Response to Reviewer 1

Thank you to the reviewers for your additional comments which have improved the quality of the paper.

Review of revisions to Intended and Unintended Consequences of Atmospheric Methane Oxidation Enhancement by Hannah Marie Horowitz, egusphere-2024-3139

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Overview / Summary

The revised manuscript is substantially improved and reflects careful and thoughtful engagement with the reviews. The author has clarified key assumptions, corrected important model issues, and strengthened the discussion of uncertainties and model limitations. The additional figures and expanded discussion of resolution effects, chlorine partitioning, and evaluation of the Chen et al. (2024) parameterization significantly enhance the manuscript.

We are particularly encouraged that the Chen and van Herpen parameterizations now give much more similar results. This convergence increases confidence in the simulations and suggests that the representation of chlorine chemistry is now more consistent with observational constraints, including $\delta^{13}C$ in CO isotope observations at Barbados. While some of the remaining questions we raised previously—such as the role of aerosol surface area and chloride availability—cannot be fully resolved within the scope of this modeling study, we agree that these issues will ultimately need to be addressed through targeted laboratory and observational investigations.

Overall, this is an important and timely contribution to the discussion of atmospheric oxidation enhancement (AOE), and we recommend publication after minor revision.

Scientific Comments

1. Efficiency of Cl_2 production from iron emissions

We believe the most important remaining issue concerns the efficiency of chlorine production from iron emissions.

Van Herpen et al. reported ~70 g Cl_2 per g of photoactive Fe emission per day under relevant conditions. If the underlying mechanisms are comparable, one would expect that an emission of

565 Tg iron in the present model would produce a chlorine response at least comparable to, or exceeding, that of the 1250 Tg Cl_2 emission scenario. Instead, the modeled response is substantially smaller.

To illustrate the discrepancy: emission of 565 Tg Fe in the form of $FeCl_3$ would contain approximately 1100 Tg of chlorine. A single photoreduction cycle of $FeCl_3$ would already release ~360 Tg Cl_2, and multiple catalytic cycles would be expected under atmospheric conditions. This suggests a substantial difference between expected chlorine production from $FeCl_3$ and the modeled outcome.

The explanation may lie in the implementation: the manuscript describes emissions of "particulate iron (pFe)." Although iron-chloride emission is referenced, it appears that the model may not treat the emitted iron as fully photoactive $FeCl_3$. For example, the model may apply solubility limitations or other speciation constraints before Fe(III) becomes available for photochemistry.

We therefore recommend that the author:

Provide the total increase in Fe(III) resulting from the modeled iron emissions.

Clarify whether the emitted iron is assumed to be fully photoactive $FeCl_3$ or treated as generic particulate iron.

Discuss how an intervention involving direct $FeCl_3$ emission might differ in efficiency from the particulate iron emissions implemented here.

This clarification is important for interpreting the environmental implications of iron-based AOE scenarios and for reconciling the model output with expected photochemical chlorine production.

I add a more explicit reference to the photoactive fraction of pFe explicitly in the main text: "The photoactive fraction of the emitted particulate iron for AOE model experiments is the same as other anthropogenic pFe, and is 26.8% (see Table S3) by accounting for both the solubility and Fe(III) speciation fractions."

I added clarifying text to Table S3 (Comparison of van Herpen et al. (2023) and Current Study for Iron and Chloride Scenarios) that the anthropogenic iron in the table "includes pFe emitted in the Iron and Iron_Chloride AOE experiments"

I add text addressing this to the results: "In addition, the properties of the emitted iron would affect the amount of iron needed to increase Cl_2. Meidan et al. (2024) emitted combustion-type iron (initially 6% soluble with 31.6% of that as photoactive, with a parameterization allowing the conversion of insoluble to soluble iron), similar to my approach of emitting anthropogenic iron (here, 40% soluble with 67% of that as photoactive, see Section 2.2.2.3). Pure $FeCl_3$ may require less total mass due to its higher solubility and pure Fe(III) speciation."

2. Oxidant-limited air pollution formation vs. "zero-sum" framing

In our original review, we raised the conceptual issue that for a fixed e.g. VOC emission, oxidation enhancement may alter the timing and spatial distribution of smog formation (O3 and PM) without a significant change in the global stoichiometric yield.

In the revision, the manuscript states that prior work suggests aerosol formation can be oxidant-limited (Shah et al., 2018; Mayhew and Haskins, 2025). These studies demonstrate that PM formation is oxidant limited for specific regional conditions e.g., winter sulfate formation over the eastern United States, but they don't show that the global yield is oxidant limited.

It would strengthen the manuscript to clarify that both perspectives can be valid:

Regionally and seasonally, aerosol production can indeed be oxidant-limited.
Globally and over longer time scales, oxidation enhancement may primarily redistribute the timing and spatial location of pollutant formation rather than substantially altering total yield.

