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Discussions

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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 #3

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This study investigated the DTT activity of different types of SOA (toluene, TMB, isoprene, a-pinene) formed in the presence of NOx. Experiments are conducted in an outdoor chamber facility with different levels of NOx. Results showed that in the presence of relatively higher levels of NOx, DTT activity of toluene SOA is 2-5 times higher than other SOA. Isoprene SOA has lower DTT with increasing NOx. Other SOA appears to be insensitive to NOx. The results are discussed in the context of different DTT modulator compounds.

This is an interesting study and will be of interest to the greater research community. I have a number of questions regarding the experimental design/protocols and how the data are interpreted. Further, the conclusions need to be better justified.

The experiments are conducted with very high levels of hydrocarbon and NOx. It is not clear what the NOx levels in this study mean in terms of the reaction pathways. It appears that the authors assume that under the "low-NOx" conditions in this study, the dominate fate of the peroxy is reaction with HO2. It is not immediately clear how this is the case, especially with the high levels of hydrocarbon and NOx, and without an external HO2 source. To what extent does RO2+HO2 proceed in these experiments and whether organic hydroperoxide should be produced in the first place?

The results in this study should be compared with prior literature and discussed. For instance, Kramer et al. (2016) found that for isoprene SOA, high-NOx conditions produce SOA that is more oxidizing compared low-NOx conditions. But, the results in this work suggest the opposite. Results from SOA formed from different hydrocarbons should also be compared to prior literature when available (e.g., Rattanavaraha et al., 2011, Tuet et al., 2017a; Tuet et al., 2017b). Tuet et al. found the DTT activity of different SOA to be fairly insensitive to RO2 fate.

Further, the same authors of this manuscript published a recent paper in Atmos Environ (Jiang et al. 2016) on similar experiments, but the results under similar reaction conditions are not the same as those reported in this study. Please clarify and discuss accordingly.

It was noted that the SOA yields in this study are consistent with prior studies. SOA yields should be compared in the context of organic mass loadings. It does not appear that the yields in this work are in line with literature. Based on the numbers provided in Table 1, the SOA yields calculated are very different from prior studies. Please see detailed comments below. The implications of these differences should be considered and discussed. If the yields are so different, what does it imply regarding their corresponding SOA composition and their health effects? On a related note, the organic mass loadings (one can calculate them based on Table 1) are high in these experiments, which will result in partitioning of more volatile species into the particle phase compared to ambient. The implications of this on the measured DTT activity in this

study and how they can be applied to ambient should also be discussed.

The authors attributed the difference in [OHP]m between low and high NOx experiments to sample collection times and associated aging. I do not think this is well-justified. Many other parameters are also changing at the same time.

Finally, the basis for comparison of DTT activity is time of the sample collection in many cases. Is that chosen to represent OH exposure? But if so, it is not clear that [OH] are constant and comparable across different experiments.

Overall, I recommend publication with major revisions. More detailed comments below.

1. Page 1, line 14. Define clearly what is considered as high vs. low NOx conditions in this study.

2. Page 4, methods.

a. Was seed aerosols used in the experiments? Please state clearly.

b. The NOx levels in this study were very high in all experiments. The authors need to define LNOx and HNOx clearly in the methods.

c. HONO was used only in toluene experiments, why? The other experiments used NOx (was that NO or NO2? Or both? In what ratio?)

d. The authors should provide figures (in the SI) to show the typical time series of hydrocarbon, NO, NO2, ozone, SOA mass for an experiment using HONO vs an experiment using NOx. This is critical to give some context regarding the conditions under which the SOA samples were collected for DTT analysis. (for instance, what was the NOx levels when the SOA samples were collected? This has important implications on the SOA composition and whether the results from different SOA samples can be directly compared.)

e. What is the collection efficiency of the PILS? How is it calculated? How is it validated? As the DTT values was normalized by mass, the authors need to provide more

details to justify the accuracy of the SOA mass values used in the DTT calculations.

3. Page 6, line 17. It was noted that "The SOA mass applied to DTT assay was constrained to ensure that the DTT consumption remained less than 50 % of DTT0." Why?

4. Page 6, line 20 onwards, the NPBA assay. It is not clear how the authors treat (or correct for) potential interference from other SOA components in the NPBA assay measurements.

a. It was noted that absorbance at 406 nm (authors referring to 4-nitrophenol) of SOA before reaction with NPBA was negligible. I do not understand why this is the case. The oxidation of aromatic compounds (such as toluene) by OH in the presence can result in the formation of 4-nitrophenol? If so, why is the absorbance at 406nm negligible?

b. In terms of potential interference from alcohols, it was noted that glycerol aqueous solutions were tested using the NPBA method and no measurable absorption appeared in UV spectrum. The authors then concluded that the UV absorption spectrum was originated from 4-nitrophenol. Multi-functional alcohols can be formed from the oxidation of hydrocarbons. How do the authors justify that the results from glycerol is representative and that the measured absorption is purely from 4-nitrophenol formed by NPBA reactions with organic peroxides, without any interference from other SOA components?

c. Why "no more than 10 ug SOA was applied to the NPBA assay"?

5. Page 7, line 16 onwards, PAN analysis. Please provide further details to show that PAN are completely hydrolyzed in 15 mins.

