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 #1 (Remarks to the Author):

Major Comments

The study by Zhang et al. measured atmospheric GEM concentrations and isotopic compositions at long-term monitoring urban site and multiple short-term monitoring urban, suburban, rural sites in China and Pakistan. Based on the comprehensive observations, the authors show notable declines in GEM concentrations and clear changes in the isotopic compositions in the urban atmosphere. By using a Hg isotope mixing model, they quantify the relative contributions of anthropogenic emissions and evidence that the GEM declines are mainly driven by the control of anthropogenic emissions. This research is well designated. I broadly agree with the interpretations throughout the manuscript. I would suggest a minor revision of this manuscript (the manuscript is well written currently). Some of the minor suggestions are presented below.

RE: We sincerely appreciate the reviewer's constructive comments for improving the clarity and rigor of the manuscript. All comments have been carefully addressed in the revised version, as detailed below.

The source apportionment: in this study, the authors use a δ^{202}Hg and Δ^{199}Hg mixing model to quantify the source contributions. I would suggest to use the Δ^{199}Hg and Δ^{200}Hg mixing model as previous studies. This is because the GEM δ^{202}Hg in the boundary layer apt to modified by vegetation uptake process (particularly at the suburban and rural sites in this study), while the Hg-MIF signals are relative stable. As seen from Fig. 3a, some of the δ^{202}Hg and Δ^{199}Hg assemble especially in the background areas are not fully encompassed by δ^{202}Hg and Δ^{199}Hg of the three source endmembers. The authors argue that the Δ^{200}Hg of anthropogenic emissions overlap surface re-emissions. However, the Δ^{199}Hg of anthropogenic emissions and surface re-emissions are distinguishable, and this could enable the source quantification of these two sources. In addition, the Tianjin sampling site is close to seas, and the seawater re-emissions should be also considered. A recent study reported mean Δ^{199}Hg and Δ^{200}Hg values of -0.13‰ and 0.02‰, respectively, for ocean emissions (Fu et al., 2026, NSR). This oceanic signature is identical to soil re-emissions. Therefore, using the Δ^{199}Hg and Δ^{200}Hg mixing model would help to understand the contributions from the two most important natural emissions (e.g., soil + seawater reemission).

RE: Thank you for this important and insightful comment. We agree that MIF signatures are generally more conservative than δ^{202}Hg, and appreciate your suggestion to consider potential seawater re-emission. We now explicitly acknowledge the potential limitation of using δ^{202}Hg in boundary-layer environments, and adopted your proposed Δ^{199}Hg–Δ^{200}Hg model. We have also expanded the discussion of natural re-emission sources by considering the possible contribution of marine Hg re-emission. It is noted that the apportionment results from the new Δ^{199}Hg–Δ^{200}Hg model are generally consistent with those of the original δ^{202}Hg–Δ^{199}Hg model. Thus, our main conclusion (i.e., the observed decline in urban GEM was primarily driven by reduced anthropogenic emissions, while natural re-emission sources may become relatively more important under conditions of lower anthropogenic input) is still valid.

Revised text (Line 206): Given Tianjin's proximity to the Bohai Sea, seawater re-emissions are also expected to contribute to surface Hg fluxes. Recent field measurements report mean δ^{202}Hg, Δ^{199}Hg, and Δ^{200}Hg values of −1.04 ± 0.32‰, −0.13 ± 0.10‰ and 0.02 ± 0.02‰, respectively, for marine re-emissions (Fu et al., 2026). These values closely overlap with those reported for urban soil re-emissions (Zhu et al., 2022). As a result, marine and urban soil surface re-emissions are combined into a single surface re-emission endmember, with its Hg isotope values represented by those of urban soil re-emissions (Zhu et al., 2022).

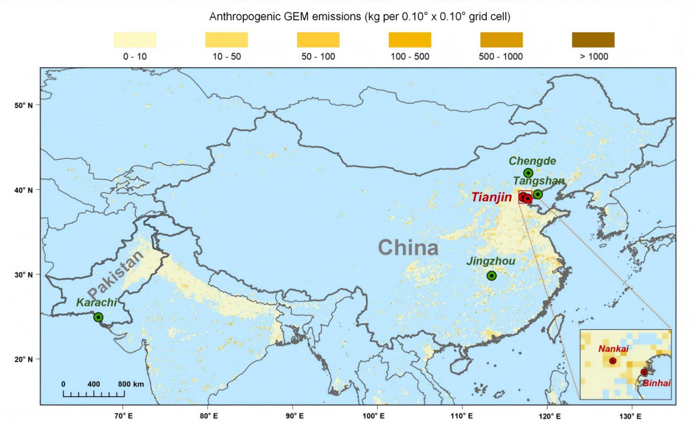
Specific comments:
Line 13: please add 'mean' before GEM concentration.

