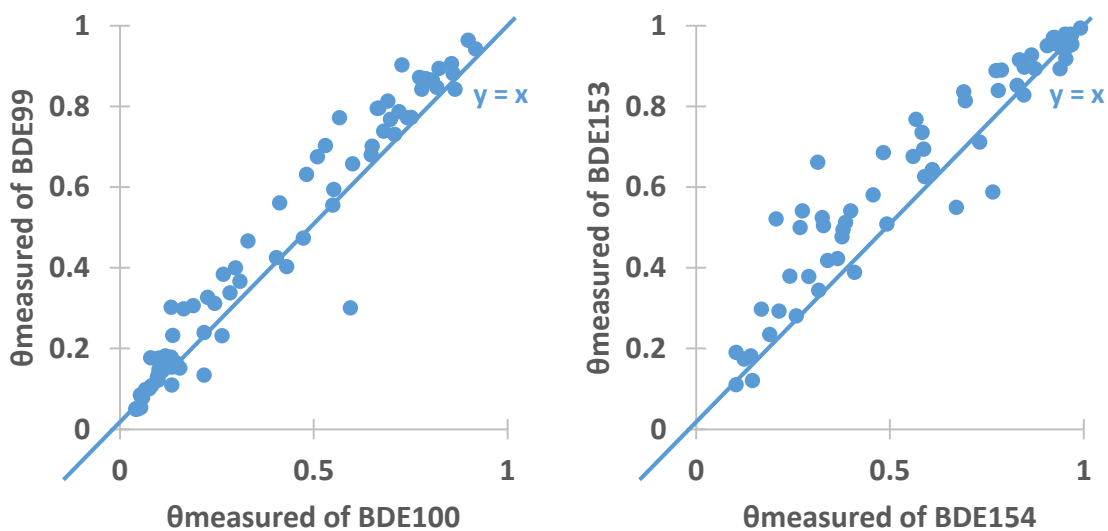
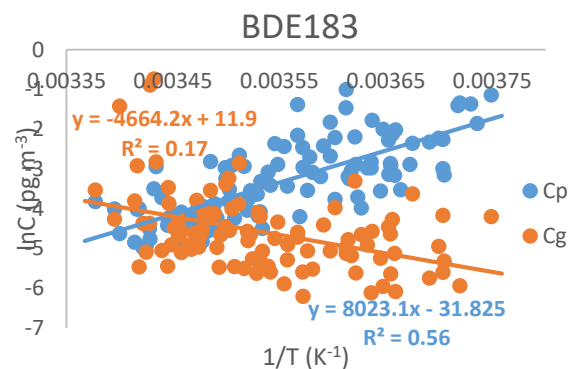
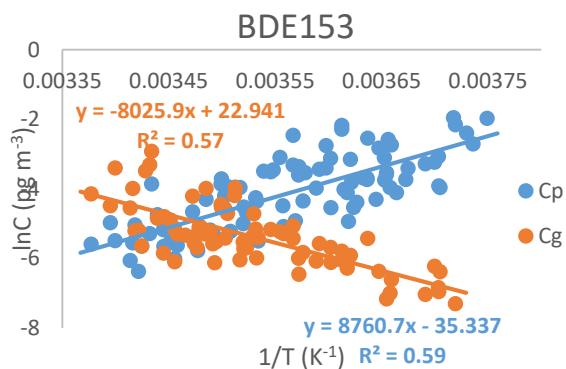
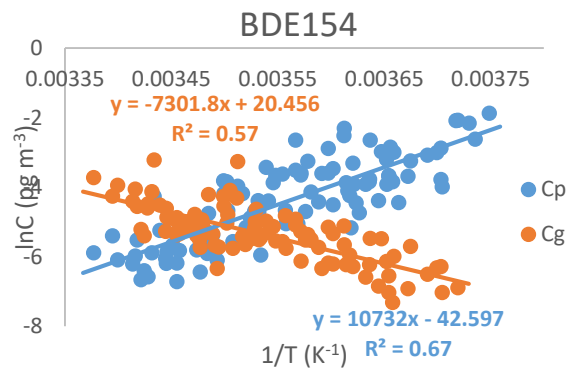
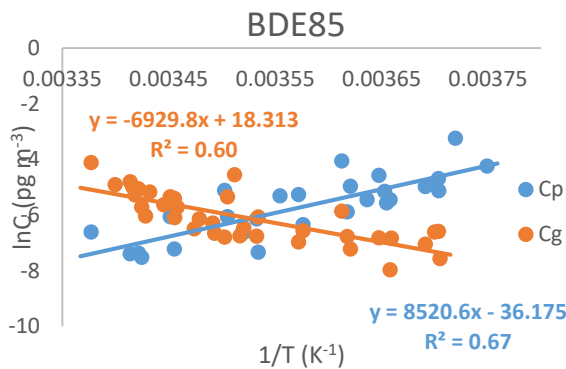
