Review of “Development of iron-mediated molecular chlorine chemistry in GEOS-Chem: model description, evaluation and global atmospheric implication” by Chen et al. 2026, Atmospheric Chemistry and Physics (ACP).

Reviewed by: M.M.J.W. van Herpen

This manuscript describes an improved iron-mediated Cl_2 formation mechanism that is implemented into the GEOS-Chem global model. The mechanism is based on earlier work by van Herpen2023 [1], who used the CESM global model. The authors have made important improvements to the mechanism that are critical to enable a global evaluation of the mechanism. The authors have implemented five tracers for iron bearing species with different properties, along with a representation of acid processing for iron solubility. This enables the authors to evaluate the mechanism globally, while the mechanism used by vanHerpen2023 was only adapted for the North Atlantic region. The resulting model output was compared with observed Cl_2 concentrations, and shows improved correlation. The authors analyze the model output to provide a global evaluation of the mechanism’s environmental impact, and describe the impact on atmospheric oxidation capacity, ClOx, HOx, NOx and secondary aerosol (PM 2.5).

Overall, I believe this work represents an important improvement to the mechanism and provides important conclusions, making it suitable for publication in ACP. Below I provide some comments that I believe are important to address before publication.

Detailed comments

Line 34-35: Add reference for field studies to Röckmann2024 [2].

Line113-114: What is meant with ‘fine and coarse modes’? Please specify the aerosol diameters. Was this added to the DST1 – DST4 bins described in lines 90-95, or are these separate bins?

Line 115-116: Antropogenic non-BB Fe emissions are scaled to primary sulfate emissions. What is the impact of recently reduced sulfur emissions in shipping on this?

Line 126: Can you elaborate why non-dust uses hydrophilic and hydrophobic black carbon properties, and how this is implemented. Considering the high solubility of biomass burning Fe, would that not imply at least some hydrophillic properties?

Line 140-145: What are the K values used for the different dust types in the model? The authors refer to Meskhidze, who found that calcite ($CaCO_3$) strongly buffers deliquesced dust aerosols with a pH that remains close to 8 until the amount of acid added to the aerosol solution exceeds $CaCO_3$ alkalinity. The implication reported by Meskhidze is that very high intensity dust events would have very low soluble iron. It is not clear whether or how the authors have taken this into account in their model. Considering the authors only include hematite, illite and smectite in the model (Table 1), I am concerned that calcite and its effect on H+ is not included. That would have substantial implications for the conclusions.

Line 151: It is known from Wittmer2014 [3] that oxalate has two opposite types of impact on iron-mediated chlorine production. First, oxalate forms a stable and dominant complex with Fe(III) that diminishes the Fe(III)–Cl complexation and thus the direct activation of chloride. At the same time, the photolysis of the Fe(III)–oxalate complexes leads to a formation of H_2O_2 and this stimulates the reoxidation of Fe(II) (rate k1 of equation 6 at line 180), accelerating the production rate of Cl_2. This creates an uncertainty for the model implementation of the IMC mechanism. The authors should discuss this in more detail, and ideally would also include a sensitivity assessment, for example through a model run that excludes ligand-mediated dissolution.

Line 182-183: The rate k1 of equation 6 is based on VanHerpen2023, who based this rate on a typical aerosol H_2O_2 concentration of 50 µM. A suggestion for an improvement to the mechanism is to make k1 dependent on modelled H_2O_2 concentrations in GEOS-Chem. I understand that this suggestion might be beyond the scope of the current work, but if the authors would consider this improvement, it would add important additional value to the manuscript.

Line 225 (results section): Can the authors provide total Cl_2 production values for the different Fe sources? In other words, what Fe source from Table 1 is the main contributor to Cl_2 production?

Line 266: I don't agree with the authors that the ~30% magnitude of Cl_2 concentrations reflects the inability for the FixFeS scenario to represent realistic photoactive Fe abundances in certain regions, because an increase in the reaction rates of equation 6 would increase it in line with the observations. Thus, the lower Cl_2 concentrations are more likely indicating an underestimation of the rates in equation 6. Instead, I would agree if the authors would use the correlation coefficient to argue for better performance by the VarFeS scenario.

Line 265: The fixed 1.8% fraction is based on the assumption that the photoactive fraction is not the same as soluble fraction, but it is the fraction of soluble iron that can be oxidized and reduced repeatedly (VanHerpen2023). This is represented by the FixFeS scenario in the manuscript. The VarFeS scenario assumes that photoactive fraction is equal to the soluble fraction. However, the sentence at line 265 that refers to "photoactive Fe reaches 32%" should be rephrased to "soluble Fe reaches 32%", because the number reported in the reference is the total soluble iron fraction.

