

We thank reviewer #1 for her/his insightful comments. Our responses to the comments are provided below, with the reviewer's comments italicized.

*I really liked this paper, as an important modeling exercise to demonstrate the potential for HO<sub>2</sub> 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 HO<sub>2</sub> 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 H<sub>2</sub>O from this chemistry, and not the product that is usually assumed, H<sub>2</sub>O<sub>2</sub>. This has an impact on the atmosphere, as indicated by GEOS-CHEM CTM modeling runs that show that this chemistry can lower OH, O<sub>3</sub>, and affect CO levels in a manner that leads to better agreement with observations.*

*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?*

**Response:** We now state in the text:

“There are several reasons why such high  $\gamma(\text{HO}_2)$  values might not be representative of the global troposphere. As shown in Figure 3C,  $\gamma(\text{HO}_2)$  becomes insignificant for  $[\text{Cu}] < 1 \times 10^{-4}$  M, and the importance of such a threshold was previously noted by Thornton et al. (2008) for Cu-only chemistry. Cu concentrations could be much lower than assumed here in the remote troposphere and at high altitudes. Also the Cu and Fe may not be distributed over all particles, they may be complexed in a non-reactive form, they may be less soluble than assumed here, or the particles may not be aqueous. The higher solubility of HO<sub>2</sub> at colder temperatures would partly compensate by increasing  $\gamma(\text{HO}_2)$  (Mao et al., 2010). As pointed out in Table 1, field studies suggest the need for  $\gamma(\text{HO}_2) \sim 1$  to explain HO<sub>2</sub> observations, and there is some evidence that H<sub>2</sub>O<sub>2</sub> is not the product. Other mechanisms than the Cu-Fe-HO<sub>x</sub> redox chemistry described here could contribute to HO<sub>2</sub> conversion to H<sub>2</sub>O in aqueous aerosols (Section 2 in supplementary material).”

*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.*

**Response:** we add a new paragraph at the end:

“A better understanding of aqueous HO<sub>2</sub> chemistry in atmospheric aerosols requires substantial work in many aspects. Measurements of aerosol Cu and Fe speciation would be of particular value as speciation could greatly affect the kinetics. More information is needed for the remote troposphere on Cu and Fe concentrations, solubility, and internal mixing across aerosol types. Redox coupling involving other TMI present in atmospheric aerosols (Heal et al., 2005) should be investigated (Marcus, 1993). Better characterization of aqueous-phase kinetics is needed including reaction rate constants and complexation equilibria with ionic strength and temperature dependences. The field evidence for HO<sub>2</sub> conversion to H<sub>2</sub>O in aerosols, together with our work proposing a possible mechanism and showing major potential effects on oxidant concentrations (with implications for air quality and climate change), should strongly motivate further work to better understand HO<sub>2</sub> heterogeneous chemistry.”

*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.*

**Response:** We now state in the text:

“Cu concentrations could be much lower than assumed here in the remote troposphere and at high altitudes.”

#### Reference

Heal, M. R., Hibbs, L. R., Agius, R. M., and Beverland, I. J.: Total and water-soluble trace metal content of urban background PM<sub>10</sub>, PM<sub>2.5</sub> and black smoke in Edinburgh, UK, Atmos. Environ., 39, 1417-1430, 10.1016/j.atmosenv.2004.11.026, 2005.

Mao, J., Jacob, D. J., Evans, M. J., Olson, J. R., Ren, X., Brune, W. H., Clair, J. M. S., Crouse, J. D., Spencer, K. M., Beaver, M. R., Wennberg, P. O., Cubison, M. J., Jimenez, J. L., Fried, A., Weibring, P., Walega, J. G., Hall, S. R., Weinheimer, A. J., Cohen, R. C., Chen, G., Crawford, J. H., McNaughton, C., Clarke, A. D., Jaeglé, L., Fisher, J. A., Yantosca, R. M., Le Sager, P., and Carouge, C.: Chemistry of hydrogen oxide radicals (HOx) in the Arctic troposphere in spring, *Atmos. Chem. Phys.*, 10, 5823-5838, 10.5194/acp-10-5823-2010, 2010.

Marcus, R. A.: Electron transfer reactions in chemistry. Theory and experiment, *Reviews of Modern Physics*, 65, 599-610, 1993.