

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 $\delta^{13}\text{C}$ 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 FeCl₃ or treated as generic particulate iron.

Discuss how an intervention involving direct FeCl₃ 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.

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.

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.

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.

4. Chlorine background levels and comparison to CESM

For the Cl₂ 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.

Technical Comments

5. Ensure consistent terminology distinguishing chloride (Cl^-) from chlorine (Cl , Cl_2) throughout, especially in emission scenarios.
6. Verify that all percentage changes in tables and supplementary material are clearly labeled “%” in column headers.
7. Check typographical consistency in reaction rate formatting (e.g., exponential notation and spacing around units).
8. Confirm that references to updated figures (e.g., Figures 2, 3, S4, Table S7) match final numbering.
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.

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.