Response to Reviewer #2's Comments

Anonymous Referee #2:

Major comments:

In this study, the authors investigated the contributions of anthropogenic and natural sources to atmospheric mercury in the marine environment in eastern China based on island, cruise, and inland campaigns. Correlation analyses were performed between TGM and meteorological factors. The TGM/BC ratios were calculated. PMF models were developed for two sites to disentangle anthropogenic and natural contributions, and correlations between BC and anthropogenic TGM were established. The sea-air exchange fluxes of mercury were estimated based on TGM and DGM. The impacts of anthropogenic emissions on marine Hg evasion were quantified. Overall, the study is well designed, and results from this study provide more evidence for the contribution of anthropogenic sources to TGM in the marine boundary layer in eastern China and the compensation effect of marine Hg evasion when the anthropogenic contribution is reduced. However, the methods part lacks some detailed information, and the results and discussion part needs improvement to address the novelty of this study. There are many speculative statements in the discussion part, the expression of which could be improved. Therefore, in my opinion, major revision is required before the manuscript is acceptable for publication on Atmospheric Chemistry and Physics.

We sincerely thank for your in-depth comments and helpful suggestions on this manuscript. Based on the specific comments, we have responded to all the comments point-by-point and made corresponding changes in the manuscript as highlighted in the track change mode. You have raised a number of issues and we quite agree. We feel the substantial revisions based on your comments have greatly improved the quality of this manuscript. Please check the detailed responses to all the comments as below.

Specific comments:

1. Line 46: Typo of "can cycles".

Response: Thank you for pointing out this error. We have corrected "can cycles" to "can cycle".

2. Lines 60–71: The statements of these literatures are inadequate. For example, Fu et al. (2018) and Wang et al. (2020) are not considered as qualitative assessment. They have provided quantitative evidence for the contributions of anthropogenic Hg emissions. I suggest these statements be rephrased.

Response: Thanks for your comments. In the revised manuscript, we have modified the original statement as below.

Line 79-85: "Although isotopic signatures have been widely applied to source apportionment of atmospheric mercury, current isotopic methods still exhibit significant uncertainties due to the poor understanding of isotopic compositions of gaseous elemental mercury emitted from various sources and fractionation processes of Hg isotopes during atmospheric transformations

(Fu et al., 2018). Additionally, this approach requires specialized isotopic measurements unavailable for routine monitoring. At present, quantitative analyses of anthropogenic contributions to marine atmospheric mercury remain limited."

3. Section 2.2: The QA/QC results for TGM/GEM measurement should be further illustrated. For example, what are the average duplication rates between A and B traps for the Tekran 2537B and the modified 2600 analyzer, respectively? What measures did the authors take to prevent or abate the impacts of high humidity on the Tekran analyzers?

Response: Thanks for your comments. For the Tekran 2537B, the average duplication rate between the A and B traps is 99%, with deviations between the two traps consistently below 3%. To mitigate the impact of high humidity on the instrument, samples are first passed through a soda lime drying tube for dehumidification before entering the detector.

The modified Tekran 2600 adopts a simplified design without separating A and B traps. Instead, it utilizes two gold traps for mercury collection and analysis. During operation, atmospheric mercury is adsorbed onto the first gold trap over a 24-minute sampling period. After sampling, the mercury on the first gold trap is thermally desorbed and transferred to the second gold trap. The second trap is then analyzed by the detector during a 6-minute detection phase, resulting in an overall 30-minute sample resolution. To ensure data quality during cruise observations, the instrument is calibrated daily using the external calibration unit Tekran 2505. Similar to the 2537B, samples are also pre-dried via a soda lime drying tube prior to detector entry to prevent humidity interference.

In the revised manuscript, we have added the following contents to Section 2.2.

Line 190-193: For the Tekran 2537B, the average duplication rate between the A and B traps is 99%, with deviations between the two traps consistently below 3%. To mitigate the impact of high humidity on the instrument, samples are first passed through a soda lime drying tube for dehumidification before entering the detector.

Line 166-173: During the operation of the modified Tekran 2600, atmospheric mercury was adsorbed onto the first gold trap over a 24-minute sampling period. After sampling, the mercury on the first gold trap was thermally desorbed and transferred to the second gold trap. The second trap was then analyzed by the detector during a 6-minute detection phase, resulting in an overall 30-minute sample resolution. To ensure data quality during cruise observations, the instrument was calibrated daily using the external calibration unit Tekran 2505. Samples were pre-dried via a soda lime drying tube prior to detector entry to prevent humidity interference.

