Author's response

Reviewer 1

This manuscript provides a study of the concentrations in the gas and particulate phase of the PAHs, RPAHs, NPAHs and OPAHs in the Mediterranean Sea and around the Arabian Peninsula including the Red Sea, Arabian Sea and the Arabian Gulf region. The study includes results about PAC particle size distribution and information about their sources in these regions.

Overall, the manuscript needs several improvements. Some parts (e.g. 3.1) are quite long and hard to follow and must be improved. In addition, the manuscript suffers of several problems in terms of chemical analytical procedures, data validation, analysis and interpretation and thus, on the results obtained. This is especially true for the source apportionment part and as it stands, the methodology applied is largely perfectible and could be improved. The probable objective of the authors was to get an understanding of PAC sources in the region. However, the PMF source apportionment approach made is not clear. I guess (not sure cause it is not clear) the authors first apportioned the PM to later understand the PAC sources. If it that the case, some major PM sources, e.g. sea salt, have not been considered at all and it is difficult to understand. The inclusion of alkylated PAHs in the PMF approach, or by applying multi-linear regression analysis or PCA between PMF outputs and key PAH ratios, would be of great benefit instead having a questionable use of PAH diagnostic ratios alone. The source attribution using NPAHs is not well done and analysed in the wrong way and so, the following discussion on the significance of the OPAHs and NPAHS sources should be removed. Finally, the PAC particle size distribution is poorly innovative and informative and could be here again largely improved.

In conclusion, the authors have really a very good database and can improve the data analysis performed and the results obtained. Thus, I would not recommend the publication of this paper in ACP in the current form. I strongly encourage the authors to resubmit their paper after major changes and revisions. Detailed comments and suggestions are provided directly into the pdf file of the text.

l. 47: IARC 1989 ->Use these references instead:
IARC: Some Chemicals Present in Industrial and Consumer Products, Food and Drinking-water, 2012.
IARC (Ed.): Diesel and gasoline engine exhaust and some nitroarenes, Lyon (France), 2013.

→ Will be added to the revised version.

l. 48: add
Idowu, O., Semple, K. T., Ramadass, K., O'Connor, W., Hansbro, P., and Thavamani, P.: Beyond the obvious: Environmental health implications of polar polycyclic aromatic hydrocarbons, Environment International, 123, 543–557, https://doi.org/10.1016/j.envint.2018.12.051, 2019.
Environmental Health Criteria (EHC) 229: Selected nitro- and nitro-oxy-polycyclic aromatic hydrocarbons, WHO Library, 2003.
→ Will be added to the revised version.

l. 50: Walgraeve et al. 2010 not relevant here
→ Yes, true. Deleted.

l. 51: Idowu, O., Semple, K. T., Ramadass, K., O'Connor, W., Hansbro, P., and Thavamani, P.: Beyond the obvious: Environmental health implications of polar polycyclic aromatic hydrocarbons, Environment International, 123, 543–557, https://doi.org/10.1016/j.envint.2018.12.051, 2019.
Environmental Health Criteria (EHC) 229: Selected nitro- and nitro-oxy-polycyclic aromatic hydrocarbons, WHO Library, 2003.
→ Will be added to the revised version.

l. 54: merge both sentences
→ Yes. Merged to: "Alkylated 3-ring-PAHs are more persistent, bioaccumulative, and toxic than the parent 3-ring-PAHs, which have been identified as substances with persistent, bioaccumulative, and/or toxic properties (PBT) (ECHA, 2021; Wassenaar and Verbruggen, 2021).

l. 56: add
Ravindra, K., Sokhi, R., and Van Grieken, R.: Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation, Atmospheric Environment, 42, 2895–2921, https://doi.org/10.1016/j.atmosenv.2007.12.010, 2008.
→ Yes, good idea. Will be added to the revised version.

l. 57: Lee et al. 2003 not relevant here
→ Yes, followed, ref. will be replaced by Yunker et al. 2002 (https://doi.org/10.1016/S0146-6380(02)00002-5)

l. 57: instead of Walgraeve et al., 2010: Use this instead:
Abbas, I., Badran, G., Verdin, A., Ledoux, F., Roumié, M., Courcot, D., and Garçon, G.: Polycyclic aromatic hydrocarbon derivatives in airborne particulate matter: sources, analysis and toxicity, Environ Chem Lett, 1–37, https://doi.org/10.1007/s10311-017-0697-0, 2018.
→ Will be done.

l. 61: Abbas, I., Badran, G., Verdin, A., Ledoux, F., Roumié, M., Courcot, D., and Garçon, G.: Polycyclic aromatic hydrocarbon derivatives in airborne particulate matter: sources, analysis and toxicity, Environ Chem Lett, 1–37, https://doi.org/10.1007/s10311-017-0697-0, 2018.
Bandowe, B. A. M. and Meusel, H.: Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) in the environment – A review, Science of The Total Environment, 581–582, 237–257, https://doi.org/10.1016/j.scitotenv.2016.12.115, 2017.
Walgraeve, C., Demeestere, K., Dewulf, J., Zimmermann, R., and Van Langenhove, H.: Oxygenated polycyclic aromatic hydrocarbons in atmospheric particulate matter: Molecular characterization and occurrence, 44, 1831–1846, https://doi.org/10.1016/j.atmosenv.2009.12.004, 2010.
→ These references will be added to the revised version.

l. 63: Atkinson, R., Arey, J., Zielinska, B., and Aschmann, S. M.: Kinetics and nitro-products of the gas-phase OH and NO3 radical-initiated reactions of naphthalene-d8, Fluoranthene-d10, and pyrene, 22, 999–1014, https://doi.org/10.1002/kin.550220910, 1990.
→ Will be added to the revised version.

l. 65: Ciccioli, P., Cecinato, A., Brancaleoni, E., Frattoni, M., Zacchei, P., Miguel, A. H., and Vasconcellos, P. de C.: Formation and transport of 2-nitrofluoranthene and 2-nitropyrene of photochemical origin in the troposphere, 101, 19567–19581, https://doi.org/10.1029/95JD02118, 1996.
→ Yes will be added to the revised version, thanks.

l. 67: Srogi, 2007: not present in the references
→ Thanks for noticing! Reference will be added to the revised version.

l.68: Jin, R., Zheng, M., Lammel, G., Bandowe, B. A. M., and Liu, G.: Chlorinated and brominated polycyclic aromatic hydrocarbons: Sources, formation mechanisms, and occurrence in the environment, Prog. Energy Combust. Sci., 76, 100803, https://doi.org/10.1016/j.pecs.2019.100803, 2020.
→ Yes very good point! Reference will be added to the revised version.

l. 69: Iakovides et al., 2021 not relevant
→ Yes, deleted reference.

l. 70: Albinet, A., Leoz-Garziandia, E., Budzinski, H., and Villenave, E.: Polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): Concentrations and sources, 384, 280–292, https://doi.org/10.1016/j.scitotenv.2007.04.028, 2007.
Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., and Jaffrezo, J.-L.: Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys: Part 1: Concentrations, sources and gas/particle partitioning, Atmospheric Environment, 42, 43–54, https://doi.org/10.1016/j.atmosenv.2007.10.009, 2008.
→ Will be added.

l. 73: Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., and Jaffrezo, J.-L.: Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys: Part 1: Concentrations, sources and gas/particle partitioning, Atmospheric Environment, 42, 43–54, https://doi.org/10.1016/j.atmosenv.2007.10.009, 2008.
→ yes, will be added.

l. 74: and Arctic
Drotikova, T., Ali, A. M., Halse, A. K., Reinardy, H. C., and Kallenborn, R.: Polycyclic aromatic hydrocarbons (PAHs), oxy- and nitro-PAHs in ambient air of Arctic town Longyearbyen, Svalbard, 1–25, https://doi.org/10.5194/acp-2020-142, 2020.
Drotikova, T., Dekhtyareva, A., Kallenborn, R., and Albinet, A.: Polycyclic aromatic hydrocarbons (PAHs) and their nitrated and oxygenated derivatives in the Arctic boundary layer: seasonal trends and local anthropogenic influence, 21, 14351–14370, https://doi.org/10.5194/acp-21-14351-2021, 2021.
→ Good point. Drotikova et al. (2021) to be added. Drotikova et al. (2020) is not really relevant as this article mainly reports and discusses local sources of PAHs and derivatives.

l. 84: add Kelly et al., 2021
→ Yes, ref. will be added.

l. 87: Results not presented neither discussed here
→ Thanks, true, we realized it after submission and deleted.

l. 111: Was it the same for HV samples below?
Please precise it.
→ Yes, it was the same. To be specified in subchapter 2.2.1: "After sampling, the filters and PUFs were stored similarly as the Digitel high-volume samples."

l. 113: 6 or 3 blanks. Later, in the SM, it is specified only 3 blanks (lines 152, 161 of the SM)
→ Yes, the phrase was somehow misleading. It was meant 6 blanks in total. To be rephrased as follows: "…collected together with 3 field blanks from each sampler, respectively."

l. 120: Please add information as above about the number of samples collected as well as the field blanks collected
→ The number of samples is written in the first sentence of that subchapter. We shall add the information about the number of blanks. Revised text: "43 air (gas and particulate phase) samples for the determination of PAHs and alkylated PAHs and 3 field blanks (3 PUFs and 3 QFFs) were collected…."

l. 121: were these PUFs also cleaned or used as they were provided by Ziemer?
What was the procedure applied?
→ Yes, to be followed. Information about the cleaning procedure to be added "(8.0 x 7.5 cm, Ziemer, Langerwehe, Germany; PUFs were washed with water and soap, followed by rinsing with ultrapure water and boiled in ultrapure water for at least 3 hours; Excess water was removed and PUFs were

extracted in a Soxhlet device with acetone (Lichrosolv, Merck) for 24h and with 1:1 mixture n-hexane/DCM (Unisolv, Merck) for another 24h)…."

l. 122: Filter weighting has been done also for PM10 ones (from DH77 sampler). Was it the same procedure applied? (1.4.2 of the SM and Table S15).
→ Yes, but we decided to delete the sentence about the determination of the TSP mass in the revised version, since the data was not used in the manuscript.

l. 129: these are the surrogates
→ Yes. Text will be changed accordingly.

l. 130: these are the internal injection standards.
Please modify the text accordingly.
→ No, these are also surrogate standards (for the PAHs). Text will be changed accordingly.

