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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Soil-air exchange controls on background atmospheric concentrations of organochlorine pesticides" *by* A. Cabrerizo et al.

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Responses to reviewer# 1:

Anonymous Referee #1

This manuscript discusses the variability of soil-air partitioning of OCPs in Europe. Its technical quality is good with detailed data analysis and presentation of the data. It has been discussed, suggested and proven by many researchers that soils might act as secondary source of OCPs to the atmosphere, especially the ones were subject to heavy application of OCPs, however previous studies were done mostly at single location. So what is unique with current manuscript is conducting multiple-site experiments

at different seasons of the year. I suggest this manuscript for publication after minor corrections listed below

Response: We thanks reviewer 1 for the constructive comments and suggestions which help us to improve the manuscript. We have modified the manuscript accordingly incorporating the corrections and comments as noted below.

General comments:

Response: All general and minor comments have been answered below and the new verstion of the manuscript modified accordingly.

I recommend authors to re-consider the number of figures to be represented in this manuscript, 7 figures seem a lot and some might be removed.

Response: We thank reviewer's suggestion but after reviewing the seven figures that appear in the manuscript we think that all of them are necessary to support the discussion that appears in the manuscript. Therefore, we conclude that it is important to keep all seven figures in the main text as they emphasise the results and contribution of this manuscript. In fact, the supplementary information already contains many other figures and ancillary data, but these seven figures are important in order to follow appropriately the discussion and justify the conclusions of the manuscript.

I suggest authors to compare and add comments whether isomer ratios of DDTs and HCHs between air and soils changes during volatilization process?

Response: We appreciate the reviewer comment, and we have considered this issue in the new version of the manuscript. For DDTs, we assume that the reviewer meant the comparison of ratios of DDT and DDEs, since we did not perform the measurement of chiral ratios in our samples. We measured ratios of ppDDE/ppDDT<1 in 3 sampling sites of the Ebro river watershed soils (Sabinánigo, Lasieso and Nájera). We have calculated ppDDE/ppDDT ratios for fugacity in soil (i.e air equilibrated with the soil) taken by the soil fugacity sampler in order to see weather the ratios in the soil and air equilibrated with the soil agree during net volatilization. Results of pp-DDE/pp-DDT for the air equilibrated with the soil for Sabiñánigo are 0.26 and 0.24 (in samples taken during consecutive days, for example) and 0.7 for Nájera. So, it can be observed that the pp-DDE/pp-DDT ratios of soil are consistent with the ratios measured in the fugacity in soil. The value reported for Lasieso in the manuscript belong to September campaign in which we only carried out soil sampling at this site but not the soil-air exchange study. Regarding HCHs, it is usually considered in the literature that if the ratio α/γ-HCH are in the range of 4-12 (Breivik et al, 1999, Vijgen, 2006), it is representative of technical HCH mixture, while lower values or nearly 1 represent important lindane inputs. For the data set reported here, overall, the ratio α/γ-HCH in soils had values lower than 4 and most of them close or lower than 1, which exception of 2 soil samples, which suggest the predominant use of lindane instead of the technical HCH mixture in the study area. Ratios of α/γ-HCH during net volatilization, in both air equilibrated with soil (fugacity in soil) and ambient air also shows that α/γ-HCH were also lower than 4. Around 80% of ambient and soil fugacities measurements had values lower than 1 consistent with results of HCH isomers in soils. All these considerations support the important role that volatilization from soil has as a control of the atmospheric occurrence of organochlorine pesticides.

There are some specific examples of literature could be mentioned in this manuscript as the scope of the manuscript is to discuss whether soils act as a secondary source to the air. For example, studies conducted by Kurt-Karakus on real-time measurement of DDTs fluxes from soil to air as well as chiral fractions of certain chiral compounds in air and soils can be added in discussion parts.

Response: Following reviewer comment we have introduced the discussion of the important work done by Kurt-Karakus and collaborators in the new version of the manuscript. Unfortunately, we do not have the chiral signature measured in our samples, but we now mention and discuss the chiral fractions and behaviour of some pesticides in soil and adjacent air as described by others.

Specific comments: In the manuscript, "ten" sites are mentioned but in Table S1, there is only nine sites reported.

Response: In the published version of the manuscript it already said “nine” sites to be accorded to what it was shown in Table 1 of Supporting Information

please remove the conflict p. 7 line 16.

Response: We have deleted the sentence from “however, the air concentrations of legacy pesticides.. ...” to be consistent with the previous sentence

RËŽužicková p. 7 ËĞ line 22.

Response: Changed as suggested

NOOA should read NOAA

Response: Changed as suggested

pp. 8, line 9. use the same notation throughout the paper, n/m3 or ng m-3

Response: We have revised all the manuscript and we have used ng m-3 throughout the manuscript

p. 9, line 4. Remove bracket before “Najera”

Response: Changed as suggested

Figure 1. the R2 and p-value both equals to 0.59. Can it be a typo?

