Response to Anonymous Referee #2 – Development of iron-mediated molecular chlorine chemistry in GEOS-Chem: model description, evaluation and global atmospheric implication

We are grateful for the feedback and guidance of reviewer. The comments and concerns have been addressed carefully. Exact comments from the reviewer are in black italic type. Our responses (indent and in normal font) and the corresponding edits in the manuscript (indent and in blue) are shown below.

Comments from Anonymous Referee #2:

Chen et al. implement an iron-mediated Cl_2 formation pathway into the GEOS-Chem CTM and present the subsequent atmospheric impacts of this scheme on tropospheric chemistry, oxidative environment and PM. The description and evaluation of this scheme is detailed and clear, showing a strong improvement to model bias for Cl_2. I have the following comments and questions for the authors.

Response in general: We are grateful to the reviewer for the very constructive comments and the recognition.

Main comments:

1. Whilst the authors evaluate the model bias changes on Cl_2, there are a number of substantial atmospheric implications from this work which are also of interest, and I believe would help to further evaluate this scheme. There is a number of ways the authors could do this, which would utilise the data they already have and not extend the analysis performed in this paper significantly. They could present tropospheric O_3 burden, global area-weighted-mean OH, methane lifetime and other key whole atmosphere diagnostics for each of the 3 model versions. Additionally with the large changes in surface O_3, all model versions could be compared to readily available observational datasets (such as from GAW or TOAR) to better understand the consequences of the additional Cl chemistry with the context of the base model performance.

Response 1: Thanks for these helpful comments.

(1) Key atmosphere diagnostics for different simulation scenarios.

We calculated several key diagnostics for the three model versions. The tropospheric O_3 burden is 367.9 Tg in the Base scenario, while it decreases to 364.8 and 357.3 Tg in the FixFeS and VarFeS scenarios, respectively. Compared to the Base scenario, the O_3 burden decreases by 2.9% in VarFeS. This reduction is mainly associated with enhanced chlorine activation under the IMC mechanism, which increases Cl radical levels and promotes direct O_3 destruction through Cl–O_3 reactions as well as $ClONO_2$ formation. In addition, perturbations to the RO*x* and HO*x* cycling further affect the global OH abundance. The global surface mean OH concentrations are 8.41×10^5, 8.33×10^5, and 8.16×10^5 molec cm^{-3} for the Base, FixFeS, and VarFeS scenarios, respectively. With the inclusion of the IMC mechanism in the FixFeS and VarFeS scenarios, OH concentrations decrease accordingly, mainly due to decreases in O_3 weaken primary OH production and conversion of HO*x* to ClO*x*.

A comprehensive assessment of the overall CH_4 lifetime is beyond the scope of the present study, as our main objective is to quantify the effects of the IMC mechanism on atmospheric oxidative capacity and $PM_{2.5}$ formation. Nevertheless, the GEOS-Chem model provides a diagnostic CH_4 lifetime with respect to OH oxidation, which can be used to evaluate the indirect influence of IMC-induced OH perturbations on CH_4 loss. The diagnosed CH_4 lifetime relative to OH are 8.32, 8.39, and 8.54 years for the Base, FixFeS, and VarFeS scenarios, respectively. Compared with the Base case, the IMC mechanism increases this CH_4 lifetime by 0.07 years (0.8%) in FixFeS and by 0.22 years (2.6%) in VarFeS, through its reduction of global OH concentrations. It should be noted that the CH_4 lifetime presented here only reflects the indirect effect of IMC through OH perturbations and does not include the direct CH_4 loss via reaction with Cl radicals. Further analysis of the CH_4 via Cl loss pathway and the full CH_4 chemical budget would help to better constrain the net impact of IMC on methane lifetime. We have added the discussion of tropospheric O_3 burden and global surface mean OH to the revised manuscript, as below.

Page 11 Line 399-400 in the revised manuscript: "With the inclusion of IMC mechanism, the global annual mean surface OH concentrations decreased by 2.5×10^4 atoms cm^{-3}, which corresponds to a 5.7% relative reduction compared to the "Base" scenario."

Page 12 Line 431-433 in the revised manuscript: "Consistent with the widespread decreases in surface O_3 outside high-NO*x* source regions, the tropospheric O_3 burden declines from 367.9 Tg in the Base scenario to 357.3 Tg in the VarFeS scenario, corresponding to a 2.9% reduction."

