We would like to thank the referees for their careful reading, review and useful questions and comments, which definitely will help to improve a revised version of the paper. We have addressed all comments below and indicate modifications planned for a revised version.

Replies to the comments of Referee #1

The paper represents important study of the PAH content in the atmosphere and can be published after some corrections.

Specific comments:

1. The first sentence of the abstract is not rather clear. It is not mentioned that measurements were made for the subset of PAHs (25 PAHs). May be there is also a need to characterize somehow what kind of PAHs were selected in the study (light, heavy, etc.) and may be to give the fraction in particulate phase as the range (not just one value – 8%).

yes, agree. For better clarity the first sentence of the abstract ' Polycyclic aromatic hydrocarbons (PAH) concentration in air of the central and eastern Mediterranean in summer 2010 was 1.45 (0.30–3.25) ngm−3, with ≈8% in the particulate phase, associated with particles< 0.25 μm.' will be re-phrased as 'Polycyclic aromatic hydrocarbons concentration in air of the central and eastern Mediterranean in summer 2010 was 1.45 (0.30–3.25) ngm−3 (sum of 25 PAHs), with 8 (1-17) % in the particulate phase., associated with particles < 0.25 μm.'

2. In the introduction (in the first statement) domestic heating also could me mentioned.

yes, agree, domestic heating will be mentioned in revised version

3. In section 2.1, the last paragraph might need reformulation as it is not rather clear that from the absence of difference between observed values on board of the ship it follows that ship-based sources were not significant.

yes, agree. For better clarity the sentence 'The PAH levels indicated by these samplers did not show significant differences, hence the ship-based contamination is negligible.' will be re-phrased as 'The PAH levels of these samples indicated that ship-based contamination was negligible.'

4. In section 2.3, in the first sentence it could be useful to note more clear what data set is meant. It is also mentioned that no data on soot or PM composition is available, but it could be said at least that this process can also affect partitioning. The underprediction mentioned later on may be connected with this selection of partitioning models.

yes; data set will be specified by '15 high-volume samples of separate gas and particulate phase concentrations'. Significance of soot for gas-particle partitioning will be emphasized: ' We refrain from testing dual adsorption and absorption models (e.g. Lohmann and Lammel, 2004) as no soot data or PM chemical composition data are available.' will be re-phrased as 'Adsorption to soot is a significant gas---particle partitioning processes for PAHs, but no soot data or PM chemical composition data are available. We, therefore, refrain from testing dual adsorption and absorption models (e.g. Lohmann and Lammel, 2004).' In the discussion of the results of the gas-particle partitioning models tested (section 3.2) the sentence ' The neglect of adsorption to soot, not covered by the gas-particle partitioning models tested, may explain a at least part of the underprediction' will be added.

5. In section 2.5 the selection of RET for the simulations of air-sea exchange can be somehow explained.

yes, agree. Short sentence 'RET is selected, because of the prevalence of one dominating source.' will be added to section 2.5.

6. In section 2.6 there is a need to give more detailed information on the generation of these retroplumes and their use for identification of potential sources.

agree. 1st paragraph of section 2.6 will start in the revised version with an introductory sentence, providing also references to respective applications i.e., 'Distributions of potential sources can be identified by inverse modelling using meteorological input data (Stohl et al., 2003; Eckhardt et al., 2007).'

7. Section 3.1: the value of total PAH concentration and its range differ from that given in the Table 1a.

The values differ because the mean values in Table 1a are referring to all 15 samples, regardless whether exceeding LOQ or not, with the ones < LOQ replaced by LOQ/2. To avoid confusion the value in the table will be mentioned in the text, too, explaining the difference.

Some comments would be useful on those PAHs that were higher than previously measured. For gaseous phase (Table 2a) these are FLT and PYR, but for particulate phase (Table 2b) there are more PAHs that were higher that previously measured. This might be connected with difference in seasons or something else. . .

Agree, although the basis for comparison of this and previous studies is limited, as emphasized. The discussion of the results will be expanded: 'The variability of advection or advection in combination with different routes taken by a vessel being influenced differently by coastal or ship emission plumes may explain this difference.' will be changed to:

'In the ISS some PAHs are found somewhat higher than previously measured i.e., FLT and PYR (in the gas-phase) and BAP and PER (in the particulate phase). Due to a sampling artefact BAP and other particulate phase PAHs could be underestimated by up to 25% (aforementioned, section 2.1). The seasonality of emissions and the variability of advection or advection in combination with different cruise routes being influenced differently by coastal or ship emission plumes can have a large influence and may explain these differences. On the other hand, the duration of temporal averaging atmospheric concentrations was similar across the various studies.'

8. In section 3.2 again effect of sorption on OC and EC could be mentioned, not just the absence of data.

yes; a respective sentence will be added in the revised version i.e., 'The neglect of adsorption to soot, not covered by the gas-particle partitioning models tested, may explain at least part of the underprediction.'

9. In section 3.3, the units of (> 50 ngm3 d?1) seems to be wrong.

yes, thanks, should be ng m^{-2} d^{-1}

10. In section 4, conclusions, it should be added that for most of measured PAHs the levels were lower than previously measured,

This conclusion is anyway drawn (first sentence of the section reads 'PAH pollution of the atmospheric Mediterranean environment was below previous observations at the beginning of the decade (2001-02; Tsapakis and Stephanou, 2005a; Tsapakis et al., 2006),

again effect of sorption on OC and EC could be mentioned. Potential sources of pollution of marine atmosphere could also be mentioned as it was evaluated through the use of FLEXPART model.

We refrain from drawing a conclusion on gas-particle partitioning because of the lack of data needed to test all relevant models.

A conclusion section should include conclusions, nothing else. The results on long-range transport paths (to the ship's position, using the inverse model FLEXPART) are mentioned in the results section and are the subject of an on-going study, to be published soon.

11. Table 3a provides observed and predicted fractions of particulate phase, but the units mentioned are ng m-3 that seems to be not correct.

Yes, thanks, unit will be removed.

Replies to the comments of Referee #2

This paper on the air-sea exchange of PAHs in the Mediterranean is based on a unique dataset of air and water samples and gives new insights into the cycling of PAHs between different environmental compartments. While the idea of the paper is compelling and in general suitable for publication in ACP the paper suffers from a variety of shortcomings. Thus, I can only support publication of this work after major revisions.

First of all, the paper would strongly benefit from a revision by a native speaker. Some sentences are obscure and it is not clear what exactly the authors want to say. A few examples:

p5967 l20,21 'Each one' [...] 'as far as possible identical manipulations on site'

will be re-phrased for better clarity: "Field blank values, b, were gained from GFFs and PUFs manipulated in the field, as far as possible identical to the samples, except without switching the high-volume sampler on."

p5972 l16 'corresponds with no or beging hit of such areas'

will be re-phrased for better clarity: "…, vice versa, low concentrations corresponded with no apparent passage of such areas"

p5972 l16 'This perception' should probably be 'This finding'

yes, agree

p5973 l17,18 '...PAH was almost exclusively quantified in particle size fraction <0.25μm' should probably mean 'the majority of the particulate PAHs were found in the size fraction <0.25 μm'?

yes, agree. Will be modified to "most of the particulate PAH mass was found in the size fraction <0.25μm."

p5974 l3 'FLT and PYR are indicated to be close to phase equilibrium' should probably mean 'were found to be'

yes, agree

p5974 l24 'observable' should be 'observed'

yes, agree

Secondly, besides the title '... aerosols and air-sea exchange ...' there is only little information on the actual findings about PAHs in/on aerosols. Also the air-sea exchange was only investigated for 3 PAHs.

PAHs in aerosols: The gas-particle partitioning of semivolatile PAHs is presented in Sections 3.2 and S2.1 (and Tables 2, S2). We refrained from reporting trivial findings (e.g., on gas-particle partitioning of more volatile and non-volatile PAHs, which was expectedly close to 0 and close to 1, respectively), not needed to be communicated 25 years after publication of key literature in this topic.

PAHs air-sea exchange: Only for 4 PAHs surface seawater concentrations >LOQ were found (Table 1b). This will be stressed for better clarity in the text of section 3.1 and caption of Table 1. We prefer to refrain from speculating about air-sea exchange of PAHs which could not be quantified in surface seawater.

detailed comments:

ABSTRACT: In the Abstract (p5964 l1-6) Why are only the findings of particles <0.25µm discussed? What is the total percentage of particulate PAHs, how is the size distribution? It is later stated (p5966 l3) that particles were collected with 2.5, 1.0, 0.5, and 0.25µm filters. But the size distribution is never discussed in the paper.

Will be re-phrased for better specification. The PAH mass size distributions will be presented (new Table S4) and discussed including more literature (following suggestions of ref. #3).

Further, with the strong focus on air-sea exchange at least a rough estimate about the total annual flux should be made.

Agree. A rough estimate of total annual flux of particulate phase PAHs can be made for the season (but not annually) and will be included in the conclusion section and abstract of a revised version:

The residence time in the troposphere is longest for particles around 0.2 µm of size, with ≈ 0.01 cm s^{-1} being a characteristic corresponding dry deposition velocity (Franklin et al., 2000), which translates into a residence time of ≈ 120 days in the MBL (depth of 1000 m; see Table S3) and deposition fluxes $F_{dep} = c \times v = 0.03\text{-}0.13$ µg m^{-2} year^{-1}, for the individual PAHs associated with the particulate phase ($c = 0.01\text{-}0.04$ ng m^{-3}; Table 2b), such as BAP, and 0.80 and 0.35 µg m^{-2} year^{-1}, respectively, for the total flux of particulate phase PAHs in the ISS and SEM in summer, respectively. The flux will be higher in winter because of the seasonality of the emissions.

Ref.: Franklin et al.: Quantitative determination of persistence in air. In: Criteria for persistence and long-range transport of chemicals in the environment (Klečka et al., eds.), Pensacola, USA (SETAC Press), pp. 7-62, 2000.

p5964 l10-12: 'It is concluded that future negative emission trends or interannual variability of regional sources may trigger the sea to become a secondary PAH source' How large could this source be compared to the primary sources in the Mediterranean?

Thank you for this question. This should indeed be quantified and added to the paper (conclusions). For retene it is found that one third was returned to the atmosphere during the study period: While the flux of secondary retene emissions (from surface seawaters) in the study area was 1.0 µg m^{-2} year^{-1} (mean of 6 years,_UEPS), the primary sources amounted to 3.1 µg m^{-2} year^{-1} (mean of 6 years). This result will be included into the abstract of the revised version ('One third of primary retene sources to the sea region in the period 2005-2010 returned to the atmosphere as secondary emissions from surface seawaters.')

METHODOLOGY: p5968 l3: Abbreviation LOQ should be explained the first time it is used.

yes, abbreviation LOQ introduced at first time mentioned

Section 2.4 seems a bit too short. It should be made clear how kw and ka were calculated. Also it should be discussed whether the air-sea exchange is dominated by ka or kw. For most species one of the two mass transfer coefficients clearly dominates the exchange process. Also the difference between 2 and 4 ring PAHs should be discussed here (e.g. what values were used to describe the diffusivity of the different species, was a temperature dependency taken into account). In general, readers of the paper should be able to reproduce the calculations done by the authors. Giving the formula and the reference to Schwarzenbach et al. is not enough here.