Response: We thank reviewer suggestion. Reviewer was right and it was a typo. We have corrected this in the new version of the manuscript

Please check references, some are reported with issue numbers but some not, please keep consistency on reference reporting

Response: All the references have been concisely checked in the new version to keep consistency

Anonymous Referee #2

Response: We thanks reviewer 2 for his/her constructive comments to improve the new version of the manuscript, and we have considered all the corrections and comments in the new version of the manuscript.

The manuscript reports on the seasonal and spatial variability of soil-air partitioning of organochlorine pesticides (OCPs) in Europe. It is concisely written with detail statistical analysis and graphical presentation. The ïňĄnding of soils being secondary source of OCPs to the atmosphere is not novel, but being able to carry out such experiments in multiple sites and different times of the year is rare and adds valuable information about soil-air partitioning. Publication is recommended after consideration of the following comments.

General comments:

Response: All the general and minor comments have been answered below and a short discussion when needed have been added in the new version of the manuscript.

Did you see breakthrough of HCB while sampling in the summer months? This may worth to mention in the analytical section, as the loss of HCB may affect the data interpretation. HCB does not showed seasonality like other pesticides. Is there a reason for this?

Response: We appreciate this comment and it was already considered in the previous version. Indeed, Reviewer 1 is right at pointing this as a potential artefact in the measurements, even though we think this is not the cause of the odd behaviour of HCB when compared with others organochlorine pesticides. Breakthrough of HCB could be a sampling artefact, since it has the highest vapour pressure (0.303 Pa) (Mackay et al 1992) of selected OCPs and it has indeed reported in the literature (Lee et al 1999) as a potential artefact to explain the lack of temperature dependence. We have now considered this possibility in the manuscript but its vapour pressure is not very different

than those of phenanthrene (0.11 Pa) (Mackay et al 1992), for which we did observe temperature dependence (Cabrerizo et al. EST 2011). In this study we sampled 10-15m3, at which volumes and with PUF of the size used, and the low flow rates, there is not significant breakthrough for the studied OCl even for the warmer periods. Our estimation of the breakthrough for PUFs of the size used in this study is around 80 m3 for chemicals such as HCB. It is also noteworthy, that for HCB the samples from the summer sampling in the Ebro river catchments could not be determined due to an analytical problem (this was already stated in the text), then the range of temperatures considered is narrow than for other OCl and it can lead easily to a lack of correlation with temperature. A lack of correlation with temperature could also be due of the enthalpy of volatilization from the pure compound is not significantly different than the enthalpy of solubilization in organic matter from the pure compounds. All these observations have been introduced in the new version. Other studies have reported previously an odd behaviour of HCBs in terms of their temperature dependence as discussed in the manuscript.

p. 6 line 13. The recoveries of for some of the chemicals were low, i.e. 50% in both air and soil. Are these the same chemical? Do you think this would be a problem if one chemical's recovery is not consistent, e.g. say in soil is 50% and in air is 90%?

Response: We understand reviewer concern in this issue, but recoveries showed in the manuscript are a range of recoveries, from minimum to a maximum, but with most of air and soil samples recoveries around 75% for air samples and 80% for soil samples, which we think that they are good and acceptable recoveries. The lowest recoveries belong to the same chemical. Regarding reviewer question, we think that it might be a problem if one chemicalÊijs recovery is not consistent with the parallel soil sample in order to calculated KSA, and for this reason, concentrations are usually corrected by recoveries, but we have not detected this inconsistency in our data, so data were not corrected by recoveries. If this un-consistency exist it may only be for isolated measurements that can not modify the trends detected and discussed. In any case, the fugacity ratios are already assessed considering a 30% uncertainty in their measurement.

p. 6, last sentence. Why is altitude an appropriate proxy for organic matter (OM) quality? I don't see the importance of altitude here in the paper. I think it is a very indirect factor which other variables such as soil organic carbon or nitrogen content, pH, vegetation type, organic carbon aromaticity etc. may be a better proxy. Can you provide some reference to show the relevance of altitude.

Response: We agree with reviewer that altitude is an indirect parameter of the organic carbon quality but altitude can influence in the last term vegetation type and so on the amount/quality of soil organic matter found in the soils, so for this reason we included the importance of altitude as a proxy for organic matter quality. In addition, there is quite a "tradition" of studying the influence of altitude on organic pollutant's concentrations (see work by Grimalt and coworkers). For example, Ribes et al. (EST 2002) reported that concentrations of PCBs in soils of different altitudes (Teide, Canary Islands, Spain) correlated with soil organic carbon but that the slope of the correlations was significantly different than one, which for us suggests that the amount of organic matter is not the only descriptor able to predict the soil concentrations of POPs, since organic matter quality may also be different at different soils. But we agree with reviewer that there are better parameters as proxy of OM quality such as those reviewer have already pointed pH, organic carbon and nitrogen content, etc, and which in fact were already considered in the manuscript. We have emphasized this in the new version of the manuscript.

p. 9. It is interesting to see ppDDE/ppDDT<1 at some sites. What is the ratio in the air?In fact, I would like to see the authors compare the isomer ratios (e.g. a/g-HCH ratio) between air and soils. It would be interesting to see if the isomer ratios of soil and air agree during net volatilization. Chiral analysis would also be a good tool to study the soil-air exchange but unfortunately it is not within the scope of the study.

