

Response to comments from referee #3 (Manuscript Ref. NO: acp-2017-214)

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We really appreciate the referee for providing these constructive comments. The detailed responses are presented as below.

This study investigated the DTT activity of different types of SOA (toluene, TMB, isoprene, α -pinene) formed in the presence of NO_x. Experiments are conducted in an outdoor chamber facility with different levels of NO_x. Results showed that in the presence of relatively higher levels of NO_x, DTT activity of toluene SOA is 2-5 times higher than other SOA. Isoprene SOA has lower DTT with increasing NO_x. Other SOA appears to be insensitive to NO_x. 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 NO_x. It is not clear what the NO_x levels in this study mean in terms of the reaction pathways. It appears that the authors assume that under the “low-NO_x” 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 NO_x, 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?

Response: Please find the response to question 11 (a) below.

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-NO_x conditions produce SOA that is more oxidizing compared low-NO_x 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.

Response: Please find the response to question 7(b).

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.

Response: Please find the response to question 11(c).

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.

Response: Please find the response to question 6(a), 6(b) and 11(d).

The authors attributed the difference in [OHP]_m between low and high NO_x 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.

Response: Please find the response to question 11(d).

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.

Response: Please find the response to question 11(d).

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

Major comments:

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

Response: The high NO_x condition represents the initial HC/NO_x ratio <10 ppbC/ppb. The low NO_x condition represents the initial HC/NO_x ratio >10 ppbC/ppb. We clarified the definition of high and low NO_x conditions in the revised manuscript (Section 2.1, Figure 2 and Figure 5).

2. Page 4, methods.

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

Response: We added one sentence to the revised manuscript (Section 2.1): “No seed aerosols were added in this study.”

b. The NO_x levels in this study were very high in all experiments. The authors need to define LNO_x and HNO_x clearly in the methods.

Response: Please find the response to question 1.

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

Response: The HONO was injected during toluene experiments to accelerate the photooxidation of toluene. NO (2% in N₂, Airgas) was injected as NO_x source in other experiments. We clarified the injection of HONO and NO_x in the revised manuscript (Section 2.1), and read now, “HC and NO (2% in N₂, Airgas) were injected to the chamber before sunrise. For photooxidation experiments of toluene, HONO generated from the reaction of 0.1 M NaNO₂ solution and 10 % w/w H₂SO₄ solution was injected into the chamber as a source of OH radicals.”

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 NO_x. 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 NO_x 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.)

Response: The reaction of toluene with OH radicals is much slower than other VOCs. Thus, we added HONO to the chamber at the beginning of the experiment. All toluene experiments were conducted in the presence of HONO except one experiment on Feb/12/2016. For the consistency in toluene SOA data, the toluene experiment without HONO has been removed in the revised manuscript. In order to response to the reviewer, the time profiles of NO, NO_x, HC, ozone, and SOA mass concentrations have been included in supporting information (Figure S1). SOA samples were collected when the SOA mass concentration reached nearly to the maximum point.

