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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 with Referee #2 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

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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 a title change to “Naphthalene SOA: Redox Activity and Naphthoquinone Gas-Particle Partitioning” to better reflect the focus of the paper. This is in light of the major comment raised by Referee 2, and is addressed in more detail in the response to Referee 2’s review.

The response to the major points raised by Referee #1 are as follows:

1. The authors reported a large discrepancy in recovery of the quinone analytes using a SPE technique for naphthalene SOA samples and oxidized two-stroke engine particle samples. In this SPE technique, phosphate buffer extracts of the samples passed through a C18-based SPE cartridge, followed by elution of the analytes using acetonitrile. For the engine particle samples, the recoveries are satisfactory for 1, 4-naphthoquinone (92+/-10%) and 9,10-phenanthrenequinone (87+/-22%), but very low for 1, 2-naphthoquinone (21+/-15%). For the nap-SOA samples, the recovery of the same analytical procedure was very low for both 1,2- and 1,4- naphthoquinone (1-3%). Such a discrepancy is difficult to comprehend and is worrisome. Was this a concentration effect (as it appears that the quinones are present in higher amounts in the NAP-SOA samples than the engine emission particles, in the text lines 25-26 on page 9117 and lines 1-2 on page 9118)? The authors ought to conduct more experiments to characterize the analytical method. Otherwise it is unconvincing how the predicted redox activities for the NAP-SOA samples could be compared with the redox activities for the engine particle samples, if the concentrations of quinones are based on different analytical approaches.

We agree that the discrepancy between the recoveries of the engine samples and the naphthalene SOA samples is quite puzzling. We do not believe that this is a concentration effect, at least not due to the relatively high concentrations of quinones; naphthoquinone standards prepared in phosphate buffer at a similar concentration to what is

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present in the filters (based on the organic extraction method) perform well in the SPE method. There appears to be something unique about the naphthalene SOA matrix that results in either (a) a lack of retention in the SPE cartridge, causing the quinone species to be drawn off with the eluent; or (b) unusually high retention, preventing the acetonitrile from washing the quinones from the column during extraction. At this point, we are more inclined to believe the former since the 2-methyl-1,4-naphthoquinone internal standard does not appear to have the same effect. One possibility is that the amount of soluble organic material in the aqueous SOA extracts increased the strength of the eluent to the point that the more polar 1,2- and 1,4-naphthoquinone analytes are drawn off the C18 cartridge but not the internal standard.

The main purpose of the short engine section was to highlight that we have even more challenge in accounting for redox activity in the more complex, previously studied engine exhaust samples in comparison to naphthalene SOA. We agree, however, that we should be approaching these results as much more uncertain and more qualitative than we have perhaps presented in the submitted manuscript. Given that the focus of the manuscript is upon naphthalene SOA, we have removed all the work related to the two-stroke engine exhaust.

2. The authors should provide more analytical details, such as the method detection limits for the filter samples, the analytical procedure and performance (e.g., recovery) for determining the quinone compounds in the XAD cartridge samples.

The method quantification limits have been operationally defined in this study as the lowest standard on the calibration curve since we are working well above the detection limits; typically this is 0.05 micrograms per extraction sample, or 0.2 micrograms based on extraction of one-quarter of the SOA filter sample. For engine samples at lower concentrations, quantification limits of 0.007 micrograms per filter were used. More precise detection limits based on a standard deviation of many blank samples were not determined. Recovery of the XAD samples was assumed to be 100%. This would imply that if the recovery is lower than 100%, the gas-phase concentrations are under-

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estimated, which places the partitioning coefficients as a lower bound. The manuscript has been updated to reflect this.

3. The authors assume that the redox activities are additive for mixtures of multiple redox active compounds in predicting redox activity of complex SOA and oxidized engine emission particles. It will be good if the authors can have actual data to support such an assumption, such as comparing the redox activities of NAP-SOA vs. NAP-SOA+ known amounts of quinones.

We neglected to refer to findings of a previous study (Charrier and Anastasio, 2012; supporting information), where combinations of redox active species including quinones and transition metals were examined to test their additivity. In the case of 1,2-naphthoquinone/phenanthrenequinone and phenanthrenequinone/iron(II) mixtures, there was no significant difference between the added individual redox activities of the individual species and the redox activity of the mixture; in the case of phenanthrenequinone/copper(II) and iron(II)/copper(II) mixtures, there was a slight statistically significant difference, but the added individual redox activities were only 14% and 18% different from the mixture, respectively. We have updated the manuscript with this reference.

4. Section 3.5: it will be good to have a table to list the DTT and quinone analysis results for the oxidized engine particle samples (similar to Table 3 for the NAP-SOA samples).

As discussed in the response to comment 1, in light of the qualitative nature of the finding and the considerable uncertainty in the values due to the low 1,2-naphthoquinone recoveries using the SPE method, we have removed the engine particle data from this manuscript.

Reference:

Charrier, J. G. and Anastasio, C.: On dithiothreitol (DTT) as a measure of oxidative

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potential for ambient particles: evidence for the importance of soluble transition metals,
Atmos. Chem. Phys., 12, 9321–9333, 2012.

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