

Interactive comment on “Increasing and decreasing trends of the atmospheric deposition of organochlorine compounds in European remote areas during the last decade” by L. Arellano et al.

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This paper is a follow-up of authors' another paper on PBDE deposition published on the same journal in 2014. The manuscript presents monitored POPs atmospheric deposition to several mountain areas across Europe. Authors investigated connections between spatial and temporal patterns of bulk deposition and environmental factors and elucidated potential mechanisms contributing to changes in deposition fluxes at different mountain sites where samplings were taken. The title of the manuscript appears not really consistent with the major objectives of this paper.

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Response. Although other results are discussed in this manuscript, we think that the most relevant outcomes of this study are the temporal trends observed in atmospheric deposition of OC in high mountain regions, and the fact that these trends are compound-dependent, with some compounds showing increasing concentrations, while other showed the opposite. This main result has been emphasized even more in the revised version. Anyway, we have modified the text for clarification.

With limited ambient data collected by authors one cannot expect any statistical significant trend to be detected.

Response. Our results are statistically significant. Temperature, precipitation and total deposited particles have been described as the main factors governing POP deposition in previous studies. These parameters have been measured in the present study in all four sampling sites. Another main source of information for the understanding of the origin of the POPs deposited in remote sites are backwards air mass trajectories and these have been measured every two days during the whole sampling period (2 years in Gossenkölle, Redon and Skalnaté Pleso and 2.8 years in Lochnagar). In each case, these measurements encompassed the reconstruction of the backwards air mass trajectories for the last 3 days at intervals of 6 hours using 12 end-points (longitude, latitude and altitude). These backwards air mass trajectories were representative of the air masses above the sampling sites. A total of 1900 air mass retrotrajectories were calculated which involved a considerable effort of computing and man-power. Concerning field work, one different team of sampling and field analysis had to be devoted to each of the sites. The conclusions of this study are based on the largest sampling and analytical effort ever performed in remote sites for the study of POPs considering the spatial coverage and the period of study. The work followed strict quality standards and it has provided reliable and statistically significant results for the evolution of POP deposition in Europe.

Some technique details of this paper relays to some extent on their previous paper on ACP, e.g., bulk atmospheric deposition sampler. Authors should state clearly that they

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collected wet and dry deposition flux.

Response. Yes, most of the technical details are given in our previous paper; however, in the present paper we included all fundamental details for the present study. For example, it is mentioned throughout the manuscript that we analyzed bulk atmospheric deposition samples, which implies dry+wet deposition. This is clearly stated now in section 2.2 Sampling.

Air mass trajectories were also presented in their last ACP paper but only for the sampling period of 2004 through 2007. Present study also assessed POPs deposition fluxes for another two periods of time from 1997-98 and 2001-02. Are those backward trajectories collected in 2004-07 applied also in these two periods of time?

Response. No, the air mass trajectories discussed in this manuscript correspond only to those calculated for the time period between 2004 and 2007.

For instance, the strongest ENSO event over the last half century took place in 1997-98 which altered considerably the large scale wind pattern in Europe. The weak El Niño winter of 2006/2007 was unusually mild in Europe. All these would affect environmental fate and deposition of POPs in Europe.

Response. Certainly, these meteorological events could affect POP transport and deposition in Europe. However, the period chosen for sampling in our study ended in September 2006, before the weak El Niño event. In principle, this phenomenon should not have influenced our results. The strong ENSO of 1997-1998 could have influenced on the results of these previous studies that we were using for comparison. Nevertheless, this phenomenon will also have a great effect on other ambient variables like temperature and precipitation, which have also been taken into account in our temporal trend discussion. As mentioned in the text, no difference in mean annual temperature was observed between the time periods considered. In addition, the precipitation data indicate an increase in rainfall from 1997-1998 to 2001-2002 in Redon, but a decrease in 2005-2006 in this site as well as in Gossenköllesee.

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Could authors explain further why HCB deposition was lowest, even lower than HCH? HCB is very stable with longest life time (aprox 2 yr) in air among those OCs investigated in this study. HCB is of higher Henry's law constant similar to PCBs and high volatility similar to α -HCH. Atmospheric level of HCB is still relatively higher as compared with PCBs and HCHs in the Northern Hemisphere (e., Hung et al 2010). Under the same meteorological conditions, the authors' result showed lower deposition with higher air concentration of HCB. This seems weird.

Response. Regarding the physical-chemical properties of HCB compared to the other OCs included in our study, we have performed a literature search to obtain comparable values among the wide range of constants published for these compounds. The main conclusion is that, in terms of volatility, HCB has a behavior equivalent to a high volatility PCB. It is more volatile than the most volatile congener considered in this study (PCB 28). This is also reflected in the H of HCB, which is the highest among the studied compounds. These two high PL and H imply low tendency to deposit by any of the deposition mechanisms (dry deposition, wet deposition or air-water exchange), therefore the low deposition fluxes measured for this compound in our study are coherent with its physical-chemical properties.

