Responses to Reviewers' Comments

We sincerely thank the reviewer for the constructive and thoughtful comments, which have significantly improved our manuscript. We have carefully considered all comments and revised the manuscript accordingly. Below are our detailed responses to your comments. Revised texts are marked red in the revised manuscript.

Reviewers' comments:

Reviewer #2 (Remarks to the Author):

This paper characterizes the decreasing trends of GEM and shifts in Hg isotopes in Chinese and Pakistani atmospheres. The authors conclude that decreased anthropogenic emissions are the main driver of this decline. Although the study is clearly presented, the accuracy of the source apportionment remains questionable due to significant gaps in the sampling periods, which may bias the seasonal representation. Please find my specific comments below;

RE: We sincerely appreciate the reviewer's constructive suggestions for improving the clarity and rigor of the manuscript. In the revised manuscript, we have strengthened the relevant methodological descriptions, explicitly discussed the temporal coverage of our sampling, and moderated several interpretations to better reflect the scope and uncertainty of our dataset.

Major comments:

- 2.1 The samplers were installed on the rooftop of Tianjin University. Has the influence of local exhaust systems (e.g., laboratory vents or heating units) been evaluated? It is necessary to confirm that the collected GEM represents the ambient urban atmosphere rather than localized emissions.

RE: Thank you for this important comment. We agree that the representativeness of the rooftop site should be clarified more explicitly. Several lines of evidence indicate that the TJ-Nankai site is representative of the ambient urban atmosphere rather than being influenced by localized emissions. First, to our knowledge, there are no known Hg point sources or local exhaust systems in the vicinity of the sampling site, which is situated on a rooftop ~21 m above ground level. Second, this rooftop has served as a long-term urban observation platform for multiple studies, including measurements of urban $PM_{2.5}$ and airborne microbial communities (Zhang et al., 2022; Zhao et al., 2023; Dong et al., 2024; Jin et al., 2025; Shuai et al., 2025). Third, active and passive GEM measurements were consistent in both concentrations and isotopic compositions during overlapping periods, and comparisons between the urban TJ-Nankai site and the suburban TJ-Binhai site, under similar air-mass conditions, revealed only modest differences in both concentrations and isotopic compositions.

We have clarified the representativeness of TJ-Nankai site in the revised manuscript.

Revised text (Line 109): This site is representative of typical urban conditions and has served as a long-term urban observation platform for multiple studies, including measurements of urban $PM_{2.5}$ and airborne microbial communities (Zhang et al., 2022; Dong et al., 2024; Jin et al., 2025).

References:

Dong, Z., Pavuluri, C.M., Li, P., Xu, Z., Deng, J., Zhao, Xueyan, Zhao, Xiaomai, Fu, P., Liu, C.-Q., 2024. Measurement report: optical characterization, seasonality, and sources of brown carbon in fine aerosols from Tianjin, north China: year-round observations. Atmos. Chem. Phys. 24, 5887–5905. https://doi.org/10.5194/acp-24-5887-2024

Jin, R., Hu, W., Duan, P., Sheng, M., Liu, D., Huang, Z., Niu, M., Wu, L., Deng, J., Fu, P., 2025. Exometabolomic exploration of culturable airborne microorganisms from an urban atmosphere. Atmos. Chem. Phys. 25, 1805–1829. https://doi.org/10.5194/acp-25-1805-2025

Shuai, W., Zhang, K., Zhang, T., Zheng, W., Liu, Y., Lang, Y., Fu, P., Feng, Y., Peng, J., Chen, J., 2025. Unraveling the origin of atmospheric soluble iron during asian dust storms. Environ. Sci. Technol. 59, 23962–23973. https://doi.org/10.1021/acs.est.5c10539

Zhang, K., Zheng, W., Sun, R., He, S., Shuai, W., Fan, X., Yuan, S., Fu, P., Deng, J., Li, X., Wang, S., Chen, J., 2022. Stable isotopes reveal photoreduction of particle-bound mercury driven by water-soluble organic carbon during severe haze. Environ. Sci. Technol. 56, 10619–10628. https://doi.org/10.1021/acs.est.2c01933

Zhao, X., Pavuluri, C.M., Dong, Z., Xu, Z., Nirmalkar, J., Jung, J., Fu, P., Liu, C.-Q., 2023. Molecular distributions and13 C isotopic composition of dicarboxylic acids, oxocarboxylic acids, and α -dicarbonyls in wintertime PM2.5 at three sites over northeast Asia: implications for origins and long-range atmospheric transport. J. Geophys. Res.: Atmos. 128, e2023JD038864. https://doi.org/10.1029/2023JD038864

- 2.6 There are significant temporal gaps in the dataset across Phases I to III. Notably, Phase II lacks data from the winter heating season (most of December to March). The current source apportionment may represent an optimized solution for the measured periods, but it likely carries a substantial bias as an annual average for 2021-22 due to the missing winter data.

