Comment on acp-2021-483

Anonymous Referee #2

Referee comment on "The number fraction of iron-containing particles affects OH, HO$_2$ and H$_2$O$_2$ budgets in the atmospheric aqueous phase" by Amina Khaled et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-483-RC2, 2021

In the manuscript at hand, Khaled and co-workers investigate the effect of iron concentration heterogeneity within a population of aerosol or cloud particles on the overall concentrations and turnover rates of reactive oxygen species (ROS) using a kinetic model. This idea is novel and unique and the results are quite significant. The topic fits well within the scope of ACP and should be interesting to most readers. The biggest challenge of this work is to communicate the model setup and results clearly, and to derive general conclusions. The paper is written well from a technical perspective, but is a slow and cumbersome read due to the inherent complexity of the model calculations and some inaccuracies in language and writing. I can recommend publication of this article after a few points, outlined below, are addressed.

General Comments

- Role of the gas phase: The gas phase is a source of ROS in most of the presented calculations, but l. 108 states that gas phase concentrations are not replenished. Can the authors comment on the initial conditions of ROS in the gas phase, what were they based on? What is the time evolution / how strongly are gas phase ROS concentrations affected by presence of cloud and aerosol particles? Is a steady state achieved? How different is this steady state from the initial conditions? L. 547 states "We find that H2O2 concentrations in cloud water are not affected by FN,Fe as H2O2 is in thermodynamic equilibrium between the gas phase and all droplets". Is this because the gas phase is a (near-)infinite source of H2O2?
- What I could not understand when reading this paper: Why are the OH concentrations in cloud droplets lower for the FeBulk case, compared to both, the iron-rich and the iron-deprived particles in the FeN<100 case? (l. 144-149).
- The results of the model simulations are highly complex and I wonder if they could be reduced / simplified in the main text of this manuscript. Is the presentation of two iron concentrations m_Fe = 10 and 50 ng m-3 in the main text really necessary? This addition makes Figs. 6 and 7 very dense. What does the presentation of epsilon values for many different conditions (Fig. 3) really add to the paper?
- I worry about the conclusions being made on oxidative potential and health effects of particles. ROS species are generally not thought of as being inhaled with the particles,

but rather being generated *in situ* upon inhalation of redox-active PM constituents (Lakey et al. 2016). This should be especially true for transient species such as OH and HO2. For H2O2, it would be interesting to see an estimate: How does the amount of H2O2 that is present in these particles compare to the H2O2 production that occurs after dissolution of PM in the lung (e.g. Tong et al. 2016)? In line 510, I do not understand the meaning of this sentence: "Therefore, this dependence together with the [ROS] dependence on FN,Fe might explain the different conclusions regarding the trends of ROS budgets in particles of different air masses."

- l. 549 reads: "However, since H2O2 has been found to partitioning more efficiently into aerosol than into pure water ($K_{Heff,H2O2}$ = 2.7·108 M atm-1 550), We find that H2O2 concentrations in cloud water might be underestimated by the FeBulk approach whereas it maybe overestimated in aerosol water." I do not understand this sentence (and there are several typos; "partitioning" -> partition, "We" -> we, "it" -> they, and "maybe" -> may be). How can cloud water be affected by a parameterization that is used for aerosol? Prior it was stated that "H2O2 concentrations in cloud water are not affected by FN,Fe" (l. 547).

Technical Comments

There are several inconsistencies with italicized vs. non-italicized variables and constants.

l. 12 – there is a superfluous "of" in "As the main reduction of process of Fe(III)"

l. 69 – "We perform box model simulations a box model with a detailed gas and aqueous phase chemical mechanism" – sentence seems missing a word.

l. 88 – Loss rates in units g_{air}^{-1} is a bit curious. What is the advantage here, would it not better to use air volume?

l. 126 – There seems to be a word missing, please explain - "For all three ROS, the ratio of the phase transfer rates near the ratio of the LWCs of the two droplet classes (98% : 2%)."

Figure 2: The boxes at the bottom after "bulk aqueous phase concentrations" confused me at first as they appear to be part of the figure legend below. A stronger visual divide between the two might be worthwhile. In l. 150, bulk aqueous phase concentrations are referred to as "at the bottom of Fig. 2b", but that is where the legend is.

Figure 3 is quite confusing and raises more questions than it answers. After several minutes looking at this figure, I am not sure what I learned. Is epsilon a useful parameter

or would total concentrations be easier to understand and put in context?

l. 515: articles -> particles

l. 555, 559: HO2/O2-

References

Lakey, P. S. J.; Berkemeier, T.; Tong, H.; Arangio, A. M.; Lucas, K.; Pöschl, U.; Shiraiwa, M. Chemical Exposure-Response Relationship between Air Pollutants and Reactive Oxygen Species in the Human Respiratory Tract. *Sci. Rep.* **2016**, *6* (1), 32916. https://doi.org/10.1038/srep32916.

Tong, H.; Arangio, A. M.; Lakey, P. S. J.; Berkemeier, T.; Liu, F.; Kampf, C. J.; Brune, W. H.; Pöschl, U.; Shiraiwa, M. Hydroxyl Radicals from Secondary Organic Aerosol Decomposition in Water. *Atmospheric Chem. Phys.* **2016**, *16* (3), 1761–1771. https://doi.org/10.5194/acp-16-1761-2016.