4. Section 2.5: More illustration on the PMF method need to be included instead of just referring to the authors' previous study. For example, at least what indicators were used in the PMF model should be introduced. According to Section 3.3, air temperature (I assume it is air temperature instead of seawater temperature) has been included in the model. What unit did the authors use? I think Kelvin makes more sense than °C since the indicators need to be positive for applying PMF.

Response: Thanks for your comments. The original description of the PMF model was indeed simplified. In the revised manuscript, we have addressed this by:

1. Adding the formula for calculating the Q-value (the objective function) in Section 2.5, along with a detailed explanation of its significance.
2. Elaborating on the criteria for selecting the number of factors (tested from 3 to 8) based on the slope of the Q-value versus the number of factors.

The updated text in Section 2.5 now reads (Line 274-292):

"The objective function, defined in Eq. (2) below, represents the sum of the squared differences between measured and modeled concentrations, weighted by concentration uncertainties. Minimizing this function allows the PMF model to determine optimal non-negative factor profiles and contributions:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{X_{ij} - \sum_{k=1}^{p} A_{ik} F_{kj}}{S_{ij}} \right)^2$$

Where X_{ij} denotes the concentration of the j^{th} pollutant in the i^{th} sample, A_{ik} represents the contribution of the k^{th} factor to the i^{th} sample, F_{kj} is the mass fraction of the j^{th} pollutant in the j^{th} pollutant in k^{th} factor, S_{ij} is the uncertainty of the j^{th} pollutant in the i^{th} sample, and p is the number of factors.

TGM, air temperature (unit: Kelvin), gaseous pollutants, and major aerosol chemical species were used as inputs for the PMF model. We tested factor numbers ranging from 3 to 8, with the optimal solution determined by analyzing the slope of the Q-value versus factor count. Model stability was assessed through residual analysis, correlation coefficients between observed and predicted concentrations, and Q-value trends. A six-factor solution in DSL and a five-factor solution at JHI provided the most stable and interpretable results.

For the air temperature input, we confirm that values were converted to Kelvin (°C + 273.15) prior to PMF analysis. This aligns with the non-negativity constraint inherent to PMF's mathematical framework, as rightly noted by the reviewer.

5. Lines 249–250: The reference here for background level in Northern Hemisphere is outdated. Please refer to more recent studies (e.g., Bencardino et al., 2024). It is also encouraged to give the value range in the text.

Response: Thanks for your comments. Following updates from recent literature, this statement in the revised manuscript has been modified in Line 327-330.

"The mean TGM concentrations reached 2.36 ± 0.65 ng/m^3 and 2.16 ± 0.81 ng/m^3 over the Yellow Sea and East China Sea, respectively, significantly higher than the background level in the Northern Hemisphere (1.58 ± 0.31 ng/m^3) (Bencardino et al., 2024).".

6. Lines 250–253: Similarly, it is recommended to list the mean values and standard deviations of TGM concentrations in these studies.

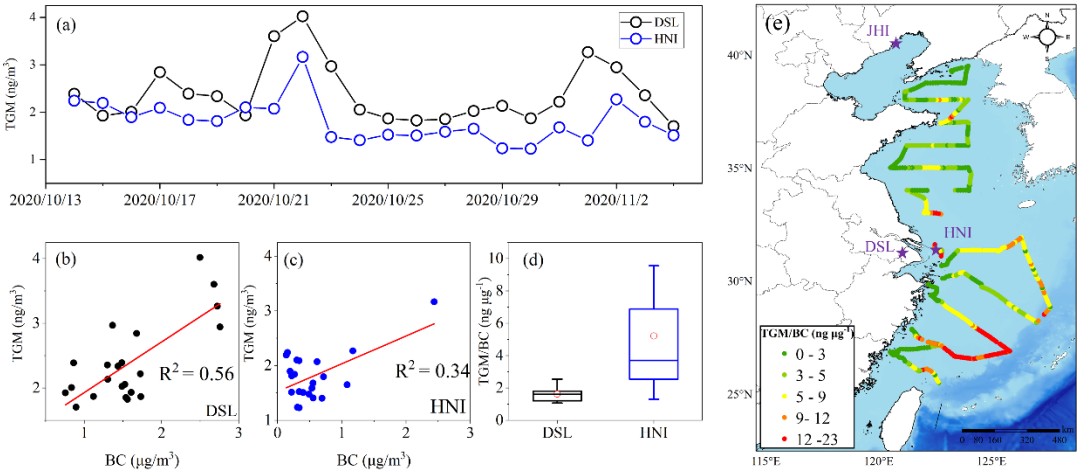
Response: Following your suggestion, we have listed the mean values and standard deviations of TGM concentrations from comparative studies. This sentence is revised in Line 332-335.

