Reviewer #1

This study provides a comprehensive analysis of the global distribution, spatial variation, and source apportionment of polycyclic aromatic hydrocarbons (PAHs) and their derivatives in the marine atmosphere through large-scale sampling and the PMF model. Notably, the findings fill a knowledge gap regarding the occurrence and composition of particle-phase alkylated, nitrated, and oxygenated PAHs in marine aerosols. These results will facilitate the understanding of the impact of PAH derivatives pollution on marine ecosystems. Therefore, I recommend that the manuscript be published in this journal after minor revisions.

However, the quality assurance/quality control (QA/QC) section requires further elaboration. More detailed explanations regarding the background signal subtraction in mass spectrometry data processing, the calculation of the method detection limit (MDL) and the method quantification limit (MQL), and the linear range of the standard curves should be provided. Moreover, the construction of the PMF model and the description of pollution sources need to be further clarified. Specific comments are provided below.

Response: Thank for reviewer's suggestions. We have significantly revised the manuscript based on reviewer's suggestions.

Specific comments:

Comment 1: Line 48: Replace "spatiotemporal characteristics" with "spatial characteristics", as the introduction and results in this study focus on spatial rather than temporal trends. Temporal aspects (e.g., seasonal influences) could be emphasized in the implication section.

Response: I agree with reviewer's suggestions. (Line 50) "spatiotemporal" has been changed into "spatial".

Comment 2: Lines 84 – 87: Please specify the reference standards used in the mass spectrometric analysis and whether internal standards were added to evaluate the recovery and instrument stability.

Response: Thank for reviewer's suggestions. (Line 124-127) The reference standards of PAHs (Pyr-d10 and BaP-d12; Wako Pure Chemicals, Osaka, Japan), OPAHs (purchased from First Standard (Alta Scientific Co., Tianjin, China), RPAHs (AccuStandard (New Haven, CT, USA)), and NPAHs (2-fluoro-7-nitrofluorene; Aldrich Chemical Company, Osaka, Japan) were used for calibrating quantification. We have added internal standards to evaluate the recovery and instrument stability.

Comment 3: Lines 114 – 116: To avoid bias introduced by missing data, did the authors use the MDL/2 method for statistical analysis when handling concentration data below the detection limit?

Response: Thank for reviewer's suggestions. Yes, we used the MDL/2 method for statistical analysis when handling concentration data below the detection limit.

Comment 4: Line 129 – 131: The range of predefined factor numbers, the ratio of QRobust to QTrue, and the optimal number of factors should be provided when constructing the PMF model.

Response: Thank for reviewer's suggestions. (Line 142-145) The range of predefined factor numbers were from 2 to 6. The ratio of QRobust to QTrue is 0.93. The optimal number of factors is 3.

Comment 5: Line 138 – 140: To ensure model reliability, the coefficient of determination (R^2) between the predicted and observed concentrations of PAHs and their derivatives, along with the significance p-value, should also be provided.

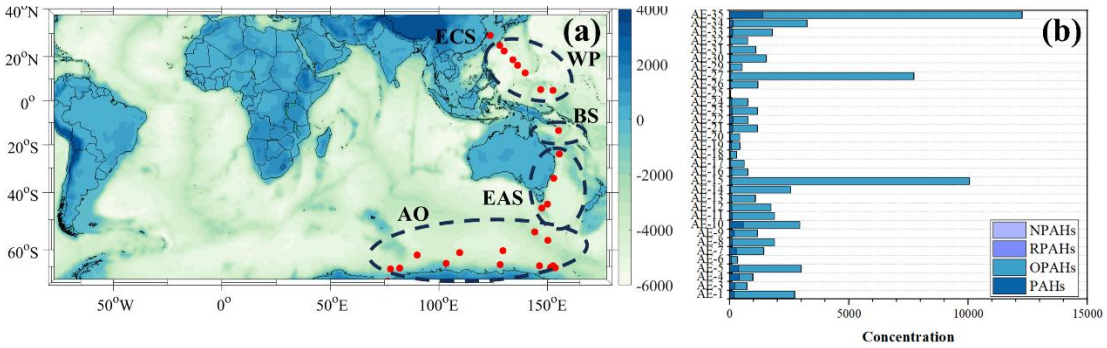
Response: Thank for reviewer's suggestions. (Line 144-145) We have added the coefficients of determination (R^2) between the predicted and observed concentrations of PAHs and their derivatives in Table S2.

