

Interactive comment on “Dithiothreitol Activity by Particulate Oxidizers of SOA Produced from Photooxidation of Hydrocarbons under Varied NO_x Levels” by Huanhuan Jiang et al.

Anonymous Referee #2

Received and published: 17 April 2017

In this work, Jiang et al. studied the oxidative potential of Secondary Organic Aerosol (SOA) generated in laboratory chambers. The authors investigated the role of various oxygenated compounds within complex SOA systems in contributing to oxidative decay of sulfhydryl groups, which is believed to be the main mechanism by which particulate matter causes adverse cardiopulmonary outcomes. The authors systematically varied experimental conditions and carefully measured various functional groups, and relate the composition to OP measured (using the DTT assay). Based on the experimental results, they conclude that organic hydroperoxides (ROOH) are a major source of oxidative potential, and suggest that electron-deficient alkenes (such as acrolein) may also be important too.

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The experiments are done with sufficient controls, and carefully interpreted. The DTT activity of SOA has recently become a topic of great interest within the atmospheric community. The work is within the scope of ACP and should be published after considering the following minor comments.

Major comments:

- The suggestion about electron-deficient alkenes being important is worth noting. Acrolein seems to be the only example that has significant DTT activity. All others are an order of magnitude lower. Are there example compounds that are more relevant to toluene/benzene system? I would imagine that aromatic compounds would yield conjugated compounds, which according to Figure 7 and Section 3.4, would have negligible DTT activity. Also, acrolein has very high vapor pressure and is unlikely to be in the particle phase.
- Related to the previous note, in Section 3.1, the decrease in DTT activity is on the same timescale of acrolein. That is not a fair comparison because acrolein is reacting in the gas phase, where the DTT measurement is for compounds in the particle phase, which likely have longer lifetimes than acrolein in the gas phase.
- On that note, why is it called “electron-deficient alkenes”? Why not “unsaturated carbonyls”? Reaction with DTT is likely on the oxygenated group, rather than on the C=C double bond. Also, from a fundamental perspective, does the C=C double bond need to be adjacent to the C=O group? Have the authors investigated, say, 3-pentenal?
- Also, if acrolein indeed contributes high DTT activity, I would imagine that SOA from 1,3-butadiene would have very high DTT activity. Have the authors done any experiments to suggest that is the case?
- Another suggestion for additional experiments (optional but would really strengthen the argument): if the authors can pass ozone over the SOA (e.g. collected on the filter), the ozone should selectively remove the double bonds. This way the authors

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can isolate the contribution to DTT from these electron deficient alkenes. While this may create additional organic hydroperoxides, the authors can easily correct for that increase by measuring total OHP with the NPBA assay.

- Does the UNIPAR model describe the abundance of electron deficient alkenes under low-NO_x? I would imagine under high NO_x there would be more electron deficient alkenes where C-C bond scission and ring-opening reactions are dominant, but the “unaccounted” DTT activity seems to be higher under low NO_x for toluene (from Fig. 6).

- I understand that the proposal about measuring DTT_m as a proxy for maximum capacity (described in Section 3.1) is useful for a chemist. But I wonder what the biological relevance is. What is the lifetime of particles deposited in the lungs? I am not a lung expert, but I wonder if mucociliary clearance would make the lifetime shorter than 2 hours, and therefore DTT_m at 2 h may not be that relevant.

- For DTT_m to be meaningful, DTT must be in large excess compared to amount of SOA. What is the estimated ratio of DTT to SOA (100 uL of DTT, 700 uL of SOA solution)? Is DTT in large excess? This is not an issue when looking at the catalytic activity, because both DTT and quinones can be regenerated through catalytic cycles. But this issue arises when it is a one-step reaction with these particulate oxidizers.

- If hydroperoxides (and PANs) are indeed unstable at room temperature (as suggested in Section 2.3.2), did the decrease in ROOH amount correspond to an increase in DTT_t or DTT_m?

- There are large fluctuations in experiment temperatures (more than 20K). Are there systematic differences in chemical composition?

Minor comments:

- Section 2.2: Please provide define PILS and provide details of the PILS method. Was steam used to grow particles for impaction and collection? If so, is there concern

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about the high temperatures leading to decomposition of thermally labile compounds important for oxidative potential?

- Section 2.3.1 Line 1: it is unclear what “two steps” mean in parentheses. Perhaps re-word to “The two-step DTT assay. . .”

- Section 2.3.1 Line 2: What does SOA sample mean? Is this the aqueous solution?

- Section 2.3.1 Page 6 Line 1: What is the pH of the PBS?

- Section 2.3.1 Page 6 Line 1: “shaken in a sonicator” is confusing. Particularly since in the later section “shaking” was compared to “sonicating”.

- Section 2.3.2: Can 4-nitrophenol be formed in high NO_x SOA from toluene? If so, are there any negative controls?

- Section 3.1 heading: remove period after title

- Section 3.3 Line 5: Grek et al. does not provide any evidence that PANs can oxidize sulfhydryl groups. They only include peroxy nitrates as an RNS, but PANs are peroxy nitrates.

- Section 4 Line 25: remove (DTT modulator: quinones)

- Section 4 Page 14 Line 8: An assay that is not water-based may not be relevant, since cells are water-based

- Table 1 and throughout manuscript: Does HC/NO_x ratio refer to the initial or average HC/NO_x? If it is the average, over what time range is the HC/NO_x calculated?

- Table 1 Mid-collection time: is this local time?

- Figure 4: why is one data series labeled with experiment date, but others are not?

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-214, 2017.

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