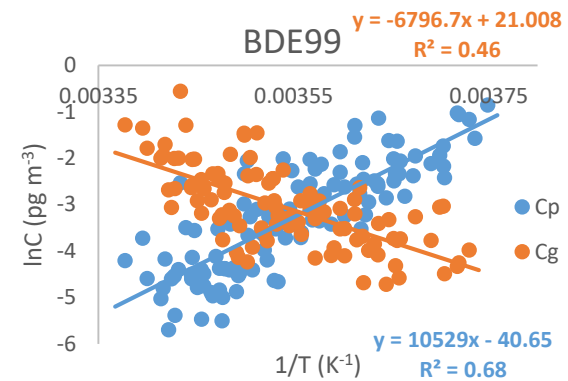
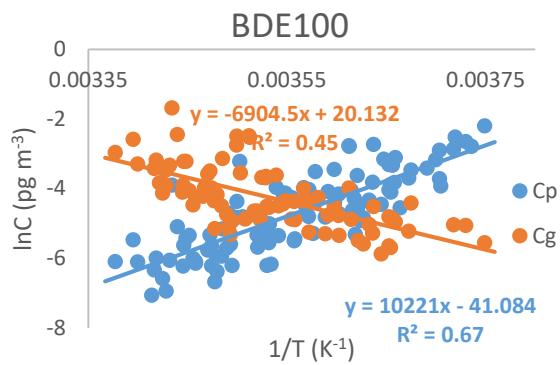
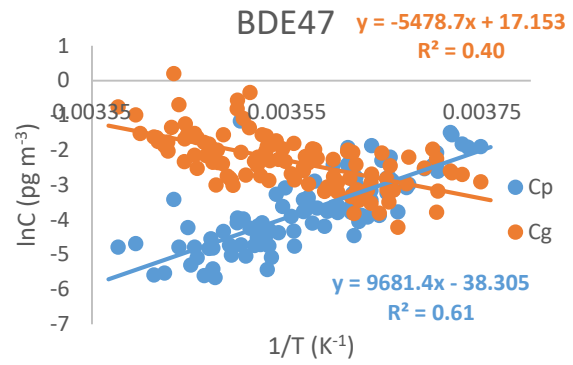
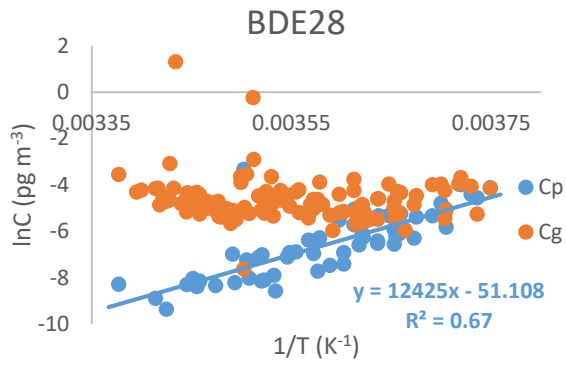