In addition, the recoveries discussed in 1.5.2.1 of SM are about the surrogate standards, right? This is not clear in the text.
→ True, text in SM to be changed to: "The recoveries for of the surrogate standards (deuterated PAHs and NPAHs/OPAHs) for gaseous (PUF) samples ranged 66-94 % (disregarded NAP-d8) and 41-74 %, respectively."

l. 156: please provide here the same level of details as in 2.3.1.
→ Will be added in the new version as follows: "For alkylated PAHs, particulate and gas-phase samples were extracted separately following a procedure described in detail elsewhere (Iakovides et al., 2021) with certain modifications. Briefly, each sample was spiked before the extraction with a known amount of surrogate standard (2 – 15 ng of phenanthrene-d10, Dr. Ehrenstorfer) and Soxhlet-extracted with 1:1 n-hexane : dichloromethane (Unisolv, Merck) mixture for 24 h and each extract was concentrated, using a rotary evaporator (Rotavap RV 300, Büchi, Flawil, Switzerland), to 5 mL. Subsequently, 10% of the extract was used for PAH analysis. The extract for PAH analysis was cleaned-up by liquid-liquid partitioning with 5% deactivated-DMF (N,N dimethylformamide containing 5% water)/n-hexane for the isolation of polyaromatic from the aliphatic compounds (N,N dimethylformamide, Suprasolv, Merck). The aromatic compounds fraction was subsequently loaded into a micro-column of non-activated granular silica gel (0.015-0.040 mm; Merck) and anhydrous sodium sulphate (ACS reagent; Sigma-Aldrich), in order to remove any water/DMF traces (Iakovides et al., 2019). Subsequently, the eluents were reduced to approximately 0.3 mL by rotary evaporation evaporation (using a rotary evaporation system (Rotavap RV 300, Büchi); vacuum electronically controlled; no heating of the water bath), transferred with iso-octane (Suprasolv, Merck) to 1.1 mL GC vials and further evaporated almost to dryness under a gentle stream of nitrogen (purity grade 5.0) at -10 °C to minimize evaporation losses."

l. 159: internal injection standard
→ Yes, will be changed accordingly.

l. 160: not the analytes but the surrogate standards I guess (line 160 of the SM)
→ Yes, new text in the SI will read:
"The recovery of the surrogate standard phenanthrene-d10 (Dr. Ehrenstorfer) for the PAHs and RPAHs from the second high volume sampler standard ranged 75 – 119 %."
New text in the main manuscript will read:
"Prior to GC/MS analysis, a known amount of internal injection standard mixture (4-20 ng of anthracene-d10 in iso-octane) was added in each GC vial to assess the analyte recovery of the surrogate standard phenanthrene-d10 (Dr. Ehrenstorfer) in the collected samples."

l. 161: Phenanthrene was analyzed by both labs on both sample types (HVS and DH77). Have you performed any comparison of the concentrations obtained It would be useful to show something about that and to include it in the QA/AC procedure

→ The sampling protocols of the two sampling types was not identical, but sampling times overlapped partly. Therefore, such a comparison would not be conclusive, unfortunately.

l. 178: Please specify here using PAS 2000 PAH monitor

→ Yes, to be changed to: "...and surface PAH concentrations using a photoelectric PAH sensor (EcoChem PAS2000, Ansyco, Karlsruhe, Germany)..."

l. 179: Please specify hre using AE33, multiwavelenght aethalometer. This is a crucial information for the later source apportionment study. You might discriminate BCff and have additionnal information using BC1 in the UV range.

→ Yes, text to be specified: "(BC, using a multiwavelength aethalometer, AE33, Magee Scientific)...."

l. 188: It is not clear how the PMF has been performed.

a) Is the first goal was to apportion PM and then see how the PAC are distrubuted among the OM sources?

b) Or the strategy was directly to apportion PACs?

In case a), other PM sources such as sea salt, secondary inorganics must be considered and with the key PM species to apportion them (including anions/cations for instance).

In case b, how did you apportion the PM as shown on Fig 5?

→ The goal was to apportion PM$_{10}$ (set as total variable) and focus on the factors with high PAC contributions. Number of samples limited the number of input variables (matrix dimension limitation). PMF was run using two different groups of parameters as input variables. PACs, heavy metals, OC and EC (as suitable tracers) were selected as variables. Secondary inorganic ions were not represented by a tracer. Nevertheless, for groups 1 and 2, the correlation between observed and modelled species was, r^2=0.75 and r^2=0.74, respectively.

In the new simulation, we have replaced BC by Na$^+$ to acquire a tracer for sea salt. We will add the following sentence: ". In addition, we added Na+ as input parameter. However, it has to be considered that the data coverage was only about 65 % of the sampling time." BC was somewhat redundant (see following comment/reply). We are aware of the missing SIA factor since the main ions, SO$_4^{2-}$, NH$_3^-$ and NH$_4^+$, were not among the input variables.

The revised figure will present the species' contributions to the total variable PM$_{10}$.

Based on the new PMF runs (with Na$^+$ but without BC), all numbers (e.g. factor contributions, correlation coefficients) were adjusted and the following sentences added to the chapter of the PMF results: "Last factor (the fifth in PMF group 2) ascribed as sea salt dominated by Na$^+$ (Pey et al., 2013; Chembari et al., 2014; Bove et al., 2016). The factor contributed by 2% and 4% to PM$_{10}$ (Fig. S4). Considering the data coverage of only around 65 % of the sampling time, the contribution of sea salt to PM might be higher than based on the PMF output."

l. 189: Why did you use as PMF input both, EC and BC? They don't have the same meaning.

In addition instead of using BC you might use BCff or use BC1 (in the UV) as the final goal is to apportion PAC. have you checked the correlations between BC1 and total PM PAC content?

→ Yes, EC (thermal) and BC (optical parameter) are different. Since the BC was determined in a different size range of PM (i.e., PM$_{2.5}$) than the other species (PM$_{10}$), and the number of input variables was limited, we have replaced BC in the new input matrix by the sea salt tracer Na$^+$. We have not checked the correlations between BC1 and total PM PAC content as we decided to focus on EC instead of BC due to the reason stated above. Input parameters of the PMF:

Variable – Group 1	**r^2**
EC	0.76

OC	0.52
Na+	0.67
Ti	0.96
V	0.89
Cr	0.57
Mn	0.85
Fe	0.99
Co	0.99
Ni	0.62
Cu	0.76
Zn	0.80
Mo	0.54
Cd	0.28
Pb	0.95
PCB7	0.69
HCH3	0.59
DDX6	0.49
endos.sulfate	0.46
drins	0.49
FLT	0.64
Σ16PAHs	0.55
Σ18NPAHs	0.60
BAN	0.81
Σ11OPAHs	0.57
PM10	0.75

Variable – Group 2	**r2**
EC	0.75
OC	0.70
Na+	0.41
Ti	0.96
V	0.94
Cr	0.58
Mn	0.85
Fe	0.99
Co	0.95
Ni	0.28
Cu	0.69
Zn	0.85
Mo	0.48
Cd	0.30
Pb	0.92
PHE	0.77
FLT	0.87
PYR	0.97
BAP	0.24
BEP	0.46

3NPHE	0.57
2NFLT	0.55
1NPYR	0.27
2NPYR	0.76
11OBaFLN	0.88
BAN	0.84
(712)O2BAA	0.81
(512)O2NAC	0.77
PM10	0.74

l. 189: Information and disucssion is missing on the selection of the PMF inputs species. Was it based on S/N, data above LQ, specific marker (tracer) species?
→ Selection criteria will be stated in the Section 2.5 Aerosol source apportionment as follows: "The PMF input species were selected based on following criteria: trace species with focus on PACs, data above LOQ, signal to noise ratio (S/N), and last, but not least the matrix dimension limitation."

l. 192: IN PMF, the ratio species (variables) to number of samples should about 1/3. So the selection of the species is hightly critical.
→ We had considered this. This is one reason why we ran the PMF with 2 different groups of parameters as input variables.

l. 194-200: What was the correlation between observed and modelled species? What about the reconstruction of the PM mass?
→ Thanks for the question, we will add the following sentence: "The correlation between observed and modelled species was r^2=0.75 and r^2=0.74 for group 1 and group 2, respectively."
We are aware of this fact. Therefore, we have carefully considered all input variables. However, there was no problem to run the model and all runs converged for both groups/matrices.

l. 207: This is well explained.
However, in the end, from the PMF outputs, is there an agreement between the possible contaminated samples by the own ship exhaust and the high concentration peak events observed on the ship emission factor?
→ Very good point: The following text will be added in subchapter 3.3.1: "The model output and the filtering of possibly stack contaminated samples strongly agree. Samples filtered for stack contamination also show a contribution from fresh shipping emissions (e.g. samples D2, D3 from 26-28 June; D16-D23 from 14-22 July D26-D28 from 25-28 July). The stack filtering has rejected even a few samples without significant contribution from the factor (D9-D11 from 4-7 July). In contrast, a minor contribution to the factor of fresh shipping emissions was found in the Mediterranean Sea for samples around 30 August, which were not excluded by our filtering. This might be explained by fresh emissions from other ships close to the strait of Messina."

l. 208: of the surrogates not of the targeted species
→ True, information will be added.

l. 209: There extensive tables about the LOQs (blank corrected) and I am not sure they are really useful (in additin not provided for RPAHs) or at least the data are not used in a good way.
→ The complexity of the LOQs (split into gas and particulate phase) is necessary since we evaluated each phase separately. The separation of instrumental and field blank LOQ might be skipped and only one LOQ (maximum of both LOQs) reported, but we prefer to keep it for the sake of tracking uncertainty / high LOQ values.

