Response to the comment to the Anonymous Referee #2

This study reports concentrations of particle-bound environmentally persistent free radicals (EPFR) and radical forms of reactive oxygen species (ROS) using electron paramagnetic resonance (EPR) spectroscopy. ROS species quantified after release by extraction of submicron particle samples in water include OH, O2-, carbon- and oxygen-centered organic radicals; the authors further report concentrations as a function of particle size. The study proposes that the formation of ROS is due to the decomposition of organic hydroperoxides interacting with semiquinones in soot and/or HULIS particles, while EPFR are likely from semiquinone radicals. The study is well written and relevant to the atmosphere and human health concerns. I recommend publication in ACP after the following questions and comments are addressed.

Response:

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

Comments:

-How do the concentrations of ROS (spins μg-1) compare to those previously reported? It may be useful to include a note in the Methods section about the context of these units in terms of their relationship to standard particle concentrations.

Response:

This study provided the concentrations of radical forms of ROS (e.g., sum of OH, O_2^-, C- and O-centered organic radicals), which is the first measurement to the best of our knowledge. Thus, we cannot make direct comparison with previous studies. Instead, we have made comparison with previous measurements of redox activity and oxidative potential of PM by the dichlorofluorescein (DCFH) and dithiothreitol (DTT) assays, as discussed in Sect. 3.2. Assuming that the consumption of one DTT molecule would correspond to the generation of one ROS molecule (e.g., H_2O_2), these values are about a few orders of magnitude higher than concentrations of radical forms of ROS measured in this study. This is reasonable as H_2O_2 is closed shell and much more stable than open-shell radical ROS. The standard unit for the particle mass concentration is μg m^{-3}, which indicates μg of particle mass in 1 m^3 of air; whereas the unit (spins μg^{-1}) of ROS or EPFR concentrations used in this study indicates the number of spins (or radicals) per unit of particle mass. We will clarify this point in the method section of the revised manuscript.

-A mention of g-factor before the Results section may be helpful as written it is difficult to understand the importance of the parameter and how unique a g-factor is to each measurable species.

Response:

Thanks for your suggestion. We will add the following sentence in the method section:

"Paramagnetic species are characterized based on their g-factor values. Free electrons have a g-factor value of 2.0023 and organic radicals have higher g-factor values (2.0030 – 2.0060), depending on the number of oxygen atom in the molecule (B. Dellinger et al. 2007)"

-Figure 1 - what does the structure at 560 nm indicate?

Response:

The spectrum for 560 nm particles indicates that no radicals have been found for this size range particles. The high background, probably due to metal oxides, causes the spectrum to be steep in shape and the fine structure seems to be not significant.

-Lines 83-98. Can you expand a bit on any transmission effects of the impactor, especially for the coarse particles?

Response:

For impactor such as MOUDI, the transmission effect of particles collected on a stage is considered to be a step function with boundaries of the steps corresponding to the cut-off sizes of the upper and lower stages. That is, each stage has an efficiency of 50% in collecting particles with the diameter comparable to its nominal cut-off size. The collection efficiency reaches 100% for particles with diameter just bigger than the nominal cut-off size of the upper stage (Marple et. al. 1991). However, the collection efficiency of particles with the diameter comparable to the nominal cut-off size of a stage can be lower than 50% due to bouncing effects. Due to bouncing, particles that are supposed to impact on a stage can be transferred to the next stage. This process is much more influential for particles in the coarse fraction. We will add the below sentence in the revised manuscript:

"Note that transmission and bouncing effects may cause mixing of particles exhibiting relatively different sizes on one stage, particularly for coarse particles (Gomes et al., 1990; Bateman et al., 2014)."

-Figure 2. What do the error bars indicate? Is there any significance that both ROS and EPFR have minima at the same size (560 nm)?

Response:

The error bars represent standard errors based on uncertainties of the particle mass and signal integration of EPR spectra. We will add this information in the figure caption. The minimum in the EPFR and ROS concentration for particles at 560 nm is likely due to a low mass loading in this stage.

-Lines 99-113. What are the background concentrations of these species? Is there any signal when EPFR are not present?

Response:

Blank measurements confirmed that there are no background concentrations of EPFR. In the absence of EPFR, the signal is just a horizontal line, when the concentrations of other paramagnetic species (e.g., transition metals) are below the detection limit.

-Figure 3. Can the authors expand on why rain events do not seem to dampen concentrations of EPFR in 100 nm particles as much as 180 nm particles?

Response:

EPFR concentrations in both 100 and 180 nm particle decreased substantially after rain events on May 30 (Saturday), but it was not very obvious, on June 1 (Monday), 2015. EPFR concentrations are controlled by both emission and deposition. The road traffic can be a main contributor of $PM_{2.5}$ in the area around the sampling site and it is generally very limited during the weekend. This means that emission or production rates of EPFR on June 1 must be higher than on May 30. Moreover, scavenging efficiency of particles depends on rainfall intensity and sizes of rain droplet and particle (Seinfeld & Pandis, 2006), which might have caused the difference for 100 and 180 nm particles.

Figure 5. The authors may find it useful to note the total ROS concentrations to further illustrate the size dependence. For the largest particles (1.8 μm especially), OH seemingly dominates the total ROS concentrations

Response:

The total ROS concentrations as a function of the particle diameter are shown as the red line in Figure 2. Figure 5 shows the relative contribution of each type of ROS to the total amount of ROS at each stage.

-did OH significantly contribute to the total ROS concentration at 1.8 µm or is this due to the smaller ROS concentrations skewing the total contributions of each species?

Response:
Yes, OH contributed up to about 90 % of the total ROS released by 1.8 µm particles.

-Lines 308-319. Is our lung capacity inhalation dependent on the total concentration (spins µg-1) of these ROS/EPFR species? Is there an amount of ROS/EPFR that our lungs can safely inhale without potential health harm?

Response:
This is a very interesting and important question to be addressed. We have recently reported that fine particulate matter (PM2.5) containing redox-active transition metals, quinones, and secondary organic aerosols can increase ROS concentrations in the lung lining fluid to levels characteristic for respiratory diseases (~100 nM) (Lakey et al., 2016). Further studies are required to unravel threshold concentrations of ROS/EPFR that are harmful to human health. We will add this aspect in the revised manuscript.

References:
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