Figure S7: Comparison of the measured particulate fractions ( $\theta_{\text{measured}}$ ) of two sets of isomers. Cases when each isomers were detected in both the gaseous and particulate phases were considered



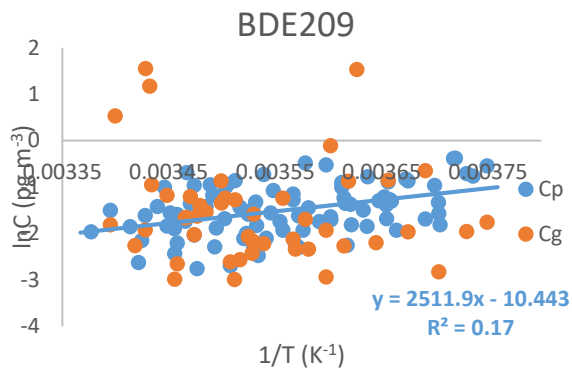


Figure S8: Correlation between the gaseous (orange dots) or the particulate (blue dots) concentration of individual PBDEs (ln transformed) with the inverse of temperature. The regression lines are shown only for cases statistically significant ( $p < 0.05$ )

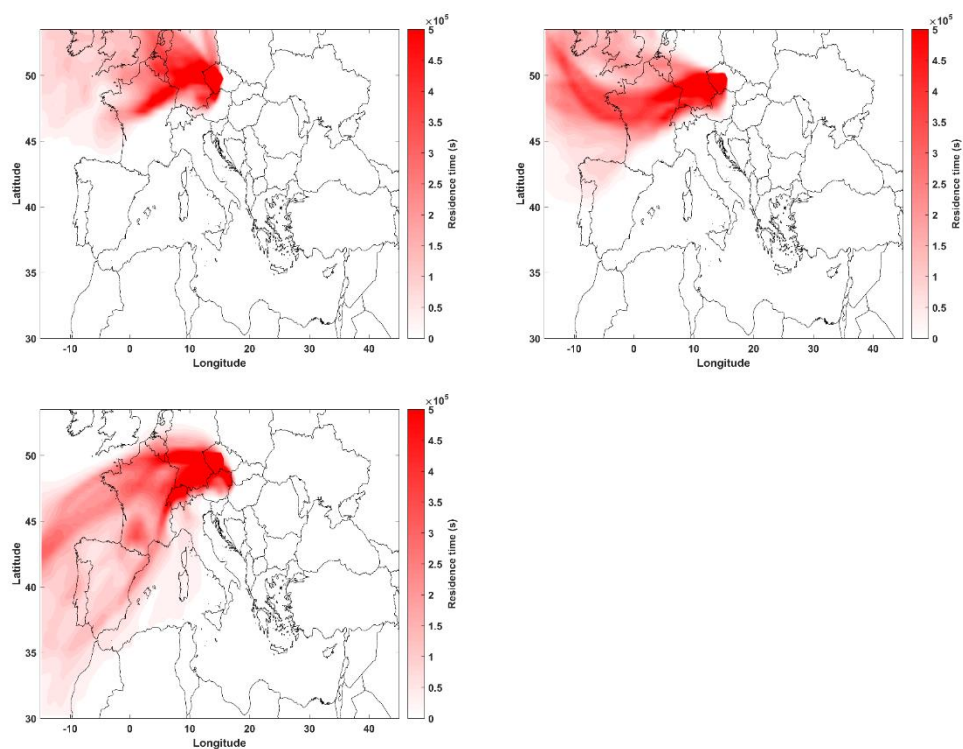


Figure S9: Selected examples of 5 days backward trajectories of samples associated with the lowest PBDE concentrations