For instance, in the end, you observed very low Naphthalene contribution in the PAH chemical profiles that is very surprising knowing it is largely the major PAH in ambient or for any combustion process. The concentrations data reported for this compound are similar or lower than the LOQ. This is first not correct and second this highlight several troubles in the quantification of this compound meaning it should not be considered; the same apply for other compounds such as ACY, 9-NA (which is usually very abundant), 1-NNA etc...
For these both latter, such results also highlight possible high contamination of the blanks inducing, after correction, very low sample concentrations.
Overall, you may check carefully again your data and exclude them if necessary (like NAPH for sure).
→ All values presented are QA/QC controlled, detailed in sections 2.7 and S1.5. Contamination of samples was minimal as all sample manipulation (including the field blank samples) could be done in a special under-deck lab with clean desk, reserved for clean-desk operations following usual lab standards.
The reported naphthalene (NAP) levels are low. They are not reported lower than LOQ (such values were given as '<xxx', LOQs (<x): x in Table S10a often higher than values for NAP due to the differentiation between gas and particulate phase. Sometimes quantified in particulate phase (but with low concentrations) but <LOQ given as the LOQ of the gas phase (which was quite high).
Low levels of naphthalene in the marine boundary layer are not uncommon (see e.g. González-Gaya et al. 2019, https://doi.org/10.1038/s41561-018-0285-3), and as such alone do not justify doubt. Low NAP levels may be dominated by the relative degradability of aged PAH mixtures. More general on interpretation of NPAH (and OPAH) substance patterns: Apparently unusual patterns when comparing with reports in the literature are not conclusive, as the mix of sources influencing the observation usually varies, and, in particular, the literature does not provide any comparison with marine boundary layer air or even a marine type of source mix.
However, NAP levels, unlike all other targeted PAHs or derivatives, were indeed subject to high blank levels. Previously in our lab, when the NAP blank level has been high and varying, NAP was excluded from the analysis. During the time of the analysis of this campaign's samples, the blank level was not varying. Nevertheless, to be on the very safe side and following the recommendation of the reviewer, in the revised version, NAP will be excluded i.e., NAP concentrations will not be reported.
ACY: please see below, comment on line 364
9-NANT: please see below, comment on line 413
1-NNAP: please see below, comment on line 418-425

l. 209: see comments above
→ Yes, also replied above

l. 211:
Overall, this part is very long and hard to read. It could be improved and probably reorganized. Maybe split into two parts in one the discussion of the concentration levels all along the travel and comparison between the seas and in the second one, comparison with the litterature data.
→ Thank you for this good idea; to be followed.

l. 214: not on the figure
→ Yes right, thank you. Will be deleted as anyway included in the $\sum_{26}$PAHs.

l. 214: why?
→ RET was measured by the Digitel sampler, while all other RPAHs were measured with the GMWL sampler. Due to the different sampling intervals, the direct allocation of the retene concentration to the concentration of the RPAHs of the individual samples was not possible. Brief explanation will be added to the text and as footnote to Table S11.

l. 221: Which one? Ref?
So to be removed from the objectives

→ Yes, the mentioning of phase distribution will be removed from the objective.

l. 225-226: Why? It does not exist. You should replace by LOD/2. LOD?
→ Yes, to be deleted in the revised version, because of low added value of that information.

l. 228: By comparison to what? References? Same seasons, same site typology?
→ Deleted here. More details will be given in the new sub-chapter 3.1.1 (Comparison to literature).

l. 250: Replace by:
Keyte, I. J., Albinet, A., and Harrison, R. M.: On-road traffic emissions of polycyclic aromatic hydrocarbons and their oxy- and nitro-derivative compounds measured in road tunnel environments, Science of The Total Environment, 566–567, 1131–1142, https://doi.org/10.1016/j.scitotenv.2016.05.152, 2016.
Zielinska, B., Sagebiel, J., McDonald, J. D., Whitney, K., and Lawson, D. R.: Emission rates and comparative chemical composition from selected in-use diesel and gasoline-fueled vehicles, J. Air Waste Manag. Assoc., 54, 1138–50, 2004a.
Zielinska, B., Sagebiel, J., Arnott, W. P., Rogers, C. F., Kelly, K. E., Wagner, D. A., Lighty, J. S., Sarofim, A. F., and Palmer, G.: Phase and Size Distribution of Polycyclic Aromatic Hydrocarbons in Diesel and Gasoline Vehicle Emissions, Environ. Sci. Technol., 38, 2557–2567, https://doi.org/10.1021/es030518d, 2004b.
→ Appropriate ref. is given / two more refs. will be added to the new version.

l. 259-261: They are all comparable
→ Yes, indeed not significantly different. Text will be changed to: "…which was comparable but slightly higher than…."

l. 262: same here. Theye are similar and not lower
→ MS and OG are statistically similar (according to t-test) but not MS and AG (not significantly similar or different). Text will be changed to: "The concentration of the $\sum_{19}$RPAHs over the Mediterranean Sea (0.81 ng m-3) was similar to the Gulf of Oman (0.83 ng m^{-3}) and comparable but lower than over the Arabian Gulf (1.12 ng m^{-3}), too."

l. 285: This figure in colour would be more ligible
→ True, changed the figure accordingly.

l. 297: Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., and Jaffrezo, J.-L.: Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys: Part 1: Concentrations, sources and gas/particle partitioning, Atmospheric Environment, 42, 43–54, https://doi.org/10.1016/j.atmosenv.2007.10.009, 2008.
→ True, ref. will be added.

l. 303: 2.8. Let's avoid to show 2 decimals cause it is not realistic to determine 0.01 pg/m3.
→ Good point. Will be changed to 1 decimal.

l. 309: 0.4, 0.9, 0.1
→ See above.

l. 360: why only the 16 ones?
→ Only slightly more information could be given (small mass share of the remaining 10 PAHs), but the figure would be less readable would it include all 27 PAHs (26 PAHs in the revised version).

l. 360: Retene?
→ Since retene was measured with another sampler with different sampling times, the relative contribution of retene to the sum of RPAHs could not be calculated.

l. 360: why only these 7 ones?
→ All quantified NPAHs (7) are shown in this Fig. 3d. Will be explained in the revised version specifying "Only quantified species included in the legends".

l. 364-370: As said before, there is a huge problem with NAP and probably ACY and they should be excluded.
You may discuss these chemical profiles by considering first both, gaseous and particulate (total) PAHs (PACs) and then, considering only the particulate phase (and so compounds mainly associated to this phase)
→ All values presented are QA/QC controlled (see comment above). The dominance of phenanthrene (PHE) among parent PAHs in marine boundary layer air is not uncommon and no reason to doubt (NAP or other 3-ring PAH concentration data (ACY, ACE, PHE, FLN) see e.g., Ding et al. 2007 (https://doi.org/10.1016/j.atmosenv.2006.11.002); van Drooge et al. 2010 (https://doi.org/10.1007/s11356-010-0296-0); Lohmann et al. 2013 (https://doi.org/10.1021/es304764e), Kim & Chae 2016 (https://doi.org/10.1016/j.marpolbul.2016.05.078), González-Gaya et al. 2019 (https://doi.org/10.1038/s41561-018-0285-3). NAP will not be reported in the revised version (see comment above); no change on ACY values (see comment above).
PAHs are semivolatiles, which are subject to gas-particle partitioning on short time scales (fast in comparison with temporal averaging corresponding to sampling periods in this study). Correspondingly, substance patterns can only meaningful be discussed when based on the total i.e., gas + particulate phase concentrations.

l. 380: Tomaz, S., Shahpoury, P., Jaffrezo, J.-L., Lammel, G., Perraudin, E., Villenave, E., and Albinet, A.: One-year study of polycyclic aromatic compounds at an urban site in Grenoble (France): Seasonal variations, gas/particle partitioning and cancer risk estimation, Science of The Total Environment, 565, 1071–1083, https://doi.org/10.1016/j.scitotenv.2016.05.137, 2016.
Also useful for 1,4-O2NAP discussion below
→ True. Will be added to revised version.

l. 388: This compound can be also primarly emitted:
Tomaz, S., Jaffrezo, J.-L., Favez, O., Perraudin, E., Villenave, E., and Albinet, A.: Sources and atmospheric chemistry of oxy- and nitro-PAHs in the ambient air of Grenoble (France), Atmospheric Environment, 161, 144–154, https://doi.org/10.1016/j.atmosenv.2017.04.042, 2017.
Nalin, F., Golly, B., Besombes, J.-L., Pelletier, C., Aujay-Plouzeau, R., Verlhac, S., Dermigny, A., Fievet, A., Karoski, N., Dubois, P., Collet, S., Favez, O., and Albinet, A.: Fast oxidation processes from emission to ambient air introduction of aerosol emitted by residential log wood stoves, Atmospheric Environment, 143, 15–26, https://doi.org/10.1016/j.atmosenv.2016.08.002, 2016.
→ Right. We shall add the sentence: "In addition, it needs to be considered that 1,4-O2NAP is also emitted primarily (Nalin et al., 2016; Tomaz et al., 2017; Clergé et al., 2019)."

L. 389: it may also be supported by this:
Nalin, F., Golly, B., Besombes, J.-L., Pelletier, C., Aujay-Plouzeau, R., Verlhac, S., Dermigny, A., Fievet, A., Karoski, N., Dubois, P., Collet, S., Favez, O., and Albinet, A.: Fast oxidation processes from emission to ambient air introduction of aerosol emitted by residential log wood stoves, Atmospheric Environment, 143, 15–26, https://doi.org/10.1016/j.atmosenv.2016.08.002, 2016.
→ Thanks for the suggestion, but the paper does not provide clear evidence on naphthoquinone sources.

