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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Atmospheric occurrence, transport and deposition of polychlorinated biphenyls and hexachlorobenzene in the Mediterranean and Black Seas" *by* N. Berrojalbiz et al.

**Anonymous Referee #2**

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The manuscript reports a comprehensive assessment of PCBs and HCB distribution in the atmosphere of the Mediterranean sea. The document presents one of the first full-scale monitoring data set of the targeted compounds in this region. Data interpretation and the discussion are developed in a quantitative way through the mathematical parameterization of major sink and source processes. Such an approach is very valuable when interpreting data from regional scale monitoring, and therefore this paper, in my opinion, deserves publication on this journal. There are some points in the methodological description that can be improved, and some omitted information has to be



added. The discussion also can be reconsidered in some parts.

See my specific comments below:

Sample collection. Concerning air sampling, the total sampled volume and flow rates used in this study are very high. In one case a total volume of 950 m3 was reached. The second air sampler (for dioxin-like PCBs) was operated even at much larger rates. In both cases, only one single PUF was used to trap gas phase. It appears that there was no quality control measures set in place to investigate possible breakthrough. Some volatile substance (including HCB and lighter PCBs) might have undergone breakthrough. These sampling conditions were adopted also in previous studies, however breakthrough check was unfortunately omitted in many recent paper. This may results in repeated bias in air concentration dataset, because sampling methods are used outside their effective operation domain. It is important to add a critical comment here and some consideration regarding the possible magnitude of breakthrough related artifacts. Reference to some key methodological paper on active air sampling for POPs will be relevant here.

Line 6 page 9750: Remove "," after "ecosystem"

Line 15 page 9751: Please change as: "both high volume air samplers were controlled by a weather station to . . ."

Line 20 page 9751: Change "preceding" with "prior"

Line 6 page 9752 remove "of" before hexane.

Line 12 page 9752. It is not clear what the authors mean with "as indicated for gas phase samples. The resultant extract. . ..". Please specify.

Line 1 page 9753. Better to report here the range (or mean and variance ) of recoveries.

Line 23 page 9753. Can you provide a reference for the temperature and salinity

correction of H'

Line 13-15 page 9754: The 0.3-3 range for taking into account the uncertainty on fugacity ratios was often adopted in similar studies. I still think it is good for the reader and the quality of the paper to briefly report the rationale behind this range. This addition will make it appearing much less arbitrary.

Line 19 page 9755: "...what was found by Iwata..." in which geographic area?

Line 1 page 9756: "volumetric concentration" please specify. Is this erm used to distinguish it from particle mass based concentrations? The units of atmospheric concentrations were already specified earlier in the text, therefore it might be convenient to remove the word "volumetric" here.

Line 5 page 9756. Here the concentration of aerosol (ng/g) is introduced for the first time. There is no explanation in the methods on how the mass of aerosol was determined in the samples. Please add.

Line 18 page 9756: change "...in the lower range than those..." with "...the lower range of those..."

Line 20 page 9756: change "levels" with "those"

Line 21 page 9757: "A PCA was performed..." there is no information on how such an analysis was conducted. This information can be either be added here or in a dedicated chapter of the method section. Such a section should also report information on the method used for trend analysis. Very likely the distribution of the data used to feed these analyses was not normal and this has an implication for the selection of the methods, therefore statistical method selection is not trivial. Please clarify.

Section 3.2. I could not find any methodological information on how the Aerosol bulk composition was determined. Please add a description in the method section.

Line 24 Page 9758: how Koa was corrected for temperature. What was the source of



chemical physical property data (both Koa and H) used in this study?

Line 26 page 9758 and following: Here the results of gas particle partitioning are described in terms of correlation between kp and Koa. This approach was used before and parameters for such model are available in literature. It would be nice to mention this and compare obtained results with previously reported parameters for this relationship.

Figure 3. Are the error bars referring to the ranges of kp and Koa calculated considering all samples. Please add in the captions.

Line 8-9 page 9759: Please quote this statement and briefly discuss it in relationship to existing Kp vs Koa models. Line 16-25 page 9759. This explanation appears to be quite speculative since it is provided only in qualitative terms. Can you provide a comparison among the magnitude of air-water exchange velocity and air-particle exchange velocity? In this way your arguments will be more convincing. It is in fact difficult to build an intuitive figure to compare these two, very different, processes. Surface/volume ratio of atmospheric particles is very high, and I expect it to be quite efficient if compared to the air-water exchange which on the other side is likely more easily kinetically limited, by the complexity of the interface, especially during low wind conditions.

Line 10-22 page 9760. I really think that you could not see any dependence of air concentration on temperature mainly because of the narrow range of temperature you observed during the campaign. The argument on the equilibrium you provided at line 16 appears fragile to me. Temperature dependence should be present mainly under equilibrium conditions as a result of the temperature dependence of H', right? I would omit this part of the explanation, and just mention the narrow range of temperatures observed in this campaign.

Line 10 page 9761 change "they potentially could receive" with "the could have potentially received"

Line 24 page 9761 Change calculating with estimating

Line 7 page 9763 what is the source of information on Coh used here?

The Section 3.3.5 Seasonal changes... sounds very descriptive and it is not strictly necessary for the scope of describing the results of the present study. I suggest removing it. If you want to keep it, instead, it has to be brought to the same standard and quantitative approach as the previous sections. For example you mention here how process influence can change seasonally only in qualitative terms. It is quite straight forward to provide estimates of the relative magnitude of this change by re-parameterizing the models of individual process under the conditions of different seasons. Some of the changes you described qualitatively (such as the shift in gas particle partitioning) is likely negligible for these substances, however this this does not emerge from the current discussion.

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 9747, 2014.