Comment 6: Lines 182 – 187: While the absolute concentrations of OPAHs at some high-latitude sites were comparable to or slightly lower than those of PAHs, the total concentrations of OPAHs were significantly higher than those of PAHs ($p < 0.01$). Could this significant difference be attributed to the higher concentrations of O_3 and OH radicals at lower latitudes, which promote the oxidation of PAHs? The current explanation seems somewhat unclear.

Response: Thank for reviewer's suggestions. This sentence suggested that many previous studies confirmed the OPAHs concentrations were often lower than PAHs concentrations especially in high-latitude regions. However, in our study, OPAHs concentrations were even higher than PAHs concentrations especially in some tropical regions. Indeed, the significant difference could be attributed to the higher concentrations of O_3 and OH radicals at lower latitudes, which promote the oxidation of PAHs.

Comment 7: Line 194 – 197: It is recommended to add a figure illustrating the distribution of sampling points in the five areas to facilitate understanding.

Response: Thank for reviewer's suggestions. We have added the distribution of sampling points in the five areas in Figure 1a.



Comment 8: Line 213 – 215: The claim that Pyr, BeP, and BaP levels in the Antarctic Ocean (AO) exceed those in the East China Sea (ECS) due to shipping emissions could be misleading, as it may imply that the AO has more shipping activity. I recommend removing this statement and instead emphasizing the impact of wildfires on BbF levels.

Response: I agree with reviewer's suggestions. We have deleted this sentence.

Comment 9: Line 261-262: Consider removing "Compared with other PAH derivatives, RPAHs showed low correlation coefficient with meteorological parameters", as it does not support the conclusion of this paragraph. If retained, provide an explanation for this observation.

Response: I agree with reviewer's suggestions. We have removed "Compared with other PAH derivatives, RPAHs showed low correlation coefficient with meteorological parameters".

Comment 10: Line 506-518: In Figure 4, using identical numbers for different compounds is confusing. It would be clearer to use compound names or their abbreviations instead. Moreover, please clarify what "B" represents on the y-axis of Figures 4c – 4d in the figure caption.

Response: Thank for reviewer's suggestions. A1 (B1), A2 (B2), A3 (B3), A4 (B4), A5 (B5), A6 (B6), A7 (B7), A8 (B8), A9 (B9), A10 (B10), and A11 (B11) in (c) represent 1,4-Naphthoquinone, 1-Naphthaldehyd, 1-Ancenaphthenaquinone, 9-Fluorenone, Ancenaphthenaquinone, Anthraquinone, Benzanthrone, Benzo(a)anthracene-7,12-dione, 1,4-Chysenequione, 5,12-

Naphthacenequione, and 6H-Benzo(cd)pyrene-6-one, respectively. The correlation coefficients and log (1/p values) of RPAH species (d). A1 (B1), A2 (B2), A3 (B3), A4 (B4), A5 (B5), A6 (B6), A7 (B7), A8 (B8), and A9 (B9) in (d) denote 2-Methylnaphthalene, 1-Methylnaphthalene, 2,6-Dimethylnaphthalene, 1,3-Dimethylnaphthalene, 1,6,7-Trimethylnaphthalene, 2-Methylanthracene, 1-Methylphenanthrene, 1-methylanthracene, 1-Methylfluoranthene, respectively. The correlation coefficients and log (1/p values) of NPAH species (e). A1 (B1), A2 (B2), A3 (B3), A4 (B4), A5 (B5), A6 (B6), and A7 (B7) in (e) reflects 1-Nitronaphthalene, 2-Nitronaphthalene, 1,3-Dinitronaphthalene, 5-Nitroacenaphthene, 2-Nitrofluorene, 9-Nitroanthracene, 1,8-Dinitronaphthalene, respectively. For Figure 3c, 3d, and 3e, A and B represent different compounds, which have been clarified in the caption. In the original version, we tried to use the abbreviation to instead of A or B. However, the contents in each panel are too small to see for readers. Therefore, we only used the A and B to replace them. The detailed implications of A and B were revealed in the caption.

Reviewer #2

This manuscript reports measurements of aerosol particle phase polycyclic aromatic hydrocarbons (PAH) and their derivatives along a transect from China to Antarctica based on high volume filter samples obtained during a ship cruise. Such measurements are scarce, and they thus provide valuable new data over regions rarely cover so far and contribute to increasing the global coverage of PAHs over the oceans, especially in remote locations. Apart from reporting the measurements, the authors use specific compound ratios as well as a statistical source apportionment method to address the potential sources of PAH in the different regions. This allows to place the measurements in the context of potential source regions as well as oxidation during transport favoring the formation of oxygenated PAHs. The analytical procedures are well described and the data analysis appears sound. The overall conclusions remain somewhat limited due to the limitations also clearly described in the manuscript, e.g., lack of gas phase measurements or of surface water measurements. Therefore, I am supportive of publication as a measurement report.

