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Interactive comment on "Are atmospheric PBDE levels declining in Central Europe? Examination of the seasonal variations, gas-particle partitioning and implications for long-range atmospheric transport" *by* Céline Degrendele et al.

Anonymous Referee #2

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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

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Discussion paper

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. Breakthrough: Given the extremely large volumes collects, I am surprised that the breakthrough is so limited. Nevertheless, the breakthrough for BDE209 and BDE183 is a bit unsettling. I agree with the other reviewer in that it's particularly interesting that in certain samples 100% of these two congeners were detected in the second PUF. The authors speculate that this effect could be due to lab contamination but lab blanks would clearly reflect that and blank subtraction would equalize samples. A relatively simpler explanation that the authors didn't consider in the paper is the filter pore size. Here the filter cutoff is 2.2 um, which is quite high. For example, IADN employs QFF with a cutoff of 0.3 um. It's quite plausible that fine particles slips through the filter and end us in the PUF. This behavior should also be taken into account for the gas-particle partitioning. 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? Gas-particle partitioning and modeling: the measured values for the particle fractions are certainly affected by the large filter cutoff, as discussed above. This artifact is certainly playing a significant role in the modeling and consequent interpretation. It is quite clear that the Koa model does a better job at describing this relationship than the other ones. If the gas phase concentrations were overestimated based on the larger than usual cutoff of the filters, the Kp would be smaller than expected. In this scenario, rather than the Koa based model overestimating the Kp, it's the measured Kp that is underestimated. 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. 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.

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. Page 3 Bottom half Remove references to PCBs and dioxins since they are not relevant here. 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. Page 6, Line 16 How was the 4% underestimation calculated? Page 6, Line 9 The reference to indoor studies is unnecessary since it's unfair to compare the two concentrations. 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). Page 7, line 26 Table S2 I wonder if this volume of 5264 m3 is a representative number. In line 11, the authors report that the sampling volume ranged from 4015 m3 to 5864 m3 for samples collected in 2015. The average is closer to 5000 m3. Page 9, line 6 Backward air trajectory was not properly introduced and it seems abruptly introduced here. Page 13, line 11 Add also Liu et al., 2016. 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. Figures in main text: They are quite blurry and hard to read. Figure 2 Define the blue lines in caption. Figure 3 If trends are significant, include R and p value on plot. If they are not significant, remove the trend line. 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. 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. Figure S12 If trends are significant, include R and p value on plot. If they are not significant, remove the trend line.

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