

Interactive comment on “Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols” by J. Mao et al.

Anonymous Referee #1

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I really liked this paper, as an important modeling exercise to demonstrate the potential for HO₂ loss on tropospheric aerosol. The main point in the paper is that dissolved transition metal ions may be sufficiently concentrated in aerosol water (i.e. much more concentrated than in cloud water), so that they may play an important role as catalysts in the loss of HO₂ being taken up from the gas phase. This general idea is not new, first gaining prominence from, for example, the experimental work of Mozurkewich in the late 1980s. However, what is new in this paper is the suggestion that couplings between the reactions of copper and iron ions can lead to the production of H₂O from this chemistry, and not the product that is usually assumed, H₂O₂. This has an impact on the atmosphere, as indicated by GEOS-CHEM CTM modeling runs that show that this chemistry can lower OH, O₃, and affect CO levels in a manner that leads to better agreement with observations.

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I recommend the paper for publication, but I would like to see the authors consider the following points before publication.

The modeled effects are dependent on a number of assumptions including: internally mixed aerosol, the concentrations of transition metals ions, that all aerosol is aqueous, and that the assumed kinetics/chemistry is correct. While the authors mention that this modeling result is likely an upper limit to the effects, I think it should be pointed out more forcefully. Indeed, I view this paper as more of a modeling exercise to suggest possibly important chemistry rather than a definitive report of what actually happens.

For example, we know that not all aerosol is aqueous. GEOS-CHEM has composition-resolved aerosol and so this modeling choice puzzled me somewhat. Why not assume only the sulfate/organic aerosol is aqueous? Surely black carbon and (most of) mineral dust is not. Also, is it not likely that the transition metal ions are likely to be associated with the mineral dust particles which are not the particles expected to be most aqueous?

Likewise, the reactions are likely much more complex than the authors model with potential complicating factors, with just one being the role of organics. Small di-acids, such as oxalate, are known to complex with transition metal ions. What impact would this chemistry have? The answer may not be known but I suggest that the authors highlight some of the uncertainties that are inherent, as suggestions for future research. Another example is the aqueous phase rate constants. How accurate are they? If some have only been measured once, then there is the potential for uncertainties there as well.

Lastly, the transition metal ion concentrations used in the modeling will be biased high by being ground level measurements, i.e. close to dust and industrial sources. I would imagine that the ratio of the transition metal ion concentrations to those of other, secondary constituents will drop as altitude increases.