We would like to thank for the comments and suggestions. We have addressed all comments below and have indicated the corresponding modifications in the revised version of the manuscript. The line numbers mentioned in our responses refer to those in the ACPD paper.

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.