(2) Surface ozone concentration evaluation

For the surface O_3 evaluation, we used in-situ observations from several publicly available air-quality monitoring datasets, including OpenAQ (https://openaq.org), the China National Environmental Monitoring Centre (http://www.cnemc.cn), the U.S. Environmental Protection Agency (https://www.epa.gov), and the European Environment Agency (https://www.eea.europa.eu/en). Simulation results were sampled at the observation sites and annual mean O_3 concentrations were used for comparation. As shown in Fig. R1, including the IMC mechanism systematically enhances model performance. Specifically, the correlation coefficient increases from 0.64 for Base scenario to 0.65 and 0.72, while the RMSE drops from 15.44 to 14.92 and 13.62 $\mu g\ m^{-3}$ and the mean bias decreases from 6.68 to 6.04 and 5.26 $\mu g\ m^{-3}$ for FixFeS and VarFeS scenario, respectively. These results indicate that the inclusion of the IMC mechanism improves the model representation of annual mean surface O_3, with the most pronounced improvement obtained in the VarFeS scenario.

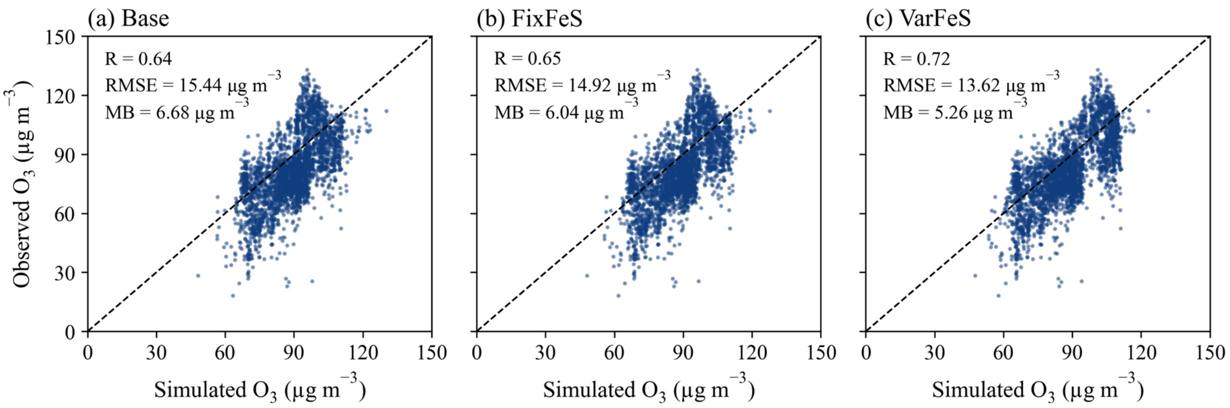

Figure R1. Comparison of observed and simulated annual mean surface O_3 concentrations for the (a) Base, (b) FixFeS, and (c) VarFeS scenarios. The dashed line denotes the 1:1 line. R, RMSE, and MB represent the correlation coefficient, root mean square error, and mean bias, respectively.

We have added a new section, "Text S1: Evaluation of surface O_3 concentrations", to the revised supplementary materials, and the corresponding statement has also been included in the revised manuscript, as below.

Page 12 Line 425-426 in the revised manuscript: "Including the IMC mechanism improves the model representation of surface O_3 relative to the Base scenario (Text S1 in the supplementary Materials), this provides further context for interpreting the simulated O_3 responses."

Page 11 in the revised supplementary materials: "To further assess whether the inclusion of the IMC mechanism affects the model representation of surface ozone, we compared simulated annual mean surface O_3 concentrations with in-situ observations from publicly available air-quality monitoring datasets, including OpenAQ (https://openaq.org), the China National Environmental Monitoring Centre (http://www.cnemc.cn), the U.S. Environmental Protection Agency (https://www.epa.gov), and the European Environment Agency (https://www.eea.europa.eu/en). As shown in Fig. S13, the inclusion of the IMC mechanism improves the model–observation agreement for surface O_3. Specifically, the correlation coefficient increases from 0.64 in the Base simulation to 0.65 and 0.72 in the FixFeS and VarFeS simulations, respectively. Meanwhile, the RMSE decreases from 15.44 μg m^{-3} to 14.92 and 13.62 μg m^{-3}, and the mean bias decreases from 6.68 μg m^{-3} to 6.04 and 5.26 μg m^{-3}, respectively. These results suggest that the including IMC mechanism improves the annual mean model performance, with the most pronounced improvement in the VarFeS scenario."