L. 413: I guess it is more related to some contamination.
9-NANT is usually one of th most abundant NPAH

→ Yes, 9-NANT is usually one of the most abundant NPAHs (in continental air, stated in the manuscript). As shown by Lammel et al. (2017; doi:10.5194/acp-17-6257-2017 in the Supplement, 9-NANT has a significantly lower contribution in the marine air than at the continental site. However, you are right that we found relatively high field blank levels which translated into elevated LOQs (which is derived as mean of field blanks + 3 standard deviations of field blanks) and a low quantification frequency. The relatively high LOQ was identified as influencing the 9-NANT concentrations. Particular care in interpretation will be stressed in the revised version by pointing to this problem and removing the sentences about the higher photodegradation of 9-NANT.

l. 414: Like the other ones. I don't think there is any data showing different photolysis rates of the NPAH (except Fan et al., 1996)
→ Yes, true. The reference to photolysis as a possible selective sink will be removed in the revised version.

l. 415: But also cause it is primarly emitted.
→ Yes, true. As said in the next sentence ("seasonal variation in the emission sources").

l. 418-425: I think it is more realated to some contamination troubles.
We experienced one time such contamination, especially on 1- and 2-NNAP, due to the silica SPE or silica alone). You may check the lab blanks (not the field ones) (if you have any).
→ Thanks for sharing the experience. We checked the lab blanks again, and there is no contamination of 1- or 2-NNAP.
On interpretation of NPAH (and OPAH) substance patterns: Apparently unusual patterns when comparing with reports in the literature are not conclusive, as the mix of sources influencing the observation usually varies, and, in particular, the literature does not provide any comparison with marine boundary layer air or even a marine type of source mix. No changes to be made to the text.

l. 434: Keyte, I. J., Albinet, A., and Harrison, R. M.: On-road traffic emissions of polycyclic aromatic hydrocarbons and their oxy- and nitro- derivative compounds measured in road tunnel environments, Science of The Total Environment, 566–567, 1131–1142, https://doi.org/10.1016/j.scitotenv.2016.05.152, 2016.
Schulte, J. K., Fox, J. R., Oron, A. P., Larson, T. V., Simpson, C. D., Paulsen, M., Beaudet, N., Kaufman, J. D., and Magzamen, S.: Neighborhood-Scale Spatial Models of Diesel Exhaust Concentration Profile Using 1-Nitropyrene and Other Nitroarenes, 49, 13422–13430, https://doi.org/10.1021/acs.est.5b03639, 2015.
Srivastava, D., Tomaz, S., Favez, O., Lanzafame, G. M., Golly, B., Besombes, J.-L., Alleman, L. Y., Jaffrezo, J.-L., Jacob, V., Perraudin, E., Villenave, E., and Albinet, A.: Speciation of organic fraction does matter for source apportionment. Part 1: A one-year campaign in Grenoble (France), Science of The Total Environment, 624, 1598–1611, https://doi.org/10.1016/j.scitotenv.2017.12.135, 2018a.
Srivastava, D., Favez, O., Bonnaire, N., Lucarelli, F., Haeffelin, M., Perraudin, E., Gros, V., Villenave, E., and Albinet, A.: Speciation of organic fractions does matter for aerosol source apportionment. Part 2: Intensive short-term campaign in the Paris area (France), Science of The Total Environment, 634, 267–278, https://doi.org/10.1016/j.scitotenv.2018.03.296, 2018b.
Srivastava, D., Favez, O., Petit, J.-E., Zhang, Y., Sofowote, U. M., Hopke, P. K., Bonnaire, N., Perraudin, E., Gros, V., Villenave, E., and Albinet, A.: Speciation of organic fractions does matter for aerosol source apportionment. Part 3: Combining off-line and on-line measurements, Science of The Total Environment, 690, 944–955, https://doi.org/10.1016/j.scitotenv.2019.06.378, 2019.
Lanzafame, G. M., Srivastava, D., Favez, O., Bandowe, B. A. M., Shahpoury, P., Lammel, G., Bonnaire, N., Alleman, L. Y., Couvidat, F., Bessagnet, B., and Albinet, A.: One-year measurements of secondary organic aerosol (SOA) markers in the Paris region (France): Concentrations, gas/particle partitioning and SOA source apportionment, Science of The Total Environment, 757, 143921, https://doi.org/10.1016/j.scitotenv.2020.143921, 2021.

→ Thanks for suggestions, but we decided to not add more references on fossil fuel NPAH sources, as the literature (including the suggested ref's) is anyway road-biased, while the study was in another type of environment i.e., marine.

l. 436: and photolysis
→ Photodegradation includes photolysis, hence adequate here.

l. 436: Fan, Z., Kamens, R. M., Hu, J., Zhang, J., and McDow, S.: Photostability of nitro-polycyclic aromatic hydrocarbons on combustion soot particles in sunlight, 30, 1358–1364, 1996.
→ Yes, thanks, this ref. will be added.

l. 443 Not realy as shown later using 2-NFLT/1-NPYR ratio
→ Thanks. Yes, not true for Arabian Sea as shown later. We will delete the Arabian Sea in this sentence.

l. 444: Based on the references cited, 3-NPHE is more secondary than primary
→ Yes, true. We will add information and some literature sources. Reads as follows: "3-NPHE, which has primary (primary: Bamford et al., 2003; mainly primary: Zhuo et al., 2017) and secondary sources (secondary: Atkinson and Arey, 1994; Ringuet et al., 2012a; mainly secondary: Tomaz et al., 2017),[...]."

l.445: Tomaz, S., Jaffrezo, J.-L., Favez, O., Perraudin, E., Villenave, E., and Albinet, A.: Sources and atmospheric chemistry of oxy- and nitro-PAHs in the ambient air of Grenoble (France), Atmospheric Environment, 161, 144–154, https://doi.org/10.1016/j.atmosenv.2017.04.042, 2017.
→ Yes, to be added.

l. 448: First, you should consider the comments made before about the PMF approach.
Second, you have attributed sources to the factors obtained but nothing is explained how you have identified the sources. It is then commented which species are observed in each sources while it should be in the other way round.
You should explain why the factors are attributed to the given source based on the major contributions of specific species. This is first missing in the text and true too for the SM (2.4.1).
All of this section should be further updated accordingly and following a deep improvement of the PMF approach applied here.
→ Yes, thank you. We have improved the PMF approach (see comments above). Will be extended and updated in the revised version.
The identification of the sources for the different factors were made according to marker substances. This has been detailed in the SM subchapter S2.4.1 and will be given in more detail in the revised version. To be clearer, S2.4.1 will be titled 'Identification of PMF factors'.
We decided to present this in the SM rather than in the main text, because it is based on PM_{10} as the total variable, while in the main text these factors are then used in sub-chapter 3.3.1.

l. 536:
Source attribution using PAH diagnostic ratio is still questionable (see references below).
Instead of using them alone, it would be preferable to include them (or key RPAHs) in the PMF or to perform some multilinear regression (MLR) analysis or PCA between the PMF outputs and such PH ratios. This would be of great value in order to confirm the PMF source apportionment obtained as already done using SO2, CO, O3, etc... (SM, 2.4.1).
Dvorská, A., Lammel, G., and Klánová, J.: Use of diagnostic ratios for studying source apportionment and reactivity of ambient polycyclic aromatic hydrocarbons over Central Europe, Atmos. Environ., 45, 420–427, https://doi.org/10.1016/j.atmosenv.2010.09.063, 2011.
Galarneau, E.: Source specificity and atmospheric processing of airborne PAHs: Implications for source apportionment, Atmos. Environ., 42, 8139–8149, https://doi.org/10.1016/j.atmosenv.2008.07.025, 2008.

Katsoyiannis, A., Sweetman, A. J., and Jones, K. C.: PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation using two decades of source inventory and air concentration data from the UK, Env. Sci Technol, 45, 8897–8906, https://doi.org/10.1021/es202277u, 2011.
Tobiszewski, M. and Namieśnik, J.: PAH diagnostic ratios for the identification of pollution emission sources, Environ. Pollut., 162, 110–119, https://doi.org/10.1016/j.envpol.2011.10.025, 2012.
Wu, Y., Salamova, A., and Venier, M.: Using diagnostic ratios to characterize sources of polycyclic aromatic hydrocarbons in the Great Lakes atmosphere, Sci. Total Environ., 761, 143240, https://doi.org/10.1016/j.scitotenv.2020.143240, 2021.
→ Thanks for the suggestion. We agree on the limited conclusiveness of diagnostic ratios (DRs) (and stressed this in previous papers including Dvorská et al. 2012), in particular in aged air masses (because of non-conservative tracers).
RPAH data were not used as parameter in PMF, as the RPAH sampling followed another sampling protocol, with only very few similar sampling times. The following sentence will be added to the text: "The RPAHs could not be included into any multivariate analysis since the RPAH sampling followed another sampling protocol than the PAHs, OPAHs and NPAHs with only very few similar sampling times."
Following the suggestion, we have extended the data analysis to PCA. The PCA score plot confirms the finding indicated by the usage of the diagnostic ratio for photochemistry (2-NFLT/1-NPYR) with regard to 7,12-O_2BAA, 2-NNAP apart from 2-NPYR. The results will be described in the text in Section 3.3.4 (see below comment l. 686) and as Fig. S6 (see below comment l. 686).