RE: We agree that the temporal coverage is uneven across the three phases, and that Phase II does not include most of the winter heating season (December to March). This is due to due to sampling constraints during the COVID-19 lockdown. We have now acknowledged this limitation more explicitly in the revised manuscript. Importantly, we would like to mention that our intention was not to construct a complete seasonal representativeness for each phase, but rather to use the three broad phases to represent contrasting emission/activity regimes and to evaluate whether the concentration and isotopic signatures of urban GEM shifted across these regimes. We note that, despite the missing winter-heating-period coverage in Phase II, both active and passive observations during Phase II already showed low GEM concentrations and background-like isotopic signatures, and similar signatures persisted into Phase III.

Revised text (Line 281): Phase II did not include most of the winter heating season. Therefore, the phase-based interpretation should be viewed as a comparison among emission regimes rather than a fully balanced seasonal comparison.

Please clarify which datasets (active only, or a combination of active and passive) were used for the mixing model. While passive samplers were deployed during the periods when active sampling was unavailable, these provide only 30-50 day integrated averages, making them difficult to compare directly with high-resolution active data.

RE: We agree that passive sampling provides time-integrated observations and is not directly comparable to high-temporal-resolution active sampling. Due to practical constraints, continuous active sampling throughout the entire study period was not feasible. Therefore, passive sampling was employed to complement active sampling by providing extended temporal coverage. As active and passive GEM measurements showed good agreement in both concentrations and isotopic compositions during overlapping periods, both datasets were used in the source apportionment analysis. This has now been explicitly clarified in Section 2.6.

Revised text (Line 369): To integrate the evidence from long-term trends, diurnal variability, and spatial comparisons, we employed a ternary isotope mixing model to quantitatively constrain the sources of GEM in urban Tianjin (Figure 6). Both active pump-trap and passive MerPAS samples are used for source apportionment analysis to provide a full temporal coverage.

In Phase II, δ202Hg values range from -0.49‰ to 1.38‰. Since 1.38‰ exceeds the defined background end-member (≈ 0.50‰), how was the contribution calculated for such samples?

RE: Thank you for this important comment. We acknowledge that a small subset of samples with high δ^{202}Hg values falls outside the original δ^{202}Hg–Δ^{199}Hg mixing space. Following the suggestion of Reviewer #1, we have adopted a Δ^{200}Hg–Δ^{199}Hg framework, which provides a more robust constraint for this dataset. Notably, all samples fall within the Δ^{200}Hg–Δ^{199}Hg mixing space. Accordingly, we have replaced the original δ^{202}Hg–Δ^{199}Hg mixing model with a Δ^{200}Hg–Δ^{199}Hg mixing model. This revised framework avoids the limitations associated with δ^{202}Hg, which is more sensitive to environmental processes and subject to larger uncertainties in passive sampling due to MDF correction. This also prevents the limitation of δ^{202}Hg, because δ^{202}Hg is more sensitive to environmental processes and δ^{202}Hg values of passive samples are associated large uncertainty arisen from MDF correction factor.

All source-apportionment results, related figures, and discussion have been updated accordingly. Importantly, the results derived from the new Δ^{199}Hg–Δ^{200}Hg model are broadly consistent with those obtained using the original δ^{202}Hg–Δ^{199}Hg approach. Therefore, our main conclusion remains unchanged: the observed decline in urban GEM is primarily driven by reductions in anthropogenic emissions, while the relative contribution of natural re-emission sources becomes more pronounced under lower emission conditions.

Revised section 2.6 (Line 195): …This approach leverages the complementary diagnostic power of odd-MIF (Δ^{199}Hg) and even-MIF (Δ^{200}Hg) to resolve the relative contributions of three dominant GEM sources: primary anthropogenic emissions (ant), tropospheric background air (bg), and secondary urban surface (legacy) re-emissions (sur)… ,,, Uncertainties in source contributions were evaluated using a Monte Carlo simulation approach (n = 50,000), in which uncertainties associated with Δ^{199}Hg and Δ^{200}Hg values for both samples and endmembers were propagated.

Please provide a quantitative estimate of the errors/uncertainties associated with the source contribution results.