2. The authors could further explore the effects of this scheme on particulate matter with further discussion on both the areas of increase and decrease and the respective drivers of these.

Response 2: Thanks for this critical comment. We have enriched the discussion regarding the spatial heterogeneity of $PM_{2.5}$ changes in the revised manuscript, as below.

Page 13 Line 453-484 in the revised manuscript: "Including the IMC mechanism significantly reshapes the global AOC by modulating radical cycling, which subsequently exerts a distinct influence on the formation and spatial distribution of fine particulate matter ($PM_{2.5}$) pollution, as shown in Fig. 6.

Spatially, $PM_{2.5}$ enhancements are primarily concentrated in the mid-to-high latitude land areas of the Northern Hemisphere. While slight increases of roughly 0.5% are found in western Europe, northern America, Canada, and parts of the Arctic Ocean, the most pronounced response appears over the NCP, where $PM_{2.5}$ rises by up to 2.5% (+2.2 $\mu g\ m^{-3}$). From the perspective of chemical composition (Fig. S10), the $PM_{2.5}$ enhancement is predominantly driven by nitrate formation. Over the NCP, nitrate rises by 1.9 $\mu g\ m^{-3}$, accompanied by a smaller increase in ammonium (+0.4 $\mu g\ m^{-3}$). This nitrate-dominated response is closely linked to elevated Cl_2 concentrations. Photolysis of Cl_2 generates highly reactive Cl radicals that substantially increase OH levels over the NCP. Since OH radicals are the critical daytime oxidants driving the conversion of nitrogen oxides into nitrate (Liu et al., 2020; Wang et al., 2026), the strengthened oxidizing environment accelerates nitrate formation and thereby increases $PM_{2.5}$ mass concentration. This is consistent with previous studies reporting that increasing AOC significantly contributes to enhanced nitrate and $PM_{2.5}$ concentrations (Feng et al., 2021; Fu et al., 2020; Zang et al., 2022). Importantly, this mechanism is further amplified under wintertime conditions, when stagnant meteorology and elevated precursor emissions coexist. In winter over the NCP, $PM_{2.5}$ increases can reach up to 6.2% (Fig. S11). High NO_x levels, frequent stagnation, shallow boundary layers, and low-temperature conditions favorable for particulate nitrate stability collectively promote the partitioning of HNO_3 into the particle phase. As a result, nitrate formation is substantially enhanced, leading to a pronounced increase in $PM_{2.5}$ in this region.

In contrast, regions located downwind of the enhanced Cl_2 production zones, as well as adjacent marine areas, exhibit a general decrease in $PM_{2.5}$ concentrations. This reduction is likely attributable to the accelerated oxidation of NO_x and other precursors near the source regions under strengthened AOC. As NO_x is more rapidly converted to HNO_3 and subsequently to particulate nitrate, these species undergo earlier deposition and removal, thereby diminishing the reservoir of precursors available for long-range transport and secondary aerosol formation. Consequently, the downwind regions experience lower $PM_{2.5}$ levels. In addition, this decreasing pattern is also consistent with the spatial distribution of sulfate reductions (Fig. S10). Under conditions of enhanced HO_x cycling, nitrate and sulfate do not respond uniformly to the IMC mechanism. While nitrate formation is strongly driven by increased OH oxidation (Liu et al., 2020; Wang et al., 2026), sulfate production is governed not only by gas-phase OH oxidation of SO_2 but also by aqueous, heterogeneous, and transition-metal-catalyzed oxidation pathways (Guo et al., 2024; Gao et al., 2024; He et al., 2025). Besides, hydroxymethanesulfonate (HMS) formed through the reaction between dissolved SO_2 and HCHO can subsequently be oxidized by aqueous OH radicals to sulfate (Song et al., 2019, Ma et al., 2020, Dovrou et al., 2022). Though elevated regional OH levels promote HCHO production which further increases the concentration of HMS (Fig.S12), HMS formation may temporarily sequester precursor SO_2, and its subsequent oxidation is likely insufficient to offset the suppression of sulfate formation via direct SO_2 oxidation. Therefore, sulfate concentrations slightly decrease over the NCP despite the enhanced OH levels."

