

Interactive comment on “Spatial variability of POPs in European background air” by A. K. Halse et al.

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General comments:

The authors present results from an ambitious study in which passive air samplers (PAS) were deployed at EMEP monitoring sites around Europe for four months, then collected and analyzed for persistent organic pollutants (POPs). As described by the authors, this study is important because at present the spatial coverage of air monitoring for POPs within the EMEP program is highly biased towards sites in Northern and Western Europe, where active air samplers are used. Expanding this coverage to more EMEP sites using passive samplers would be a marked improvement over the current situation because it would provide data that is required to better evaluate fate & transport models and emission inventories. However, there are challenges associated

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with the use of passive samplers, since they provide only semi-quantitative information about concentrations of POPs in air.

The study appears to have been quite successful. Where it was possible to make comparisons, the PAS-measured concentrations are in reasonable agreement with active samplers. As discussed in the paper, the spatial variability in concentrations of a range of POPs measured in the campaign is consistent with current understanding of the sources and atmospheric fate & transport of these substances. The most valuable new contribution provided by the paper are the measurement data themselves, which provide a snapshot of spatial variability of concentrations of POPs in air in the European domain, and which will be invaluable to model developers working within the framework of the CLRTAP convention. The success of the study is also highly significant finding because it points the way to improving EMEP's monitoring program. As such I believe the paper will be of interest to readers of Atmospheric Chemistry & Physics, and that it should be published. That said, prior to publication I strongly suggest that the authors add a full reporting of the raw data collected in the study to the Supplementary Material. This should include estimated sampling rates at all sites, and details of the method and field blank levels for all substances analyzed, preferably as an Excel spreadsheet or in annotated text files. Modelers will require these raw data and will not be interested in summary statistics such as presented in Table 1, or the semi-quantitative information presented in Figure S3.

The data requested are now included as Supporting information (excel spreadsheet). Estimated sampling rates are available in Table S1.

In addition, I believe there are many opportunities to improve the readability and clarity of the paper. The presentation and discussion of the data lacks polish throughout, and conveys the impression that the authors rushed this work to completion. This is a shame because the paper reports highly significant findings that have resulted from the concerted efforts of numerous collaborators and volunteers. I have provided several specific suggestions to improve the manuscript in the section below, with a focus on

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the first part of the paper. But, this is definitely not an exhaustive list of areas where improvements are possible, and I encourage the authors to critically edit the entire manuscript to address issues similar to those raised below.

We thank anonymous Referee #1 for the favourable review overall, and for insightful comments and specific recommendations in the following paragraphs. As a result of the helpful suggestions by both referees, we believe the clarity as well as readability of the manuscript has been much improved compared to the initial version.

Specific comments:

P. 22587, Line 6: Are POPs really 'common'? In what sense? Certainly only a small fraction of all chemicals in existence have properties that make them POPs. What is 'common' about that?

Rephrased: "POPs constitute a group of organic chemicals that are semi-volatile,..."

Line 9: Why use the word 'components' here when you are talking about discrete chemical substances that are not components of anything!

Rephrased: "A key feature of these chemicals is their intrinsic potential..."

Line 11: I don't believe the goal of either the Stockholm Convention or the CLRTAP is 'to reduce future environmental burdens in remote areas'. Why be imprecise about what the goals really are?

Rephrased: "Two international agreements have come into effect in order to protect human health and the environment from these substances."

P. 22588, Line 11: delete the word 'potential' that is modifying 'similarities'.

The word "potential" has been deleted.

P. 22591, Line 11: change were -> where.

Corrected.

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P. 22597, Line 25 – 26: 'greater higher'?

Corrected: "greater" has been deleted.

P. 22598, Section 4.2: What happened to the results from Aspvreten in the comparison between passive and active sampling in this section? It is listed on Line 23 along with other sites, but no results are shown for any compounds.

Unfortunately, one of the samples from Aspvreten was never returned. This is now clarified in the text as follows: "Regrettably, one of the samplers from the Aspvreten site was lost. The comparison for this EMEP AAS site is thus restricted to one PAS sample only".

Also, the spelling of Råd is inconsistent between this section of the text and Figures 2 & 3.

Råd is now used consistently throughout manuscript

P. 22599, Line 10 – 15: The discussion in this section is quite confusing. Differences in windspeed are proposed as a possible explanation for different concentrations of PCBs measured in duplicate samplers. But in the next paragraph, it is stated that results for the HCHs show no evidence that different windspeeds affected the samplers. The same samplers were used for PCBs and HCHs, so they should have experienced the same windspeeds! Couldn't the whole question of effective windspeed be resolved by comparing the rate of depletion of the performance reference compounds in the duplicate samplers? This is not even discussed in the paper at present.

