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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Quantification of environmentally persistent free radicals and reactive oxygen species in atmospheric aerosol particles" *by* Andrea M. Arangio et al.

Anonymous Referee #3

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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 hydropreoxides 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 Atmo-

spheric Chemistry and Physics after the following comments have been addressed.

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?

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?

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?

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

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.

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

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.

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.

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

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