3. For emission inventories, many in GEOS-Chem will cycle the most recent year available if the current year the model is being run in is unavailable. Could the authors specify the emission years for the CEDS inventories as more recent changes (such as to sulfur emission standards for shipping) may not be captured in this study and could have a potential impact on the results presented.

Response 3: Thank you for this insightful comment. The CEDS anthropogenic emissions used in this study are from CEDS v2025-04 (https://doi.org/10.5281/zenodo.15059443) which extends to 2023 and updates shipping fuel sulfur content by incorporating IMO sulfur-content agreements. For our simulations, the corresponding-year CEDS emissions were used directly rather than being cycled from an earlier available year. Therefore, the effect of recent shipping sulfur reductions associated with the IMO 2020 low-sulfur regulation for shipping has been represented in the CEDS emissions as well.

We have clarified the year used for the different inventories in the revised manuscript, as below.

Page 4 Line 124-127 in the revised manuscript: "In this study, anthropogenic non-BB Fe emissions are scaled to anthropogenic primary sulfate emissions from the Community Emissions Data System (CEDS) emission inventory which extends to 2023 and updates shipping fuel sulfur content by incorporating IMO sulfur-content agreements, assuming a fixed mass ratio of 1:30 following previous studies (Chen et al., 2024; Alexander et al., 2009)."

Page 6 Line 231-232 in the revised manuscript: "All emission inputs correspond to the simulation year 2023 except for AEIC aircraft emissions and AFCID, which are based on year 2019 and 2015 due to data availability."

4. The authors have employed a 6-month spin-up period, the atmospheric impacts are substantial and it is more common for such changes (especially concerning O_3) to run for 1 year or more for this spin-up period. Could the authors consider a longer spin-up period to align this more closely with other studies and further settle any changes in longer-lived species.

Response 4: Thanks for your constructive suggestion. To address this concern, we conducted an additional sensitivity simulation with a 1-year spin-up period and compared the O_3 responses induced by the Fe(III)-mediated Cl_2 formation mechanism under the two spin-up settings. As shown in Fig. R2, the absolute O_3 changes between 'VarFeS' and 'Base' scenarios are highly consistent between the 6-month and 1-year spin-up simulations, with the vast majority of regions showing negligible deviations, indicating that the mechanism-induced O_3 perturbation is not sensitive to extending the spin-up period from 6 months to 1 year. Since our study primarily investigates the impacts of iron-mediated Cl_2 formation on relatively short-lived reactive species (e.g., reactive chlorine species, RO_2, HO_x) and their immediate influence on O_3 and $PM_{2.5}$, we believe the 6-month spin-up duration is acceptable for this study. We appreciate this perspective and will ensure that a longer spin-up period is implemented in our future work, particularly for studies involving complex cycles of long-lived species.