RE: "mean" is now added before "GEM concentration".

Fig.1: better to show the location of Karachi in this figure.

RE: The location of Karachi is now added in the updated Fig. 1.

Revised figure:



Line 127: please specify whether the sampling flow rate is operated under the standard temperature and air pressure.

RE: The reported flow rate of 4.0–5.5 L min^{-1} refers to the measured ambient flow rate during sampling. For concentration calculation, the cumulative sampled air volume was normalized to standard temperature and pressure (273.15 K and 101.325 kPa) using the recorded ambient temperature and pressure. We have clarified this point in the revised manuscript.

Revised text:
Line 128: Air was drawn through the traps at ambient flow rates of 4.0–5.5 L min^{-1}, with particulate matter removed upstream using a 47 mm quartz fiber filter housed in a Teflon filter pack.

Line 182: For active pump-trap sampling, GEM concentration was calculated as the blank-corrected Hg mass collected on each CLC trap divided by the sampled air volume normalized to standard temperature and pressure (273.15 K and 101.325 kPa).

Section 2.2: please provide the sampling interval or duration for each sample at the sampling sites, including the pump-trap and passive samples.

RE: We have provided the sampling durations for both active pump-trap and passive samples. Specifically, the deployment dates and sampling durations of passive samples are provided in Tables S2–S3, while the start/end times of active pump-trap samples are provided in Tables S5–S7. To improve clarity, we have further added sampling duration information in the Section 2.2.

Revised text (Line 135): At Tianjin (TJ-Nankai and TJ-Binhai), active sampling campaigns were conducted in November 2018 (Phase I, ~1 day per sample), from October 2021 to September 2022 (Phase II, 1–3 days per sample), and from December 2024 to January 2025 (Phase III, with separate day (07:00–18:00) - night (18:00–07:00) samples) at TJ-Nankai, but only from December 2024 to January 2025 (Phase III, ~1 day per sample) at TJ-Binhai (Tables S5–S7 of the Supplementary Material). To facilitate long-term monitoring and inter-city comparisons, paired MerPAS samplers were deployed at all study sites. For the long-term monitoring at TJ-Nankai, individual passive samples were deployed for 40–53 days in Phase II and 29–56 days in Phase III, yielding total monitoring periods of 192 and 343 days, respectively (Tables S2–S3 of the Supplementary Material).

Section 2.5: please add the method for the calculation of GEM concentrations using the pump-trap. Are all concentrations reported for the STP conditions?

RE: Yes, all reported concentrations were normalized to STP conditions.

Revised text (Line 182): For active pump-trap sampling, GEM concentration was calculated as the blank-corrected Hg mass collected on each CLC trap divided by the sampled air volume normalized to standard temperature and pressure (273.15 K and 101.325 kPa).

Line 221: add ‘mean±1sd’ after the values.

RE: To avoid repeatedly adding ‘mean±1sd’, 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.

Line 223: please note ‘mean±1sd’ for the values reported in Beijing and Shijiazhuang.

RE: Please see our response to your comment at Line 225.

Line 235: add ‘mean,’ before n =35.

RE: Please see our response to your comment at Line 225.

Line 240: better to show the exact p value when it is higher than 0.05.

RE: We have shown the exact *p* value.

Revised text (Line 257): Relative to Phase I, GEM concentrations declined by ~68% in Phase II and ~66% in Phase III, with no statistically significant difference between Phases II and III (independent sample *t*-test, $p = 0.59$).

Line 245: add 'mean' before δ^{202}Hg.

RE: Please see our response to your comment at Line 225.

Line 246: change 'directly' to 'mainly'?

RE: We agree and have changed "directly" to "mainly".

Line 247-248: add 'mean±1sd' before n=16. Same in line 249, 251 and 255.

RE: Please see our response to your comment at Line 225.

Line 257: show the real value instead of >0.05.

RE: We have shown the exact p value.

Revised text: Hg isotopic compositions were broadly similar between Phases II and III, with no significant differences in δ^{202}Hg (independent sample *t*-test, $p = 0.75$) or Δ^{200}Hg (independent sample *t*-test, $p = 0.35$), although Δ^{199}Hg differed significantly (independent sample *t*-test, $p = 0.04$). Nevertheless, both Phase II and Phase III differed significantly (independent sample t-test, all $p < 0.01$) from Phase I in δ^{202}Hg, Δ^{199}Hg, and Δ^{200}Hg.

Line 262: add mean before GEM.

RE: Please see our response to your comment at Line 225.

Line 267-268: not note these are mean values.

RE: Please see our response to your comment at Line 225.

Line 277: add 'mean' before values.

RE: Please see our response to your comment at Line 225.

