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).