"also surpassing measurements recorded in the other open ocean areas such as the South China Sea (1.52±0.32 ng/m^3), Mediterranean Sea (1.8± 1.0 ng/m^3), Bering Sea (1.1 ± 0.3 ng/m^3), Pacific Ocean (1.15-1.32ng/m^3), and Atlantic Ocean (1.63 ± 0.08 ng/m^3)".

7. Lines 331–333: These TGM/BC ratio ranges are a bit strange. These values were

automatically generated on mapping. I suggest the authors reset the ranges and use rounded values instead.

Response: Thanks for your suggestion. We have now adjusted the TGM/BC ratio ranges. The revised Figure 4 (see below) now reflects these modifications.



8. Lines 363–370: The method for measuring the concentrations of heavy metals at DSL was not mentioned in Section 2. Was it an online or offline method? How big was the dataset?

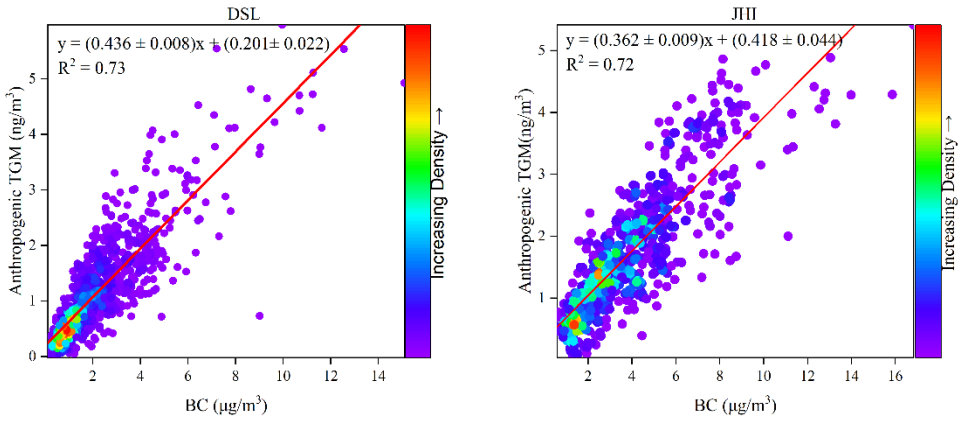
Response: In the revised manuscript, we have introduced the online methodology for measuring heavy metals in Section 2. The data used in this study covers the period from October to December, 2020 with a temporal resolution of 1 hour.

The details are added in Line 251-256.

"Trace metals in $PM_{2.5}$ (Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Sr, Cd, Sn, Sb, Ba, Tl, Pb, and Bi)were continuously measured using an Xact multi-metals monitor (Model Xact™ 625, Cooper Environmental Services LLT, OR, USA). It operated at a flow rate of 16.7 L min^{-1} with hourly resolution. Particles in the airflow passed through a PM2.5 cyclone inlet and were deposited onto a Teflon filter tape, then the samples were transported into a spectrometer for analysis via nondestructive energy-dispersive X-ray fluorescence."

9. Figure 5 (c and d): It seems to me that the two relationships are quite similar. The relationship for JHI is highly influenced by the top right data point, which is not robust. Therefore, I suggest the authors integrate the data points of these two sites and establish a uniform relationship.

Response: Thanks for your comments. The relationships between anthropogenic GEM and BC were originally derived from the daily average data. Now, we have used the original hourly data to re-calculate the linear regressions, which are shown in the figure below. It could be seen that even there is a number of high concentration data on the top right, the regression equations are close to the original relationships based on daily data. This indicates that the relationship between anthropogenic GEM and BC is still robust.



We appreciate for your suggestion that a uniform relationship can be established by integrating the data points of two sites. However, it could be seen that regression slopes at the two sites have discernible differences. This was reasonable as northern China and southern China have different energy structures, thus the relationship between anthropogenic GEM and BC should be different to some extents. In this regard, we didn't use the uniform relationship for the further data analysis.

10. Figure 6 (a-d): These relationships are all based on nonlinear regressions which are not consistent with the linear assumption for PMF.