In general, the manuscript is well written and structured, though the English language could be improved in some places, especially in terms of using articles. The authors should do another round for that, as the quality of language and grammar decreases towards the end of the manuscript, simply meaning that focusing on these aspects again from the beginning to the end would be important. Remaining corrections could be done at the copy-editing stage. The content is nowhere obscured due to this.

Response: Thank for reviewer's suggestions. We have significantly revised the manuscript based on reviewer's suggestions.

A few specific comments are listed below.

Comment 1: Introduction section, and maybe also in the discussion of the results: I was wondering why the study by Zhang et al. (2022) was not cited, as this seems to be related quite a bit to the topic of the present work.

Response: Thank for reviewer's suggestions. Zhang et al. (2022) was citied in the discussion of our study (Zhang et al. 2022a) because it is strongly related with the topic of our study and give us many important implications (Line 230 and Line 490-493).

Comment 2: line 51: A growing body of literature...

Response: Thank for reviewer's suggestions. (Line 53) We have changed "researches" into "literature".

Comment 3: line 60: better 'oceans' than 'seas' (also everywhere else in the text), and 'with intense anthropogenic activities'

Response: Thank for reviewer's suggestions. (Line 62) We have changed "seas" into "oceans". "dense" has been replaced by "intense".

Comment 4: line 65: 'volatilization from soil and snow...'

Response: Thank for reviewer's suggestions. (Line 68) We have corrected the error in this sentence.

Comment 5: line 72/73: This sentence is not clear. If these studies simultaneously study different regional oceans, they would also get global coverage. maybe just delete 'simultaneously' if that is then more correct.

Response: Thank for reviewer's suggestions. (Line 80) "simultaneously" has been removed.

Comment 6: line 75: 'It is important...' (or 'urgent')

Response: Thank for reviewer's suggestions. (Line 82) We have used the "important" instead of "highly necessary".

Comment 7: line 88: if the end of the cruise refers to the continent of Antarctica, it should be called 'Antarctica', not Antarctic. Please amend throughout the manuscript. In the abstract it is already correct.

Response: Thank for reviewer's suggestions. (Line 86) We have replaced "Antarctic" by "Antarctica" throughout the manuscript.

Comment 8: line 89: '...of the shipping route...'

Response: Thank for reviewer's suggestions. (Line 96) The sentence has been changed into "The detailed information of the shipping route is depicted in Figure S1 and 1".

Comment 9: line 209: what is the basis for assuming that Australia features low PAH emissions? This could also be brought back where the sources with the various indicators and PMF are discussed.

Response: Thank for reviewer's suggestions. (Line 312-315) We assumed that Australia possessed low PAH emission based on the global PAH emission inventory derived from PKU-Fuel (Shen et al., 2013). We have also added the discussions in the PMF analysis.

Comment 10: line 212: '...than those in ECS, and the BbF levels were...'

Response: Thank for reviewer's suggestions. (Line 226) We have corrected this error based on reviewer's suggestions.

Comment 11: line 215: '...that the marine aerosol in AO was...'. Here you refer to a single aerosol type, so it should be used in singular. Otherwise you should talk about aerosol particles. Please try to be consistent with this throughout the manuscript.

Response: Thank for reviewer's suggestions. We have corrected this error throughout the manuscript.

Comment 12: line 217: could oxidation also be the reason for the low PAH content outside Australia?

Response: Thank for reviewer's suggestions. I think the high oxidation capacity in Australia might be an important reason for the low particulate PAH content in the adjacent seas of Australia.

Comment 13: line 232: PAH do not have oxidation capacity. What do you want to say here? The potential of PAH to get oxidised?

Response: Thank for reviewer's suggestions. In this part, we want to say PAHs in BS and EAS were more easily to be oxidated to OPAHs. Indeed, the oxidation potentials of PAHs in BS and

EAS were much higher compared with other oceans because both of OH radical and O_3 concentration in these regions were much higher than many other seas.

Comment 14: line 235: 'displayed similar...'

Response: Thank for reviewer's suggestions. (Line 249) "the" has been deleted in the revised version.

Comment 15: line 243: 'It has been well documented...'

Response: Thank for reviewer's suggestions. (Line 257) "was" has been changed by "has been".

Comment 16: line 246: '... in the Southern hemisphere'

Response: Thank for reviewer's suggestions. (Line 260) "South" has been replaced by "Southern".

