Anonymous Referee #2

We appreciate the time and effort made by Anonymous Referee #2. We have reproduced the reviewer's comments below in black, and provided detailed responses in blue.

This paper investigates the sources of atmospheric oxidized mercury at a mountain top site combining ambient measurements with a chemical transport model. This paper demonstrates that chemical transport model underestimates oxidized mercury concentrations, yet current sensitivity modeling experiments are insufficient to pinpoint the causes. The measurements seem to be appropriate and state-of-the-art.

- We thank the reviewer for this synopsis.

I recommend that this study should include several additional sensitivity experiments, such as examining iodine oxidation effects and deposition rate variations. These experiments could help unravel the reasons behind the observed underestimation of oxidized mercury levels. Unfortunately, the current analysis lacks this critical component. Thus I suggest major revisions of the current manuscript.

- We have performed sensitivity experiments on dry deposition rate variations. The results of these experiments are in Section 3.2 of the manuscript with changes tracked.
- We did not perform sensitivity tests with iodine oxidation. While Lee et al. (2024; https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2024GL109247) speculate that iodine *could be* an important oxidant of elemental Hg, the 5th paragraph of their introduction cites several papers that provide evidence against the viability of iodine as an oxidant of elemental Hg because of fast thermal decomposition of HgI. Also, Lee et al. found discrepancies between measured IO and IO modeled by GEOS-Chem, which means any work we did in this area would be influenced by this bias. We thus choose not to make assumptions about oxidation by iodine radical until at least some computational chemistry work shows the reaction might be viable.

Anonymous Referee #1

We appreciate the time and effort made by Anonymous Referee #1. We have reproduced the reviewer's comments below in black, and provided detailed responses in blue.

This study uses an atmospheric mercury chemistry model (GEOS-Chem) to analyze a measurement campaign conducted at a mountaintop site in the Western US. The authors identify that GEOS-Chem significantly underestimates the amount of oxidized mercury measured during this campaign. This highlights an important knowledge gap in Hg models.

- We thank the reviewer for this synopsis.

However, it is an issue that has been identified in many previous publications about GEOS-Chem (e.g., Gustin et al., 2023; Shah et al., 2021; Shah et al., 2016) and the 3 sensitivity simulations conducted here are not sufficient to bring us closer to resolving this issue.

- We disagree that the three articles listed here provide overly similar information to our manuscript. Our manuscript builds on these studies and adds significant new information, including:
    - Shah et al. (2016) used a much different (simpler) version of GEOS-Chem that only involved direct oxidation of Hg^0 by Br radical. There have been a large increase in understanding of atmospheric Hg chemistry since that paper, and the Shah et al. (2021) paper provides a dramatic update and increase in complexity of the Hg chemical mechanism. It is significant that, even with this update, the model suffers from the same problem. We added text to the Conclusions section to highlight this.
    - Figure S6 in Shah et al. (2021) (referred to as S7 in the text of the paper) indeed shows an underestimation of simulated Hg^{II} compared to measurements in the inland western U.S., just as our paper shows, and this underestimation is especially striking given that the measurements used for comparison were made with KCl denuder-based methods that have been shown in ~20 different peer-reviewed papers to be biased low. While they acknowledge the low Hg^{II} bias in simulations, their paper is focused on the Hg model as a whole, and they were not able to give the bias comprehensive treatment. Our paper aims to provide a better understanding of the extent of the bias, at least for some locations. We added text to the Comparison with Others' Work and Conclusions sections to highlight the work already done by Shah et al. (2021) and other researchers and put it in the context of our study.
    - Gustin et al. (2023) show a low bias in GEOS-Chem using the Shah et al. mechanism, but they did nothing to investigate the cause of the bias. We already include a comparison of their findings with ours in the Comparison with Others' Work section of the paper.

I believe that more sensitivity simulations and analysis would be required to yield more actionable results, and I suggest some ideas below. As it currently stands, I believe the article is more suitable as a measurement report due to the limited scope.

- We thank the reviewer for this synopsis.

Main Issues:

1) The sensitivity simulations aim to test the impact of different oxidation rates on the comparison with the observed results. However, there is no simultaneous adjustment of the photoreduction rate or total Hg emissions, which leads to a highly unlikely Hg0 budget for SA1 (Figure 3). Because there is too little total Hg in the atmosphere, it is not surprising that for SA1 there is too little oxidized Hg. The authors admit this issue at several points, but it would strengthen the paper to have a scenario where the model is retuned (using higher emissions or photoreduction) so that a high oxidation scenario can be fairly compared to the results of the Base scenarios.

- We have completed sensitivity runs for SA1 in which the rate of the photoreduction reaction $Hg^{II}P(org) + h\nu \rightarrow Hg^0$ was adjusted iteratively to increase atmospheric Hg^0, following the method outlined by Shah et al. (2021). The results of these experiments are now the final paragraph of Section 3.2, and the revised supplemental contains a new figure to show our findings. While adjusting the photoreduction frequency increased Hg^0, we found that Hg^{II} stayed in the same range as the original SA1 results. We hypothesize that the decrease in total Hg^{II} caused by the increase in photoreduction frequency was balanced by an increase in Hg^{II} because more Hg^0 was available for oxidation.

I would also consider doing simulations where oxidation rates are only adjusted locally rather than globally, as the authors state that this episode is likely due to a in-situ oxidation process (P7L158).