Transfer coefficients were calculated for one 3 ring and two 4 ring PAHs (stated in section 3.3), $k_w \ll k_a$ throughout (will be specified section 3.3). Derivation of k_w and k_a now explained in detail, including the references to the input data sources: '$k_a = (0.2U_{10} + 0.3)*(D_{i,air}/D_{H2O,air})^{0.61}*36$, $k_w = (0.45U_{10}^{1.64})*(Sc_i/Sc_{CO2})^{-0.5}*0.01$. U_{10} is the wind speed at 10 meter height above sea level (m s^{-1}), $D_{i,air}$ and $D_{H2O,air}$ are the temperature dependent diffusivities of substance i and H_2O in air, and Sc_i and Sc_{CO2} are the Schmidt numbers for substance i and CO_2 (see Bidleman and McConnell, 1995; Zhong et al. 2012; and references therein). U_{10}, T_a, T_w and air pressure are taken from the ship based measurements.'

Section 2.5: Is river runoff considered as a source for PAHs? Is it an important source?

Many PAHs are enriched in coastal waters as opposed to the open sea, most likely as river runoff is a significant source. As retene is rarely monitored this is not obvious for this substance. In an urban estuary in the USA, the linkage with river runoff was found less obvious for retene than for other PAHs (Lohmann et al., Env Sci Technol 2011, 45, 2655-2662). The neglect of the riverine retene source in our modelling may cause an underestimate of the emission flux, Faw, and might explain part of the discrepancy (underestimate when compared to observed flux). This will be added to the discussion text (section 3.6): The sentence ' The sensitivity to input uncertainties (SM S1.2) may explain part of the underestimate, but not up to one order of magnitude.' will be extended: 'Neglected retene sources to seawater, such as riverine input may explain part of the discrepancy.'

Section 2.6 is much too short (2 sentences) to justify an additional section.

This part of the methodology is different from others. Its results are included in the text of section 3.1 (1st paragraph).

RESULTS: Section 3.1: It should be discussed whether earlier crusies are comparable. Different seasons, different wind conditions, different cruise routes can potentially have a large influence on the observed concentrations.

This discussion is expanded as suggested by reviewer #1. ('The seasonality of emissions and the variability of advection or advection in combination with different cruise routes being influenced differently by coastal or ship emission plumes can have a large influence and may explain these differences. On the other hand, the duration of temporal averaging atmospheric concentrations was similar across the various studies.')

Table 2 should state precisely when the different cruises were taking place.

Months identified in the revised version

The reference (1) in Table 2b is not used.

Ref. (1) is used in Table 2a

Section 3.2: As stated before there should be more information about the size distribution of the PAHs from the 2.5, 1.0, 0.5, 0.25µm filters.

The PAH mass size distributions will be presented, listed for the size range <0.25µm (below, new Table S4) and discussed including an earlier study of size segregated PAH measurements in the eastern Mediteranean (Kavouras and Stephanou, JGR 2002).

Table S4. Concentrations of 4-6 ring PAHs found in particulate phase size fraction corresponding to <0.25 µm a.e.d. (ng m^{-3}) as time-weighted mean (min-max). n_{LOQ} = number of samples > LOQ (out of 3). PAHs with concentrations <LOQ in all size fractions not listed. LOQ = 0.001 ng m^{-3} except for FLT (0.011) and PYR (0.020).

	n_{LOQ}	mean (min-max)
FLT	3	0.046 (0.035–0.054)
PYR	3	0.047 (0.040–0.051)
RET	3	0.048 (0.046–0.050)
CPP	1	0.007 (<0.001–0.022)
CHR	1	0.002 (<0.001–0.005)
BJF	1	0.002 (<0.001–0.007)
BEP	1	0.003 (<0.001–0.008)

CONCLUSIONS: The Conclusions seem to be very short. It would be beneficial to give an estimate about the relation of total annual RET deposition to net revolatilisation. Also there should be more information about the differences between the observed PAHs and on the observed particulate PAHs.

In the revised version retene deposition will be compared with revolatilisation (detailed above).

The results on PAH level trends are partly inconclusive (discussion in section 3.1, expanded as suggested by reviewer #1). We prefer to refrain from drawing conclusion from inconclusive results.

Replies to the comments of Referee #3

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)

agree, title changed into 'Air-sea exchange and gas-particle partitioning 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 ozone.

This is anyway clarified in the text of section 2.1 ('Based on such sampling artefact quantification studies (Tsapakis and Stephanou, 2003; Galarneau et al., 2006) and ozone levels (Table 1a) and sampling times (Table S1) we expect that total PAHs are underestimated by up to 50% in the gas-phase and by up to 25% in the particulate phase.'). Implications now included in the discussion (section 3.1).

- 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.

agree, will be modified accordingly

- Section 2.2: It is stated that no 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.

agree, will be specified in section 2.2 ('No QFF field blank was taken for impactor sampling. As no PAHs were detected in the stages corresponding to 2.5-10 μm (all PAHs < limit of detection in all such samples), instead the mean of values of the QFF substrates of the 2 uppermost impactor stages (in total 5) was taken.')

- 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 suspended particles) were determined (those presented in Table 1b).

Indeed total PAH concentrations were determined and dissolved concentrations used for mass exchange calculations: To this end dissolved aqueous concentrations were derived from the bulk seawater concentrations using Cw = Cbulk /(1 + kPOC*CPOC + kDOC * [DOC]), with POC and DOC from Pujo-Pay et al 2011, and kPOC and kDOC from Lüers & ten Hulscher 1996, Ma et al 2012, Karickhoff et al 1981, and Rowe et al 2009. This sentence now added to the section text.

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

unit is correct, ng m^{-3}.

- 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".

will be clarified by re-phrasing (virtual particles)

Results and discussion

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

Agree; will be re-phrased for better clarity, as 'corresponded with air masses having resided over large urban areas, and, vice versa, low concentrations corresponded with air masses without apparent passage of such areas'

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

Sum concentration will be included and referred to in the text

- 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.

The data are consistent. The apparent inconsistency is the consequence of time-weighted averaging of different data subsets, 15 samples in Table 1a, but each 5 samples in Table 2 for ISS and SEM data subsets.

- 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.

Thanks for pointing to the presentation of these data, which was imperfect. No data suggest unplausible gas-particle partitioning, but the way they were presented (Table 2b) was misleading: mean values <LOQ were erroneously not flagged as such (but only the range shown in brackets showed values for min and max eventually flagged for <LOQ). Will be corrected unambiguously. Also the number of valid digits will be harmonized.

- 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.

Yes, will be compared with earlier data, which suggests similar levels: These observed seawater contamination levels are comparable to levels found in the region 2 and 1 decades ago (Lipiatou et al., 1997; Tsapakis et al., 2003).

– 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 (21-27C). I encourage them to examine the logKp-logPLo relationship and evaluate the slope and intercept values.

Such type of examination was inspiring the research research 2 decades ago (Pankow & Bidleman Atmos Environ 1992; Pankow et al. Environ Sci Technol 1994), but is inherently inconclusive, at least as long as supporting parameters are not measured (but fixed values adopted assuming standard or characteristic conditions) and time resolution is not improved. We have been applying this method and will continue to do so for the interpretation of field data, assuring measured (rather than default) aerosol parameters, high time resolution, and an extended chemical characterization of the particulate phase (Lammel et al Atmos Environ 2010, J Environ Mon 2011, and unpublished in urban environments). Neither of these was possible on board RV Urania (our data set).

The examination's limitations apart from lack of supporting parameters are as follows: If the gas-phase concentrations were controlled by local relaxation to (liquid–vapour) phase equilibrium, then the relationship between these and ambient temperature should be described by the Clausius–Clapeyron equation, physically equivalent to plots of the form

log K_P = A/T + B. log K_p of PAHs based on differentiating sampling of the gaseous and particulate fractions was found to be correlated with 1/T (or log p_{L0}) in a number of studies, but these tests were largely inconclusive for several reasons: Correlation with 1/T is in accordance with both adsorptive and absorptive mechanisms of gas-particle partitioning (Pankow et al. Environ Sci Technol 1994). Adsorption had been claimed to lead to a slope of -1, inconclusively, however, as various possible reasons for non-ideality exist which usually cannot be addressed (such as non-equilibrium, temperature change during sampling, and absorption into OM; Pankow & Bidleman Atmos Environ 1992; Goss & Schwarzenbach Environ Sci Technol 1998). This would in particular apply to our data set, as OM was not quantified and long sampling intervals, >12h, with significant temperature variation during sampling prevailed. Non-equilibrium can be caused by kinetic constraints (introduction of fresh particles or clean air) or by the presence of nonexchangeable compounds in the particles. None of these hypotheses explanations could be rejected based on our data set. Furthermore, standard or characteristic aerosol parameters had to be assumed (rather than determined). A large data scatter is anyway expected, as attributed to lack of representativeness of the temperature measurement for the volatilisation process (which may have occurred several days back, in particular if local substance levels are influenced by long-range transport; Hoff et al.: Non-linearities in the slope of Clausius-Clapeyron plots for semivolatile organic compounds. Environ. Sci. Technol. 1998, 32, 1793–1798), again, certainly also in our data set.

The explanation given in the text ('little temperature variation') will be replaced by one sentence identifying the key limitations of the method with regard to its application to our data set.

- 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.

Re-phrased for better specification in the abstract (following suggestion of ref. #1). More results from impactor samples presented (see above, following ref. #2)

- 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.

We limited the substances studied for testing gas-particle partitioning models to those showing obvious semivolatility i.e., concentrations in both atmospheric phases, C_g and C_p, >LOQ in at least half of the samples (n = 15), and with input data available. This led to the rejection of FLT and PYR, BBN (C_p <LOQ), CPP, BBF, BJF (C_g <LOQ), and BGF (no p0_L available). These criteria will be explained in the revised version.

- 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.

Indeed total PAH concentrations were determined and dissolved concentrations used for FR and mass exchange calculations (detailed above)

- 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. Please, make the appropriate corrections and clarifications.

Yes, µg/m³, now corrected in Fig. S2.

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 (_PAHs).

The discussion of these results has now been expanded to the individual PAH level (as suggested by reviewers #1 and #2)

1 **Air-sea exchange and gas-particle partitioning of p**olycyclic aromatic hydrocarbons in

2 **the Mediterranean**

3 Marie D. Mulder[a], Angelika Heil[b], Petr Kukučka[a], Jana Klánová[a], Jan Kuta[a], Roman Prokeš[a],

4 Francesca Sprovieri[c], Gerhard Lammel[a,d*]

5 [a] Masaryk University, Research Centre for Toxic Compounds in the Environment, Brno,

6 Czech Republic

7 [b] Helmholtz Research Centre Jülich, Institute for Energy & Climate Research, Jülich,

8 Germany

9 [c] CNR, Institute for Atmospheric Pollution Research, Rende, Italy

10 [d] Max Planck Institute for Chemistry, Mainz, Germany

11 * phone +420-54949-4106, fax +420-54949-2840, lammel@recetox.muni.cz

12

13 **Abstract**

14 Polycyclic aromatic hydrocarbons concentration in air of the central and eastern

15 Mediterranean in summer 2010 was 1.45 (0.30-3.25) ng m^{-3} (sum of 25 PAHs), with 8 (1-17)

16 % in the particulate phase, almost exclusively associated with particles <0.25 μm. The total

17 deposition flux of particulate PAHs was 0.35-0.80 μg m^{-2} year^{-1}. The diffusive air-sea

18 exchange fluxes of fluoranthene and pyrene were mostly found net-depositional or close to

19 phase equilibrium, while retene was net-volatilisational in a large sea region. Regional fire

20 activity records in combination with box model simulations suggest that seasonal

21 depositional input of retene from biomass burning into the surface waters during summer is

22 followed by an annual reversal of air-sea exchange, while inter-annual variability is

23 dominated by the variability of the fire season. One third of primary retene sources to the sea

region in the period 2005-2010 returned to the atmosphere as secondary emissions from surface seawaters. It is concluded that future negative emission trends or interannual variability of regional sources may trigger the sea to become a secondary PAH source through reversal of diffusive air-sea exchange.

