

We thank reviewer #2 for her/his insightful comments. Our responses to the comments are provided below, with the reviewer's comments italicized.

*This is an interesting contribution on the role of TMI interaction of Fe and Cu with HO<sub>2</sub>. As discussed before and elsewhere, HO<sub>2</sub> can be efficiently taken up into aqueous particles and may then be destroyed by TMI redox chemistry. The main point of the paper is the inclusion of this chemistry into GEOS-Chem where interesting things are observed upon this implementation. However, I feel that at least part of these effects have already been observed in the study by Thornton et al. (2008). So, it would be good if the authors clearly describe in how far their chemical scheme is different from Thornton's et al. chemistry and also compare the resulting effects.*

**Response:** We now state:

“The standard GEOS-Chem model includes a parameterization of  $\gamma(\text{HO}_2)$  taken from Thornton et al. (2008) for HO<sub>2</sub> uptake by pure water. The resulting  $\gamma(\text{HO}_2)$  is typically less than 0.1 and the product is H<sub>2</sub>O<sub>2</sub>, with no significant effects on global oxidant chemistry. Here we investigated the implications for oxidant chemistry of assuming as an upper limit  $\gamma(\text{HO}_2) = 1$  for all aerosols. We further assume  $Y_{\text{H}_2\text{O}_2} = 0$  (Figure 3B), since observations suggest that the dissolved Cu/Fe ratio is usually below 0.1 (Table S4); in fact, it appears from Figure 3B that  $Y_{\text{H}_2\text{O}_2}$  is more likely to be negative than positive.”

The resulting effects on global OH, CO and ozone are presented in Section 5.

*I would find it helpful if the authors could clarify that the chemistry of interest is described in CAPRAM 2.4. - a scheme not being restricted to cloud chemistry but as well addressing other tropospheric aqueous systems including aqueous aerosol particles.*

**Response:** We now state: “The chemical mechanism mainly draws from Jacob (2000), Chemical Aqueous Phase Radical Mechanism (CAPRAM) 2.4 (Ervens et al., 2003) and Deguillaume et al. (2004), with a number of modifications and updates (Tables S8 and S9).”

*The point at the end of the manuscript that speciation measurements are highly desirable is well taken. It also points to something which could require a different treatment as performed here: Many soluble TMI including those studied here could be complexed in atmospheric aqueous particles and especially under deliquescent aerosol conditions. Such complexation does not necessarily occur with organic ligand but also with inorganic solutes. It is unclear how kinetics will change from the just aquated TMs towards the corresponding complexed species. If reactivity would decrease, the present treatment could result into a too strong destruction of HO<sub>2</sub> - so, I would like to suggest to discuss this additional uncertainty. The complexation addressed here can involve other species than those already mentioned on Page 27058 - which, for the case of Fe, are*

*mainly introduced into the models because of their photochemistry. In summary, this is a very interesting and noteworthy study. If the above comments are addressed, the paper should be published.*

**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.”

#### Reference

Deguillaume, L., Leriche, M., Monod, A., and Chaumerliac, N.: The role of transition metal ions on HO<sub>x</sub> radicals in clouds: a numerical evaluation of its impact on multiphase chemistry, *Atmos. Chem. Phys.*, 4, 95-110, 10.5194/acp-4-95-2004, 2004.

Ervens, B., George, C., Williams, J. E., Buxton, G. V., Salmon, G. A., Bydder, M., Wilkinson, F., Dentener, F., Mirabel, P., Wolke, R., and Herrmann, H.: CAPRAM 2.4 (MODAC mechanism): An extended and condensed tropospheric aqueous phase mechanism and its application, *J. Geophys. Res.*, 108, 4426, 10.1029/2002jd002202, 2003.

Heal, M. R., Hibbs, L. R., Agius, R. M., and Beverland, I. J.: Total and water-soluble trace metal content of urban background PM10, PM2.5 and black smoke in Edinburgh, UK, *Atmos. Environ.*, 39, 1417-1430, 10.1016/j.atmosenv.2004.11.026, 2005.

Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, *Atmos. Environ.*, 34, 2131-2159, 2000.

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