The method will be introduced in Section 2.5 and reads as follows: "In addition, principal component analysis (PCA) was performed. Similar to the PMF, all samples were included into the analysis. The concentrations of the selected substances (based on detection frequency and importance for interpretation; i.e. 2-NNAP; 2-NFLT; 1-NPYR; 2-NPYR; 7-NBAA; 1-(CHO)NAP; 9-OFLN; 9,10-O_2ANT; 11-OBaFLN; 11-OBbFLN; BAN; 7,12-O_2BAA; 5,12-O_2NAC; 3-ring PAHs; 4-ring PAHs and 5-7 ring PAHs) were normalized by the total concentration of the NPAHs, OPAHs and PAHs, respectively. In addition, the concentration of EC, OC and the diagnostic ratios BAP/(BAP+BEP), LMW PAHs/HMW PAHs, 2-NFLT/1-NPYR; 2-NFLT/2-NPYR as well as the ratios of the PAH derivatives and their respective parent PAHs were included into the PCA."

l. 572-627: There is a long discussion about the results on the 2-NFlt/1-N-Pyr ratio while in the end, execpt for 2-3 samples in the MS, all ratio are below 5 indicating the impact of primary emissions for nitro-PAHs.
All of this part should be shortened and merged with the 3.3.4. one.
→ Text using diagnostic ratios (subchapters 3.3.2-4) will be substantially shortened in the revised version. However, the chapter 3.3.3 provides new insights in the usability and its limitations in the marine environment. Due to that, we will shorten the section but will not merge it with section 3.3.4.

l.576: Pay attention that using the Rxi-5sil MS column used, you are not able to discriminate both, 2- and 3-NFlt. 3-NFlt is primary (about 10% of the total of the isomers) and so, this has an impact on the 2-NFlt/1-NPyr used and so the limit of 5 should be considered with caution. This should be specified in the text.
→ Yes true, we were aware of that problem. The possible contribution of 3-NFLT is minor i.e., NFLT/(2-NFLT + 3-NFLT) > 0.96 (Bamford et al., 2003 besides others).
Bamford, H. A., Bezabeh, D. Z., Schantz, M. M., Wise, S. A., and Baker, J. E.: Determination and comparison of nitrated-polycyclic aromatic hydrocarbons measured in air and diesel particulate reference materials, Chemosphere, 50, 575–587, 2003.
We will add the following sentences to section 2.7 (Quality control): "The separation of the isomers 2-NFLT and 3-NFLT is incomplete using the 5MS GC column ((5%-phenyl-)methylpolysiloxane GC stationary phase. In this study, the separation of the two isomers was inadequate to quantify both isomers separately but sufficient to qualitatively report that 3 NFLT was either not detected or only detected as a small shoulder of the 2-NFLT peak, which was not integrated for the peak area of 2-

NFLT. In this study, the separation of the two isomers was inadequate to quantify both isomers separately but sufficient to qualitatively report that 3-NFLT was either not detected or only detected as a small shoulder of the 2-NFLT peak, which was not integrated for the peak area of 2-NFLT.

l. 633-648: There is no need to discuss this ratio as the secondary formation of NPAHs is low.
→ We think that the discussion of the predominant pathway of the secondary formation of NPAHs is important although the relative contribution of secondarily formed NPAHs is lower than in other studies since it is the first study measuring these compounds in these sea regions. The text will be shortened in the revised version, better emphasizing the finding. New text (last sentence of previous lines 633-648): "This finding is similar to previous observations in the marine environment, i.e. the Japanese and Mediterranean Seas (Tang et al., 2014; Lammel et al., 2017)."

l. 649 ff. This section is good.
You may also have an analysis of EC and OC using the EC tracer method in order to apportion the SOC fraction.
Srivastava, D., Favez, O., Perraudin, E., Villenave, E., and Albinet, A.: Comparison of Measurement-Based Methodologies to Apportion Secondary Organic Carbon (SOC) in PM2.5: A Review of Recent Studies, 9, 452, https://doi.org/10.3390/atmos9110452, 2018.
Day, M. C., Zhang, M., and Pandis, S. N.: Evaluation of the ability of the EC tracer method to estimate secondary organic carbon, Atmospheric Environment, 112, 317–325, https://doi.org/10.1016/j.atmosenv.2015.04.044, 2015.
Zhang, Q., Sarkar, S., Wang, X., Zhang, J., Mao, J., Yang, L., Shi, Y., and Jia, S.: Evaluation of factors influencing secondary organic carbon (SOC) estimation by CO and EC tracer methods, Science of The Total Environment, 686, 915–930, https://doi.org/10.1016/j.scitotenv.2019.05.402, 2019.
→ Thanks for the suggestion. The derivation of the contribution of secondary OC to total OC from an estimate of the ratio of EC/OC in the primary emissions is expectedly reliable (little discrepancies) the longer the time series (towards 'climatology'), the closer the receptor to the combustion source(s), and/or the less variable the mix of combustion sources influencing the receptor. With regard to all three, duration of time series, expected distances to combustion sources (coast, other ships and off-shore sources), and the variation of their mix along the cruise (coastal, shelf, open ocean), our data set does hardly qualify for such an approach.

l. 686: I don't think that your database is the most appropriate to have such discussion.
This is mainly based an related to the 2-Nflt/1-Npyr ratio and we can see on Fig 6 that only fo few samples you have clear indication of secondary processes.

I would remove all of this section.
→ Followed, the section will be largely shortened and integrated into the previous sub-chapter. The results of the PCA will be included. The new text (end of subchapter 3.3.3) will read: "We found significant positive correlations ($p<0.05$) of 9-OFLN ($r=0.33$), 1-(CHO)NAP ($r=0.41$), 7,12-O_2BAA ($r=0.83$), 2-NNAP ($r=0.46$) and 3-NPHE ($r=0.44$) with the ratio of 2-NFLT/1-NPYR, which is typically used as an indicator for the contribution of PAH derivatives formed from oxidative reactions. This supports the perception that 9-OFLN, 1-(CHO)NAP, 7,12-O_2BAA and 3-NPHE have photochemical sources apart from primary. Laboratory studies showed that 7,12-O_2BAA is formed in heterogeneous reactions of BAA with O_3 or with O_3 and NO_2 (Gao et al., 2009a; Ringuet et al., 2012a, b). The formation of 7,12-O_2BAA from the photochemical reaction of BAA has also been reported from laboratory studies (Jang and McDow, 1997; Shen et al., 2007). Lin and colleagues (2015) also found field evidence for significant secondary formation of 3-NPHE and 7-NBAA. Tomaz et al. (2017) even suggested 3-NPHE to be used as a marker for secondary formation from PHE. 1-(CHO)NAP was already reported to be secondarily formed by ozonolysis from ACY, 1-methylnaphthalene and possibly other precursors within hours (Dang et al., 2015). These indications of photochemical sources are supported by PCA: The PCA score plot shows the ratios 2-NFLT/1-NPYR and 2-NFLT/FLT as indicative for secondary

formation clustered with the parent-daughter ratios 7,12-O_2BAA/BAA and 7-NBAA/BAA. The ratio BAP/(BAP+BEP), which points to aged air samples, is clustered with 2-NPYR/PYR and 2-NNAP and close to 2-NPYR and the first cluster indicating secondary formation of 2-NPYR (as known in the literature) and 2-NNAP. For 9-OFLN, 1-(CHO)NAP and 3-NPHE, the PCA did not reveal significant secondary formation.

Accordingly, the substances identified as having secondary sources, given in both the abstract and the conclusions will be changed: The respective sentence in the abstract will read: "Apart from 2-NFLT and 2-NPYR, also benz(a)anthracene-7,12-dione and 2-NNAP had significant photochemical sources." And in the conclusion will read: "Photochemical formation of 2-NFLT, 2-NPYR, 2-NNAP, 3-NPHE, 7-NBAA, 1-(CHO)NAP, 9-OFLN, and 7,12-O_2BAA was indicated, while for 1-NPYR, 11-OBaFLN, 11-OBbFLN, BAN and 5,12-O_2NAC secondary sources were not significant."

In the Supplement the plot of PCA scores will be added:

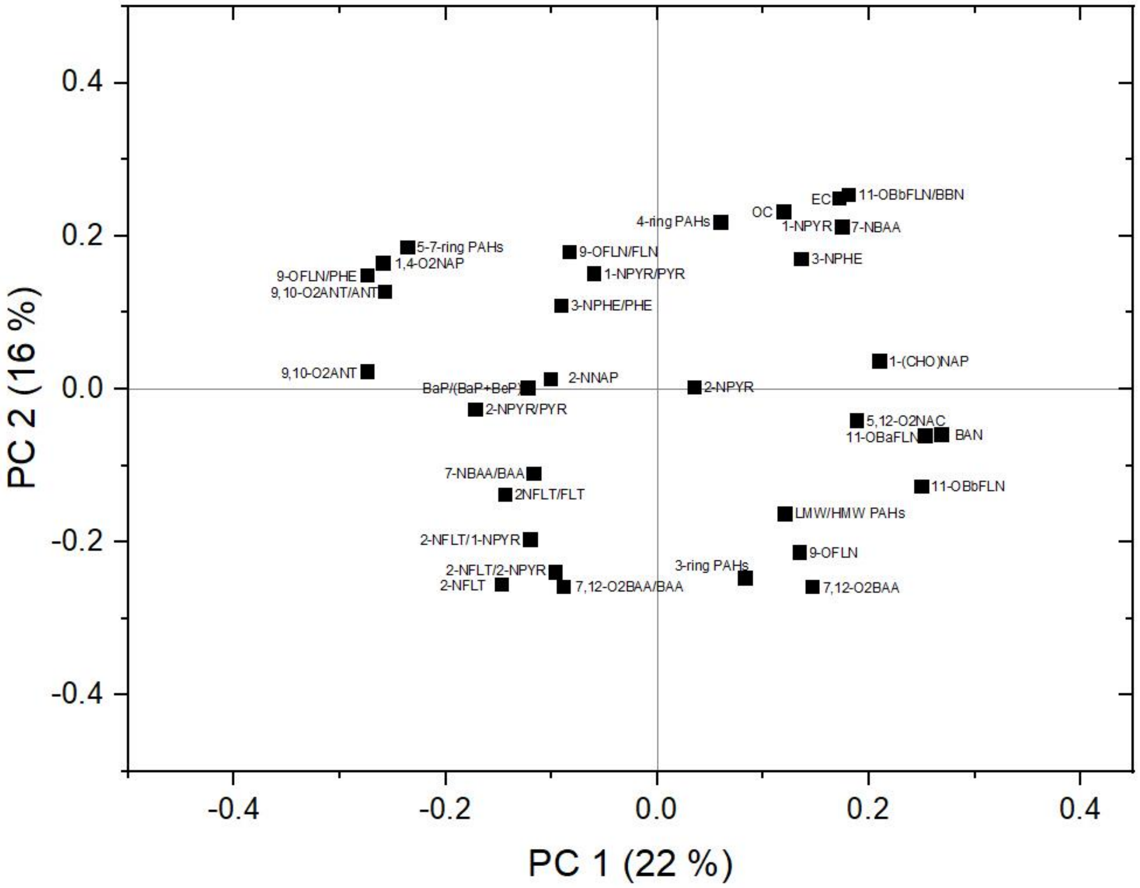

Figure S6. Principal component scores of individual PACs, groups of PACs and ratios thereof (PCA). Individual PACs' concentrations were normalized to the mass fraction in the substance class.

l. 736 ff: This section is currently poorly inovative, discussed and documented.
It could be largely improved.
First have a look to some key papers about the PAHs, OPAHs and NPAHs size distribution (see below). Second, the discussion should be focused on species mainly associated to the particulate phase or at least by making a distinction between low molecular and high moleular weight compounds (and not by summing all compounds). Discussion could be done based on individual species too. From that, the discussion could be updated.

Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., and Jaffrezo, J.-L.: Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys Part 2: Particle size distribution, Atmospheric Environment, 42, 55–64, https://doi.org/10.1016/j.atmosenv.2007.10.008, 2008.

Allen, J. O., Dookeran, N. M., Taghizadeh, K., Lafleur, A. L., Smith, K. A., and Sarofim, A. F.: Measurement of oxygenated polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol, 31, 2064–2070, 1997.

Allen, J. O., Durant, J. L., Dookeran, N. M., Taghizadeh, K., Plummer, E. F., Lafleur, A. L., Sarofim, A. F., and Smith, K. A.: Measurement of C24H14 polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol, 32, 1928–1932, 1998.

Gao, Y., Lyu, Y., and Li, X.: Size distribution of airborne particle-bound PAHs and o-PAHs and their implications for dry deposition, Environ. Sci.: Processes Impacts, 21, 1184–1192, https://doi.org/10.1039/C9EM00174C, 2019.

Miguel, A. H., Eiguren-Fernandez, A., Jaques, P. A., Froines, J. R., Grant, B. L., Mayo, P. R., and Sioutas, C.: Seasonal variation of the particle size distribution of polycyclic aromatic hydrocarbons and of major aerosol species in Claremont, California, 38, 3241–3251, https://doi.org/10.1016/j.atmosenv.2004.03.008, 2004.

Ringuet, J., Leoz-Garziandia, E., Budzinski, H., Villenave, E., and Albinet, A.: Particle size distribution of nitrated and oxygenated polycyclic aromatic hydrocarbons (NPAHs and OPAHs) on traffic and suburban sites of a European megacity: Paris (France), Atmos. Chem. Phys., 12, 8877–8887, https://doi.org/10.5194/acp-12-8877-2012, 2012.

Schnelle-Kreis, J., Gebefügi, I., Welzl, G., Jaensch, T., and Kettrup, A.: Occurrence of particle-associated polycyclic aromatic compounds in ambient air of the city of Munich, Atmospheric Environment, 35, S71–S81, https://doi.org/10.1016/S1352-2310(00)00557-4, 2001.

Venkataraman, C. and Friedlander, S. K.: Size Distributions of Polycyclic Aromatic-Hydrocarbons and Elemental Carbon .2. Ambient Measurements and Effects of Atmospheric Processes, 28, 563–572, 1994.

Venkataraman, C., Thomas, S., and Kulkarni, P.: Size distributions of polycyclic aromatic hydrocarbons-gas/particle partitioning to urban aerosols, Journal of Aerosol Science, 30, 759–770, https://doi.org/10.1016/S0021-8502(98)00761-7, 1999.

→ We agree that the compressed presentation of these size-resolved concentration data limits information and does not fully exploit the data set. In the revised version, the PACs' mass size distributions will be shown for more substance classes (Fig. S7, Chapter S2.5) and will be discussed in the light of substance vapour pressure, illustrated by an additional figure (Fig. S9). The new text of Section 3.4 will read:

"The highest concentrations of PAHs, OPAHs and NPAHs are found in the sub-micrometre fraction of particulate matter, PM_1, i.e. 58%, 89 % and 93 % of PAHs, OPAHs and NPAHs, respectively. For 1-NPYR and 2-NFLT the fractions were 92% and 83% in the Mediterranean Sea, while previously 68% and 86%, respectively, were reported (Lammel et al., 2017). The finding has two main implications. First, due to the low share of pollutants in particles >1 µm, deposition lifetime against wet and especially against dry particle deposition is long (Pryor et al., 2013; Škrdlíková et al., 2013). Similar shares of OPAHs and NPAHs in PM_1 had been reported from urban sites (Eastern Mediterranean and central Europe; Kitanovski et al., 2020). Second, a higher share in the ultrafine particle fraction might lead to higher adverse health effects since these ultrafine particles can penetrate deeper into the lung than bigger particles (Hussain et al., 2011). The result suggests a higher risk (assuming same toxicity) for PAH derivatives since the higher relative amount of OPAHs and NPAHs in the ultrafine fraction can reach deeper into the lung.

Fig. 8 shows the campaign average mass size distributions (MSDs) of the PAHs and PAH derivatives. The MSDs of PAHs, NPAHs and OPAHs are mainly unimodal given the coarse size resolution of the impactor with 6 size ranges within PM_{10}. The maximum was found in particles with an aerodynamic diameter <0.49 µm. For the sum of PAHs, four samples showed an apparently unimodal distribution with a maximum at a particle diameter of 0.49–0.95 µm in the accumulation mode instead of the lowest particle size. In addition, three samples (two in the Arabian Gulf and one in the Arabian Sea) showed a bimodal distribution with maxima in particles with an aerodynamic diameter <0.49 µm and of 0.95–1.5 µm. For the sum of NPAHs, only one sample (in the Mediterranean Sea) showed an apparently unimodal distribution with a maximum in another aerodynamic particle diameter range than <0.49 µm (0.49–0.95 µm). Since we did not resolve the <0.49 µm size fraction, more modes in the sub-micrometre fraction, as found by di Filippo et al. (2010) cannot be excluded.

The ratio between the concentrations in particles <0.49 µm compared to the concentrations in coarse mode PM particles is greater for high-molecular-weight PACs compared to low-molecular-weight PACs (Fig. S7 a and b) and higher for PAH derivatives compared to the parent-PAHs (Fig. S7 c, d and e). This can be explained by the lower vapour pressure of PAH derivatives and high-molecular-weight PAHs compared to the parent-PAHs and low-molecular-weight PAHs. Compounds with lower vapour pressure are less subject to redistribution across particles sizes during transport (Degrendele et al., 2014). The process of redistribution is more effective that the pollutants reach higher particle size fractions than the process of coagulation of particles to form larger particles, which would transfer low vapour pressure PACs to bigger particle size fractions. For PAHs, the mass median diameter (MMD) is significantly positively correlated with the subcooled liquid vapour pressure ($r = 0.54$, $p < 0.05$). The same is true for the NPAHs and OPAHs ($r = 0.98$, $p < 0.05$). The latter correlation is strongly biased by the high MMD of 1-(CHO)NAP. 1-(CHO)NAP was the only PAH derivative with relatively high vapour pressure which was quantified on the filters regularly. MMDs of the targeted substances are shown with their subcooled liquid vapour pressures in Fig. S9 (plotting all PACs with a detection frequency of >30 % in the impactor samples). It is striking that the MMD increases with increasing vapour pressure but that dependence differs between PAHs and PAH derivatives, with the lower MMDs at same vapour pressure for the latter. Semivolatile compounds are subject to redistribution across the size spectrum of aerosols during transport, which could be suppressed by specifically high affinity to the matrix of mode(s). The higher MMD diameter of PAHs indicates that high affinity of PAHs to BC (or EC; see e.g., Lohmann and Lammel, 2004) was not significant. BC (or EC) was concentrated in sub-micrometer particles (Fig. S8). This is not surprising in aerosols which chemical compositions are dominated by sea salt and mineral dust. It seems that NPAHs and OPAHs were less subject to redistribution than PAHs, possibly related to specific affinity to particles <0.49 µm (Fig. 8, Fig S7). Different mass size distributions between PAHs and PAH derivatives despite similar vapour pressures were reported from polluted rural environment and explained by differences in the chemical affinity of the PACs to the PM matrix (Albinet et al., 2008b). The NPAHs generally had a low concentration in our study and most low-molecular-weight PACs were not abundant in PM since these substances are preferable in the gas phase. The campaign average MMDs of the target compounds are shown in the Supplement Table S19. As shown by Gao et al. (2019), the MSDs influence the dry deposition velocities since coarse mode particles have a higher dry deposition velocity than the particles in the fine particle fraction.

Since the process of redistribution depends on time, a shift of the MMD to larger particles sizes is found for aged aerosols (see exemplary Fig. S10). For instance, Lammel et al. (2017) found two maxima for the 4-ring PAHs at a marine background site (same cascade impactor as the one used in this study). The second maximum was explained by aged aerosols at the marine site. The samples showing a maximum of the sum of PAHs at higher particle diameters in our study can also be attributed to aged aerosols (aged samples C6 and C7 in Arabian Gulf; C27, C28 in Mediterranean Sea without close primary emission sources; C22 in very clean air over the Arabian Sea, C24 in southern Red Sea possibly because of Saharan dust).

For compounds with similar vapour pressures and polarity (or sorption to the PM matrix), differences in the MSDs could point to a different origin and/or time elapsed since release or formation of the compounds. The relative amount of the primarily emitted 1-NPYR in the fraction with a particle size of <0.49 µm was higher and the MMD lower than of the secondarily formed 2-NFLT and 2-NPYR. This is also reflected by the ratio 2-NFLT/1-NPYR, indicative for the relative amount of secondarily formed PACs, which was highest in the accumulation mode (0.95-1.5 µm). This is in contrast to the findings of Ringuet et al. (2012b), who observed the highest ratios in the finest particle fraction, attributed to condensation of secondarily formed 2-NFLT to the aerosol surface, which size distribution peaked in the finest fraction. Albinet et al. (2008b) did not find an influence of primary or secondary origin of the PAH derivatives on their mass size distributions at polluted rural sites. One reason for the difference could be the lower relative amount of ultrafine particles in the marine atmosphere due to less primary sources and less new particle formation as compared to the polluted continental environment (Seinfeld and Pandis, 2016). However, even in a cloud-free atmosphere the uncontrolled influencing parameters are too many and more process-oriented studies would be needed to elucidate individual PAH derivatives' MSDs."

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Wiley, New York, USA, 2016.

Albinet A, Leoz-Garziandia E, Budzinski H, Villenave E, and Jaffrezo J.L.: Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys Part 2: particle-size distribution, Atmos. Environ., 42, 55–64, https://doi.org/10.1016/j.atmosenv.2007.10.008, 2008b.