Capsule: Polycyclic aromatic hydrocarbons phase distributions in marine aerosols, direction of air-sea exchange and open fires as a possible source characterised in the Mediterranean

Keywords: polycyclic aromatic hydrocarbons, long-range transport, air-sea exchange, open fires

1. Introduction

The marine atmospheric environment is a receptor for polycyclic aromatic hydrocarbons (PAHs) which are advected from combustion sources on land (power plants, biomass burning, road transport, domestic heating). Marine sources may be significant near transport routes (ship exhaust). Long-range transport from urban and industrial sources on land are the predominant sources of PAHs in the Mediterranean (Masclet et al., 1988; Tsapakis et. al, 2003 and 2006; Tsapakis and Stephanou, 2005a). A number of PAHs are semivolatile (vapour pressures at 298 K in the range 10^{-6}-10^{-2} Pa) and, hence partition between the gas and particulate phases of the atmospheric aerosol, influenced by temperature, particulate phase chemical composition and particle size (Keyte et al., 2013). Upon deposition to surface water PAHs partition between the aqueous and particulate (colloidal and sinking) phases and may bioaccumulate in marine food chains (Lipiatou and Saliot, 1991; Dachs et al., 1997; Tsapakis

47 et. al, 2003; Berrojalbiz et al., 2011). They were also found enriched in the sea-surface

48 microlayer relative to subsurface water (Lim et al., 2007; Guitart et al., 2010). Semivolatile

49 PAHs may be subject to re-volatilisation from the sea surface (reversal of air-sea exchange),

50 similar to chlorinated semivolatile organics (Bidleman and McConnell, 1995), in case high

51 concentrations in surface water would build up. This had been predicted by

52 multicompartmental modelling for 2-4 ring PAHs for polluted coastal waters and also the

53 open ocean (Greenfield and Davis, 2005; Lammel et al., 2009a) and was indeed observed in

54 coastal waters off the northeastern United States (Lohmann et al., 2011). Field studies in the

55 open sea found net-deposition to prevail whenever determined (e.g. Tsapakis et al., 2006;

56 Balasubramanian and He, 2010; Guitart et al., 2010; Castro-Jiménez et al., 2012; Mai, 2012).

57 However, some 3-4 ring parent PAHs, among them fluorene (FLU), fluoranthene (FLT) and

58 pyrene (PYR), were reported to be close to phase equilibrium in the Mediterranean, Black

59 and North seas (Castro-Jiménez et al., 2012; Mai, 2012), and net volatilisation of FLT and

60 PYR was observed in the open southeastern Mediterranean Sea in spring 2007 (Castro-

61 Jiménez et al., 2012).

62 The aim of the measurements on board RV Urania was to investigate levels of organic

63 pollutants in summer in Mediterranean air and gain insights about sources and phase

64 partitioning in the aerosol of these substances. This study is on the cycling of PAHs in the

65 marine atmosphere.

66

67 **2. Methods**

68 **2.1 Sampling**

Samples were taken during the RV Urania cruise, 27 August – 12 September 2010 (see Supplementary Material (SM), Fig. S1). PAHs were collected in the gaseous and particulate phases using high volume samplers (Digitel) equipped with one glass fibre filter (Whatman) and one polyurethane foam (PUF) plug (Gumotex Břeclav, density 0.030 g cm^{-3}, 50 mm diameter, cleaned by extraction in acetone and dichloromethane, 8 h each, placed in a glass cartridge) in series. Particle size was classified in the particulate phase using high-volume filter sampling (F = 68 m³ h^{-1}, model HVS110, Baghirra, Prague) and low-volume impactor sampling (F = 0.54 m³ h^{-1}, Sioutas 5-stage cascade, PM$_{10}$ inlet, cutoffs 2.5, 1.0. 0.5, 0.25 μm of aerodynamic particle size and back-up filter, impaction on quartz fibre filters (QFF), SKC Inc., Eighty Four, USA, sampler Baghirra PM$_{10-35}$). In total 15 high-volume filter samples, exposed 8-36 h (230-1060 m³ of air), and 3 low-volume impactor samples, exposed 5 d, were collected. Water sampling was performed using the stainless steel ROSETTE active sampling device equipped with 24 Niskin bottles (volume of 10 l) deployed in water at 1.5 m depth for surface water sampling.

PAH sampling on GFF and in PUF can be subject to losses related to oxidation of sorbed PAH by ozone (Tsapakis and Stephanou, 2003). This artifact is species-specific and the more pronounced the higher the ozone concentration and the longer the sampling time. Among the PAHs addressed benzo(a)pyrene and pyrene have been identified as particularly vulnerable to oxidation. Based on such sampling artefact quantification studies (Tsapakis and Stephanou, 2003; Galarneau et al., 2006) and ozone levels (Table 1a) and sampling times (Table S1) we expect that total PAHs are underestimated by up to 50% in the gas-phase and by up to 25% in the particulate phase.

With the aim to characterize the potential influences of ship-bourne emissions on the samples, passive air samplers with PUF disks were exposed at 5 different locations on board during 16 days. The PAH levels of these samples indicated that ship-based contamination was negligible.

2.2 PAHs~~Organic trace substances~~ analyses and quality assurance

For PAH~~organic~~ analysis all samples were extracted with dichloromethane in an automatic extractor (Büchi B-811). Surrogate recovery standards (D8-naphthalene, D10-phenanthrene, D12-perylene) were spiked on each PUF and GFF prior to extraction. The volume was reduced after extraction under a gentle nitrogen stream at ambient temperature, and fractionation achieved on a silica gel column.

The first portion of the extract was fractionated on a silica column (5 g of silica 0.063 – 0.200 mm, activated 12 h at 150°C). The first fraction (10 mL n-hexane) containing aliphatic hydrocarbons was discarded. The second fraction (20 mL DCM) containing PAHs was collected and then reduced by stream of nitrogen in a TurboVap II (Caliper LifeSciences, USA) concentrator unit and transferred into an insert in a vial. Terphenyl was used as syringe standard, final volume was 200 μL. GC-MS analysis was performed on a 6890N GC equipped with a 60m x 0.25mm x 0.25μm DB5-MS column (Agilent J&W, USA) coupled to 5973N MS (Agilent, USA). The MS was operated in EI+ mode with selected ion recording (SIR).The targeted compounds are the 16 EPA priority PAHs (i.e., naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BAA), chrysene (CHR), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(a)pyrene (BAP),

115   indeno(123cd)pyrene (IPY), dibenzo(ah)anthracene (DBA), benzo(ghi)perylene (BPE)), 10

116   more parent PAHs (i.e., benzo(ghi)fluoranthene (BGF), cyclopenta(cd)pyrene (CPP),

117   triphenylene (TPH), benzo(j)fluoranthene (BJF), benzo(k)fluoranthene (BKF),

118   benzo(e)pyrene (BEP), perylene (PER), dibenz(ac)anthracene (DCA), anthranthrene (ATT),

119   and coronene (COR)), and one alkylated PAH, retene (RET). The injection volume was 1 μL.

120   Terphenyl was used as internal standard.

121   Field blank values, b, were gained from GFFs and PUFs manipulated in the field, as far as

122   possible identical to the samples, except without switching the high-volume sampler on. No

123   QFF field blank was taken for impactor sampling. As no PAHs were detectedin the stages

124   corresponding to 2.5-10 μm (all PAHs < limit of detection in all such samples), but instead

125   the mean of values of the QFF substrates of the 2 uppermost impactor stages (in total 6) was

126   taken. The respective b value was subtracted from sample values. The limit of quantification

127   needs to take the accuracy of the blank level into account. In lack of a measure for the

128   variation of the field blank, the relative standard deviation (SD) of field blanks from earlier

129   field campaigns, (σ_c/b_c), on a high-mountain site (high-volume sampling summer 2007, n = 5;

130   Lammel et al., 2009b) and in the Mediterranean (impactor sampling summer 2008, n = 6;

131   Lammel et al., 2010a) was used ($\sigma = (\sigma_c/b_c) \times b$). The identical samplers, sampling and

132   analysis protocols for all analytes had been applied. Values below the sum of the field blank

133   value (from this campaign) and 3 relative SDs of the field blank values (from the previous

134   campaigns) were considered <LOQ (LOQ = b + 3σ). NAP and ACY were excluded from the

135   data set, because of the lack of blank values. The field blank values of most other analytes

136   were below instrument LOQ in high-volume PUF and GFF samples. However, higher field

137   LOQs, up to (6-25) pg m^{-3} (according to sampled volume of air) resulted for ANT, PYR and

138 RET, and up to (45-180) pg m^{-3} for ACE, FLN, PHE and FLT in PUF. Field LOQs of PAHs in

139 impactor QFF samples were below instrumental LOQ for most substances, but in the range

140 (8-15) pg m^{-3} for ACE, ANT, and FLT, ≈55 pg m^{-3} for FLN, and 120-140 pg m^{-3} for NAP and

141 PHE.

142 The instrument limit of quantification (LOQ), which is based on the lowest concentration of

143 calibration standards used, was 0.5 ng, corresponding to 0.5-2.5 pg m^{-3} for high-volume

144 samples, ≈8 pg m^{-3} for impactor samples, 6-10 pg m^{-3} for semivolatile PAHs determined in

145 passive air samples and up to 200 pg m^{-3} for non volatile PAHs in passive air samples.

146 Water samples (2-2.5 L) were extracted immediately after their collection using solid phase

147 extraction on C$_{18}$ Empore discs using a vacuum manifold device. Disks were stored closed in

148 glass vials in a freezer and transported to the processing laboratory, PAHs were eluted from

149 disks using 40 mL of dichloromethane. The above listed PAHs were analysed on GC/MS

150 (Agilent GC 6890N coupled to an Agilent single quadrupole MS 5973N operating in electron

151 impact ionisation mode). LOQ was 0.1 ng L^{-1}.

152

153 **Other trace constituents and meteorological parameters**

154 Ozone was measured with an absorption method (Teledyne–API model 400A UV) on the top

155 deck (10 m above sea surface). Meteorological parameters (air temperature, humidity, wind

156 direction and velocity) and oceanographic parameters were determined aboard.