Line 303: please add 'mean±1sd' after the D200Hg values.

RE: Please see our response to your comment at Line 225.

Line 309: add 'mean' before GEM.

RE: Please see our response to your comment at Line 225.

Line 324: please add 'mean' before δ202Hg and D199Hg. please also check other place if the values are referred to mean values.

RE: Please see our response to your comment at Line 225.

Line 343: please add 'on average' before contributing.

RE: We have added "on average" before "contributing".

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 Δ^{199}Hg and Δ^{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).

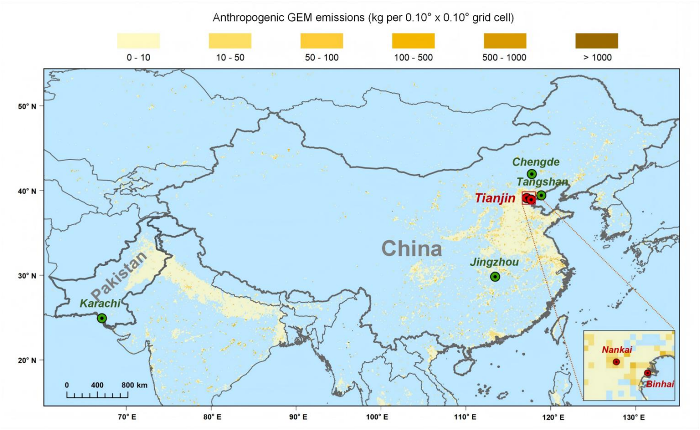
RE: We have clarified the data description at the beginning of the “Results and discussion” section: In the following, data is reported as mean ± 1SD uncertainty for each category of samples, unless otherwise indicated. In addition, the corresponding sample number (n) has been added consistently.

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.

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 #3 (Remarks to the Author):

This paper presents a long term GEM concentration - isotope record spanning pre-control, lockdown, and post-pandemic phases (2018–2025) in E China and S Pakistan. Certainly, it documents a fundamental shift in urban atmospheric mercury quality in Tianjin, China. The study is timely, policy-relevant (Minamata Convention), and methodologically advanced. However, I have a number of comments:

RE: We sincerely appreciate the reviewer's constructive suggestions for improving the clarity and rigor of the manuscript. We have revised the manuscript to better define the representativeness and limitations of the dataset, improve the statistical description, and further refine the interpretation of the isotope results.

Major comments:

1. **Representativeness of sampling sites**. Please discuss the possibility of the sampling site being a receptor of localized emissions rather than urban ambient atmosphere.

RE: We thank the reviewer for this important comment. We did not perform a dedicated engineering evaluation of individual rooftop exhaust outlets (e.g., laboratory vents or heating units). However, several lines of evidence suggest that the TJ-Nankai site is representative of the ambient urban atmosphere rather than being persistently dominated by localized exhaust emissions. First, the sampling site is located on the rooftop of Building No. 19 at Tianjin University, approximately 21 m above ground level, and was selected to minimize direct surface interference. Second, the same Tianjin University urban rooftop setting has been used in previous published atmospheric studies, including year-round urban $PM_{2.5}$ observations and airborne microbial sampling (Zhang et al., 2022; Zhao et al., 2023; Dong et al., 2024; Jin et al., 2025; Shuai et al., 2025), supporting its suitability as an urban atmospheric observation platform. Specifically, active and passive GEM measurements were consistent during overlapping periods, and the urban–suburban comparison between TJ-Nankai and TJ-Binhai revealed only modest concentration and isotopic differences with similar air-mass origins.

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. **Small sample sizes in Phase I (2018)** – consists of only 3 active samples collected in a single month (November). Please acknowledge this as a limitation, but also note that Phase I isotopic values are consistent with a larger compilation of Chinese urban GEM (Zhang and Sun, Earth-Science Reviews, 2026).

RE: We have acknowledged this limitation more explicitly in the revised manuscript and noted their isotope consistency with the larger compilation of Chinese urban GEM isotope data.

Revised text (Line 267): Such values largely overlap the range commonly observed in China urban GEM that is mainly influenced by primary anthropogenic sources such as coal combustion and metal smelting (mean ± 1 SD, δ^{202}Hg= –0.52 ± 0.27‰; Δ^{199}Hg = -0.05 ± 0.04‰; Δ200Hg = -0.01 ± 0.02‰, n = 16 sites) (Zhang and Sun, 2026) (Figure 3). This consistency suggests that Phase I captured a representative urban GEM isotope signature, despite the limited sample size.

3. **Statistical treatment of trends** The paper states that GEM concentrations and isotopic compositions differ significantly between phases ($p<0.05$), but no trend analysis (e.g., Mann-Kendall, Theil-Sen) is applied to the continuous time series within Phase II and III. Add trend analysis for Phase II–III; report statistical tests in figure captions.