RE: We have provided the uncertainties for source contributions. In addition, we have clarified that the source contributions were estimated following the binary Δ^{199}Hg-Δ^{200}Hg mixing model using a Monte Carlo simulation approach (n = 50,000 times), in which uncertainties from both the samples and the endmembers were propagated.

Revised text (Line 211): Uncertainties in source contributions were evaluated using a Monte Carlo simulation approach (n = 50,000), in which uncertainties associated with $\Delta^{199}Hg$ and $\Delta^{200}Hg$ values for both samples and endmembers were propagated.

- The authors attribute the decline in GEM concentrations to mercury emission regulations. Are there any auxiliary atmospheric composition data (e.g., SOx, NOx) available to support this claim and verify the reduction in combustion-related emissions?

RE: Yes. We have added SOx, NOx, and other related air-pollutant data in the Supplementary Information as supporting evidence. These auxiliary data such as PM 2.5, SOx, and NOx show two times declines from Phase I to Phases II–III, consistent with the reduction in combustion-related emissions and the observed decrease in GEM concentrations. We have revised the text to clarify that the GEM decline is supported not only by the Hg concentration and isotope data, but also by the co-occurring decreases in conventional combustion-related air pollutants.

Revised text (Line 260): The absence of a post-pandemic rebound indicates that the decline in urban GEM is not a transient effect of reduced activity, but rather reflects a sustained weakening of anthropogenic Hg emissions, aligning with broader regional trends observed elsewhere in China (Cui et al., 2024; Feng et al., 2024; Sun et al., 2025). This interpretation is further supported by simultaneous decreases in conventional combustion-related air pollutants (e.g., $PM_{2.5}$, NO_2, and SO_2; Table S9 of the Supplementary Information).

Minor comments:

- L164 The expression (***Hg/198Hg)NIST3133 should be revised to "NIST SRM 3133" in accordance with Equation (1).

RE: Revised.

- For all data presented in the text, please specify whether the indicated errors represent 1SD or 2SD, and consistently include the number of samples (n).

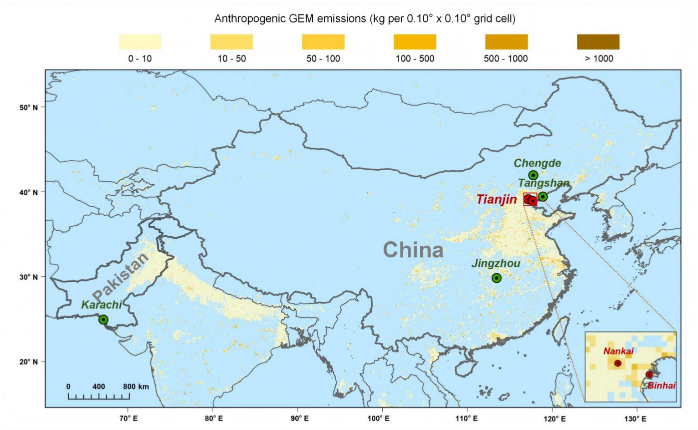
RE: We have clarified the data description at the beginning of the "Results and discussion" section: In the following, data is reported as mean ± 1SD uncertainty for each category of samples, unless otherwise indicated. In addition, the corresponding sample number (n) has been added consistently.

Added text (Line 225): Data is reported as mean ± 1SD uncertainty for each category of samples, unless otherwise indicated.

- Figure 1 The text in Figure 1 is difficult to read, and the scale of the enlarged map is unclear. Additionally, the sampling point for Karachi should be explicitly marked on the map.

RE: We have enlarged the text labels, revised the scale of the enlarged map, and marked the sampling location of Karachi.

Revised figure:



- A systematic offset in δ^{202}Hg exists between active and passive sampling. While the authors performed baseline experiments (Figure S2) and applied corrections (Table S4), it is recommended to use labels such as "corrected-δ202Hg" in both the main text and supplementary figures to avoid confusion.

RE: In the revised manuscript and supplementary materials, we now mark the corrected δ^{202}Hg values with an asterisk (δ^{202}Hg*) and clarify that δ^{202}Hg* denotes corrected δ^{202}Hg values for passive MerPAS in the relevant figures/tables (Fig 3, Table S4, and Table S8).

- Figure 6b There is a symbol resembling a stop button. Is this symbol necessary? If not, please remove it to maintain graphical clarity.

RE: We have removed the unnecessary symbol from Figure 6b to improve graphical clarity.

- The use of the minus sign (hyphen vs. en-dash) is inconsistent throughout the manuscript. Please unify the mathematical symbols.

RE: We have carefully checked the manuscript and unified the use of minus signs, hyphens, and en-dashes.