157

158 **2.3 Models of gas-particle partitioning**

159 The data set (15 high-volume samples of separate gas and particulate phase concentrations)

160 is used to test gas-particle partitioning models for semivolatile organics in terms of the

161   organics' mass size distribution and size dependent particulate matter (PM) composition. The

162   models assume different processes to determine gas-particle partitioning, i.e. an adsorption

163   model (Junge-Pankow; Pankow, 1987), and two absorption models (i.e. K_{OA} models; Finizio

164   et al., 1997; Harner and Bidleman, 1998). Absorption is into particulate OM. Adsorption to

165   soot is a significant gas---particle partitioning processes for PAHs, but no soot data or PM

166   chemical composition data are available. We, therefore, refrain from testing dual adsorption

167   and absorption models (e.g. Lohmann and Lammel, 2004). Particulate mass fraction, θ, and

168   partitioning coefficient, K_p, are defined by the concentrations in the 2 phases:

169

170     $\theta = c_p / (c_p + c_g)$

171

172     $K_p = c_p / (c_g \times c_{TSP}) = \theta / [(1 - \theta) \times c_{TSP}]$

173

174   with c_p and c_g in units of ng m^{-3}, c_p representing the whole particle size spectrum.

175   Different models describe different processes to quantify differences in ad- and absorption

176   between compounds. The Junge-Pankow model uses the vapour pressure of the subcooled

177   liquid p_L^0, $\theta = c_J S/(p_L^0 + c_J S)$, (data taken from Lei et al., 2002), c_J should be approximately

178   171 Pa cm for PAHs (Pankow, 1987). The aerosol particle surface, S, was not measured and

179   a typical value for maritime aerosols is adopted instead (4.32×10^{-7} cm^{-1}; Jaenicke, 1988).

180   Harner and Bidleman, 1998, use the log K_{OA} and f_{OM}: log K_p = log K_{OA}+log f_{OM} -11.91; and

181   Finizio et al., 1997, uses only the K_{OA} as predictor (data taken from Ma et al., 2010): log K_p

182     $= 0.79 \times$log K_{OA} - 10.01. The range of the fraction of OM used here is based on Putaud et al.,

183   2004 (16% lower limit) and Spindler et al., 2012 (45% upper limit).

184

2.4 Air-sea diffusive mass exchange calculations

State of phase equilibrium is addressed by fugacity calculation, based on the Whitman two-film model (Liss and Slater, 1974; Bidleman and McConnell, 1995). The fugacity ratio (FR) is calculated as:

$FR = f_a/f_w = C_a R T_a / (C_w H_{Tw,salt})$

with gas-phase concentration C_a (ng m^3), dissolved aqueous concentration C_w (ng m^3), universal gas constant R (Pa m^3 mol^{-1} K^{-1}), water temperature and salinity corrected Henry's law constant $H_{Tw,salt}$ (Pa m^3 mol^{-1}), and air temperature T_a (K). C_w is derived from the bulk seawater concentration:

$C_w = C_{bulk} /(1 + K_{POC} C_{POC} + K_{DOC} C_{DOC})$

with C_{POC} and C_{DOC} from Pujo-Pay et al., 2011, K_{POC} and K_{DOC} from Karickhoff et al, 1981, Lüers and ten Hulscher 1996, Rowe et al, 2009, and Ma et al, 2010. Values 0.3< FR <3.0 are conservatively considered to not safely differ from phase equilibrium, as propagating from the uncertainty of the Henry's law constant, $H_{Tw,salt}$, and measured concentrations (e.g., Bruhn et al., 2003; Castro-Jiménez et al., 2012; Zhong et al., 2012). This conservative uncertainty margin is also adopted here, while FR >3.0 indicates net deposition and FR <0.3 net volatilisation. The diffusive air–seawater gas exchange flux (F_{aw}, ng m^{-2} day^{-1}) is calculated

206   according to the Whitman two-film model (Bidleman and McConnell, 1995; Schwarzenbach

207   et al., 2003):

208

209     $F_{aw} = k_{ol} (C_w - C_a RT_a/H_{Tw,salt})$

210

211   with air-water gas exchange mass transfer coefficient k_{ol} (m h^{-1}), accounting for resistances

212   to mass transfer in both water (k_w, m h^{-1}) and air (k_a, m h^{-1}), defined as

213

214     $1/k_{ol} = 1/k_w + RT_a/(k_a H_{Tw,salt})$

215

216   with $k_a = (0.2U_{10} + 0.3)*(D_{i,air}/D_{H2O,air})^{0.61} \times 36$, $k_w = (0.45U_{10}^{1.64}) \times (Sc_i/Sc_{CO2})^{-0.5} \times 0.01$. U_{10}

217   is the wind speed at 10 meter height above sea level (m s^{-1}), $D_{i,air}$ and $D_{H2O,air}$ are the

218   temperature dependent diffusivities of substance i and H_2O in air, and Sc_i and Sc_{CO2} are the

219   Schmidt numbers for substance i and CO_2 (see Bidleman and McConnell, 1995; Zhong et al.

220   2012; and references therein). U_{10}, T_a, T_w and air pressure are taken from the ship based

221   measurements.

222

223

224   **2.5 Non-steady state 2-box model**

225   The air–sea mass exchange flux of RET is simulated by a non-steady state zero-dimensional

226   model of intercompartmental mass exchange (Lammel, 2004). RET is selected, because of

227   the prevalence of one dominating source. This 2-box model predicts concentrations by

228   integration of two coupled ordinary differential equations that solve the mass balances for the

229 two compartments, namely the atmospheric marine boundary layer (MBL) and seawater

230 surface mixed layer. Processes considered in air are dry (particle) deposition, removal from

231 air by reaction with the hydroxyl radical, and air-sea mass exchange flux (dry gaseous

232 deposition), while in seawater export (settling) velocity, deposition flux from air, air-sea

233 mass exchange flux (volatilisation), and degradation (as 1st order process) are considered. All

234 input parameters are listed in the SM, Table S2.

235 Atmospheric depositions related to emissions from open fires are assumed to provide the

236 only source for seawater RET. These are available as daily time series for the East

237 Mediterranean domain (28-45°N, 8-30°E) through the fire-related $PM_{2.5}$ emissions as

238 provided by the Global Fire Assimilation System (GFASv1.0; Kaiser et al., 2012) in

239 combination with an emission factor (207 mg RET in $PM_{2.5}$ (kg fuel burnt)$^{-1}$; Schmidl et al.,

240 2008). The fire emissions are averaged over the domain and assumed to disperse within the

241 MBL only. This is justified due to the assumed underestimation of the fire related emissions

242 and ignorance of other (emission) sources. The 2-box model is run for the years 2005-2010,

243 for the east Mediterranean domain (28-45°N, 8-30°E) with a 1 h time resolution. Fluxes in

244 the range $F_{em} = (0.30 \pm 1.46)$ ng m^{-2} h^{-1} (positive defined upward) are simulated (using the

245 initially estimated parameter set, Table S2). GFAS uses global satellite observations of fire

246 radiative power to estimate daily dry matter combustion rates and fire emission fluxes. The

247 GFAS system partly corrects for observational gaps (e.g. due to cloud cover) and detects fires

248 in all biomes, except for very small fires (lower detection limit of around 100-1000 m^2

249 effective fire area).

250

251 **2.6 Analysis of long-range advection of air**

252 Distributions of potential sources can be identified by inverse modelling using

253 meteorological input data (Stohl et al., 2003; Eckhardt et al., 2007). So-called retroplumes

254 are generated using operational weather prediction model data and a Lagrangian particle

255 dispersion model, FLEXPART (Stohl et al., 1998, 2005). Hereby, 50000 virtual particles per

256 hour were 'released' and followed backwards in time for 5 days. The model output is a 3-D

257 distribution of residence time.

258

259 **3. Results and discussion**

260 **3.1 PAH concentrations in air and seawater**

261 The mean total (i.e., sum of gaseous and particulate) Σ25 PAHs concentration is 1.45 ng m^{-3}

262 (time-weighted; 1.54 with values <LOQ replaced by LOQ/2, see Table 1a), and ranged from

263 0.30-3.25 ng m^{-3} (high volume samples). The spatial variability of PAH levels in the

264 Mediterranean is large, determined by long-range advection (Tsapakis and Stephanou, 2005a;

265 Tsapakis et al., 2006). The levels found in this study in the southeastern Mediterranean are

266 for most substances lower than found earlier (Table 2). In the ISS some PAHs are found

267 somewhat higher than previously measured i.e., FLT and PYR (in the gas-phase) and BAP

268 and PER (in the particulate phase). Due to a sampling artefact BAP and other particulate

269 phase PAHs could be underestimated by up to 25% (aforementioned, section 2.1). The

270 seasonality of emissions and the variability of advection or advection in combination with

271 different cruise routes taken by a vessel being influenced differently by coastal or ship

272 emission plumes can have a large influence and may explain theseis differences. On the other

273 hand, the duration of temporal averaging atmospheric concentrations was similar across the

274 various studies. Diagnostic ratios (BAA/(BAA+CHR), FLT/(FLT+PYR); Dvorská et al.,

275 2011) in some of the samples (No. 2, 4, 7, 8, and 15) reflect the influence of traffic and

276 industrial sources. We investigated the potential source distribution of individual samples

277 collected along the cruise (section 2.6) and found that indeed maxima of PAH concentrations

278 corresponded with air masses having resided over large urban areas, and, vice versa, low

279 concentrations corresponded with air masses without~~no~~ apparent passage of such areas

280 (illustrated in Fig. S5). This finding~~perception~~ is supported by the ozone data i.e., 53 (47-65)

281 ppbv during influence from urban areas but 37 (33-62) ppbv otherwise.

282 It had been pointed out that the source distribution around the Mediterranean may cause a

283 west-east gradient, leading to higher concentrations found in the Ionian Sea and Sicily region

284 (ISS) than in the southeastern Mediterranean (SEM; Berrojalbiz et al., 2011). This gradient is

285 somewhat reflected in our results, as levels in the ISS exceeded levels in the SEM (Table 2a).

286 Most PAH concentrations in surface seawater were <LOQ, while FLT, PYR and RET were

287 quantified in at least part of the samples (Table 1b). These observed seawater contamination

288 levels are comparable to levels found in the region 2 and 1 decades ago (Lipiatou et al.,

289 1997; Tsapakis et al., 2003). The ~~PAH~~ concentrations ~~in seawater~~ near Crete (samples No. 7

290 and 8a) are very similar to those found in fall 2001 and winter-spring 2002 (Tsapakis et al.,

291 2006; FLT = 0.15 (0.11-0.21) ng L^{-1}, PYR = 0.12 (0.07-0.17) ng L^{-1}.

292

293 Table 1. Concentrations of PAHs found in (a.) air (total, i.e. sum of gas and particulate

294 phases, ng m^{-3}) and (b.) seawater (total, i.e. sum of dissolved and particulate, ng L^{-1}) as time-

295 weighted mean (min-max). n_{LOQ} = number of samples > LOQ (out of 15 air and 23 seawater

296 samples). PAHs with concentrations <LOQ in all samples not listed. For calculation of mean

297 values <LOQ were replaced by LOQ/2. Ozone levels are given, too (ppbv).