Based on the suggestion of Referee #2, we have moved the entire section 4.2.1 into the supplementary material (section S1.6). This section has now also been revised; In response to the specific issue above, we have (1) added the estimated sampling rate for each of the parallel PAS samples into Table S1 which conveys information on the rate of depletion of performance reference compounds, and (2) revised the discussion of possible differences in effective windspeed on the basis of a comparison of observed

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differences in the rate of depletion of PRCs (sampling rates).

P. 22601, Line 6: Again a passing reference is made to problems at the Aspvreten site that are not explained. Why is there only one PAS from this site?

This is now clarified as detailed above.

P. 22601, Line 10 – 20: Here, the possibility that the active samplers and the passive samplers at Kosetice sampled different air masses is raised. I believe the authors could evaluate this possibility quantitatively using the results from their FLEXPART modeling. Why not do so?

We have included a discussion along the lines suggested for PCB-28 (the only substance being modelled) in section 4.4.

P. 22608 & Figure 4: The agreement between the model and measurements is discussed in terms of logarithmic discrepancies (ie, 'within a factor of 2'). I believe this is appropriate, but it implies that Figure 4 should be presented as a log-log plot rather than on a linear scale.

Figure 4 (now Figure 3) is now changed into a log-log plot.

P. 22609, Line 0 – 5: What effect would secondary sources of PCB 28 have on the EC maps that are presented here? There is a recent paper by Harner and Li in ES&T that suggests air-soil fugacity ratios of the less chlorinated PCBs indicate near equilibrium distribution. If secondary sources are important, aren't the EC maps derived from primary emissions going to be highly misleading?

We agree this is a valid criticism which deserves further attention. In response, we have added a section which clearly highlights the limitations of our modelling approach with reference to a few key studies addressing the potential importance of secondary emissions, including the study mentioned above.

Fig. 1: Panel E shows the value '0' twice on the vertical axis. I would prefer to see a

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logarithmic scale used in all panels.

The duplicated "0" on the vertical axis of Panel E in Figure 1 (now Fig.S2) have been corrected. Additionally, all vertical axes in Figure 1 (now Fig.S2) have been changed to logarithmic scales.

In both Figure 1 & 2 I think some statistics should be used to determine whether differences are significant or not.

We have included error bars in Figures 1 and 2 (now Fig S2 and Fig 1, respectively) to better illustrate the uncertainties associated with PAS results: Figure 1 (now Fig S2) now include the estimated uncertainty associated with the chemical analysis alone as discussed in section 3.4, whilst Figure 2 (now Fig 1) additionally includes the relative deviations from the average value of the two parallel PAS samples (Table S4). The corresponding texts in both the main manuscript (4.2) and SI (S1.6) have been revised accordingly.

Fig. 2: Panel F says 'Hivol' where it should say 'AAS'.

This has been corrected in Fig 2 (now Fig 1).

Figure S6 – S20: The two versions of the ES and EC maps for some sites should be better explained in the figure captions. I presume these are for the active versus the passive samplers? But, if this is the case, why aren't there two versions presented for Birkenes and Kosetece in Figure 5.

Unfortunately, some ES and EC maps were duplicated in the submitted manuscript. This has now been corrected. All ES and EC maps correspond to the exact PAS deployment period at each site, except for Fig S23-24 which has additionally been included to illustrate possible differences in model outputs for the AAS sampling periods alone for the two sites mentioned above.

As noted above, separate analysis using the model for the active and passive samplers could be used to discuss the possibility that different source regions influenced levels

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measured in the two types of samplers.

An analysis along the lines indicated has now been carried out for Košetice and Birkenes where AAS and PAS sampling coverage differed the most (and hence air masses sampled). This is now summarized in section 4.4.

The scales on all of these Figures should be adjusted so that the colored portion of the ES map extends over all possible source regions identified in the EC map. It is frustrating to not be able to read quantitative information about the ES for most sites from anywhere in North America, but then to see that the east coast of North America makes a higher contribution in the EC map than many areas of Europe.

The figures show the values on a logarithmic scale. The contributions coming from North America are in most cases below 1%. Extending the scales would lead that nearly all areas would show up in the colour of the lowest value. No change has therefore been made to the scales of the ES maps.

Finally the map in Figure 14 does not show the location of the sampling site!

We have now modified this figure (Fig S16) so that it includes the location of the sampling site.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 22585, 2010.