6. Page 8, line 14-18. SOA yields from different hydrocarbons cannot be compared without the context of organic aerosol mass, as yield is typically a function of organic aerosol mass (Odum equation).

a. In Table 1, while one can calculate the organic mass loading from deltaHC and

yield, the authors should also provide the organic mass loadings in the table to facilitate easier comparison of yields from this study to prior studies.

b. I quickly did the calculations, but found that the yields for the different hydrocarbons are very different from the previous studies cited in the manuscript. For instance, the yield for isoprene SOA photooxidation (with NOx/isoprene ratio of ∼5) is all ∼ 5% for Kroll et al., Xu et al., and this study. However, the organic mass loading that corresponds to this 5% SOA yield in Kroll et al and Xu et al is ∼ an order of magnitude smaller than this study. This means that when plotted in the Y vs. deltaMo (Odum equation) space, the SOA yields under this specific NOx/isoprene ratio in this study is substantially lower than all previous studies. Discrepancies also exist for other hydrocarbons. The authors should conduct a detailed comparison with previous studies by showing their data in the yield curve space and comparing with others. The discrepancies should be discussed.

7. Page 9, line 8-15. Comparison of response of aerosols from different hydrocarbons. This section needs to be expanded to include more discussions (in addition to the description of results).

a. The authors noted that a previous study by Fujitani et al. (2012) with epithelial cells is consistent with this study. Can the cellular results from Fujitani et al. (2012) be directly compared to the DTT in this study? Please discuss.

b. How do results in this work compare to previous studies? For instance, recent work from Tuet et al. showed that the response from naphthalene is higher than other hydrocarbons such as m-xylene and a-pinene; McWhinney has also demonstrated previously that showed naphthalene SOA is highly redox-active. It would be useful that the authors provide some context and discuss the DTT activity of different SOA with respect to previous work.

8. Page 9, line 25. It was stated that "...DTTm of low-NOx isoprene SOA was much higher than that of high-NOx isoprene SOA". This does not seem like it is the case from

Figure 4. Some data points overlap and are within uncertainty.

9. Page 9, line 27. (and page 10) But for the "toluene LNOx-17 Nov 2016", the data are not linear? i.e., will the data also start from the origin, if so, considering the origin and the 5 data points in Figure 4, the overall trend is then non-linear? Please discuss.

10. Page 10, quinones. The authors stated that "the redox cycling of quinones was not the major mechanism underlying DTT consumption by the SOA". A small contribution of quinones to the total aerosol mass does not necessarily mean they are not important for overall toxicity? Oxidation of the aromatic compounds used in this study can lead to formation of quinones (e.g., Bloss et al., 2005). Many previous studies have pointed to the importance of quinones in ambient PM toxicity. It is not clear how the results in this work should be placed in the context of previous work that pointed to the importance of quinones for PM toxicity. Please discuss.

11. Page 11, NOx conditions.

a. Line 5 onwards. The authors noted that under low NOx conditions, RO2 predominately reacts with HO2, producing hydroperoxides (among other products). This accuracy of this statement will depends on what precisely the "low NOx conditions" are, as "low NOx conditions" do not directly (or necessarily) translate to RO2+HO2 reactions. It is not clear that RO2+HO2 is the dominant reaction under the conditions of this study. The hydrocarbon concentration used in this study is very high (hundreds of ppb to several ppm), there is abundant NOx (even under "low NOx" conditions), but no addition HO2 source (such as H2O2). With this, it is not clear how RO2+HO2 dominates. Since a large fraction of the discussions in the manuscript hinged on this, it is critical that this is justified clearly in the manuscript. The authors can perform a simple simulation of the relative importance of different RO2 reactions under their "low" and "high" NOx conditions.

b. The authors shall compare and discuss their results in the context of previous studies. For instance, a recent Kramer et al. (2016) concluded that High-NOx con-

ditions produce SOA that is more oxidizing compared low-NOx conditions. This re-sults from this work showed the opposite. Please discuss. Also, Tuet et al. (2017a, 2017b) specifically studied the toxicity of SOA (including isoprene) under RO2+HO2 vs RO2+NO reactions conditions, and found DTT activity of isoprene SOA to be similar under RO2+HO2 and RO2+NO conditions, also for other SOA except naphthalene.

c. How do the data in this study compare the results from a previous study by the same author (Jiang et al. AE, 2016). For example, the "without denuder" data in Figure 2 Jiang et al AE paper can be compared to those in the current study. But comparing this study and their previous AE publication, the results (in terms of the DTTt values) are different for each hydrocarbon under similar conditions? Please compare and discuss, and confirm self-consistency if that is the case.

d. Line 20, and figure 6. What is the x-axis (time) supposed to be a surrogate of? If it is supposed to be a surrogate for OH exposure, then the OH level should be the same is each experiment. Is this the case? The authors simply explained the differ-ence in [OHP]m between low and high NOx toluene SOA as the low-NOx SOA being collected at a later time and resulted in a lower level of [OHP]m due to further reac-tions/photooxidation. I do not think the authors can discount other factors, such as the varying RH (maybe SOA composition is different due to different RH?), organic mass loading (when I used the numbers in Table 1 and calculated the mass loadings for the toluene experiments shown in Figure 6, the loadings are very different for the two experiments), etc?

12. Table 1. Was ozone present in these experiments? If so, please include some in-formation here. This should also be specified and discussed clearly in the manuscript, in case some of the SOA is formed from ozonolysis in addition to OH oxidation.

Minor Comments:

1. Page 1, line 26. Clearly state in the abstract under what NOx conditions the sen-tence "The amount of organic hydroperoxide was substantial, while PANs were found

to be insignificant for both SOA." 2. Page 1, line 29. Clearly state what "model compound study" refers to. 3. Page 2, line 8. The author should also cite McDonald et al. (2012, Inhal. Toxicol), McWhinney et al. (2013, ACP), Kramer et al., (AE, 2016), Tuet et al. (2017, ACP), and Tuet et al. (2017, ACPD). 4. Page 4, line 7-9. The authors should state clearly that only selected (but not all) toluene and isoprene SOA samples are analyzed with the Griess and NPBA assays. 5. Page 5, line 16. Was 23 May 2016 a typo? Should it be July 22? (based on Table 1)