Gao, Y., Lyu, Y., and Li, X.: Size distribution of airborne particle-bound PAHs and o-PAHs and their implications for dry deposition, Environ. Sci. Process. Impacts, 21, 1184–1192, https://doi.org/10.1039/c9em00174c, 2019.

Lohmann, R., and Lammel, G.: Adsorptive and absorptive contributions to the gas- particle partitioning of polycyclic aromatic hydrocarbons: state of knowledge and recommended parametrization for modelling, Environ. Sci. Technol., 38, 3793–3803, https://doi.org/10.1021/es035337q, 2004.

Pryor, S. C., Gallagher, M.; Sievering, H., Larsen, S. E., Barthelmie, R. J., Birsan, F., Nemitz, E., Rinne, J., Kulmala, M., Grönholm, T., Taipale, R., and Vesala, T.: A review of measurement and modelling results of particle atmosphere−surface exchange, Tellus, Ser. B, 60, 42−75, https://doi.org/10.1111/j.1600-0889.2007.00298.x, 2008.

Škrdlíková, L., Landlová, L., Klánová, J., and Lammel, G.: Wet deposition and scavenging efficiency of gaseous and particulate phase polycyclic aromatic compounds at a central European suburban site, Atmos. Environ., 45, 4305−4312, https://doi.org/10.1016/j.atmosenv.2011.04.072, 2011.

New figures:

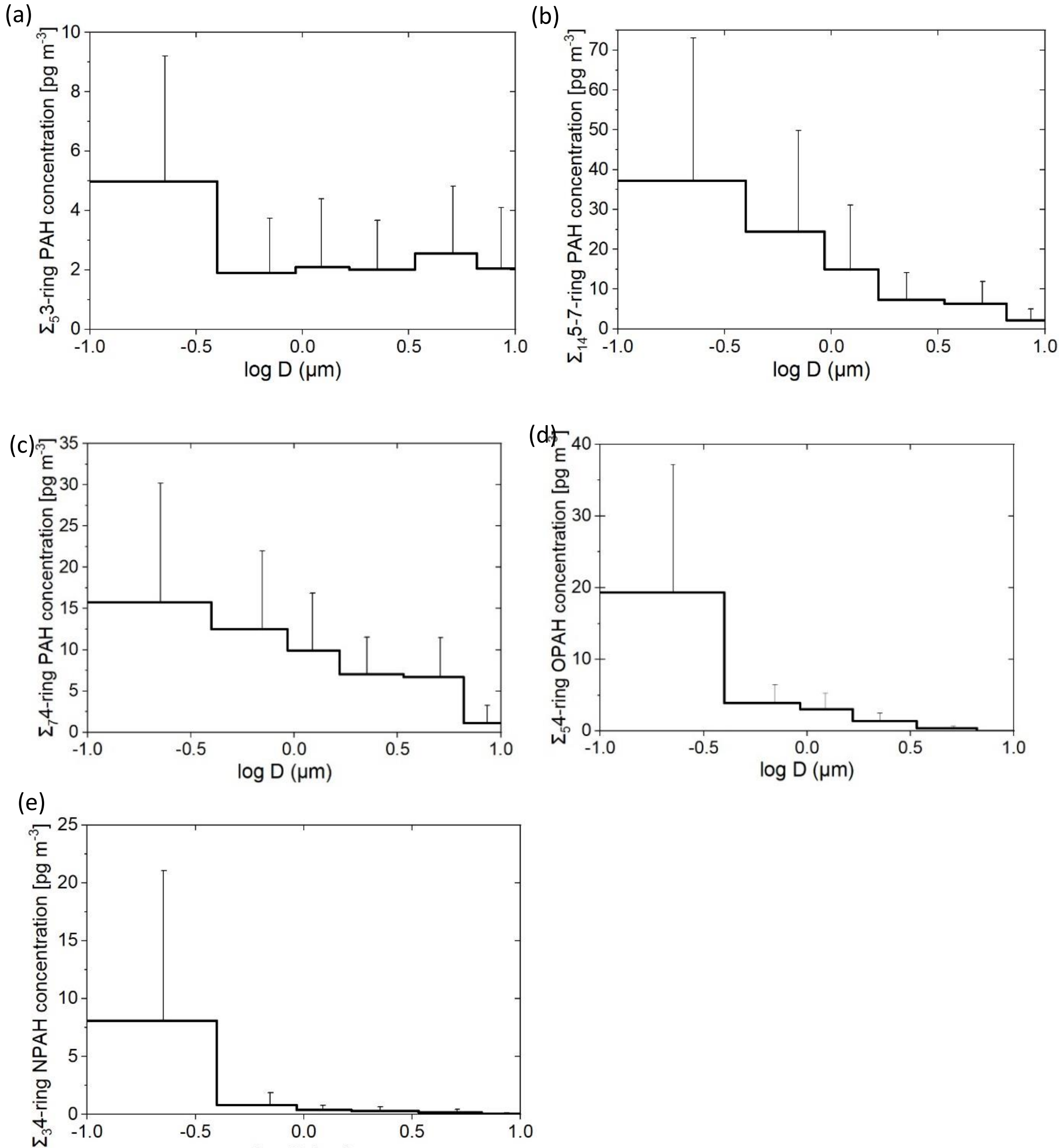

Fig. S7: Campaign average mass size distributions (MSDs) of a) $\sum_5$3-ring PAHs, b) $\sum_{14}$5-7-ring PAHs, c) $\sum_7$4-ring PAHs, d) $\sum_5$4-ring OPAHs, e) $\sum_3$4-ring NPAHs.

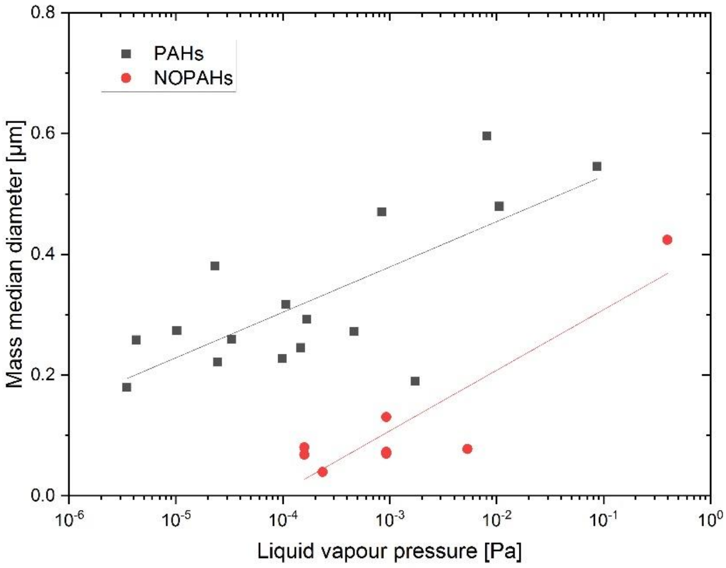

Fig. S9: Mass median diameter (MMD) of PACs in dependence of their subcooled liquid vapour pressure (only considered compounds with a detection frequency >30 %).

l. 750-752 So, distinction of low and high molecular weight would be more relevant for the discussion.
→ True, will be done, see comment above.

Reviewer 2:

Referee comment on "Polycyclic aromatic hydrocarbons (PAHs) and their alkylated-, nitro and oxy-derivatives in the atmosphere over the Mediterranean and Middle East seas" by Marco Wietzoreck et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-32-RC2, 2022

Background: The residues of a comprehensive list of PAHs and their relevant transformation products were quantified during a ship-based campaign in 2017. Polycyclic aromatic compounds (PACs) pattern, local contaminations, and distribution profiles were discussed in coastal Mediterranean and Middle East locations. For all regions, Ship associated emissions along with fossil fuel and other diffusive sources were identified as the main contributors to the PAC atmospheric profiles. Particle-associated associations for PACs were confirmed. The highest PAC levels are confirmed for the sub-mm particulate fraction during the cruise. Advances multivariate statistical methods including Positive Matrix Factorization (PMF) were applied for compound fate evaluation and source apportionment. Characteristic level and pattern differences were found, and specific coastal sources were identified.

Editorial comments
The scientific language of the manuscript has been found well-suited. The manuscript describes an advanced and completely conducted study on relevant PAC contaminants in the Mediterranean atmosphere. However, few clarifications and improvements should be considered before accepting the manuscript for publication in Atmospheric Chemistry and Physics (ACP)

General comments

- Explain all abbreviations when introducing them or provide a list of abbreviation
  Provide information on quality and origin (when introducing) of solvents and consumables.
  → Will be added to the revised version.

- Provide information on dimension and type of the Silica based clean-up column
  → Will be added to the revised version as follows: "…a silica column (with 1 cm i.d. as open tube using 5 g of silica (Merck, Darmstadt, Germany), 0.063–0.200 mm, activated at 150 °C for 12 hours, 10% deactivated with water) and 1 g Na_2SO_4 (Merck, Darmstadt, Germany)."

- Add information on the N_2 applied for volume reduction (quality, origin) as well as other gases (ie, He, air etc) applied for sample analysis and quantification.
  → Will be added to the text.

Detailed comments
Method section
Line (L) L100 ff: Please provide information about field and laboratory blank regime
→ Will be added to the SM, S1.5.2.1: "Laboratory solvent blanks were processed as one blank per max 20 samples but only the field blanks were used for blank subtraction."

