Response to the comment to the Anonymous Referee #4

This paper describes measurements of the concentrations of reactive species embedded in atmospheric aerosol collected from the roof of the MPI. It is a followup to the earlier paper this year by Tong et al which compared field samples to lab samples collected for a shorter period of time and focused on OH generation. The measurement method consists of extracting soluble molecules from the particles and reacting them with a scavenger. This is essentially a physical chemistry paper and my comments are from that perspective. This paper will be publishable after some edits to respond to the following comments.

Response:

We thank the referee for review and positive evaluation of this manuscript.

I found the terminology used by the authors to be confusing in places. Through use of words such as "we have also characterized and quantified ROS including OH, superoxide (O2-) and carbon- and oxygen-centered organic radicals, which were released upon extraction of the particle samples in water." the reader could conclude that the radicals are persistently present in the particle, rather than being formed by reaction of water with precursors during the extraction process and later scavenged. The multiple chemical steps involved in the experiment lend an ambiguity to how to relate the lab processes that are responsible for formation of detectable spins to atmospheric and physiological processes. As another example, on pages 4-5 the authors talk about spins per microgram but do not define this quantity. I presume they mean spins detected by extraction from a sample of this mass using the protocol described. The concentration of the scavenger is not given so it is not clear how closely this process is controlled or how repeatable it is. Clarification of the terminology and relation of the experimental conditions to those found in the lung and in clouds, for example, would be helpful.

Response:

Following your suggestion, we will make it clear that we measured ROS formed upon extraction into water throughout the revised manuscript. The unit for EPFR and ROS concentrations used in this study is spins μg^{-1}, which indicates the number of spins (or radicals) produced per unit of particle mass. We will add the following sentence in the revised manuscript.

"Concentrations of EPFR and ROS are reported in the unit of spins μg^{-1}, which indicates the number of spins (or radicals) per μg of particle mass."

The concentration of the scavenger was specified in the method section (350 μL of 20 mM BMPO was used). The experimental procedure was controlled well and repeatable (e.g., Tong et al., 2016).

(2) Only particles smaller than 1 micron contain extractable ROS material. Do the authors understand why this is? Since peroxides are photo labile I might have expected the opposite - the larger, more optically opaque particles would have more precursors than the smaller ones assuming the extraction processes work the same way for all particle sizes. Some discussion of the size effects would be useful.

Response:

ROS concentrations are indeed smaller for particles in the coarse mode, but ROS were formed also by particles larger than 1 μm, as shown by the red line in Fig. 2, Fig. 4a and Fig. 5. The size-dependence was discussed in L266 – 273 ("SOA particles, which may contain large amounts of organic hydroperoxides, account for a major fraction in PM1 (Jimenez et al., 2009). SOA compounds may also coat coarse particles such as biological particles (Pöhlker et al., 2012). As shown in Fig. 2, semiquinones are mostly contained in submicron particles but not in coarse particles. Thus, the release of a variety of ROS species are most likely due to the interactions of organic hydroperoxides, semiquinones, and transition metal ions, whereas the dominance of OH radicals in coarse particles may be due to the decomposition of organic hydroperoxides in the absence of semiquinones. ").

(3) The reactive oxygen species released and scavenged during the analytical protocol are well known to have rich chemistry in water and very different reactivities compared to each other. Have the authors determined how efficiently are they being detected (absolute and relative values)?

Response:

We are aware that ROS chemistry is quite complex. We are currently making efforts on synthesizing possible reactions involving ROS, organic hydroperoxides, quinones and transition metals and developing the kinetic model. We intend to present these results in the follow-up study. Regarding the detection efficiency of ROS, BMPO is known as a very efficient trapping agent for OH radicals (Tong et al., 2016). In this work, BMPO is assumed to have the same efficiency for all type of radicals. Even though there is no thorough quantitative data specifically for BMPO trapping efficiency for superoxide and organic radicals, Sueishi et al. (2015) have reported that nitrone-based spin-traps have the highest reactivity towards OH followed by carbon-centered radicals, oxygen-centered organic radicals, and superoxide. Further studies are required to fully address this issue and we will note include the below sentence in the revised manuscript.

(4) On page 9 line 269ff there is a section discussing implications for aerosol chemistry and lung chemistry. Since there are no data in this paper specifically looking at these implications but there are in Tong I recommend the reader referred back to the earlier paper instead.

Response:
Yes, we refer this aspect to Tong et al., (2016). This study itself did not show that ROS can be generated in the lung lining fluid containing antioxidants, but it did show that the particles can form ROS in water. Several previous studies have shown that redox-active components such as transition metals and quinones can induce formation of ROS species upon interactions with lung antioxidants (Charrier et al., 2014; Charrier and Anastasio, 2011). We will clarify it in the revised manuscript as below:

"Previous studies have shown that redox-active components such as transition metals and quinones can induce ROS formation in surrogate lung lining fluid upon interactions with antioxidants (Charrier et al., 2014; Charrier and Anastasio, 2011). This study also implies that ROS may be released in lung lining fluid upon inhalation and respiratory deposition of atmospheric aerosol particles."

References.

Tong, H., Arangio, A. M., Lakey, P. S. J., Berkemeier, T., Liu, F., Kampf, C. J., Brune, W. H., Pöschl, U., and Shiraiwa, M.: Hydroxyl radicals from secondary organic aerosol decomposition in water, Atmos. Chem. Phys., 16, 1761-1771, 2016.