298   a)

	n_{LOQ}	mean (min-max)
ACE	4	0.025 (<0.020–0.089)
FLN	10	0.137 (<0.030–0.396)
PHE	15	0.581 (0.144–1.41)
ANT	13	0.043 (0.008–0.22)
RET	14	0.016 (0.006–0.030)
FLT	15	0.262 (0.053–0.795)
PYR	15	0.203 (0.044–0.564)
BAA	15	0.01 (0.0014–0.031)
CHR	15	0.04 (0.012–0.092)
TPH	15	0.018 (0.007–0.032)
BBN	11	0.018 (0.001–<0.085)
BBF	15	0.021 (0.004–0.102)
BKF	14	0.012 (0.002–<0.085)
BAP	12	0.015 (0.001–<0.085)
BGF	15	0.021 (0.005–0.067)
CPP	7	0.012 (0.001–<0.085)
BJF	15	0.016 (0.002–0.079)
BEP	14	0.019 (0.004–0.088)
PER	7	0.012 (0.001–0.1)
IPY	7	0.022 (0.008–0.094)

BPE	6	0.02 (0.009–0.085)
COR	5	0.016 (0.002–0.1)
Σ25 PAHs		1.539 (0.44–4.694)
Ozone		42 (33 – 65)

299

300   b)

	n_{LOQ}	mean (min-max)
PHE	1	1.1
RET	12	0.1 (<0.1–0.5)
FLT	10	0.1 (<0.1–0.3)
PYR	7	0.2 (<0.2–0.9)

301

302   Table 2 Gaseous (a) and particulate (b) concentrations in air (time-weighted mean (min-

303   max), ng m^{-3}) of selected PAH compared to other studies in the Ionian Sea and Sicily region

304   (ISS) and in the southeastern Mediterranean (SEM). For calculation of means values <LOQ

305   were replaced by LOQ/2. RV = research vessel cruise.

306   a)

	ISS		SEM			
					Finokalia September-October 2001, February, March and July 2002 [1]	Finokalia November 2000-February 2002 [2]
	RV August-September 2010	RV 2006, June 2006, May 2007	RV August-September 2010	RV June 2006, May 2006, 2007		

	this study	Castro-Jiménez 2012	this study	Castro-Jiménez 2012	Tsapakis et al. 2006	Tsapakis & Stephanou 2005
FLN	0.186 (0.0503–0.400)	2.25 (1.27–5.65)	0.11 (<0.027–0.34)0.07 (0.02–0.34)	0.69 (0.36–1.23)	1.05 (0.15–1.67)	1.8 (0.2–5.7)
PHE	0.592 (0.145–1.110)	7.00 (3.52–15.45)	0.51 (0.14–1.41)0.35 (0.14–1.41)	3.94 (2.50–6.35)	4.78 (1.75–7.78)	7.3 (1.5–27.7)
ANT	0.064 (<0.021–0.10)	0.37 (0.18–0.55)	0.0674 (<0.013–0.22)	0.20 (0.16–0.30)	0.61 (0.12–1.31)	0.9 (0.1–4.5)
FLT	0.1538 (0.053–0.311)	0.05 (0.02–0.07)	0.150 (0.061–0.376)	0.007 (0.003–0.011)	0.82 (0.12–1.69)	1.8 (0.07–6.0)
PYR	0.1539 (0.044–0.2987)	0.04 (0.02–0.06)	0.192 (0.058–0.56)	0.006 (0.003–0.009)	0.65 (0.14–0.97)	0.9 (0.1–2.8)
CHR	0.0132 (0.0071–0.021)	0.09 (0.03–0.23)	0.0184 (0.01211–0.03737)	0.03 (0.02–0.05)	0.18 (0.06–0.33)	0.2 (<0.001–0.6)
Sum of 6 PAHs	1.1	9.8	1.0	4.9	8.1	12.9

Formatierte Tabelle

307

308   b)

	ISS		SEM		
	RV August-September 2010	RV June 2006, May 2007	RV August-September 2010	RV June 2006, May2006, 2007	Finokalia November 2000-February 2002
	this study	Castro-Jiménez 2012	this study	Castro-Jiménez 2012	Tsapakis & Stephanou 2005
FLN	≤0.9286~~0.43~~ (<0.60~~60~~–<1.1~~1.13~~)	0.001 (0.0009–0.002)	≤0.66 (<0.33–<1.4)~~<0.250 (<0.33–<1.36)~~	0.0013 (0.0011–0.0016)	0.02 (<0.001–0.01)
PHE	≤1.9~~1.760.88~~ (<1.2~~1.22~~–<2.3~~2.28~~)	0.06 (0.01–0.12)	≤1.6 (<0.66–<2.7)~~<1.02.51 (<0.67–<2.76)~~	0.04 (0.01–0.13)	0.05 (0.004–0.2)
ANT	≤0.221~~10~~ (<0.14~~14~~–<0.26~~26~~)	0.007 (0.0009–0.012)	≤0.16 (<0.07–<0.32)~~<0.1206 (<0.08–<0.32)~~	0.009 (0.0007–0.023)	0.004 (<0.001–0.02)
FLT	≤0.858~~40~~ (<0.56~~56~~–<1.0~~1.04~~)	0.099 (0.01–0.19)	≤0.62 (<0.30–<1.3)~~<0.4623 (<0.31–<1.26)~~	0.049 (0.01–0.12)	0.1 (0.04–0.2)
PYR	≤0.11~~105~~ (<0.07~~07~~–<0.13~~3~~)	0.109 (0.016–0.216)	≤0.08 (<0.044–<0.16)~~<0.063 (<0.04–<0.16)~~	0.057 (0.012–0.142)	0.04 (0.01–0.01)
BAA	0.0065~~1~~ (<0.0018~~04~~–	0.013 (0.006–	0.0030 (<0.0006–	0.018 (0.004–	0.03 (0.003–0.1)

	0.0253)	0.023)	0.0080)0.003 (0.0004–0.01)	0.046)	
CHR	0.0212 (0.0030–0.0768)	0.04 (0.01–0.08)	0.010 (0.0033–0.020)0.01 (0.003–0.02)	0.043 (0.012–0.101)	0.1 (0.02–0.3)
BBF	0.0283 (<0.00181–0.1010)	0.029 (0.012–0.045)	0.014 (0.0042–0.033)0.01 (0.004–0.03)	0.033 (0.010–0.060)	0.04 (<0.001–0.2)
BKF	0.0152 (<0.00183–0.0576)	0.015 (0.005–0.027)	0.0065 (0.0018–0.015)0.005 (0.002–0.02)	0.089 (0.005–0.333)	0.04 (<0.001–0.2)
BAP	0.0163 (<0.00092–0.0727)	0.009 (0.04–0.016)	0.0052 (<0.0011–0.0098)0.01 (<0.025–0.01)	0.034 (0.005–0.081)	0.02 (0.01–0.05)
BJF	0.0212 (<0.00181–0.0798)	0.015 (0.014–0.016)	0.011 (0.0023–0.031)0.01 (0.002–0.03)	0.010 (0.008–0.011)	-
BEP	0.0233 (<0.00181–0.0889)	0.03 (0.02–0.05)	0.011 (0.0035–0.025)0.01 (0.004–0.03)	0.046 (0.017–0.093)	0.04 (0.01–0.1)
PER	≤0.002863	0.002	≤0.00085	0.026	0.004 (<0.001–

	(<0.000962~~2~~ 0.011~~1~~)	(0.0005– 0.004)	(<0.0006– 0.0021)~~<0.024~~ ~~(<0.012–~~ ~~0.002)~~	(0.0001– 0.068)	0.01)
IPY	0.0~~2~~04 (<0.0~~0~~0962– 0.09~~4~~)	0.0~~1~~18.~~32~~ (0.006~~5.57~~ – 0.032~~1.55~~)	0.0043 (<0.00052– 0.019)~~0.02~~ ~~(<0.012–~~ ~~0.019)~~	0.009 (0.002– 0.013)	0.03 (0.009–0.2)
BPE	≤0.0~~0~~146~~3~~ (<0.000962~~xx~~ ~~–~~≤0.00184)	0.026 (0.017– 0.042)	≤0.00676~~ ~~ (<0.00052– 0.020)~~0.02~~ ~~(<0.012–0.02)~~	0.081 (0.012– 0.210)	0.03 (0.010– 0.09)
Sum of 15 PAHs	0.15	1.06	0.06	0.54	0.54

309 [1] months Sep and Oct 2001, Feb, Apr and May 2002. No particulate data reported.

310 [2] 24h per month between Feb 2000 and Feb 2002

311

312 **3.2 Gas-particle partitioning**

313 Only a small mass fraction of the total, $\theta = 0.08$, is found in the particulate phase, confirming

314 earlier findings from remote sites in the region (Tsapakis and Stephanou, 2005a; Tsapakis et

315 al., 2006; Table 3c). The particulate mass fraction, θ, of four semivolatile PAHs varied

316 considerably along track (see SM Fig. S2). θ is thought to be strongly influenced by

317 temperature and doubling per 13 K cooling was found in a Mediterranean environment

(Lammel et al., 2010b) apart from PM composition. We refrain from aAn exploration of the vapour pressure ($p_{L,0}$)temperature dependence of θ (or K_p) is not possible, because : a low time resolution implies lack of representativeness of the temperature measurement for the phase change (Pankow and Bidleman, 1992), non-equilibrium conditions cannot be excluded (but are likely as a consequence of time resolution; Hoff et al., 1998) and supporting physical and chemical aerosol parameters, necessary to relate are lacking.

of only little temperature variation during the cruise (T_{mean_sample} = 21-27°C, Fig. S2). For similar temperatures higher θ values had been observed at sites on the region influenced by urban and industrial sources (Mandalakis et al., 2002; Tsapakis and Stephanou, 2005b; Akyüz and Cabuk, 2010), which is probably related to the influence of higher organic and soot PM mass fractions. Gas-particle partitioning models (Table 3) underpredict θ, except the Finizio et al., 1997, model for one substance, TPH. θ predicted by the Junge-Pankow (JP) model comes closest. A number of semivolatile PAHs could not be included in this test of gas-particle partitioning models as concentrations in either the gas-phase (CPP, BBF, BJF), or the particulate phase (FLT, PYR, BBN) did not exceed LOQ or no insufficient input data were available (BBF). The neglect of adsorption to soot, not covered by the gas-particle partitioning models tested, may explain at least part of the underprediction (Lohmann and Lammel, 2004). Due to the lack of OC/EC data an extended examination is not possible.

In size-segregated samples particulate PAH mass was almost exclusively found in the PAH was almost exclusively quantified in particle-size fractions <0.25 µm a.e.d. (<LOQ in the other stages, except 0.002 ng m^{-3} CPP in the size fraction corresponding to 0.5-1.0 µm; S2.1, Table 1aS4). Most particulate phase PAHs, 40%, have been found associated with particles <0.5µm out of 5 size ranges in the marine background aerosol of the sea region (coast of

Crete, November 1996 – June 1997; ~~No similar measurements from the open sea or even clean coastal sites exist to compare with.~~ Kavouras and Stephanou, 2002). A~~However, the observation here is in line with observations a~~t continental sites in central and southern Europe~~: There,~~ mass median diameters of PAHs were found to be in the accumulation range, mostly 0.5-1.4 μm (Schnelle et al., 1995; Kiss et al., 1998; Lammel et al., 2010b and 2010c), but also a second, coarse mode was found (up to 2.4 μm; Chrysikou et al., 2009).