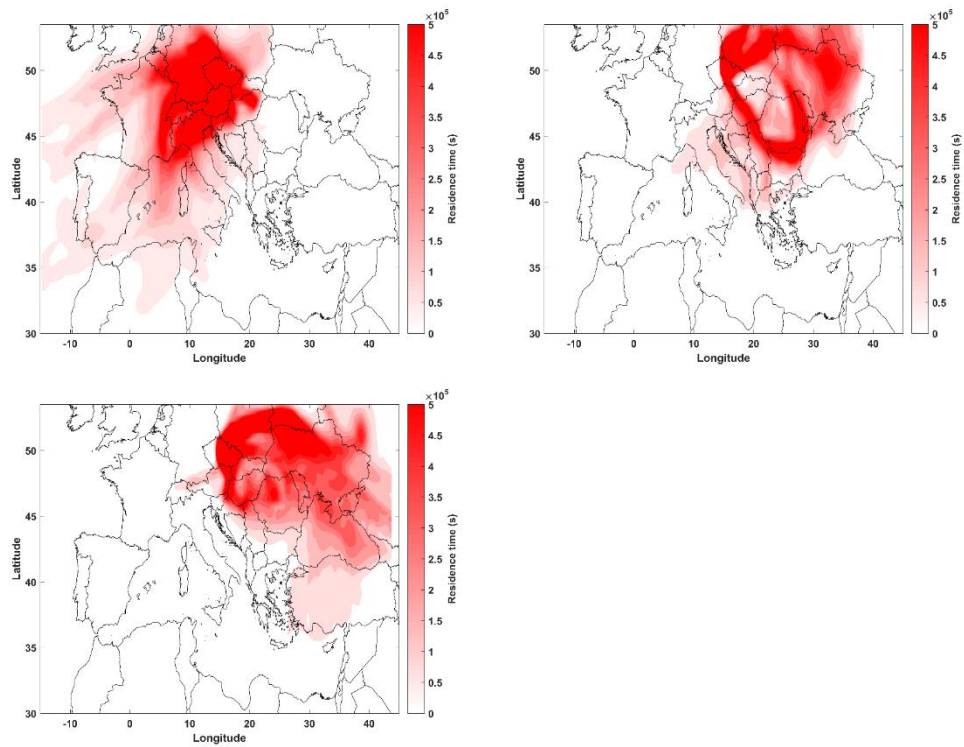


Figure S10: Selected examples of 5 days backward trajectories of samples associated with the highest PBDE concentrations

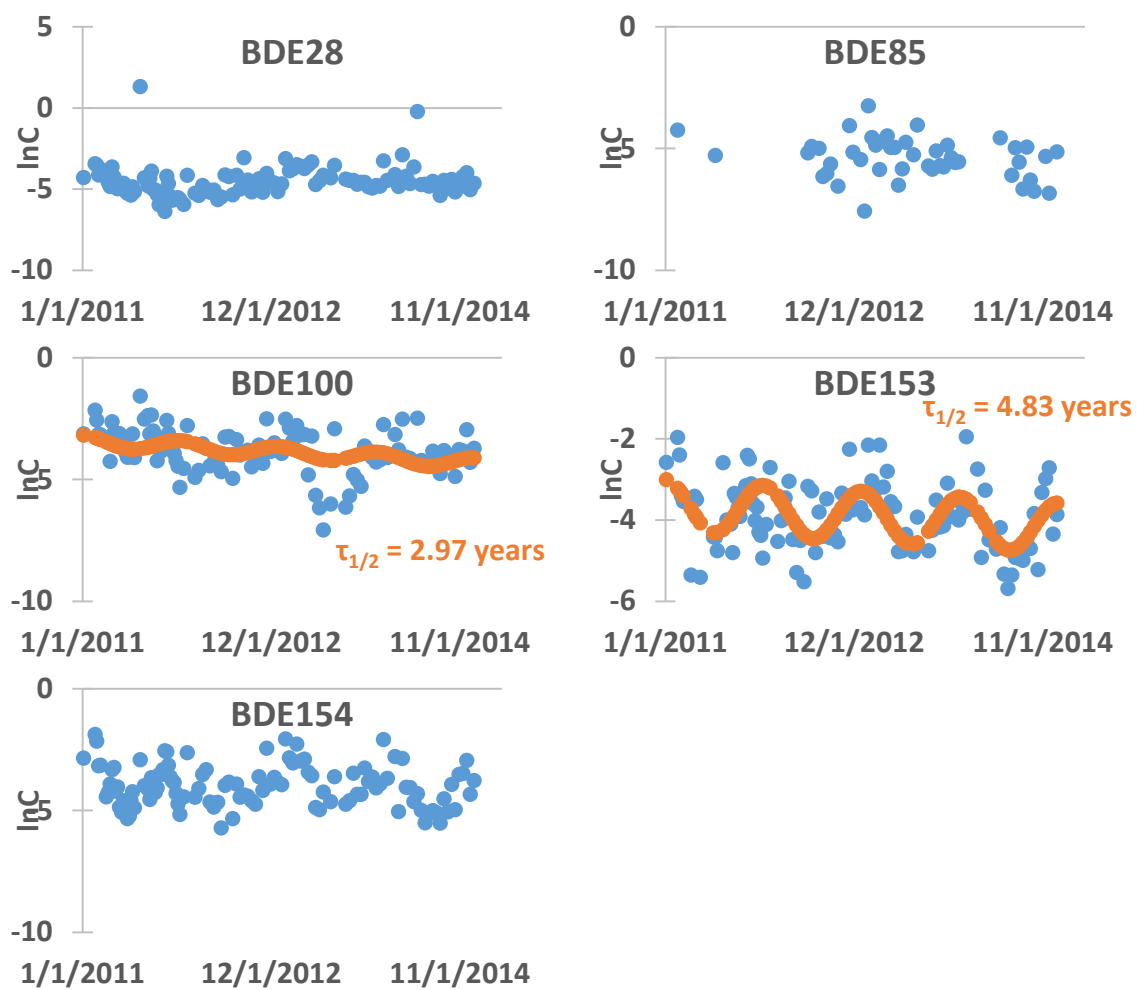


Figure S11: Multi-years trend of some PBDEs