Response: Thank you for the comments. The linearity assumption of PMF applies strictly to the additivity of factor contributions but does not constrain the intrinsic relationships among input variables. As explicitly stated in the US EPA PMF 5.0 Guide, input variables may include nonlinearly correlated features (e.g., meteorological parameters) provided their data uncertainties are properly quantified. When temperature is included in PMF as a continuous variable, its association with pollution sources may be linear or nonlinear, which does not violate the model's core assumptions. The nonlinear regressions in Figure 6 are independent of the PMF factorization process; their sole purpose is to reveal potential nonlinear modulation effects of temperature on the intensity of source contributions, serving as descriptive analyses that do not participate in PMF model computations. Therefore, the nonlinear relationships shown in Figure 6 are methodologically justified.

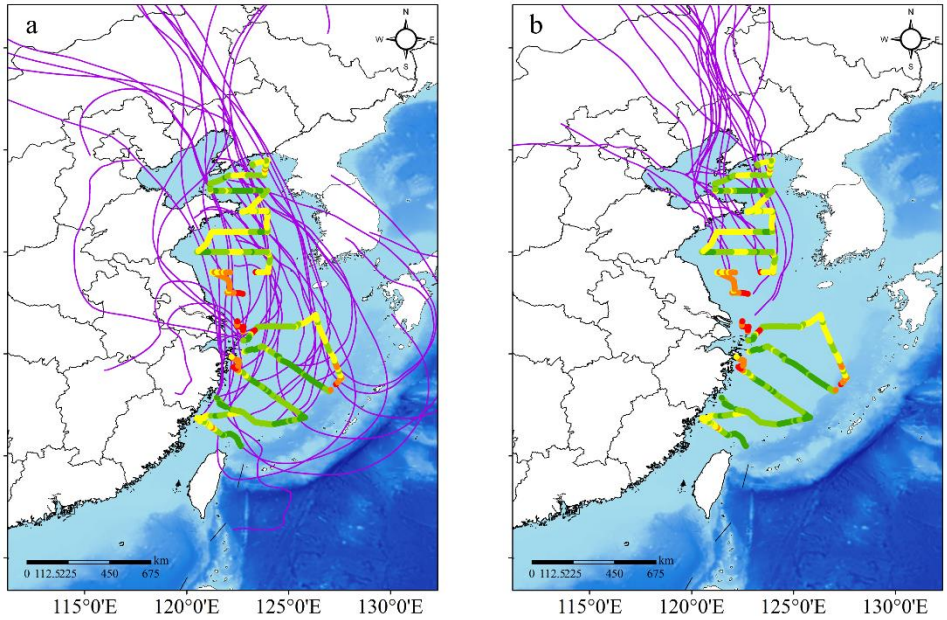
11. Lines 411–415: Could it be more likely that the Yellow Sea suffers more from the air masses from the North China Plain region which is more polluted than eastern China?

Response: Thank you for the comment. As shown in Figure S1, the backward trajectories during the Yellow Sea segment of the cruise predominantly originated from the North China Plain and Liaoning Province. We therefore agree with your perspective that "the Yellow Sea suffers more from the air masses from the North China Plain region, which is more polluted than eastern China".

In the revised manuscript, we have revised this description in Line 536-539.

"As shown in Figure S1, the backward trajectories over the Yellow Sea segment were primarily influenced by air masses from the North China Plain and Liaoning Province. The relatively

higher contribution of anthropogenic sources to the Yellow Sea during the cruise was likely attributable to the continental transport from northern China."



Bencardino, M., D'Amore, F., Angot, H., Angiuli, L., Bertrand, Y., Cairns, W., Diéguez, M. C., Dommergue, A., Ebinghaus, R., Esposito, G., Komínková, K., Labuschagne, C., Mannarino, V., Martin, L., Martino, M., Neves, L. M., Mashyanov, N., Magand, O., Nelson, P., Norstrom, C., Read, K., Sholupov, S., Skov, H., Tassone, A., Vítková, G., Cinnirella, S., Sprovieri, F., and Pirrone, N.: Patterns and trends of atmospheric mercury in the GMOS network: Insights based on a decade of measurements, Environmental Pollution, 363, 125104, https://doi.org/10.1016/j.envpol.2024.125104, 2024.

Fu, X., Yang, X., Tan, Q., Ming, L., Lin, T., Lin, C.-J., Li, X., and Feng, X.: Isotopic Composition of Gaseous Elemental Mercury in the Marine Boundary Layer of East China Sea, Journal of Geophysical Research: Atmospheres, 10.1029/2018jd028671, 2018.