Table 3. Gas-particle partitioning of selected PAHs (mean ± sd (median)~~, ng m^{-3}~~), observed and predicted by the models Junge-Pankow, 1987 (JP), Harner and Bidleman, 1998 (HB), and Finizio et al., 1997 (F), expressed as (a) particulate mass fraction, θ, and (b) log K_p of this study.

a)

	Observed	JP	HB	F
BAA	0.51 ± 0.28 (0.47)	0.18 ± 0.07 (0.18)	0.08 – 0.20	0.18
TPH	0.27 ± 0.13 (0.26)	0.24 ± 0.10 (0.24)	0.23 – 0.46	0.37
CHR	0.35 ± 0.15 (0.35)	0.31 ± 0.13 (0.32)	0.09 – 0.21	0.19
BBF	0.88 ± 0.40 (0.94)	0.91 ± 0.40 (0.97)	0.49 – 0.73	0.59

b)

	Observed	JP	HB	F
BAA	-1.28 ± 1.00 (-0.96)	-1.97 ± 1.14 (-1.84)	-2.43 – -1.98	-1.89
TPH	-1.77 ± 1.27 (1.45)	-1.80 ± 1.07 (-1.63)	-1.91 – -1.46	-1.48
CHR	-1.59 ± 1.18 (1.34)	-1.65 ± 1.01 (-1.46)	-2.41 – -1.96	-1.87

| BBF | -0.94 ± 0.19 (-0.24) | -0.52 ± 0.66 (-0.74) | $-1.41 - -0.96$ | -1.08 |

355

3.3 Fugacity ratio and air-sea exchange flux

Fugacity ratios (Fig. 1a) and vertical fluxes (Fig. 1b) could be quantified for FLT, PYR and RET. The uncertainty window of FR = f_a/f_w = 0.3 - 3.0 is based on the uncertainty of $H_{Tw,salt}$. Values FR >3.0 indicate net deposition, FR <0.3 indicate net volatilisation. For RET both water and air concentrations of sample No. 2 were <LOQ. Transfer coefficients were k_w << k_a.

Fig. 1. Air-sea exchange, (a) fugacity ratios FR = f_a/f_w (volatilisation > 3, deposition < 0.3, grey area insignificant deviation from phase equilibrium) and (b) flux F_{aw} (ng m^{-2} d^{-2}; volatilisation > 0, deposition < 0) of FLT, PYR and RET along the cruise of RV Urania. Error bars indicate sea water concentration C_w <LOQ. The x-axis depicts the correspondence of sequential pairs of air samples (1-13) and water samples (a-e).

a.
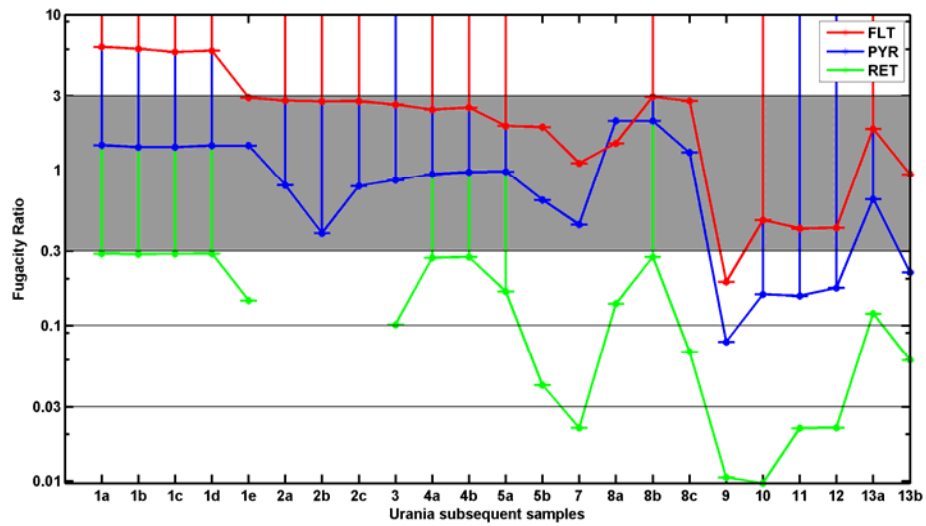
369

370   b.

371

372

373   FLT and PYR <u>were foun</u>d to be close to phase equilibrium, with most of the FR values within

374   the uncertainty range, one sample (No. 1) indicating deposition of FLT and one or two (No. 9

375   and 13) indicating volatilisation of FLT and PYR, respectively. In comparison with earlier

376 observations of FLT and PYR air-sea exchange in the SEM in 2001-02 and 2007 (Tsapakis et

377 al., 2006; Castro-Jiménez et al., 2012) and considering spatial and temporal variabilities no

378 trend, in particular no reversal of air-sea exchange is indicated. This comparison is detailed

379 in the SM, S2.2.1.

380 RET, however, is found net-volatilisational throughout most of the cruise (Fig. 1). Among the

381 highest fluxes (> 50 ng m^2 d^{-1}) are some samples with very low FR, <0.03. Fugacity of RET

382 from water is supported by its Henry's law coefficient (11 Pa m^3 mol^{-1} at 298 K) which is

383 higher than for CHR (0.53 Pa m^3 mol^{-1}) and FLT (2.0 Pa m^3 mol^{-1}). RET is commonly

384 considered as biomarker for coniferous wood combustion (Ramdahl, 1983). A decrease in

385 wildfires could explain the suspected RET volatilisation. Integrated over the domain and the

386 year 2010, fires released 7.2 PJ fire radiative energy, which translates into around 22.2 Gg of

387 $PM_{2.5}$ emitted (Fig. 2). Compared to the $PM_{2.5}$ emissions of the years 2003 to 2012, the year

388 2010 had the lowest emissions, equivalent to 46% of the 2003-2012 mean, and only 18% of

389 the peak emissions of the year 2007 (Fig. 2d). As typical for the East Mediterranean region,

390 the fire season in 2010 started by the end of June and ended by early October. The Urania

391 cruise measurements took place between 27.8. and 12.9., i.e. towards the end of the main

392 burning season (Fig. 2c). During the first half of the Urania cruise, widespread fire activity

393 was observed in the entire domain, with most intense fires occurring in Southern Italy, Sicilia

394 and along the East coast of the Adriatic and the Ionian Sea (notably in Albania and Greece)

395 (Fig. 2a).

396

397 Fig. 2. Spatial pattern of fire-related $PM_{2.5}$ emissions (Global Fire Assimilation System

398 GFASv1.0; Kaiser et al., 2012) for the East Mediterranean (28-45°N/8-30°E), (a) time

399 integral of August 10-26, (b) time integral of August 27 - September 12, 2010, given as sum

400 over each period in mg m^{-2}. Areas with no observed fire activity are displayed in white.

401 Temporal pattern of domain-integrated (c) daily total $PM_{2.5}$ emissions over 2010 (c) and

402 yearly total $PM_{2.5}$ emissions over 2003 to 2012. Labelled in red is (c) the the period of the

403 Urania cruise (27 August – 11 September 2010) (d) and the year 2010.
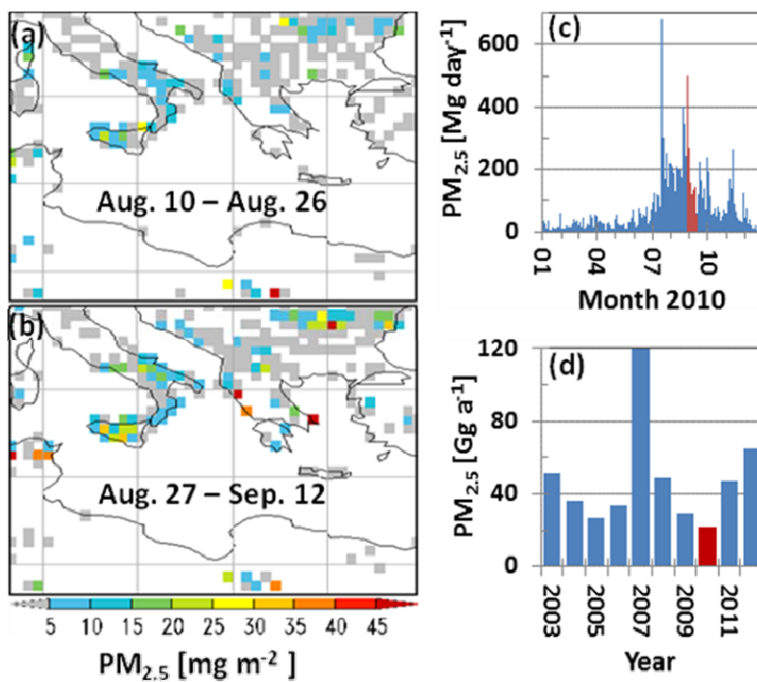
404

405

406 The hypothesis that seasonal depositional input of RET into the surface waters during the fire

407 season (summer) triggers reversal of diffusive air-sea exchange, at least in the year 2010, are

408 tested by box model (sections 2.5 and S1.3) runs. Two scenarios are considered, an 'Initially

409 Estimated Parameter Set' (IEPS) representing mean values for environmental parameters, and

410 an 'Upper Estimate Parameter Set' (UEPS) which represents realistic environmental

conditions favouring seawater pollution (SM, Table S3). Simulated diffusive air-sea exchange flux, F_{aw}, during 2005-2010 initialised by the UEPS is shown in Fig. 3a and by the IEPS in the SM, Fig. S3, and during the observations (cruise of RV Urania, 27.8.-9.9.2010) initialised by the UEPS in Fig. 3b.

The model confirms the hypothesis that seasonal depositional input of RET into the surface waters during the fire season (July-September, typically in the range $F_{aw} = 10^{-2}\text{-}10^{1}$ ng m^{-2} d^{-1} under IEPS) is followed by a period of prevailing flux reversal, typically $F_{aw} = 10^{-2}\text{-}10^{0}$ ng m^{-2} d^{-1}, which in the years 2008-10 started in October and lasted until the onset of the fire season, but eventually started later in the years 2005-07 (at least under IEPS). The volatilisation flux is predicted smaller in magnitude than the net-deposition flux during the fire season, but correspondingly, i.e. higher after intense fire seasons. The high RET volatilisation flux, indicated by measured C_a and C_w, seems to be dominated by biomass burning in the region in the previous fire season. F_{aw} is predicted highly fluctuating, also during the observational period (Fig. 3b). Even under UEPS the model is underpredicting F_{aw} (Fig. 3b). The sensitivity to input uncertainties (SM S1.2) may explain part of the underestimate, but not up to one order of magnitude. Neglected RET sources to seawater, such as riverine input may explain part of the discrepancy.

