Comment on acp-2022-32

Roland Kallenborn (Referee)

Referee comment on "Polycyclic aromatic hydrocarbons (PAHs) and their alkylated, nitrated and oxygenated 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.
- Provide information on dimension and type of the Silica based clean-up column

- 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.

Detailed comments

Method section

Line (L) L100 ff: Please provide information about field and laboratory blank regime

L115ff: Different total volumes (218 – 1428 m3) are reported for the sampling regime. Explain the reason (cruise planning and sampling during different cruise legs)

GC/MS method: essential information on the quantification method should be added incl. the complete GC temperature program incl. SSL isotherm (time)

Quality control

Provide information on method uncertainty, recovery range, instrumental LOD and MDL

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.

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.

Table1: Please add the CAS numbers for easy identification.

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).

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

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.

L203: FLEXPART please add information on the version and application mode https://doi.org/10.5194/gmd-12-4955-2019)

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

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

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

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.

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.

Supplementary material

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

Figure S4: Repetition (fig 4) omit

Figure S8 partly repetition (fig 8), omit