Oxidation to aerosol particles is not the only fate of emitted gases. Instead, they may be dry or wet deposited before they can be oxidized to form aerosol. Hence, increasing the rate of oxidation could lead to increases in aerosol production on a global scale under constant emissions due to shifting the balance between oxidation and deposition removal processes.

I modify and add text clarifying with references related to sulfate aerosol in Section 3.1.4: "There are larger impacts on $PM_{2.5}$ from the hydrogen peroxide and OH methods (up to 14–19 μg m^{-3} in an individual model gridbox) than the Cl_2 and Cl_2_BrCl_Br_2 methods (up to 6–7 μg m^{-3} in an individual gridbox). These results are consistent with prior work suggesting that aerosol production can be oxidant-limited (e.g., Mayhew and Haskins, 2025; Shah et al., 2018), and observational and model studies showing that long-term declines in sulfate aerosol are weaker than those of SO_2 on a global and regional scale due to increasing SO_2 oxidation (e.g., Manktelow et al., 2007; Aas et al., 2019; Lin et al., 2025). Globally averaged, I find annual mean increases in $PM_{2.5}$ of 0 to 0.3 μg m^{-3} for Cl-based approaches and 0.3 to 0.4 μg m^{-3} for H_2O_2 experiments (see Figure S6)."

Another study I did not include in the text is Unger et al. (2006), which specifically isolated the change in sulfate aerosol in a future climate simulation due to increases in ozone, which led to increased rates of gas-phase oxidation of SO_2 by OH; this led to a 5% increase in sulfate aerosol on a global annual mean scale, with larger changes regionally (20% increase in annual mean sulfate in China and India).

In this study, I used the simplified representation of SOA in GEOS-Chem, which means its production from precursor gases is not affected by changing oxidant concentrations. However, a recent study quantified how rapid depositional loss leads to an overestimate of the extent of VOC oxidation on the path toward SOA production (Bi and Isaacman-VanWertz, 2025), meaning that the competition between oxidation and deposition is important, suggesting an increase in the oxidation rate (e.g., by increasing oxidants) could shift this balance.

Thus the location and timing of a hypothetical oxidation enhancement intervention would be critical for determining, and minimising, exposure to air pollution (air pollution view), and at the same time, a hypothetical oxidation enhancement will not produce additional radiative forcing from O3 and PM (climate view). In fact, tropospheric O3 would decrease as methane decreases.

A clarification along these lines would avoid misunderstanding and better present the details of the environmental impacts.

I add text clarifying to section 3.1.3: "At the same time, tropospheric ozone decreases in all AOE experiments (see Table 2) which could lead to a negative radiative forcing. Full radiative transfer calculations would be needed to quantify the overall impact."

As I describe in section 3.1.3, the increases in tropospheric inorganic aerosols predicted in this study could lead to negative radiative forcing: ". Increases in the tropospheric inorganic aerosol burden could lead to an additional negative radiative forcing."

3. Resolution and plume chemistry

The added discussion of coarse model resolution and plume dilution effects is appreciated. However, the reference to Mayhew and Haskins (2025) does not fully address the concern, as their nested grid simulations at 10 to 50 km resolution still represent several hours of atmospheric dispersion under typical wind speeds. This remains substantially coarser than the spatial and temporal scales of concentrated plume chemistry. We recommend that the author clarify whether coarse resolution is expected to bias methane response upward or downward in the ISA scenarios. Even a qualitative statement would improve clarity for readers assessing feasibility and uncertainty.

The reference to Mayhew and Haskins is specifically in the context of OH-based removal. Regardless of resolution, OH reacts with many other species besides methane, which is a very slow reaction relative to other species and this is the dominant controlling factor of the efficiency of OH-based AOE.

I add text to the Uncertainties – Model resolution section regarding plumes in the context of chlorine: "In this study, I emit species for the chlorine-based AOE experiments uniformly over all global oceans rather than in concentrated ship plumes. While coarse-resolution models may underestimate methane removal within these high-ClO_x plumes, Pennacchio et al. (2025) find that due to rapid dilution, iron salt aerosol released from ships would spend most of its atmospheric lifetime in a dilute, low-ClO_x regime, likely leading to an increase in methane over most of the global oceans after accounting for background NOx and ozone levels."

4. Chlorine background levels and comparison to CESM

For the Cl_2 emission scenario, the present study finds lower methane reduction compared to Li and Meidan. The author offers several explanations. We would like to suggest an additional possibility: CESM may have a higher background chlorine burden, which could help overcome nonlinear feedbacks more efficiently. A brief discussion of differences in background Cl levels between modeling frameworks could help contextualize the discrepancy.