Fig. 3. Diffusive air-sea exchange flux, F_{aw}, of RET (ng m^{-2} d^{-1}; downward in blue and upward in red) using the upper estimate parameter set (UEPS) for the Eastern Mediterranean (28-45°N/8-30°E) (a.) model predicted for 1.1.2005-31.12.2010 and (b.) model predicted and observed (black) for 27.8.-9.9.2010. Hourly mean data filtered against off-shore winds (see text). Error bars including both signs of F_{aw} reflect C_w <LOQ.a.
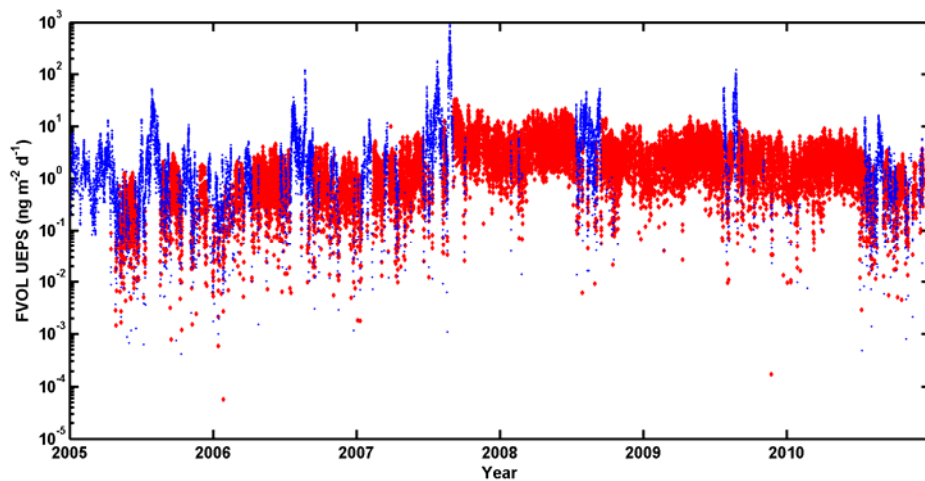
434

435

436   b.
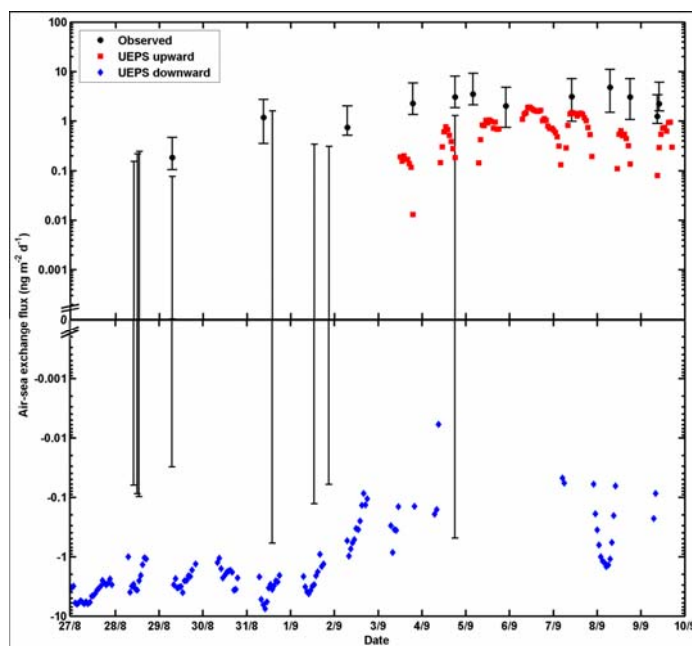
437

438

439   **4. Conclusions**

440

PAH pollution of the atmospheric Mediterranean environment was below previous observations at the beginning of the decade (2001-02; Tsapakis and Stephanou, 2005a; Tsapakis et al., 2006), also considering possible losses during sampling. This might reflect emission reductions. The particulate phase PAHs were concentrated in the size fraction < 0.25 μm a.e.d. The residence time in the troposphere is longest for particles around 0.2 μm of size, with ≈0.01 cm s^{-1} being a characteristic corresponding dry deposition velocity (Franklin et al., 2000), which translates into a residence time of ≈120 days in the MBL (depth of 1000 m; see Table S3) and deposition flux F_{dep} = c×v = 0.03-0.13 μg m^{-2} year^{-1} for the individual PAHs associated with the particulate phase (c = 0.01-0.04 ng m^{-3}; Table 2b), such as BAP, and 0.80 and 0.35 μg m^{-2} year^{-1}, respectively, for the total flux of particulate phase PAHs in the ISS and SEM in summer, respectively. The flux will be higher in winter, because of the seasonality of the emissions.

Three gas-particle partitioning models were tested and found to underpredict the particulate mass fraction in most of the samples (four PAHs i.e., BAA, TPH, CHR and BBF). Although input parameters were incomplete these results confirm the earlier insight that additional processes on the molecular level need to be included, beyond adsorption (Junge-Pankow model) and absorption in OM (K_{oa} models), namely both adsorption and absorption (Lohmann and Lammel, 2004) or even a complete description of molecular interactions between sorbate and PM matrix (Goss and Schwarzenbach, 2001).

Simulations with a non-steady state 2-box model confirm the hypothesis that seasonal depositional input of RET from biomass burning into the surface waters during summer is followed by a period of flux reversal. The volatilisation flux is smaller in magnitude than the

net-deposition flux during the previous months, but correspondingly, i.e. higher after intense fire seasons. Future negative emission trends or interannual variability of regional sources may trigger the sea to become a secondary PAH source through reversal of diffusive air-sea exchange. For the wood burning marker RET it is found that the secondary source became significant in recent years: While the flux of secondary RET emissions (from surface seawaters) in the study area was 1.0 µg m^{-2} year^{-1} (mean of years 2005-2010, UEPS), the primary sources amounted to 3.1 µg m^{-2} year^{-1}. Because of non-diffusive emission from the sea surface, such as aerosol suspension from sea spray and bubble bursting (Woolf, 1997; Qureshi et al., 2009; Albert et al., 2012), the true volatilisation may have exceeded the diffusive flux significantly.

References

Albert, M.F.M.A., Schaap, M., Manders, A.M.M., Scannell, C., O'Dowd, C.D., de Leeuw, G.: Uncertainties in the determination of global sub-micron marine organic matter emissions, Atmos. Environ., 2012, 57, 289-300.

Akyüz, M., Çabuk, H.: Gas-particle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey. Sci. Total Environ., 2010, 408, 5550-5558.

Balasubramanian, R., He, J.: Fate and transfer of persistent organic pollutants in a multimedia environment. In: Zereini, F., Wiseman, C.L.S. (eds) Urban airborne particulate matter: origins, chemistry, fate and health impacts. Springer, Heidelberg, pp. 277-307, 2010.

494   Berrojalbiz, N., Dachs, J., Ojeda, M.J., Valle, M.C., Castro Jiménez, J., Wollgast, J., Ghiani,
495   M., Hanke, G., Zaldivar, J.M.: Biogeochemical and physical controls on concentrations of
496   polycyclic aromatic hydrocarbons in water and plankton of the Mediterranean and Black
497   Seas, Glob. Biogeochem. Cycles, 2011, 25, GB4003.

498   Bidleman, T.F., McConnell, L.L.: A review of field experiments to determine air–water gas-
499   exchange of persistent organic pollutants. Sci. Total Environ., 1995, 159, 101-107.

500   Bruhn, R., Lakaschus, S., McLachlan, M.S.: Air/sea gas exchange of PCBs in the southern
501   Baltic sea. Atmos. Environ., 2003, 37, 3445–3454.

502   Castro-Jiménez, J., Berrojalbiz, N., Wollgast, J., Dachs, J.: Polycyclic aromatic hydrocarbons
503   (PAHs) in the Mediterranean Sea: Atmospheric occurrence, deposition and decoupling
504   with settling fluxes in the water column. Environ. Pollut., 2012, 166, 40-47.

505   Chrysikou, L.P., Gemenetzis, P.G., Samara, C.A.: Wintertime size distributions of polycyclic
506   aromatic hydrocarbons (PAH). polychlorinated biphenyls (PCB) and organochlorine
507   pesticides (OCPs) in the urban environment: Street- vs. rooftop-level measurements.
508   Atmos. Environ., 2009, 43, 290-300.

509   Dachs, J., Bayona, J.M., Raoux, C., Albaiges, J.: Spatial, vertical distribution and budget of
510   polycyclic aromatic hydrocarbons in the western Mediterranean seawater. Environ. Sci.
511   Technol., 1997, 31, 682-688.

512   Dvorská, A., Lammel, G., Klánová, J.: Use of diagnostic ratios for studying source
513   apportionment and reactivity of ambient polycyclic aromatic hydrocarbons over central
514   Europe. Atmos. Environ., 2011, 45, 420-427.

515   Eckhardt, S., Breivik, K., Manø, S., Stohl, A.: Record high peaks in PCB concentrations in
516   the Arctic atmosphere due to long-range transport of biomass burning emissions, Atmos.
517   Chem. Phys., 2007, 7, 4527–4536.

518   Finizio, A., Mackay, D., Bidleman, T.F., Harner, T.: Octanol-air partition coefficient as a
519   predictor of partitioning of semi-volatile organic chemicals to aerosols. Atmos. Environ.,
520   1997, 31, 2289-2296.

521   Franklin, J., Atkinson, R., Howard, P.H., Orlando, J.J., Seigneur, C., Wallington, T.J.,
522   Zetzsch, C.: Quantitative determination of persistence in air. In: Criteria for persistence
523   and long-range transport of chemicals in the environment (Klečka, G., Boethling, B.,

Formatiert: Englisch (USA)

Franklin, J., Grady, L., Graham, D., Howard, P.H., Kannan, K., Larson, R.J., Mackay, D., Muir, D., van de Meent, D., eds.), SETAC Press, Pensacola, USA, pp. 7-62, 2000.

Galarneau, E., Bidleman, T.F., Blanchard, P.: Modelling the temperature-induced blow-off and blow-on artefacts in filter-sorbent measurements of semivolatile substances. Atmos. Environ., 2006, 40, 4258-4268.

Goss, K.U., Schwarzenbach, R.P.: Linear free energy relationships used to evaluate equilibrium partitioning of organic compounds. Environ. Sci. Technol., 2001, 35, 1–9.

Greenfield, B.K., Davis, J.A.: A PAH fate model for San Francisco Bay, Chemosphere, 2005, 6, 515-530.

Guitart, C., Garcá-Flor, N., Miquel, J.C., Fowler, S.W., Albaíges, J.: Effect of accumulation PAHs in the sea surface microlayer on their coastal air-sea exchange, J. Mar. Systems, 2010, 79, 210-217

Harner, T., Bidleman, T.F.: Octanol–air partition coefficient for describing particle-gas partitioning of aromatic compounds in urban air. Environ Sci Technol,, 1998, 32, 1494 – 1502.

Hoff, E.M., Brice, K.A., Halsall, C.J.: Non-linearities in the slope of Clausius-Clapeyron plots for semivolatile organic compounds. Environ. Sci. Technol., 1998, 32, 1793–1798.

Jaenicke, R.: Aerosol physics and chemistry. In: Numerical Data and Functional Relationships in Science and Technology, ed. G. Fischer, vol. 4, pp. 391-457, Springer, Berlin, 1988.

Kaiser, J.W., Heil, A., Andreae, M.O., Benedetti, A., Chubarova, N., Jones, L., Morcrette, J.J., Razinger, M., Schultz, M.G., Suttie, M., van der Werf, G.R.: Biomass burning emissions estimated with a global fire assimilation system based on observed fire radiative power. Biogeosci., 2012, 9, 527-554.

Karickhoff, S.W.: Semiempirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere, 1981, 10, 833-849.

Kavouras, I.G., Stephanou, E.G.: Particle size distribution of organic primary and secondary aerosol constituents in urban, background marine, and forest atmosphere. J. Geophys. Res., 2002, 107, 4069.