Compound PL (Pa) H (Pam³/mol)

HCB 0.094 65

PCB 8 0.148 22.9

PCB 15 0.0575 13.49

PCB 28 0.0269 30.2

PCB 101 0.00245 24

PCB 153 6.03 x 10⁻⁴ 19.95

α -HCH 0.245 0.741

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γ -HCH 0.0759 0.309

Values of HCB from Shen and Wania, 2005. Values of HCHs from Xiao et al., 2004. Values of PCBs from Li et al., 2003.

Paper from Hung et al 2010 mentioned by the reviewer (Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993–2006) indicates an increase in the concentration of HCB in the Arctic air, which is consistent with the cold condensation theory predicting a selective accumulation of high volatility compounds like HCB in the polar areas, while moderately volatile OC would be deposited and accumulated in mountain regions. These results are also coherent with the low deposition fluxes of HCB measured in our high mountain sites. We have added a sentence in the revised manuscript to explain the physical-chemical reasons of the observed low deposition fluxes of HCB in pag 7, line 12: “In contrast, HCB exhibited the lowest deposition, generally in the range of few ng m⁻² mo⁻¹ according to its high volatility and Henry’s law constant (PL 0.094 Pa; H 65 Pam3 mol⁻¹, Shen and Wania, 2005), which inhibit its removal from the atmosphere by any of the deposition mechanisms (air-water exchange or dry and wet deposition)”.

Section 4.2. Authors should mention what data were used to estimate correlations between OC deposition flux and meteorological variables. Are these correlations from monthly deposition fluxes and monthly averaged temperature and precipitation?

Response. We obtained monthly deposition data for OCs, hence we standardized all meteorological data to a monthly basis. This is mentioned in the header of Table 4 and 5, and in the first paragraph of the 4.2 section.

Frankly, no matter how primary emission or secondary emission dominate, these chemicals always show higher level in warm season and lower level in cold season. This is a common knowledge. So such correlation analysis does not show added values to our knowledge.

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Response. We are not sure if reviewer’s comment referred to all OCs or only to those showing a positive correlation with temperature in this study. In fact, we observed this seasonality for endosulfans in the four sites (the current use pesticide), while in the case of PCBs it was only found in one of the sites, indicating that there are other factors controlling the concentration of these compounds in atmospheric deposition for the studied period in these sites. These results contrast with those found in previous studies performed in Redon and Gossenköllesee in 1996, when all compounds showed higher level in warm season than in cold season. In this sense, there are several studies reporting this lack of seasonality, mainly in remote sites such as Finokalia (Eastern Mediterranean Sea) (Mandalakis and Stephanou 2004, EST, 38, 3011-3018) or even the opposite, namely negative correlation between PCB concentration in precipitation and temperature (see for example paper on PCB in atmospheric deposition over the Baltic Sea by Agrell et al, 2002, Atmospheric Environ., 36, 371-383 and references herein). In view of the differences in seasonal behavior reported in the literature for these compounds, we think that is worth to perform this correlation analysis to study which factors have a greater influence in our specific case.

Given its short half-life in air, endosulfan (pg 15, line 13) would quickly be degraded after its application in summer.

Response. We couldn’t find any reference to endosulfan in pag 15, line 13 in any of the versions of our manuscript, therefore we do not know what the referee wanted to state with this comment. In any case, several studies have shown the occurrence of endosulfans in remote areas far from its production/application areas which indicate the long range transport potential of this compound despite its half-life.

Pg 3, line 21, “. . .with limited atmospheric transport”, not sure what does this mean.

Response. This means that pesticides with low vapor pressure and short half-lives in air have limited capacity for long-range transport. This is clearly described in Hageman et al. (2006), for instance.

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Without or with limited atmospheric transport, where deposited or mountain tracked POPs come from?

Response. Well, this is one of the objectives of our study which has been addressed investigating the relationship between air mass trajectories arriving at each site and OC deposition fluxes. Our results showed no correlation for PCBs, which is consistent with diffuse pollution from unspecific sources as the predominant origin of these compounds in these remote sites. In contrast, significant correlations between current-use pesticides and air masses flowing from the south were observed in Gossenköllesee, Lochnagar and Redön. In Gossenköllesee and Lochnagar, the relationship between pesticide concentration and southern air masses was univocal reflecting the impact of regions with intensive agricultural activities, whereas in Redön, the correlation between air masses from the south and temperature did not allow to discriminating between these two determinant factors of pesticide deposition.

A recent study by Zheng and Nizzetto et al (Environ Popl 2014, 195, 115-112) showed that soil total organic carbon dominated PCBs accumulation and distribution in mountains, not cold-trapping associated with temperature.