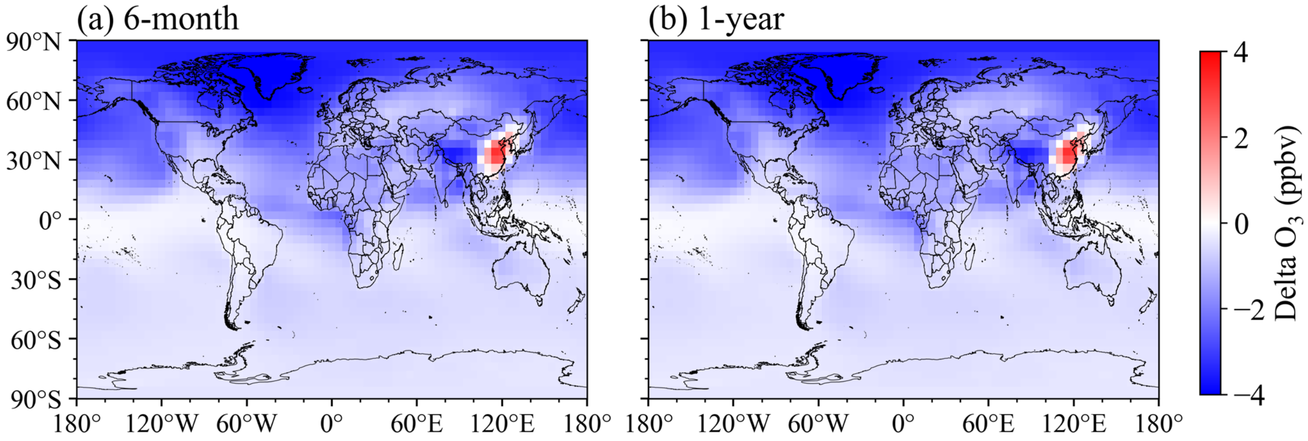

Figure R2. Comparison of absolute changes (VarFeS-Base) of O_3 for (a) 6-month and (b) 1-year spin-up simulations.

Minor/technical comments:

1. When referencing the GEOS-Chem model version (in this case 14.2.3), DOIs are available for all major and minor releases which improve the transparancy and ease of recovering the exact model version used in studies. These are archived on Zenodo and also detaild on the GEOS-Chem readthedocs/wiki.

Response 5: We have added the corresponding DOI citation for GEOS-Chem version 14.2.3 as archived on Zenodo to the revised manuscript, as shown below.

Page 2 Line 71-72 in the revised manuscript: "Global chemical transport model GEOS-Chem (version 14.2.3, https://doi.org/10.5281/zenodo.10246546) was employed to assess the influence of reactive chlorine chemistry on atmospheric processes."

2. The authors have used the reduced vertical grid for this study (47 levels). There have been several issues raised with this (some arising and being fixed by later versions). One that comes to mind is issues with the accuracy of the photolysis in the 47-layer grid, whilst this is most noticeable in the stratosphere, do the authors believe this or any other issues could have any bearing on the results they present?

Response 6: Thanks for raising this important point. We note that a specific 47-layer initialization issue has been reported for GEOS-Chem v14.6.0–v14.6.3 (https://github.com/geoschem/geos-chem/issues/3170), which may affect stratospheric species and photolysis rates. However, our simulations were performed using GEOS-Chem v14.2.3. Since this issue was confirmed not to exist before v14.6.0, our simulations are not affected by it. Regarding the general difference between the 47-layer and 72-layer configurations, the 47-layer grid preserves the native vertical structure through the troposphere and lower stratosphere, with vertical layer lumping only beginning in the stratosphere, above approximately 70–80 hPa. Therefore, the vertical resolution directly relevant to boundary-layer chemistry, surface O_3, and $PM_{2.5}$ is retained. As the present study focuses primarily on tropospheric and near-surface impacts of Fe(III)-mediated Cl_2 activation, the reduced vertical grid is unlikely to substantially influence our main conclusions. In addition, our conclusions are based on differences between paired simulations using the same vertical grid configuration, namely the Base simulation and the VarFeS simulation including the Fe(III)-mediated Cl_2 activation mechanism. Any systematic influence associated with the reduced vertical grid would thus be largely shared by both simulations and is expected to have a limited impact on the relative changes used to evaluate the chemical mechanism. Accordingly, we have added a new section, "Text S2 Other potential uncertainty analysis.", to the revised supplementary materials to discuss this uncertainty, and the corresponding statement has also been included in the revised manuscript, as below.

Page 9 Line 324 in the revised manuscript: "Other potential uncertainties are discussed in Text S2 in the supplementary materials."

Page 11 in the revised supplementary materials: "Additional uncertainties may also arise from the reduced vertical-grid configuration used in this study. This configuration reduces vertical resolution primarily in the stratosphere and mesosphere, which could introduce uncertainties in stratospheric chemical and transport processes. Since this study focuses mainly on near-surface responses and relative differences between simulations using the same vertical-grid configuration, these uncertainties are expected to have a limited influence on the main conclusions. Future studies specifically targeting stratospheric responses could adopt the full 72-layer configuration or additional sensitivity simulations to further assess the influence of vertical resolution."

3. As this work has involved several changes to the GEOS-Chem source code, it would be good practice for the authors to make these changes publicly available and archived so that results could be replicated. This could be done in a similar version to the public version of GEOS-Chem with the authors using GitHub/Zenodo.

Response 7: Thanks for this comment. The modified GEOS-Chem source-code files associated with Fe dissolution processes and Cl_2 formation mechanisms implemented in this study will be archived on Zenodo and made publicly available upon acceptance.