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Interactive comment on “Redox activity of naphthalene secondary organic aerosol” *by* R. D. McWhinney et al.

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We would like to thank the Referee for the time taken to provide helpful comments and discussion of our paper.

A common concern raised with Referee #1 was the discrepancy in recoveries from the SPE method between the naphthalene SOA and engine filter samples. Our responses are outlined below about why we believe the quinone recovery is so different between the two techniques, but we agree that the recovery difference is somewhat troubling and the poor precision in recovery prevents strong conclusions from being reached from the engine data. Since the engine results are a rather minor section of the manuscript and the findings do not influence the rest of the conclusions to any degree, for clarity we are removing this section from the manuscript for the final revision. We hope that this helps to alleviate potential confusion the reader might have with this paper.

The second change we are proposing is in light of the major comment raised by Referee 2, addressed in more detail below. In brief, the Referee mentioned the paper might be more concise without the discussion of the naphthoquinone partitioning coefficients. As the partitioning behaviour has the potential to play a major role in the influence these species may have on particle redox cycling, we believe this is a rather important discussion to remain in the paper. To reflect this, we are proposing a change to the title of the paper to “Naphthalene SOA: Redox Activity and Naphthoquinone Gas-Particle Partitioning” to better reflect the focus of the paper.

Our responses to the individual comments are as follows:

The authors argue convincingly (e.g., p. 9125) that with their experimental procedure it might difficult to determine air-particle partitioning coefficients due to the non-equilibrium conditions in the chamber (i.e., the need to add dilution air during sampling). Would this not suggest that is does not make sense to calculate partitioning coefficients?

While we certainly understand the point the reviewer makes, we respectfully disagree with the removal of this section of the paper. One of the important aspects of determining the potential impact of photochemical oxidation on health is if the products of concern will actually be in the atmospheric phase where they are of concern; in this case, it is whether the naphthoquinones observed would be found in the particle phase. This is especially important given the high concentrations our lab study works with. While our setup may not be ideal for measuring the partitioning coefficient, we believe that we have shown it to be reliable enough, and in reasonable agreement with the relatively few measurements of 1,4-naphthoquinone air-particle partitioning, to report and, in particular, to question what the impact of ambient naphthoquinones might be to the potential toxicity of particles redox cycling. We think this an important analysis to make at this point, and given the relatively few measurements that have been made of air-particle partitioning of these species and how important it is to the atmospheric relevance of this study's results, the discussion is important to leave in the paper. Certainly, it would be best if this measurement could be made using more appropriate experimental conditions in the future, but in the absence of such measurements at this time, we believe this is rather important to be in the final publication.

p.9112, line 14ff: The chamber is described rather shortly. Is there a reference giving more details on the design and operation of the chamber?

As this is the first study published using the chamber, we do not have a reference for the chamber operation, but the design is rather simple; the chamber is a rectangular cuboid shape and is illuminated by 24 UVB lamps on 4 sides. We have added these further details about the design in the manuscript to clarify.

p. 9113, line 4/5: PTRMS calibration is not clear. Did the calibration procedure assume that 100% of the injected naphthalene was present in the gas phase of the chamber, i.e., was it assumed that there were not transfer or wall losses? If yes, is this assumption justified?

The naphthalene concentrations have been calibrated based on assuming 100% of the naphthalene added is mixed into the chamber. While the naphthalene signal remains reasonably steady over the course of an experimental time scale in the absence of oxidant, we don't have definitive proof that there are no mass transfer loss effects, and will update the manuscript to reflect this. The naphthalene concentrations are given for reference only and are not used in any calculations, so this will not affect any experimental outcomes.

p. 9115, line 15ff: Why was the recovery of the naphthaquinones for SOA and engine exhaust samples so different?

As we mentioned above, due to the poor quality of the data the engine exhaust work will be removed from the final version of the paper, although we do have some hypotheses as to why the SPE recoveries were so different. Please refer to the discussion to Referee #1 for our thoughts on the naphthoquinone recoveries.

p. 9116, line 15: Please provide an original reference instead of citing a textbook.

We have changed the reference to the Pankow (1994) paper.

p. 9117, line 12: It is mentioned that the SOA was composed mainly of "hydrocarbons and oxidized hydrocarbon fragments". This statement should be explained in more detail and supported with data.

We apologize for the awkward wording of this particular section. This is referring to the AMS measured mass spectrum, which sees mostly hydrocarbon (CxHy) and oxidised hydrocarbon (CxHyOz) fragments, as shown in Table 2 and Figure 3. We have clarified this in the manuscript.

p. 9123, line 5: Please comment on the observed differences of the partitioning coefficient in this study and the model predictions.

We do not have a strong explanation as to why the partitioning coefficient as modeled is lower than what we have observed. The probable reason is that the modeled values are based on structural activity relationships (SARs) rather than experimental data. If the model does not accurately describe the intermolecular forces present in the molecule of interest, the modeled value may be off by orders of magnitude. The agreement between our partitioning coefficient and the only previously experimentally determined value leads us to believe that the SARs are inaccurately describing the volatility of 1,4-naphthoquione.

p. 9124, last sentence: word missing in this sentence.

Thank you – this sentence has been corrected.

Reference:

Pankow, J. F.: An absorption model of gas/particle partitioning of organic compounds in the atmosphere, Atmos. Environ., 28, 185-188, 1994.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 9107, 2013.