We add a sentence: "The baseline present-day tropospheric Cl burden in Li, Meidan et al. (2023) was also larger (0.7 Mg vs. 0.313 Mg in this study)."

Technical Comments

5. Ensure consistent terminology distinguishing chloride (Cl^-) from chlorine (Cl, Cl_2) throughout, especially in emission scenarios.

Confirmed. One instance was modified "chlorine salts" to "chloride salts".

6. Verify that all percentage changes in tables and supplementary material are clearly labeled "%" in column headers.

Fixed 2 tables in the SI that had this issue.

7. Check typographical consistency in reaction rate formatting (e.g., exponential notation and spacing around units).

The reaction rates have the same format throughout the table in the SI.

8. Confirm that references to updated figures (e.g., Figures 2, 3, S4, Table S7) match final numbering.

SI Tables S1 and S2 were incorporated into Table 1 so these have been renumbered again, and modified throughout the text.

9. The phrase “model concentrations remained underestimated” would be clearer if rewritten as: “The model predicts concentrations that are lower than those observed in the field study.” This improves clarity and is more objective in tone - saying that there is a difference, but not necessarily saying that the observations are correct.

Modified the sentence as follows: “While adding the mechanism greatly improved the model performance of [Cl_2] at Wangdu, increasing simulated concentrations by a factor of 28 to 48, the modeled concentrations remained lower than those observed.”

Overall Recommendation

The author has addressed the major concerns in a serious and substantive manner, and the manuscript has improved considerably. With clarification of the oxidant-limitation framing and, most importantly, clearer treatment of iron emission speciation and chlorine production efficiency, the manuscript will be suitable for publication.

Additional references in this review not included in the revised manuscript:

Bi, C., Isaacman-VanWertz, G. Formation of late-generation atmospheric compounds inhibited by rapid deposition. *Nat. Geosci.* 18, 213–218 (2025). https://doi.org/10.1038/s41561-025-01650-2

N. Unger, D.T. Shindell, D.M. Koch, & D.G. Streets, Cross influences of ozone and sulfate precursor emissions changes on air quality and climate, Proc. Natl. Acad. Sci. U.S.A. 103 (12) 4377-4380, https://doi.org/10.1073/pnas.0508769103 (2006).

Response to Reviewer 2

I wish to thank Hannah Horowitz for the very thorough reply to my initial review of the paper: "Intended and Unintended Consequences of Atmospheric Methane Oxidation Enhancement". My concerns were adequately addressed. I do have some comments on the revised version, mostly in terms of organization and explanation.

Thank you to the reviewer for your additional comments which have improved the quality of the paper.

1. Introduction (L50-L53). It would be nice to know here how what you have done differs from previous studies.

Added a sentence: "Unlike previous studies, here I use the Chen et al. (2024) chlorine production mechanism to investigate iron salt aerosol, simulate global-scale OH-based AOE and its impacts, and use the GEOS-Chem model which has different background halogen chemistry to assess Cl-based AOE."

2. Section (2.2). I find this section confusing as (i) it mixes discussing the simulations and results and (ii) it omits a number of simulations in table 1 that are discussed in the text. Moving results to the result section would clarify this section so as not to mix the results together with the description of the simulations.

I removed the results-type discussion from section 2.2.1.1 and moved the part about negligible results to the beginning of Section 3 (results) and the part about effects of stack height and daytime-only emissions in the global scenarios to Section 3.1.2. I also removed Table S1 (simulations that produced negligible results) as these are included in Table 1 and discussed in Section 3.

I would suggest explicitly adding the standard and standard plus chen simulations to table 1, and discussing these separately. I think the discussion of chen is included under the category "Iron salt aerosol". This should be listed as a separate simulation. I don't think the OH simulations are listed in the table.

At the end of section 2.1 I added a sentence describing that this represents the Standard simulation. I split section 2.2.2.3 into two sections, with section 2.2.2.3 describing the Standard + Chen simulation (I also add a sentence explicitly defining as such), and 2.2.2.4 describing the iron salt aerosol emissions experiments.

Adding H2O2_sens as a group of simulations to the table would be helpful. Then you could

discuss the various results in the results section and justify why you concentrate on the surface emissions.

I added the 4.1 Tg/yr H2O2 simulations to Table 1 (moved from Table S1), and I marked simulations with a dagger and footnote highlighting the 3 experiments for which I performed daytime-only sensitivity tests.

The OH chemical production should be added to the table.

I moved these from the supplementary Table S2 to the main table, and removed Table S2. Remaining supplementary tables have been renumbered.

3. Some more details on the aerosol scheme with respect to the emitted species would be helpful when describing the model. What exactly is "accumulation mode aerosol chloride and particulate iron (pFe) " (line 228). Is this a new aerosol type or does it have the properties of seasalt aerosol with a fixed Fe/Cl ratio? I'm uncertain about what happens to particular iron when it is emitted. Does it combine with seasalt aerosols. Which version of the model are these species emitted into?