RE: We have added Mann–Kendall trend-test to Figure 2 for the Phase II–III time series. The results show that no significant monotonic trends were detected for GEM concentration or isotopic compositions across the combined Phase II–III period.

Revised Figure 2 caption (Line 233): No significant monotonic trends were detected for GEM concentration (p = 0.80), δ^{202}Hg (p = 0.90), Δ^{199}Hg (p = 0.20) and Δ^{200}Hg (p = 0.37) within the combined Phase II–III time series, according to the Mann–Kendall trend analysis.

4. **Diurnal interpretation**

The diurnal isotopic shift (lower δ^{202}Hg, higher Δ^{199}Hg during daytime) is attributed to surface re-emissions, but atmospheric photochemical oxidation of GEM to Hg(II) can also fractionate isotopes in ways that might appear similar. The paper does not fully rule out oxidation-driven MIF changes. Please add a brief discussion.

RE: Thank you for this important comment. We agree that atmospheric oxidation of GEM can also induce isotope fractionation and therefore cannot be fully excluded as a contributor to the observed diurnal isotopic shift. In the revised manuscript, we have added a brief discussion to clarify this point.

Revised text (Line 323): In addition, atmospheric oxidation of GEM may induce similar isotope fractionation (Sun et al., 2016a) and therefore cannot be fully excluded as a contributing process. As the boundary layer expands during the day, photochemical re-emission of legacy Hg and enhanced local primary emissions may provide compensatory sources that replenish near-surface GEM. Therefore, in the low-emission era, diurnal GEM concentrations may underestimate the role of surface–atmosphere exchange, whereas isotopes remain sensitive to these secondary processes. Direct measurements of surface–atmosphere Hg exchange flux is needed to this inference. Direct measurements of surface–atmosphere Hg exchange fluxes are needed to further evaluate this interpretation. Nevertheless, the nearly constant diurnal GEM concentrations and Δ^{200}Hg values suggest that the net contributions from legacy Hg re-emission, local primary emissions, and oxidation-driven losses are relatively small.

Lack of direct flux measurements – surface re-emissions inferred but not quantified.

RE: We agree that direct flux measurements were important to validate our inference. Our discussion of surface re-emissions is intended as an inference based on the observed diurnal isotopic patterns, rather than a direct quantification of surface–atmosphere Hg exchange. We have clarified this point in the revised manuscript.

Revised text (Line 328): As the boundary layer expands during the day, photochemical re-emission of legacy Hg and enhanced local primary emissions may provide compensatory sources that replenish near-surface GEM. Therefore, in the low-emission era, diurnal GEM concentrations may underestimate the role of surface–atmosphere exchange, whereas isotopes remain sensitive to these secondary processes. Direct measurements of surface–atmosphere Hg exchange fluxes are needed to further evaluate this interpretation.

5. **Passive sampler MDF correction.** The MDF correction factor for MerPAS samplers is applied uniformly, but its uncertainty (±0.33‰) is large relative to some of the δ^{202}Hg differences reported (e.g., urban-suburban difference ~0.3‰). The potential impact on the mixing model results is not fully assessed. Perform a sensitivity analysis showing how varying the correction factor affects source apportionment, or at least discuss this uncertainty explicitly.

RE: Thank you for this important point. As suggested by other reviewers, we have replaced the original δ^{202}Hg–Δ^{199}Hg mixing model with a Δ^{200}Hg–Δ^{199}Hg-based model in the revised manuscript. 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 the MDF correction. Thus, the MDF-correction uncertainty does not propagate into the final source-contribution estimates. Please see our revised section 2.6: Source apportionment

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.

Minor comments:

Equation (2) appears incorrectly written – likely a typo.

RE: Corrected.

Figure 2 caption: The caption states "no statistically significant differences" between active and passive sampling but doesn't specify the test used or p-value.

RE: The caption of Figure 2 has also been revised to include the statistical method and corresponding *p*-value.

Revised text (Line 232): GEM concentrations and isotope values between active and passive sampling show no statistically significant differences during their overlapping periods (independent-samples *t*-test: GEM concentration, $p = 0.98$; δ^{202}Hg, $p = 0.61$; Δ^{199}Hg, $p = 0.20$; Δ^{200}Hg, $p = 0.95$).

Please add information if GEM concentrations are normalized to STP.

RE: We have clarified in the revised manuscript that all reported concentrations were normalized to STP conditions.

Revised text (Line 182): For active pump-trap sampling, GEM concentration was calculated as the blank-corrected Hg mass collected on each CLC trap divided by the cumulative sampled air volume normalized to standard temperature and pressure (273.15 K and 101.325 kPa).