553   Keyte, I.J., Harrison, R.M., Lammel, G.: Chemical reactivity and long-range transport
554   potential of polycyclic aromatic hydrocarbons – a review, Chem. Soc. Rev., 2013, 42,
555   9333-9391.
556   Kiss, G., Varga-Puchony, Z., Rohrbacher, G., Hlavay, J.: Distribution of polycyclic aromatic
557   hydrocarbons on atmospheric aerosol particles of different sizes, Atmos. Res., 1998, 46,
558   253-261.
559   Lammel, G.: Effects of time-averaging climate parameters on predicted multicompartmental
560   fate of pesticides and POPs. Environ. Pollut., 2004, 128, 291-302.
561   Lammel, G., Sehili, A.M., Bond, T.C., Feichter, J., Grassl, H.: Gas/particle partitioning and
562   global distribution of polycyclic aromatic hydrocarbons – a modelling approach.
563   Chemosphere, 2009a, 76, 98-106.
564   Lammel, G., Klánová, J., Kohoutek, J., Prokeš, R., Ries, L., Stohl, A.: Observation and origin
565   of organochlorine pesticides, polychlorinated biphenyls and polycyclic aromatic
566   hydrocarbons in the free troposphere over central Europe. Environ. Pollut., 2009b, 157,
567   3264-3271.
568   Lammel G., Klánová J., Ilić P., Kohoutek J., Gasić B., Kovacić I., Lakić N., Radić R.:
569   Polycyclic aromatic hydrocarbons on small spatial and temporal scales – I. Levels and
570   variabilities, Atmos. Environ., 2010a, 44, 5015-5021.
571   Lammel, G., Klánová, J., Ilić, P., Kohoutek, J., Gasić, B., Kovacić, I., Škrdlíková, L.:
572   Polycyclic aromatic hydrocarbons on small spatial and temporal scales – II. Mass size
573   distributions and gas-particle partitioning, Atmos. Environ., 2010b, 44, 5022-5027.
574   Lammel, G., Novák, J., Landlová, L., Dvorská, A., Klánová, J., Čupr, P., Kohoutek, J.,
575   Reimer, E., Škrdlíková, L.: Sources and distributions of polycyclic aromatic
576   hydrocarbons and toxicity of polluted atmosphere aerosols. In: Urban Airborne
577   Particulate Matter: Origins. Chemistry. Fate and Health Impacts (Zereini. F., Wiseman.
578   C.L.S., eds.), Springer, Berlin, pp. 39-62, 2010c.
579   Lei, Y.D., Chankalal, R., Chan, A., Wania, F.: Supercooled liquid vapor pressures of the
580   polycyclic aromatic hydrocarbons. J. Chem. Eng. Data, 2002, 47, 801–806.
581   Lim, L., Wurl, O., Karuppiah, S., Obbard, J.P.: Atmospheric wet deposition of PAHs to the
582   sea-surface microlayer, Mar. Poll. Bull., 2007, 54, 1212-1219.

583 Lipiatou, E., Saliot, A.: Fluxes and transport of anthropogenic and natural polycyclic
584   aromatic-hydrocarbons in the western Mediterranean Sea. Mar. Chem., 1991, 32, 51-71.

585 Lipiatou, E., Tolosa, I., Simó, R., Bouloubassi, I., Dachs, J., Marti, S., Sicre, M.A., Bayona,
586   J.M., Grimalt, J.O., Saliott, A., Albaiges J.: Mass budget and dynamics of polycyclic
587   aromatic hydrocarbons in the Mediterranean Sea, Deep Sea Res. II, 1997, 44, 881-905.

588 Liss, P.S., Slater, P.G.: Flux of gases across air–sea interface. Nature, 1974, 247, 181-184.

589 Lohmann, R., Lammel G.: Adsorptive and absorptive contributions to the gas particle
590   partitioning of polycyclic aromatic hydrocarbons: State of knowledge and recommended
591   parameterization for modelling. Environ. Sci. Technol., 2004, 38, 3793-3803.

592 Lohmann, R., Dapsis, M., Morgan, E.J., Dekany, E., Luey, P.J.: Determining airwater
593   exchange spatial and temporal trends of freely dissolved PAHs in an urban estuary using
594   passive polyethylene samplers. Environ. Sci. Technol., 2011, 45, 2655-2662.

595 Lüers, F., ten Hulscher, T.E.M.: Temperature effect on the partitioning of polycyclic aromatic
596   hydrocarbons between natural organic carbon and water. Chemosphere, 1996, 33, 643-
597   657.

598 Ma, Y.G., Lei, Y.D., Xiao, H., Wania, F., Wang, W.H.: Critical review and recommended
599   values for the physical-chemical property data of 15 polycyclic aromatic hydrocarbons at
600   25°C. J. Chem. Eng. Data, 2010, 55, 819-825

601 Mai, C.: Atmospheric deposition of organic contaminants into the North Sea and the western
602   Baltic Sea, PhD thesis, University of Hamburg, Hamburg, Germany, 444 pp., URL:
603   http://www.chemie.uni-hamburg.de/bibliothek/diss2012_/DissertationMai.pdf, 2012.

604 Mandalakis, M., Tsapakis, M., Tsoga, A., Stephanou, E.G.: Gas–particle concentrations and
605   distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of
606   Athens (Greece). Atmos. Environ., 2002, 36, 4023-4035.

607 Masclet, P., Pistikopoulos, P., Beyne, S., Mouvier, G. : Long range transport and gas/particle
608   distribution of polycyclic aromatic hydrocarbons at a remote site in the Mediterranean
609   Sea, Atmos. Environ., 1988, 22, 639–650.

610 Pankow, J.F.: Review and comparative analysis of the the theory of partitioning between the
611   gas and aerosol particulate phases in the atmosphere. Atmos. Environ., 1987, 21, 2275-
612   2283.

Pankow, J.F., Bidleman, T.F.: Interdependence of the slopes and intercepts from log-log correlations of measured gas-particle partitioning and vapor pressure. I. Theory and analysis of available data. Atmos. Environ., 1992, 26A, 1071-1080.

Pujo-Pay, M., Conan, P., Oriol, L., Cornet-Barthaux, V., Falco, C., Ghiglione, J.F., Goyet, C., Moutin, T., Prieur, L.: Integrated survey of elemental stoichiometry (C, N, P) from the western to eastern Mediterranean Sea. Biogeosci., 2011, 8, 883-899.

Rowe, C.L., Mitchelmore, C.L., Baker, J.E.: Lack of biological effects of water accommodated fractions of chemically-and physically-dispersed oil on molecular, physiological, and behavioral traits of juvenile snapping turtles following embryonic exposure. Sci. Total Environ., 2009, 407, 5344-5355.

Putaud, J.P., Raes, F., van Dingenen, R., Brüggemann, E., Facchini, M.C., Decesari, S., Fuzzi, S., Gehrig, R., Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., ten Brink, H., Tørseth, K., Wiedensohler, A.: A European aerosol phenomenology-2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. Atmos. Environ., 2004, 38, 2579–2595.

Qureshi, A., MacLeod, M., Hungerbühler, K.: Modeling aerosol suspension from soils and oceans as sources of micropollutants to air, Chemosphere, 2009, 77, 495-500.

Ramdahl, T.: Retene — a molecular marker of wood combustion in ambient air. Nature, 1983, 306, 580 - 582.

Schmidl, C., Bauer, H., Dattler, A., Hitzenberger, R., Weissenböck, G.: Chemical characterisation of particle emissions from burning leaves. Atmos. Environ., 2008, 42, 9070–9079.

Schnelle, J., Jänsch, J., Wolf, K., Gebefügi, I., Kettrup, A.: Particle size dependent concentrations of polycyclic aromatic hydrocarbons (PAH) in the outdoor air. Chemosphere, 1995, 31, 3119-3127.

Schwarzenbach, R.P., Gschwend, P.M. Imboden, D.M.: Environmental Organic Chemistry. 2nd ed., Wiley, Hoboken, USA, 2003.

Spindler, G., Gnauk, T., Grüner, A., Iinuma, Y., Müller, K., Scheinhardt, S., Herrmann, H.: Site-segregated characterization of PM_{10} at the EMEP site Melpitz (Germany) using a five-stage impactor: a six year study. J. Atmos. Chem., 2012, 69, 127-157.

Formatiert: Deutsch (Deutschland)

644 Stohl, A., Hitzenberger, M., Wotawa, G.: Validation of the Lagrangian particle dispersion
645   model FLEXPART against large scale tracer experiments. Atmos. Environ., 1998, 32,
646   4245-4264.

647 Stohl, A., Forster, C., Eckhardt, S., Spichtinger, N., Huntrieser, H., Heland, J., Schlager,
648   H.,Wilhelm, S., Arnold, F., Cooper, O.: A backward modeling study of intercontinental
649   pollution transport using aircraft measurements. J. Geophys. Res., 2003, 108, 4370,
650   doi:10.1029/2002jd002862.

651 Stohl, A., Forster, C., Frank, A., Seibert, P., Wotawa, G.: Technical Note: The Lagrangian
652   particle dispersion model FLEXPART version 6.2. Atmos. Chem. Phys., 2005, 5, 2461-
653   2474.

654 Tsapakis, M., Stephanou, E.G.: Collection of gas and particle semi-volatile organic
655   compounds: Use of an oxidant denuder to minimize polycyclic aromatic hydrocarbons
656   degradation during high-volume air sampling. Atmos. Environ., 2003, 37, 4935-4944.

657 Tsapakis, M., Stephanou, E.G.: Polycyclic aromatic hydrocarbons in the atmosphere of the
658   Eastern Mediterranean. Environ. Sci. Technol., 2005a, 39, 6584-6590.

659 Tsapakis, M., Stephanou, E.G.: Occurrence of gaseous and particulate polycyclic aromatic
660   hydrocarbons in the urban atmosphere: study of sources and ambient temperature effect
661   on the gas/particle concentration and distribution. Environ. Poll., 2005b, 133, 147-156.

662 Tsapakis, M., Stephanou, E.G., Karakassis, I.: Evaluation of atmospheric transport as a non-
663   point source of polycyclic aromatic hydrocarbons in marine sediments of the Eastern
664   Mediterranean, Mar. Chem., 2003, 80, 283-298.

665 Tsapakis, M., Apsotolaki, M., Eisenreich, S., Stephanou, E.G.: Atmospheric deposition and
666   marine sedimentation fluxes of polycyclic aromatic hydrocarbons in the Eastern
667   Mediterranean Basin, Environ. Sci. Technol., 2006, 40, 4922-4927.

668 Woolf, D.K.: Bubbles and their role in gas exchange, in: Sea Surface and Global Change
669   (Liss, P.S., Duce, R.A., eds.), Cambridge University Press, Cambridge, UK, pp. 173-206,
670   1997.

671 Zhong, G., Xie, Z., Möller, A., Halsall, C., Caba, A., Sturm, R., Tang, J., Zhang, G.,
672   Ebinghaus, R.: Currently used pesticides, hexachlorobenzene and
673   hexachlorocyclohexanes in the air and seawater of the German Bight (North Sea).
674   Environ. Chem., 2012, 9, 405-414.

675