Response. Thanks for quoting Zheng et al. We were not aware of this paper when submitting our manuscript. Actually, this study confirms the influence of the cold-trapping effect in the PCB distributions in mountain slopes. Zheng et al describe what it has been published in several papers, that is, the influence of soil organic matter (TOC) in the distribution and accumulation of persistent organic pollutants (POPs), with high organic carbon content soils accumulating higher amounts of POPs (see for example, Meijer et al, EST, 37,667-672 (2003), Ribes et al EST, 36, 1879-1885 (2002), among others); however, once soil organic carbon has been taken into account, it is possible to study the influence of other environmental factors such as temperature, precipitation, etc. In fact, one of the main conclusions of the paper from Zheng et al is the occurrence of an altitudinal gradient in TOC normalized concentrations of PCBs at increasing altitude in 16 sites out of the 20 studied (see section 3.4. Distribution along

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the altitudinal gradient, pag 118). Similar results were reported for other areas once the concentrations of PCBs in soils were normalized by TOC (Ribes et al., 2002). Zheng et al indicate that this result confirms previous evidences of orographic cold trapping in Chinese high mountains and other regions of the world. Even more, these authors reported that temperature and wet deposition were the only variables significantly correlated with PCBs enrichment trends along the slopes, which is consistent with the altitudinal cold trapping theory.

Pg 4, line 13, "POPs were determined in bulk. . .", deposition cannot determine POPs. POPs environmental fate was determined in bulk atmospheric deposition?.

Response. The reviewer is correct. This sentence had a problem. We determined POP concentrations. We had changed this sentence in the new version of the manuscript published in ACP discussions as: POP concentrations were determined in bulk atmospheric deposition samples collected monthly in four mountain areas distributed throughout Europe between 2004 and 2006

Pg 4, line 21-24: the third and fourth objectives have no significant difference.

Response. These objectives were already modified in the final version of the manuscript: (iii) to determine which environmental variables control the atmospheric deposition fluxes of OCs and to quantify their influence, and (iv) to identify potential source regions of these compounds in high mountain areas of Europe

Pg 7, line 20-21 and other places of the paper for air mass trajectories: see my previous comment.

Response. We have indicated here and in other paragraphs (when suitable) that the air mass trajectories discussed in the manuscript corresponded to the period from 2004 to 2007.

Pg 8, line 19-20:

Response. We do not know which the referee's comment for these lines is.

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Pg 13, line 19, 'in' should be 'on'.

Response. We have modified this sentence.

Section 4.4, see my general comment.

Response. See answers above.

Pg 17, line 23, PCB138 has greater long-range transport potential.

Response. According to the physical-chemical constants PCB 138 has not greater long-range transport potential than the other PCB congeners considered in this study. We observed that this congener showed the strongest increase in 2004-2006, in comparison to the time interval sampled in 1996-1998. For a more homogeneous comparison of the total PCB congener values between different time periods, we performed some calculations excluding this congener.

Pg 18, line 22-26, these statements are speculative.

Response. We agree with the referee that these statements are speculative, since we cannot demonstrate with our data that the PCB increase is related to the additional inputs due to the melting of glaciers; however our data matches with this "glacier hypothesis" in terms of the increase of the total PCB amount as well as in terms of changes in PCB composition (higher contribution of the less volatile congeners in comparison to the PCB mixtures found in 1996-98 and 2000-2001). Several studies have showed that, in these high altitude sites of Europe, environmental compartments, namely soils, aquatic organisms, sediments and snow, are enriched in less volatile PCB congeners in relation to what is found in the atmosphere. Moreover, recent studies have demonstrated that melting glaciers in high mountain regions can act as secondary sources of POPs released to Alpine lakes (Schmid et al., *Environ. Sci. Technol.*, 45, 203-208, 2011; Blais et al., *Ambio*, 30, 410-415, 2001), especially for PCBs (Bogdal et al., *Environ. Sci. Technol.*, 44, 4063-4069, 2010). Indeed, increasing concentrations of POPs have been observed recently in sediments of Lake Oberaar, a glacier-fed lake

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in Switzerland, (Bogdal et al., *Environ. Sci. Technol.*, 43, 8173-8177, 2009). Hence, although speculative, we think that these statements are plausible and may explain the temporal trend observed in PCB concentrations and composition in atmospheric deposition samples; however, this paragraph has been modified to clearly state that this is a hypothesis.

Figure 1, add more detailed information in figure captions.

Response. In the final version of the manuscript published in the ACP discussions we had changed Figure 1's caption by: Mean percentage contribution of PCB congeners considering all deposition samples (total) and for each study site.

Figure 4, define upper and lower panel as fig. 4a and 4b.

Response. Again, this was already done in the final version of the manuscript for the ACP discussions.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 15, 3415, 2015.

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