- We don’t believe local adjustments of oxidation rates would be useful, and we chose not to perform sensitivity tests with local adjustments of oxidation rates. Oxidation of Hg^0 occurs extremely slowly in the ambient atmosphere, and the in-situ oxidation event explored in the model involved oxidation over multiple days of transport from the Pacific free troposphere. We used global, rather than regional, GEOS-Chem simulations for most of our work because Hg^{II} buildup occurs slowly during global (or at least hemispheric) atmospheric transport. While it is possible that an unknown oxidant that existed locally led to the enhanced Hg^{II} observed in this study, the Derry et al. (2024) paper we cite in the manuscript provides evidence against that hypothesis.

2) I was intrigued by the discussion in Section 3.3 about using HgII:Hg0 as a potential metric for evaluating HgII deposition processes. There are definitely uncertainties related to deposition in the models in general and the parameters assigned to deposition of

different HgII species, and the paper would benefit from a more detailed discussion of these uncertainties. I think there is a clear opportunity here to conduct additional sensitivity simulations adjusting the HgII deposition rates to constrain the potential bias in HgII deposition rates, using the slope derived from observations. Without this evidence it is difficult to know how biased the HgII deposition processes are in the model, or if the HgII:Hg0 slope depends on other factors.

- We have performed sensitivity experiments on deposition rate variations. The results of these experiments are in Section 3.2 of the revised manuscript.

3) In Section 3.4, the authors use the Hg0 temporal variability as an indicator of oxidation (P14L247). However, Hg0 variability will also be affected by issues in emissions, deposition, and transport. Therefore, I believe it is too simplistic to assert that the net oxidation is four times too low in the simulations, since even the simulation with higher oxidation (SA1) does not seem to improve the simulated amplitude of Hg0 during the episode (Figure 3).

- We added the following statement to the section: “we concede that Hg^0 variability is also impacted by emissions, deposition, and transport phenomena, confounding the accuracy of this indicator.”

4) Building on the previous point: I think the change in magnitude of Hg0 can also be strongly impacted by dynamics; i.e., the specific dynamics of a mountaintop site that will be difficult to resolve in a global model. Even the high resolution simulations (~30 km x 30 km grid boxes) might not necessarily capture the dynamics above such a complicated topography. Is the model able to reproduce the variations in other atmospheric compounds measured at this site? Such a comparison would be helpful to identify whether this is a Hg-specific issue or a dynamics issue in general.

- While we agree that the change in magnitude of Hg0 can be expected to be impacted by mountain atmospheric dynamics, the impact of these dynamics is muted in the coarse resolution used in the model. Most of the work used 2.0x2.5 degrees as model resolution size, so no detailed mountain dynamics can be expected to be resolved.
- Model-measurement comparisons for IO, ozone, water vapor, and temperature were accomplished by Lee et al. (2024). We added the following text to Section 2.3 in the methods to make this clear: “Lee et al. (2024) conducted a comparison of measured and modeled ozone, temperature, and water vapor for the same base model used in this study.”

Technical/Minor Comments:

P2L35 - Recent mercury literature (Zhou et al., 2021; Sonke et al., 2023) suggests that dry Hg0 deposition is a substantial portion of the overall atmospheric Hg sink.

- We have corrected this.

P4L94 - This term is unclear to me: expanded uncertainty

- This is a statistical term. We added references to which readers can go for a discussion of the term and how it is calculated.

P7L147 - specify whether HgII here includes particulate species or only gas phase species

- We have made this change.

P13L232 - Slopes greater than -1 -> it's not clear if you mean greater in absolute magnitude or more positive (i.e., -1<slope<0).

- We feel like greater is a very clear term. -0.9 is greater than -1. -1.1 is less than -1. In our view, this is the clearest possible way to discuss the relative magnitudes of negative numbers.

P16L272 - should be Hg(OH)2

- Corrected.

P16L275 - A major reason for the predominance of HgCl2 is its stability to photoreduction compared to other Hg(II) species, see Saiz-Lopez et al., doi: 10.1038/s41467-018-07075-3 (2018)

- We understand this concept. We don't believe any changes are needed to the manuscript in response to this comment. We don't believe the manuscript implies that the reason for predominance of $HgCl_2$ among modeled HgII species is unknown, and we aren't sure repeating what is already in the Saiz-Lopez paper and the Shah et al. paper is necessary here.

P16L276 - Speciation discussion - there has been no molecular determination that these measured Hg compounds actually contain N- and S- species; it is just inferred based on similarity of thermal desorption profiles and a few Hg(iI) compounds that are available commercially (which don't include Hg(OH)2 or HgBrOH that are predicted to be prevalent)

- We completely agree with the reviewer. This is why the existing manuscript text included the words "may" and "indirect", and it is why there is a clause at the end of the sentence stating that oxidation by N- and S-containing compounds is unlikely. We don't believe additional hedging of the text is necessary.

- Table 3 - not all parameters in this table are fully understandable (HgII:Hg0 (r^2) - shouldn't this be a negative correlation?) nor are all discussed in the text (HgII:Hg0 intercept: what does this signify?)

- r2 values are always positive because the product of two negative numbers (for example, a negative Pearson r correlation) is a positive number.

- We don’t agree that it is necessary for every column in the table to be discussed explicitly in the text.
- The HgII:Hg0 intercept is the HgII concentration when Hg0 is zero, assuming linearity between Hg0 and HgII. We added a sentence to the table caption to explain what the intercept means conceptually.

- Figure 7 - add trend lines for simulations and observations, so that we can see visually how they compare

- We had trend lines originally, but we felt (and still feel) it made the figure messy, so we took them out. The slopes and other regression information are available in Table 3, and those data may be used by readers to compare the slopes of the different datasets.