

Response to comments from referee #1 (Manuscript Ref. NO: acp-2017-214)

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Thank you for your valuable comments. We modified the manuscript accordingly.

General comments: This manuscript presents a laboratory chamber study to investigate the contribution of particulate oxidizers in secondary organic aerosols to the oxidative potential measured dithiothreitol (DTT) assays. The significance of quinones, organic hydroperoxides, and peroxyacyl nitrates (PANs) in SOA samples from various precursors and conditions was characterized, and directly compared to the measured DTT activity. The authors report that the presence of particulate organic hydroperoxides can explain most of the DTT consumption of isoprene SOA (almost 1:1 correlation), and partially for toluene SOA, while the amount of PANs and quinones appears to be negligible in the SOA systems investigated here. With completely different approaches, it is intriguing to see the results reported in this study to be closely consistent with Kramer et al. (Atmos Environ, 2016) who directly measured the DTT activity of synthesized isoprene-derived hydroperoxide (ISOPOOH) standard and reported a very strong DTT response (almost comparable to the quinone compound and 3 order of magnitudes higher than other major isoprene SOA constituents).

Overall, this is a well-planned study and the manuscript is well written. I have a few specific questions and suggestions are listed below for the authors' clarification and consideration. I am in support of publication once these questions have been addressed.

Specific comments:

1. Page 5, Line 24: should the storing condition here be 4 °C instead of -4 °C?

Response: This sentence was modified and reads now,
“Before chemical analysis, all SOA samples were stored in a refrigerator at 4 °C.”

2. Page 6 Line 2: how the reaction between DTT and SOA could be quenched by adding 1 mL trichloroacetic acid (1 % w/v)? Was this to quench specific components in SOA samples before measuring the remaining DTT with DTNB? More detailed explanation is needed as it is not clear here.

Response: Trichloroacetic acid is a strong organic acid ($pK_a = 0.5$) and commonly used as a quencher of thiol oxidation (Cho et al., 2005, Fang et al. 2014, Curbo et al. 2013) by decreasing pH. Trichloroacetic acid is crystal. It is easy to prepare the quenching solution by weighing trichloroacetic acid. This sentence was modified as below:

“...the reaction between DTT and SOA was quenched by adding 1 mL 1% w/v trichloroacetic acid (a commonly used quencher of thiol oxidation).”

Reference: Cho, et al., Redox activity of airborne particulate matter at different sites in the Los Angeles Basin, Environ. Res., 99, 40-47, 2005.

Sophie Curbo et al., Is Trichloroacetic Acid an Insufficient Sample Quencher of Redox Reactions? Antioxidants & Redox Signaling, 18, 2013.

Ting Fang et al., A semi-automated system for quantifying the oxidative potential of ambient particles in aqueous extracts using the dithiothreitol (DTT) assay: results from the Southeastern Center for Air Pollution and Epidemiology (SCAPE), Atmospheric Measurement Techniques, 2014

3. Page 6 Line 13-17: how the slopes shown in Figure S1 compare to each other statistically?

Response: With significance level $\alpha = 0.05$, the slope of ΔDTT vs. time with sonicator was not significantly different from the one with shaker, tested using the statistical method which is based on the Student t-test (Andrade and Estévez-Pérez, 2014)). This sentence was modified and reads now,

“Tested using the statistical method reported by Andrade and Estévez-Pérez (Andrade and Estévez-Pérez, 2014), the DTT loss rate in blank control during sonication was not significantly different from that with shaker (significance level $\alpha = 0.05$); therefore, in this study, the influence of free radicals generated by sonication on DTT measurement was insignificant.”

4. Table 1. It looks like no seed aerosols were introduced into the chamber experiments. Did the SOA form solely because of nucleation?

Response: No, SOA was formed without seed aerosol.

5. How the chemical composition and DTT activity might change if there are pre-existing seed aerosols?

Response: It is a valuable question to think. With pre-existing aqueous seed aerosols, SOA yields will increase and SOA compositions will also change. We cannot simply answer for this question because aerosol formation is complex. What we can think is that the water content and aerosol acidity can influence the lifetime of unstable compounds, partitioning of organic species, and the reaction with atmospheric oxidants in particle phase.

6. Figure 4: why a higher concentration of potassium phosphate buffer was needed for the Toluene LNOX-17 Nov 2016 sample? Would changing buffer concentrations affect the measured DTT activity?

Response: Please find the last paragraph of Section 3.1.

“Medina-Ramos et al. (2013) reported that the electron transfer rate between glutathione (GSH) and an electrogenerated mediator ($[\text{IrCl}_6]^{2-}$) exhibited a slight acceleration when the phosphate buffer concentration was increased from 0 to 50 mM at pH = 7.0. To achieve the completion of the reaction between particle oxidizers in SOA and DTT, the DTT_m of toluene SOA (HC/NO_x=24 ppbC/ppb, 17 Nov 2016) was measured with a 0.8 mM potassium phosphate buffer in the first step of DTT assay (2 times higher than the typical buffer concentration (0.4 mM)).”

Thus, the higher concentration of potassium phosphate buffer was applied to toluene (17 Nov 2016) sample and accelerated the rate of the reaction between DTT and toluene SOA.