Comment 17: line 257: is adsorption kinetics relevant here? I would assume that equilibrium partitioning is the main parameter determining temperature dependent composition.

Response: Thank for reviewer's suggestions. Indeed, equilibrium partitioning is the main parameter determining temperature dependent composition. Although we did not measure the concentrations of PAH derivatives in the gas-phase, many previous studies also supported the inferences. Previous studies showed good agreement with our statistical analysis about the good relationship between air temperature and particulate PAH derivatives.

Comment 18: line 266-268: please clarify which ratio is attributed to which source.

Response: Thank for reviewer's suggestions. We have clarified which ratio is attributed to which source. The ratios less than 0.4, 0.4-0.5, and greater than 0.5 could be treated to be petrogenic source (0.4), petroleum combustion or biomass burning (0.4-0.5), and the coal combustion (> 0.5), respectively (Yunker et al., 2002; Zhang et al., 2021a).

Comment 19: line 269: here it might be relevant to discuss how oxidation would affect this ratio.

Response: Thank for reviewer's suggestions. (Line 278-282) Fluoran/(Fluoran +Pyr) ratio seems to be not related the atmospheric oxidation, which mainly reflects the major sources of PAH species. The ratios less than 0.4, 0.4-0.5, and greater than 0.5 could be treated to be petrogenic source (0.4), petroleum combustion or biomass burning (0.4-0.5), and the coal combustion (> 0.5), respectively (Yunker et al., 2002; Zhang et al., 2021a). In our study, the Fluoran/(Fluoran +Pyr) ratio in nearly all of the regions except AO (0.46) were higher than 0.5, indicating the impact of coal combustion on marine aerosols in most regions in Northern Hemisphere and tropical regions. Many previous studies also revealed the North Hemisphere and Southern Ocean were often affected by fossil fuel combustion and biomass burning, respectively (Na et al., 2020 MPB; Zhang et al., 2022 EST). The results were also in good agreement with our empirical knowledge.

Comment 20: line 276: better 'significant' than unignorable?

Response: I agree with reviewer's suggestions. (Line 291) We have corrected this error.

Comment 21: line 280: around this discussion: recent changes to international regulation of shipping emissions might also affect the PAH profiles. Have these changes occurred prior to or after the measurements reported here? this could also be mentioned in the introduction section.

Response: Thank for reviewer's suggestions. (Line 74-78) "Zetterdahl et al. (2016) also revealed that the shipping emission might play an important role on the PAHs in the marine atmosphere. They verified the new regulation (since late 2014) about the use of low-sulfur residual marine fuel oil instead of heavy oil significantly altered the chemical compositions of PAHs (increasing the low-ring components, while decreasing the high-ring components)" has been added in the revised version. Although the new regulation largely increased the low-ring components, the middle- and high-ring components still dominated the PAH compositions in the current shipping emissions. The

results were in good agreement with our study. Our measurements occurred after the proposal of this regulation.

Comment 22: line 297: here, at the end of the discussion, the case of low PAH levels outside Australia could be discussed again.

Response: Thank for reviewer's suggestions. (Line 312-315) We have added the discussion about the case of low PAHs levels outside Australia. "Based on the source apportionment, we verified that EAS showed relatively high secondary contribution compared with some regions such ECS and WP. It was assumed that EAS showed the higher atmospheric oxidates and low PAH emissions (Ambade et al., 2023; Shen et al., 2013), which was in good agreement the spatial variations of PAHs and OPAHs." has been added in the revised version.

Comment 23: line 306: 'can be related to precursor emissions...'

Response: Thank for reviewer's suggestions. (Line 323) "can be related to" has been added in the revised version.

Figures:

Comment 24: All figure captions need to be placed below the figures.

Response: I agree with reviewer's suggestions. We have placed all of the captions below the figures.

Comment 25: For the paneled figures: please adapt all font sizes to become equal and well readable. For Figure 2, for instance, the two plots on the left could be made more narrow with narrower symbols to allow for more space for the rest.

Response: Thank for reviewer's suggestions. We have redrawn Figure 2 and Figure 3 to meet the requirement of readers.

Reference

Xue Zhang, Zi-Feng Zhang, Xianming Zhang, Fu-Jie Zhu, Yi-Fan Li, Minghong Cai, Roland Kallenborn, Polycyclic Aromatic Hydrocarbons in the Marine Atmosphere from the Western Pacific to the Southern Ocean: Spatial Variability, Gas/Particle Partitioning, and Source Apportionment, Environmental Science & Technology, 10.1021/acs.est.1c08429, 56, 10, (6253-6261), (2022).