I add a sentence to the initial model description (Section 2.1) to clarify that "Aerosols are assumed to be fully externally mixed." and add "pFe" following the first introduction of particulate iron in this section.

I modify and add lines in this section to clarify the questions above:
"First I perform GEOS-Chem simulations with the additional reaction of iron-mediated Cl_2 release from chloride aerosol from Chen et al. (2024) (Standard + Chen simulation; section 2.2.2.3) in the absence of any additional emissions to act as a reference point for the iron salt aerosol emissions-based atmospheric oxidation enhancement experiments. Then, within the Standard + Chen simulation to release additional Cl_2 from iron salt aerosol, accumulation mode aerosol chloride (Cl^-) and particulate iron (pFe) are released over the oceans at the surface in four scenarios to assess the driving factors and compare against the direct Cl_2 scenario. Accumulation mode aerosol Cl^- and pFe are existing species within GEOS-Chem, where Cl^- is sea salt chloride with the physical properties of sea salt aerosol and the molecular weight of chlorine, and pFe represents anthropogenic particulate iron (see also Sections 2.1 and 2.2.2.3)."

4. Uncertainties. You probably should mention interannual variability as the simulations only compare one year. Also, while I understand the global CH4 burden is corrected by a feedback factor using fixed surface concentrations, I worry the surface chemistry, where a lot of the emissions occur, may be impacted by the fixed surface concentrations. Admittedly this effect

may be small due to long methane lifetime. Does the author have any thoughts on this?

I add a sentence to the uncertainties section: "The 1-year simulation also does not capture potential interannual variability in AOE effects due to meteorology or emissions."

I add a section about the fixed surface concentration :

"Fixed boundary condition for methane. **Surface-level methane concentrations are fixed, including during the AOE model experiments, potentially affecting the predicted atmospheric chemistry impacts at the surface. However, given the long lifetime of methane, methane concentrations during the 1 year of simulated AOE decrease by <1% everywhere, including just above the surface layer and at other altitudes where OH (in H_2O_2 experiments) or Cl (in Cl-based experiments) increase by more than 100%. As discussed in Section 2.1, the simplified surface representation does not impact estimates of changes in steady-state methane (e.g., Khodayari et al., 2015)."**

5. I like the idea of a summary figure but I feel the author could do more with this. The figure rather begs the question of the overall magnitude of the change. The bars showing the sign of the change could be color coded for magnitude. In addition, the table is not altogether accurate as it in some Cl experiments methane increases as it does in the Chen scheme in comparison to the standard model. The experiments represented should be explicitly given, or it might be possible to give a few by splitting the arrows into parts.

I clarified the description of the Chen scheme in response to a prior comment. I split into 5 columns of representative experiments, color-coded and changed size of arrows to represent impacts. I also removed the stratospheric ozone part as I removed this discussion based on the previous round of reviews.

Technical Comments

1. Table 2 description. This table also includes basic global budgets and not just percentages.

Changed: "Simulated global annual mean tropospheric burdens of selected species and chemical families and their percent change due to atmospheric oxidation enhancement."

2. L33: "methods appropriate for ambient concentrations". Ambient concentrations of what? The meaning here is somewhat unclear.

Added "methane" here to clarify.

3. L77: "offline at the native model resolution". Native to what?

Revised for clarity: "at the native resolution of the MERRA-2 meteorology (0.5° × 0.625°)"

4. Table 2: In terms of emitted species (Tg/yr), is this for the entire species (e.g., iron chloride) or for just Cl?

I added "by Species" to the table header ("Total Emissions by Species (Tg/yr)") so it is more clear each number in this column refers to the specific species in the column directly to the left.

5. L275 "the partitioning of gas-phase Cly shifts away from HCl toward chlorine hydroxide." In the H2O2 experiments?

Yes, added "in the H_2O_2 experiments" to clarify.

6. L324 "fully responsive concentrations at the surface". I'm not sure I follow the meaning here.

Revised for clarity : "In this region, methane levels remain high due to the surface boundary condition and long lifetime against reaction with OH; as CO does not have a fixed surface boundary condition, here it is reacted away by the additional OH, and its loss rate slows down due to its shorter lifetime."

7. L350 -15% to 50%. Probably omit the minus sign.

For consistency with the quantities in the next half of this sentence ("here –20% at steady-state vs. –45% in year 2050") I choose to add another negative sign so it is more clear: "-15% vs. -50%" .

8. L353-354: Is the vertical distribution of Cl different? Is this shown somewhere?

No, I add text clarifying. I do not have access to their model results.

"While a quantitative comparison of the vertical distribution of Cl concentrations between the two models is not able to be conducted here, I hypothesize that model differences may influence this distribution."