Line 283: change "global mean Cl_2 concentrations" into "global mean surface Cl_2 concentrations"

Line 299: Can the authors elaborate on this, because both the production (eq6) and the loss (photolysis) are depending on solar radiation. Weakened solar radiation would therefore reduce both Cl_2 production and Cl_2 photolysis at the same time, so why would this explain accumulation of Cl_2 at the surface?

Line 305: Could the authors include in the supplemental information a figure that shows Cl_2 production rate (molec/cm^3/s). This helps the reader distinguish between production effects and loss effects for Cl_2.

Line 332: The authors should refer to Pennacchio2025 [4] in this section, where the effects of Cl_2 emission on atmospheric oxidation capacity have been investigated, including the role of NOx and ozone. Pennacchio2025 reported that $ClONO_2$ hydrolysis is an important reaction that influences AOC. Do the authors see the same in the GEOS-Chem model output?

Line 365: Following Pennacchio2025, the impacts of Cl_2 emission are strongly depending on the local intensity of Cl_2 emissions. This can explain part of the difference between the NCP region and other regions, because the NCP region has the highest intensity of Cl_2 emissions.

Line 385: While the authors are discussing increased PM2.5 in certain regions, they fail to point out that in other regions the PM2.5 decreases. The authors note that the reason for the PM2.5 increase in the NCP region is the accelerated conversion of nitrogen oxides into nitrate (line 393). What the authors should include in this discussion is that this also implies that PM2.5 is reduced in other locations. This is visible in Figure 6, which shows reduced PM2.5 downstream of the NCP region. This is an important finding, because it means that the location of chlorine enhancement will determine whether air quality improves or declines in certain population zones. Or in other words, it appears PM2.5 is not increased globally, but instead it is displaced geographically.

Line 385: The model uses only a short spin-up period of 6 months. For the conversion of nitrogen oxides into nitrate this is sufficient spin-up time. However, is it sufficient to create a stable state for other important mechanisms that produce fine particle matters?

Line 417: The conclusions should note that PM2.5 is also reduced elsewhere. E.g. the conclusion could be rephrased to say "with localized PM2.5 surges reaching 6%, while PM2.5 is reduced downstream."

Line 20 (abstract): Similar to my comments on PM2.5 above, the authors should also rephrase line 20 in the abstract to include that PM2.5 is reduced downstream of the region with enhanced AOC.

Line 403: There are two relevant studies that implemented an iron-mediated chlorine production mechanism in a global model, to which the authors should compare their result. The first one is Chen2024 [5] from the same group as the current manuscript, but uses a very different mechanism. The second study is Meidan2024 [6], who also implemented an IMC mechanism combined with iron dissolution.

Supplemental information: Figure S5: Adjusting the color scale of the top of the figure will improve visibility. Also, can the authors also include a list of Cl_2 observations in the supplemental info?

References

1. van Herpen, M.M., Li, Q., Saiz-Lopez, A., Liisberg, J.B., Röckmann, T., Cuevas, C.A., Fernandez, R.P., Mak, J.E., Mahowald, N.M., Hess, P. and Meidan, D., 2023. Photocatalytic chlorine atom production on mineral dust–sea spray aerosols over the North Atlantic. Proceedings of the National Academy of Sciences, 120(31), p.e2303974120.
2. Thomas Röckmann et al 2024 Environ. Res. Lett. 19 064054, https://iopscience.iop.org/article/10.1088/1748-9326/ad4375
3. Julian Wittmer, Sergej Bleicher, and Cornelius Zetzsch, Iron(III)-Induced Activation of Chloride and Bromide from Modeled Salt Pans, The Journal of Physical Chemistry A 2015 119 (19), 4373-4385 DOI: 10.1021/jp508006s https://pubs.acs.org/doi/10.1021/jp508006s
4. Luisa Pennacchio, Maarten van Herpen, Daphne Meidan, Alfonso Saiz-Lopez, and Matthew S. Johnson, Catalytic Efficiencies for Methane Removal: Impact of HOx, NOx, and Chemistry in the High-Chlorine Regime, ACS Earth and Space Chemistry 2025 9 (3), 504-512 DOI: 10.1021/acsearthspacechem.4c00283 https://pubs.acs.org/doi/abs/10.1021/acsearthspacechem.4c00283
5. Chen, Q., Wang, X., Fu, X., Li, X., Alexander, B., Peng, X., Wang, W., Xia, M., Tan, Y., Gao, J., Chen, J., Mu, Y., Liu, P., and Wang, T.: Impact of molecular chlorine production from aerosol iron photochemistry on atmospheric oxidative capacity in North China, Environ. Sci. Technol., 58, 12585-12597,doi: 10.1021/acs.est.4c02534, 2024.
6. Daphne Meidan et al 2024 Environ. Res. Lett. 19 054023, https://iopscience.iop.org/article/10.1088/1748-9326/ad3d72