Dear Prof. Ralf Ebinghaus,

Please, find attached the revised version of the manuscript "Atmospheric occurrence, transport and deposition of polychlorinated biphenyls and hexachlorobenzen in the Mediterranean and Black Seas" for its consideration in Atmospheric Chemistry and Physics.

We appreciate the constructive comments of the two reviewers which have allowed us to significantly improve the manuscript and clarify some issues. We hope that the manuscript is now ready for its acceptance. We attach as well the detailed responses to the two reviewers.

Looking forward to hearing from you,

Jordi Dachs

Responses to Reviewer 1

We appreciate the positive appreciation from Reviewer 1 about our work and the contribution that is does on the knowledge of POP pollution for the Mediterranean basin. We respond below the comments raised by reviewer.

- Concerning the comment on the Thresholds cruises, the objectives of these cruises funded by the Spanish Government included, indeed, the assessment of air-water-phytoplankton interactions, but also other objectives such as covering a gap of the current knowledge of the processes affecting the occurrence in the atmosphere and seawater of a number of organic pollutants at the basin level. Previous efforts were limited to local/regional studies. In our previous work (Berrojalbiz et al. 2011) we evaluated the occurrence and processes driving the concentrations in water, seawater particles and phytoplankton. However, in the present work we evaluate the atmospheric occurrence and processes affecting it for PCBs and HCB (not only the water side of the story). We do evaluate the role of the air-water exchange on the atmospheric occurrence. Because the Mediterranean Sea is oligotrophic, there is a small influence of phytoplankton uptake lowering the surface water concentrations of POPs, thus leading to air and water concentrations close to equilibrium conditions for most sampling events, as already discussed in the text.

- Concerning the sampling of gas and aerosol phase with the high volume sampler operating at a flow rate of 40 m^3 $hour^{-1}$, we should say that this was the programmed flow rate, but the real ranged between 30 and 40 m^3 $hour^{-1}$. The details of the breakthrough for the gas phase compounds have been discussed as a response to Reviewer 2 and the details included in the supplementary material of the manuscript. Concerning the potential breakthrough of particles from the QMA filters, we did not check this during the thresholds campaigns. The reason is that the aerosol phase concentrations of PCBs and HCB are very low for the marine atmosphere, and our experience is that in the marine/oceanic atmosphere it is not possible to detect most organic compounds in a second filter. However, there are indications that there is no significant breakthrough of small particles because for example, when the samples were analyzed for PAHs (Castro-Jiménez et al. 2012), there were no measurable amounts of high MW PAHs retained in the PUF (used for measuring the gas phase).

- The residence times (R) estimated in this study correspond to the residence times of PCBs and HCB during their transport over the Mediterranean Sea. However, these are not the half-lives of PCBs in the environment comprising all the compartments (air, water, soil, vegetation, PCB reservoirs in primary sources). All half-lives are not equal. PCBs are semivolatile compounds, and only a small fraction of them can be found in the atmosphere (less than 0.1%), most of the PCBs reservoirs are in soils, vegetation, waters,

and sediments. A rapid change of PCB concentrations in the atmosphere in the scale of days, do not imply that their concentrations in the environment decrease in a time period of one or two decades. The apparent lack of decline of atmospheric concentrations over time is not contradictory with the short atmospheric residence times. It implies that there are large primary and secondary sources of PCBs, probably in land, that continuously supply PCBs to the Mediterranean atmosphere. We have improved the explanation on these processes in the new version.

Responses to Reviewer 2

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 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 cm^3), 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 cm^3). 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 m^3 $hour^{-1}$, the larger PUFs of sampler A were operated at 40 m^3 $hour^{-1}$. 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 m^3 h^{-1}. Thus, in reality, the A sampler usually operated at flow rates between 30 and 40 m^3 $hour^{-1}$. 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 m^3, but were larger than 600 m^3 for only 5 of the 34 gas phase samples (see Figure 1).
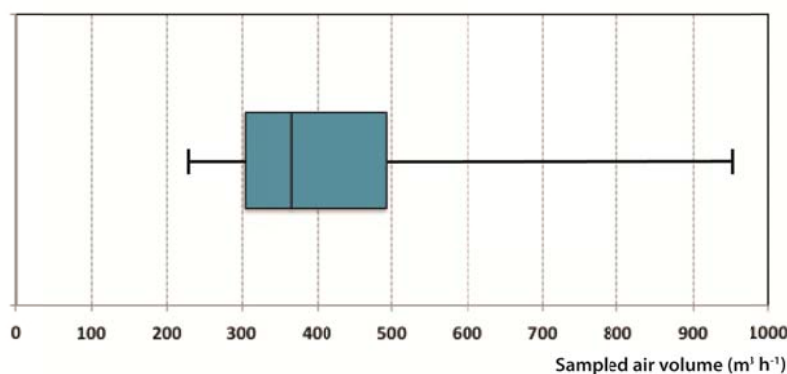
FIGURE 1: sampled air volumes by sampler A (34 samples). The box plot graph represents the minimum, the lowest quartile, the median, the upper quartile and the maximum value of the sampled air volume.

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 25°C.

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.

- 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 25°C 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 (K$_{OA}$) 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 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, 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.