L115ff: Different total volumes (218 – 1428 m3) are reported for the sampling regime. Explain the reason (cruise planning and sampling during different cruise legs)
→ As described in Table S1 (see caption), samples were obtained from different sampling devices (Digitel, Cascade and GMWL), pumping on different sampling volumes (sub-tables a, b, and c in Table S1, respectively). Sampling times and volumes were separately and constantly monitored for each device. Most of the samples were collected for 24 h but due to different reasons (explained below), the sampling time was changed for some samples.
The text in the revised version will read: "The sampling duration varied from 6 to 24 h (mostly 24 h) and the total volume of each air sample ranged from 318 to 1428 m3 (mainly around 700 m^3) which was based on the cruise planning, but also influenced by limited access to sampling spots on the ship due to either bad weather or other extrinsic conditions on the ship (e.g. power failures, sudden short access restrictions)"

GC/MS method: essential information on the quantification method should be added incl. the complete GC temperature program incl. SSL isotherm (time)
→ The SSL injector was operated at a constant temperature. Added to the text: "). 1 µL of sample was injected splitless at a constant temperature of 280 °C with He as carrier gas (purity grade 5.5, SIAD, Czech Republic) at a constant flow rate of 1.5 mL min^{-1}."
The GC temperature programs are provided in the main text, MRMs and other details are part of Table S3.
The following information about the quantification method will be included in the revised manuscript: "Target compounds were quantified using internal standard method, with calibration in the range of 1-1000 ng mL^{-1}. Calibration curves were set as linear fit."

Quality control
Provide information on method uncertainty, recovery range, instrumental LOD and MDL
→ We added the method uncertainty in subchapter 1.5.2 in the SI and a short summary of the quality control to subchapter 2.7 in the main manuscript:
"In short, the recovery of the surrogate standards of the high volume samples ranged 41-119 %. The reported concentrations are blank corrected by using the average of three field blanks but not recovery corrected. The instrumental limits of quantification (iLOQs) of the PAHs, OPAHs and NPAHs ranged 0.10-53 ng $sample^{-1}$, 0.11-1.96 ng $sample^{-1}$ (ignoring 9,10-phenanthrenequinone) and 0.02-8.33 ng $sample^{-1}$, respectively. For the evaluation the maximum of the iLOQ and the LOQ of field blank samples (fbLOQs). The fbLOQs of the PAHs, OPAHs and NPAHs ranged 0.12-54.64 ng $sample^{-1}$, <iLOQ-72.76 ng $sample^{-1}$ and <iLOQ-2.67 ng $sample^{-1}$, respectively. The method uncertainty for all target compounds ranged between 4 and 28 %."

Results:
L118: PM10 particles were collected for particle bound N-O-PAHs and TSP was collected for parent PAHs & RPAHs. Please discuss comparability issues and how this may affect the statistical interpretation as a part of the QC section.
→ Important point. Just for clarification: PAHs were measured in PM_{10} (same sampler as N-O-PAHs) as well as in TSP (same sampler as RPAHs). For the interpretation, we used the concentrations in PM_{10}, expect for the section when discussing the RPAH concentrations/ratios.

Nevertheless, we will discuss in the revised version adding the following sentence:
"Particulate phase PAHs, OPAHs and NPAHs were sampled as PM10, while RPAHs were collected as TSP. The difference of PAC concentrations in TSP compared to PM10 is expected to be not significant as reported by Menichini and Monfredini (1995) and Ringuet et al. (2012b) for PAHs and PAH derivatives due to low concentrations of PACs in coarse mode particles."

L155: Rotary evaporation was used for volume reduction. However, no information on vacuum control is provided. Please add information on the vacuum control system used and how the loss of volatile PACs (s – 3 ring PACs) was minimized.

→ Added the information. It now reads: "Each fraction was reduced to approximately 0.3 mL by rotary evaporation (using a rotary evaporation system (Rotavap RV 300, Büchi, Flawil, Switzerland); vacuum electronically controlled; no heating of the water bath; approx. 0.5 mL of iso-octane (Unisolv grade, Merck, Darmstadt, Germany) was added as solvent keeper)"
Each step of the protocol of analysis has been isolated and potential losses have been determined. For this particular step (Rotavap), PAH recoveries ranged ca. from 99-100% (pyrene to benzo[ghi]perylene) to 97% (phenanthrene to fluoranthene).

Table1: Please add the CAS numbers for easy identification.

→ We refrain from adding the CAS number to Table 1 due to the limited space. However, we added the following sentence to the caption of the table: "CAS numbers and physicochemical properties are shown in Table S2 in the Supplement."

L 185: POPs were not discussed earlier. Elaborate on the reason why OCBs, OCPS and DDTs were suddenly included in the discussions (without introducing the quantification methods and QC properly).

→ POPs (OCBs, OCPS, DDTs) will be published in a separate paper (in preparation). That is the reason why these data are not presented here in detail. However, the sum of these substance classes were used in the first group of parameters of the PMF results. That's the reason why we introduce shortly how these substances were measured.

L188: Explain the rationale for applying PMF in favor of other suitable multivariate statistical methods. Usually, PMF is applied for larger data sets as available for the here reported study (https://doi.org/10.1016/j.scitotenv.2015.01.022)
Describe the procedure how "non detects" were treated during the PMF analysis

→ There are several receptor model approaches of which factor analysis (FA) is the most frequently used to estimate the number and chemical profiles of the sources and their contributions to the receptor concentrations (Belis at al., 2013). Recent air quality studies use the advanced variant of the FA, Positive Matrix Factorization (PMF) (Paatero, 1997) bilinear model, where input datasets are generally two dimensional with temporal variability of aerosol chemical composition and mass. Previously, PMF has been successfully applied to datasets with a limited number of samples (Contini et al. 2014; Diapouli et al. 2017; Kozáková et al., 2019). The following text discussing data below LOQ (DL) and missing data will be added to Section 2.5, Aerosol source apportionment:
"The data matrix was prepared in compliance with the procedure described by Polissar et al. (1998); i) data below LOQ was replaced with the value LOQ/2, and (5/6)*LOQ was used as the corresponding uncertainty value, and ii) for missing data geometric mean of species value and a multiple of 3 for the uncertainty value was utilized."

Belis CA, Karagulian F, Larsen BR, Hopke PK (2013) Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe. Atmos Environ 69:94–108. https://doi.org/10.1016/j.atmosenv.2012.11.009
Contini D, Cesari D, Genga A, Siciliano M, Ielpo P, GuascitoMR, Conte M(2014) Source apportionment of size-segregated atmospheric particles based on the major water-soluble components in Lecce (Italy). Sci Total Environ 472:248–261. https://doi.org/10.1016/j.scitotenv.2013.10.127
Diapouli E, ManousakasM, Vratolis S, Vasilatou V,Maggos T, Saraga D (2017) Evolution of air pollution source contributions over one decade, derived by PM 10 and PM 2 .5 source apportionment in two metropolitan urban areas in Greece. Atmos Environ 164:416–430.

https://doi.org/10.1016/j.atmosenv.2017.06.016
Kozáková J, Pokorná P, Vodička P, Ondráčková L, Ondráček J, Křůmal K, Mikuška P, Hovorka J, Moravec P, Schwarz J, 2019. Influence of regional air pollution transport at a European air pollution hotspot. Environmental Science and Pollution Research 26, 1675-1692. https://doi.org/10.1007/s11356-018-3670-y
Paatero P., 1997. Chemometrics and Intelligent Laboratory System 37, 23-35. https://doi.org/10.1016/S0169-7439(96)00044-5

L190: Earlier only GMW & TISCH-based sample equipment were introduced. Obviously, samples for POP analysis were collected with DIGITEL (CH) high-volume equipment (not previously described). Add this to the Method section or refer to a suitable publication.

→ Modified one sentence in subchapter 2.7: "The measurement of polychlorinated biphenyls (PCBs), hexachlorocyclohexanes (HCHs), dichlorodiphenyl-trichloroethane and isomers (DDX), other organochlorine pesticides (drins) from the same samples as used for the measurement of PAHs, OPAHs and NPAHs was done similar to Lammel et al. (2016)."

L203: FLEXPART please add information on the version and application mode

→ Followed, to be specified "… were studied using the FLEXPART Lagrangian particle dispersion model (FLEXPART version 10.4; Pisso et al., 2019), …" -> https://doi.org/10.5194/gmd-12-4955-2019)

L234: RV Kommandor Iona: Provide IMO Registration (8401999) and country of registration (UK).

→ Followed, IMO registration no. to be added. Hence, direct access to other relevant information now provided.

L244: Add coordinates for sample location D58 and all other locations when specifically referring to the location or refer to tableS1 which contains this information

→ Yes, information "(coordinates in Table S1)" to be added.

L294, Figure 2: The spatial concentration differences (indicated by the color code blue to read), especially in the background level regions may be within the overall method uncertainty which is expected to be of ca 30-40% in the respective concentration range. Please discuss the implication of method uncertainty for the here performed statistical Interpretation

→ Yes, the method uncertainty of the concentration at very remote sites can be around 30 %. However, as shown in Fig. 1, the differences in the concentrations of several samples of the Arabian Sea or the Southern Red Sea showed a relatively low standard deviation. Sentence to be added to Subchapter 3.1:

"Furthermore, it needs to be considered that the uncertainty at very low concentrations can be relatively high (up to 28 %, see SI, subchapter S1.5.2.2), similar to some of the spatial gradients indicated in Fig. 2."

L 305: Concentrations listed with 3 digits behind the comma at the pg/m3 level imply a method accuracy (<1%) which is not warranted by the here used methods and the associated method uncertainty, especially in pg/m3 range.

→ Yes, right. Will be changed to one digit behind the comma for concentrations given in pg/m3.

L540 ff: Source attribution: parent-daughter compound relationship ratios have earlier provided helpful information on transformation processes, source strength estimation, source elucidation. I, hence, strongly recommend considering this type of interpretation in addition to the diagnostic ratios already applied.

→ Yes, thanks. We have extended this data analysis using another multivariate analysis, PCA, where we included parent-daughter ratios. The results support the previous findings and will be presented in subchapter 3.3.4 and S2.4.4 (see above comment on l. 536 and l. 686)

Supplementary material

Add a complete QA/QC section including, method uncertainty estimate, LOD, MDL, recovery rate, and range.

→ Alright. We modified the QA/QC section in the Supplement with more details and added the method uncertainty estimate as subchapter S1.5.2.2 to the Supplement.

Figure S4: Repetition (fig 4) omit
→ It is not a repetition, it is another PMF run with slightly different input parameters.

Figure S8 partly repetition (fig 8), omit
→ There is no Fig. S8 but I guess you mean Fig. S6. In the main text (Fig. 8), there is the average MSD of the substance classes but in Fig. S6, there are the MSDs of 3 specific samples shown.