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

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We appreciate the positive and constructive comments of Reviewer 2 which have allowed us to complement the information given in the previous version, and significantly improve the manuscript. We provide below the responses to the comments and information on how the manuscript has been improved.

All the minor modifications indicated by the reviewer have been included/corrected in the new version. We provide here the detailed responses for those that require detailed

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explanations.

- Methods. Breakthrough volumes

The reviewer raises concerns on the large volumes of air sampled. As explained in the manuscript, we had three air volumes operated in parallel. One of samplers was used for the analysis of 41 PCBs and HCB, while the other two were used for the determination of 8 dl-PCBs and dioxins (PCDD/F) collecting larger volumes of air than the first one. The latters have already been used previously to report the PCDD/F concentrations in the Mediterranean atmosphere (see Castro-Jiménez et al. 2010). As reported in this previous study by Castro Jiménez et al., there was no breakthrough of dioxins to a second PUF. Unfortunately we omitted the results of breakthrough for the dl-PCBs in the previous version of this manuscript, but we have included these in the revised version. Briefly, we performed three controls with 2 PUFs, and the percentages of dl-PCBs in the second PUF range from 0.4% to 4% with a very small standard deviations. The details of these controls have been included in the supplementary material of the manuscript. The high volume air samplers for the 8 dl-PCBs (called sampler B to simplify the discussion) used PUFs with 6.5 cm of diameter and 7 cm long (volume of 995 cm3), while the high volume air sampler operated for sampling 41 PCBs and HCB (sampler A) used a larger PUF of 10 cm of diameter and 10 cm long (volume of 3142 cm3). These larger PUF allow operating the sampler with a larger flow rate. While the smaller PUFs of the B sampler were sampled at 12-15 m3 hour-1, the larger PUFs of sampler A were operated at 40 m3 hour-1. The later is a theoretical maximum flow rate (the programmed flow rate for the sampler) because the pump cannot keep a continuous flow rate of 40 m3 h-1. Thus, in reality, the A sampler usually operated at flow rates between 30 and 40 m3 hour-1 . Since the volume of the PUF of this sampler A is three times higher, the flow rate can also be operated at three times the flow rate of the smaller PUF of B sampler, obtaining similar breakthrough results.

Concerning the sampled air volumes by sampler A (using the larger PUFs and discussed sampling flow rates), these ranged between 230 and 950 m3, but were larger

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than 600 m3 for only 5 of the 34 gas phase samples (see Figure 1 in attached file).

We have published the breakthrough tests for the larger PUFs and large air volumes before (see Del Vento et al. 2007 for results of phenanthrene), and the percentages are always a few percent (less than 6%) for the more volatile compounds such as low chlorinated PCBs and lighter PAHs, even at 25oC.

During the THRESHOLDS campaigns in the Mediterranean Sea, the breakthrough was only evaluated for the smaller PUFs of the sampler B which were used to sample the larger air volumes needed for dioxins (previously published) and 8 dl-PCBs (reported now in the new version of the manuscript).

In addition, these are the results or extended discussion included now in the main text or supplementary material of the new version of the manuscript.

- The rationale of the 0.3-3 range in the fugacity ratios comes from the uncertainty of the measures, but especially on the uncertainty on the Henry's law constants. This is now explicitly commented in the manuscript.

- The mass of aerosols was determined by gravimetry, it is now commented in the methods section.

- We include comments on the details of the PCA analysis in the new version of the text summarizing the information given in the supporting information. Briefly, gas- and aerosol-phase samples were analyzed separately, including as variables in both matrices the sum of the concentrations of PCBs with the same amount of Cls (i.e. sum of tri- to hepta-chlorinated biphenyls), temperature and total suspended particles (TSP) of each sample. PCA was performed on normalized (subtraction of mean and division by standard deviation) data.

- The aerosol content of organic and elemental carbon was determined by using the thermal optical transmittance in a sunset laboratory carbon analyzer using the NIOSH temperature protocol. This information has been included in the manuscript.

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- Koa values were obtained from Harner and Bidleman (1996), Komp and McLachlan (1997) and Shoeib and Harner (2002), which includes the correction for temperature. The H values used were those of Harner and Bidleman (1996), Bamford et al. (2002), Li et al. (2003) and Shen and Wania (2005) using an enthalpy phase exchange of 65 kJ mol-1. The temperature correction has a little effect in this study since the temperatures were very close to 25oC for all sampling events. The references are,

Bamford, H. A., Poster, D. L., Huie, R., and Baker J. E.: Using extrathermodynamic relationships to model the temperature dependence of Henry's law constants of 209 PCB congeners, Environ. Sci. Technol., 36, 4395–4402, doi:10.1021/es020599y, 2002.

Harner, T. and Bidleman, T. F: Measurement of octanol-air partition coefficients for polychlorinated biphenyls, J. Chem. Eng. Data, 41, 895–899, 1996.

Kömp, P. and McLachlan, M. S.: Octanol/air partitioning of polychlorinated biphenyls. Environmental Toxicology and Chemistry, 16: 2433–2437, 1997. doi: 10.1002/etc.5620161201

Li, N., Wania, F., Lei, Y. D., and Daly, G. L.: A comprehensive and critical compilation, evaluation, and selection of physical-chemical property data for selected polychlorinated biphenyls, J. Phys. Chem. Ref. Data, 32, 1545–1590, doi:10.1063/1.1562632, 2003.

Shen, L., and Wania, F.: Compilation, Evaluation, and Selection of Physical−Chemical Property Data for Organochlorine Pesticides, J. Chem. Eng. Data., 50 (3), 742-768, 2005.

Shoeib, M. and Harner, T.:Using measured octanol-air partition coefficients (KOA) to explain environmental partitioning of organochlorine pesticides. Environ. Tox. Chem. 21:984-990, 2002.

- Concerning the comparison of air-water exchange and gas-aerosol partitioning, the reviewer is right that the discussion was qualitative, and it is likely than gas-aerosol

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exchange may be a much faster process than air-water exchange. Therefore, we have removed this paragraph.

- We agree with the reviewer that the lack of temperature dependence of gas phase concentrations may be mainly due to the narrow range of temperatures, and we have removed the second part of the explanation.

- We have not removed section 3.3.5 as suggested by the reviewer, but we have significantly simplified it. We do not discuss the seasonality, since the estimations of the relative magnitude of the seasonal changes (by reparameterizing the models of individual process under the conditions of different seasons) will increase the length of the manuscript to a great extent. Section 3.3.5 is now limited to the comment of the loss fluxes (Figure 6). Nevertheless, we have inserted a couple of consideration on seasonal variations when we think this was relevant, especially for the strength of the biological pump.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C4371/2014/acpd-14-C4371-2014-supplement.pdf

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