

Response to the comment to the Anonymous Referee #3

In this study, the authors report size-resolved measurements of EPFR and ROS radicals using EPR spectroscopy and LC-MS for samples collected for one week in Mainz as a demonstration. They show size-dependent variations in the proportion of radicals of ROS and EPFR, with concentrations of both peaking in the accumulation mode, and find that carbon-centered radicals contribute the largest proportions to radical species in ROS for PM1. Using laboratory generated spectra, they further propose that mechanisms for ROS generation in these samples require a combination of transition metals with organic hydroperoxides and quinones. The work is of high technical quality with important implications for understanding atmospheric processes and air quality, and the manuscript is well-written. The work is thus recommended for publication in Atmospheric Chemistry and Physics after the following comments have been addressed.

Response:

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

General comments regarding the measurement method:

1. Are there any transformation artifacts from the initial measurement of EPFR? For example, if the authors use collocated measurements and analyze ROS directly on the second filter, would they expect to find the same ROS concentrations measured after the filter has been used for quantification of EPFR?

Response:

EPR measurements for the EPFR detection are non-destructive measurements. The microwave radiation used during EPR analysis does not induce any changes in the chemical composition of the sample itself. Indeed, the intensity EPFR signal did not change when monitored over the experimental time. Thus, initial EPFR measurements would not affect subsequent ROS measurements of particle extracts in water.

2. On p.3, line 95, it is stated that "BMPO is an efficient spin-trapping agent [...]." Is the efficiency effectively considered to be 100% for all, or are there biases for certain radicals?

Response:

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 nitron-based spin traps have the highest reactivity towards OH and somewhat lower reactivity towards 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.

3. In the drying process with N₂, is it possible that negative artifacts are introduced? How is the dried extract introduced into the EPR spectrometer?

Response:

The text was misleading. The water extracts were exposed to a N₂ flow to reduce the volume of the solution to 50 µL. 20 µL are then introduced into a glass capillary for EPR analysis. As N₂ is inert towards BMPO-trapped radicals, we do not think artifacts would be introduced. We will clarify it in the revised manuscript.

4. Is the detection limit reported the instrument detection limit, or analytical detection limit derived from blanks?

Response:

The reported detection limit refers to the detection limit of the instrument.

General comments regarding the reported concentrations:

1. Would it be meaningful to plot radiation intensity alongside Fig. 3 to discuss the potential role of photochemistry? For instance, on 02/06/2015, the concentration is also high even though the conditions are presumably cloudy according to descriptions in text. In this regard, the radical concentrations appear to depend on many factors and underscores the benefit of integrating this technique into larger measurement campaigns.

Response:

This is a very good idea as photochemistry may be related to EPFR formation; however, unfortunately we do not have data of radiation intensity.

2. Are the proportions in Fig. 5 meant to be representative of those observed during the entire measurement campaign?

Response:

The proportions in Fig. 5 are referred to samples collected for 48h in June 2015 and extracted in presence of BMPO. We will clarify it in the revised manuscript.

Minor comments:

1. p. 3, line 92: The authors discuss pre-cleaning and weighing, and then discuss particle extraction. It would be helpful if the description were explicit in the pre-sampling and post-sampling procedures.

Response:

Following your suggestion, we will describe explicitly the pre-sampling and the post-sampling procedures as follow:

“Particles were collected on 47 mm diameter Teflon filters (100 nm pore size, Merck Chemicals GmbH). Before sampling, each filter was cleaned and sonicated for 10 min with pure ethanol and ultra-pure water and dried with nitrogen gas before weighing. Teflon filters were weighed four times using a balance (Mettler Toledo XSE105DU) and mounted in the MOUDI. After the sampling, each filter has been conditioned for at least one hour in the lab atmosphere (22 C and 40-50 RH) and weighted four times.”

2. p. 5, line 152: This is just a semantic issue, but it would seem more appropriate to say that the values in this work are comparable with the EPFR concentrations measured by Shaltout et al. (2015) - instead of the other way around - since their work preceded this one and sets the precedent to which following studies should be compared.

Response:

Following your comment, we will revise the sentence in the revised manuscript.

3. In the conclusions, the measurement location and period should be restated so the reported concentrations are placed in the proper context.

Response:

We thank referee 3 for pointing this out. We will include this information.

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.