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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Polycyclic aromatic hydrocarbons in atmospheric aerosols and air–sea exchange in the Mediterranean" *by* M. D. Mulder et al.

Anonymous Referee #3

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General comments The current manuscript presents PAHs concentrations in the air and the seawater that were obtained during a 15-day cruise (27 Aug-12 Sept 2010) of the research vessel Urania across central and southeastern Mediterranean. Although the g-p partitioning of PAHs is presented, the authors focus mainly at the diffusive air-sea exchange fluxes of the three PAHs measured in sea water. The manuscript contains interesting original data concerning the occurrence of PAHs in the open sea atmosphere. Nevertheless, it suffers from various scientific and technical deficiencies (several obscurities, inconsistencies, insufficient comparison with literature data, etc), most of which are listed below. In my opinion, the manuscript needs revision before it

can be accepted for publication in ACP.

Specific comments Title The tile of the manuscript is not consistent with the content, I would suggest the following (Gas-particle partitioning and air-sea exchange of polycyclic aromatic hydrocarbons in the Mediterranean)

Methods - Section 2.1: It should be clarified whether results presented in the manuscript have been corrected for possible losses during sampling due to oxidation by ozon.

- Section 2.2: The section title about organic trace substances is confusing, please, change to the following "PAHs analyses and quality assurance". Also, change "organic" with "PAHs" in the first sentence of this section.

- Section 2.2: It is stated that ÂńNo QFF field blank was taken for impactor sampling, but instead the mean of values of the QFF substrates of the 2 uppermost impactor stages (in total 5) was taken". Hence, more information about the concentrations of PAHs in the 1-2.5 μm and the 2.5-10 μm particle fractions needs to be provided.

- Section 2.4: It is unclear which concentrations were used in the air-sea diffusive mass exchange calculations. The FR equation requires the dissolved aqueous concentration Cw. However, as stated in Section 2.2,"Water samples (2-2.5 L) were extracted immediately after their collection using solid phase extraction on C18 Empore discs", which means that total PAHs concentrations (dissolved and adsorbed on suspeneded particles) were determined (those presented in Table 1b).

- Section 2.4: Please correct the concentration units for Cw.

- Section 2.6: The analysis of the long-range advection of air needs further clarifications, especially the statement "Hereby, 50000 particles per hour were released and followed backwards in time for 5 days".

Results and discussion

- Section 3.1: Statement about the long-range transport (illustrated in Fig. S5) is not very clear.

- Section 3.1: The west-east gradient of PAHs concentrations could be evidenced if the sum concentration of PAHs (ΣPAHs) for ISS and SEM were included in Tables 2a and 2b.

- Table 1a: Total concentrations (sum of gaseous and particulate phase) of PAHs provided in the Table are not consistent with the values provided in Table 2a and 2b for the separate phases (For instance, the total concentration of PHE is 0.581 ng/m3, whereas the gaseous and particulate phase concentrations are 0.35 and 0.51 ng/m3). Please, check and correct wherever needed.

- Table 2a,b: Some of the data provided in these Tables indicate an unexpected g/p partitioning for certain PAHs, for instance, for PHE and FLT greater distribution in the particle than in the gaseous phase is shown. This strange g/p partitioning should be explained.

- Table 1b: Only 3 PAHs (PYR, FLT, RET) were quantifiable in sea water? Some comparison with literature data for open sea levels of PAHS would be useful.

– Section 3.2: The g/p partioning of PAHs should be more thoroughly investigated. The authors are claiming that the effect of temperature was not possible to be examined because of only little temperature variation during the cruise (21-27°C). I encourage them to examine the logKp-logPLo relationship and evaluate the slope and intercept values.

- The paragraph concerning the size distribution of PAHs needs substantial improvement, otherwise remove. Results are presented in one single phrase “In size-segregated samples PAH was almost exclusively quantified in particle size fractions <0.25 μm a.e.d.” The particle mass size distribution is not reported. The authors are claiming that there are no available data in literature for the size distribution of PAHs in

the open sea atmosphere; however comparison could be made with some background coastal sites in Mediterranean, such as Finokalia on the Crete Island, for which there are published PAH size distribution data.

- Table 3: Table 3 provides calculated theta and logKp values for 4 PAHs only, whereas values for PAHs that were quantified in both phases (such as for FLN, PHE, ANT, FLT, PYR) are missing. Missing data shall be provided.

- Section 3.3: The FR values reported for FLT, PYR and RET appear to follow the same order with the water solubility of the specific PAHs, FLT (265 μg/L) > PYR (135 μg/L) > RET (0 μg/L). Consequently, I am concerned that, if FRs were calculated from the total (soluble+adsorbed) concentrations in sea water, the FR of RET has been possibly underestimated. The FR equation requires the dissolved aqueous concentration Cw to be known. However, as described in Section 2.2, sea water samples were extracted immediately after their collection without filtration, which means that total PAHs concentrations (dissolved and adsorbed) were determined. The authors need to address this issue.

- Figure S2: Should I suppose that the units of the PM10 concentrations presented in Fig. S2 are μg/m3 and not ng/m3. Moreover, PM10 concentrations need to be clarified regarding the way they were obtained. If they were obtained from the low volume impactor sampling, they could not be more than 3 (according to sampling description in Section 2.1.). If they were obtained from the high volume sampling, they should be reported as TSP because the high volume sampler was not equipped with a PM10 inlet. Plkease, make the appropriate corrections and clarifications.

Conclusions The conclusion that “PAH pollution of the atmospheric Mediterranean environment was below previous observations at the beginning of the decade (2001-02; Tsapakis and Stephanou, 2005; Tsapakis et al., 2006)” is not true, since some PAHs such as FLT, PHE and ANT in the particle phase were found in the current study at much higher concentrations. Therefore, it would be better if comparisons were made on the sum concentration of PAHs (ΣPAHs).

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 5963, 2014.