Response: We appreciate reviewer comment, and we have considered reviewer suggestion in the new manuscript. The answer is the same as that given to reviewer 1. We measured ratios of ppDDE/ppDDT<1 in 3 sampling sites of the Ebro river watershed soils (Sabinánigo, Lasieso and Nájera). We have calculated pp-DDE/pp-DDT ratios for fugacity in soil (i.e air equilibrated with the soil) taken by the soil fugacity sampler in order to see weather the isomer ratios of soil and air equilibrated with the soil agree during net volatilization. Results of pp-DDE/pp-DDT for the air equilibrated with the soil for Sabiñánigo is 0.26 and 0.24 (in samples taken during consecutive days, for example) and 0.7 for Nájera. So, it can be observed that the pp-DDE/pp-DDT ratios of soil are consistent with the ratios measured in the fugacity in soil. The value reported for Lasieso in the manuscript belong to the September campaign in which we only carried out soil sampling at this site but not the soil-air exchange study.

Regarding HCHs, it is usually considered in the literature that if the ratio α/γ-HCH are in the range of 4-12 (Breivik et al, 1999, Vijgen, 2006), it is representative of technical HCH mixture, while lower values or nearly 1 represent lindane inputs. For the data set reported here, overall, the ratio α/γ-HCH in soils had values lower than 4 and most of them lower or close to 1, which exception of 2 soil samples, which suggest the predominant use of lindane instead of the technical HCH mixture in the study area. Ratios of α/γ-HCH during net volatilization, in both air equilibrated with soil (fugacity in soil) and ambient air also shows that α/γ-HCH were also lower than 4. Around 80% of ambient and soil fugacities measurements had values lower than 1 consistent with results of HCH in soils

We agree with reviewer that chiral analysis is a good tool to study enantiomeric composition of chiral pesticide residues and would provide further evidence of the volatilization process as a control of atmospheric concentrations, but unfortunately it was not the scope of the manuscript

SpeciïňĄc comments:

Response: All specific comments have been considered and changed in the new version of the manuscript

In Section 2.1, first line. It says “ten” sites, but I can only find nine (see Table S1). Please clarify

Response: In the published version of the manuscript it already said nine sites and we have checked this in the new version.

p. 7 lines 8-13. This part sounds contradictory. At first it says the OCP concentrations showed seasonality, and then the next sentence says that they do not change dramatically as the PCBs. Suggest to re-phrase the statements.

Response: We have deleted the second sentence to avoid confusion as reviewer suggested.

p. 7 line 10. Please specify which “legacy pesticides”. Do you mean the OCPs in the current study?

Response: With the term legacy pesticides, we refer to those pesticides used in the past (we have considered DDT, HCH and HCB in this study), now legally banned and being eliminated under the United Nations Economic Commission for Europe (UN-ECE) and the Stockholm Convection, but due to its physico-chemical properties and stability in the environmental compartments, they are still detected worldwide. The term “legacy pesticides” is not new and there are many papers which use these terms to refer to HCB, HCH and DDT. For example, see works from Bidleman and co-workers. Anyway, we have clarified in the new version of the manuscript that the manuscript we have studied belongs to this classification.

p. 7 line 16. RĚŽužicková, not RĚŽuŽi ĚĞ ckovâ Response: Changed as suggested

p. 7 line 22. NOOA should be NOAA - National Oceanic and Atmospheric Administration.

Response: Changed as suggested

p. 8 lines 5-11. The fugacity of air is described and presented here. However, the authors do not provide any context or interpretation of the data. I wonder if this is the appropriate place to bring this up. It might be better if it is described in the latter section (e.g. section 3.5) where fs/fa is discussed.

Response: We understand the point raised by reviewer here, but we think it is better to introduce the fugacity of air in this section since it was derived from the ambient air concentration presented in the same section.

p. 8, line 9. To be consistent with the notation of fraction, use ng m-3 instead of ng/m3.

Response: We have revised all the manuscript and we have used ng m-3 to be consistent throughout the manuscript.

p. 9, line 4. Delete bracket before “Najera”

Response: Changed as suggested

p. 12, equation 3. Please provide unit for Ksa.

Response: Units for KSA (l kg-1) have been added in the new version of the manuscript

p. 12, line 4. References for Su et al. (and others) report temperature correlation with HCHs in air rather than Ksa.

Response: We agree with reviewer suggestion, but the correct way to express enthalpies from vanÊijt Hoff equation is to derive them from partition coefficients rather than from concentrations. It is true that other studies report enthalpies derived from air measurements, and the implicit assumption in those studies is that the surface concentration is always the same. In any case, this is an important distinction and we have described it in the new version of the manuscript.

Figure 1. Caption for b-HCH, the R2 and p-value both equals to 0.59. Please check whether there is a typo for the p-value.

Response: We appreciate reviewer comment and we have corrected the value in the new version since it was a typo.

References are not consistent. Some references have issue no. but some don't. Please check.

Response: All the references have been concisely checked in the new version to keep consistency.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 25937, 2011.