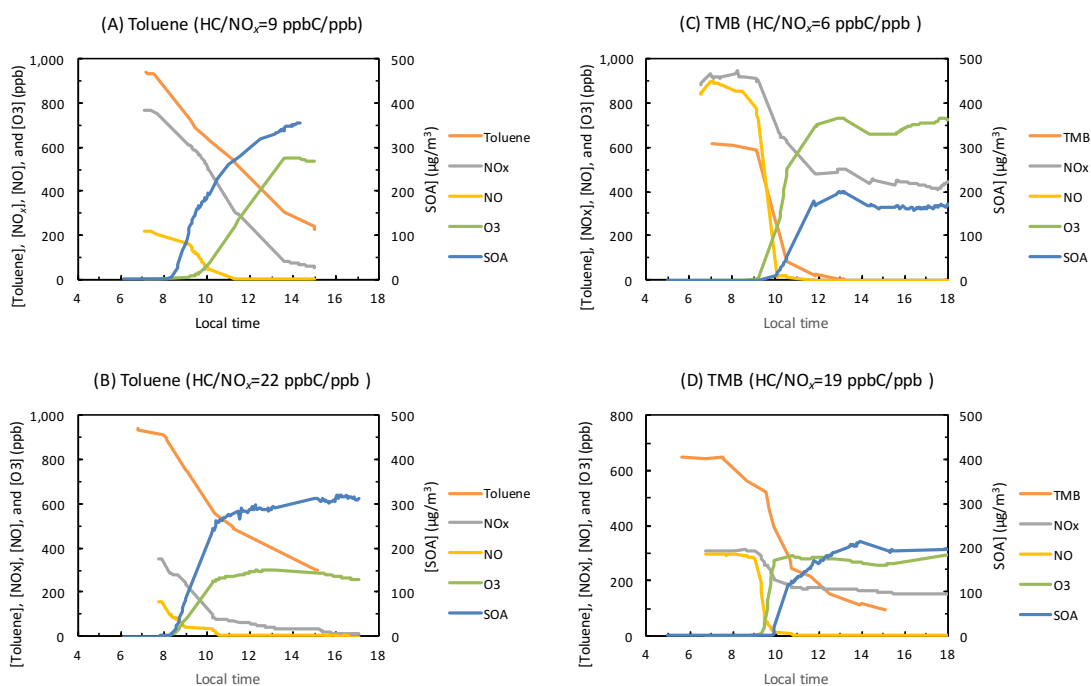


Figure S1. The time profile of SOA mass concentration, toluene, TMB, NO_x, NO and O₃ mixing ratios through the experiment.

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.

Response: The collection efficiency of PILS for was published by Orsini et al (2003). We clarified the collection efficiency in the revised manuscript (Section 2.2) as below:

“The sampling efficiency of PILS is greater than 95 % for particle size ranging from 0.03 to 6 μm (Orsini et al., 2003).” A value of 95% was used as the collection efficiency of PILS.

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?

Response: We modified this sentence as follows:

“To ensure the pseudo-1st-order reaction between DTT and redox-active species in SOA, the SOA mass applied to DTT assay was constrained so that the DTT consumption remained less than 50 % of DTT₀.”

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?

Response: 4-Nitrophenol can be found in toluene SOA. The influence of 4-nitrophenol in SOA on NPBA assay was discussed in Section 4.2 (revised supporting information) and reads now, “4-Nitrophenol, a NPBA assay product, can also be found in toluene SOA and potentially influences on NPBA data. However, the light absorption of the SOA sample collected using PILS was negligible at 406 nm, suggesting that NPBA data is not influenced by the light absorbing materials in SOA products.”

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?

Response: The mechanism of NPBA assay is the production of 4-nitrophenol from the reaction between OOH functional group and NPBA. The SOA contains a lot of OH functional groups, which might also react with NPBA. To make sure that the OH functional groups don't interfere with the detection of hydroperoxides, we did the test of glycerol and found that there was no 4-nitrophenol produced from the mixture of glycerol and NPBA. The influence of multi-alcohols on NPBA assay was moved to Section S4.2 (revised supporting information) and reads now (next page),

“The influence of multi-alcohols and 4-nitrophenol on NPBA assay. It has been reported that boronic acid can react with multi-alcohols to form colorful products (Kim et al., 2007). SOA products are often multifunctional including multi-alcohols. To examine the possible interference by alcohol adducts, the glycerol aqueous solution was tested for the NPBA method. However, no measurable absorption appeared in the UV spectrum.”

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

Response: We removed this sentence in the revised manuscript.

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

Response: The information of hydrolysis time for Griess assay was included in supporting information (S4.3) and reads now,

“Hydrolysis time of PAN products in SOA. In this study, the hydrolysis time for PANs was set to 15 min. To ensure that 15 min is enough to hydrolyse the PANs in SOA products, the Griess response with 15-min hydrolysis was compared to that with 30-min hydrolysis. There was no significant difference in Griess response between a 15-min hydrolysis and a 30-min hydrolysis. “

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 ΔHC 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.

Response: The SOA mass loadings were included in Table 1. The new table is shown in the next page:

Table 1. Outdoor chamber experiment conditions

HC and Date	Initial HC ppb	Initial NO _x (HONO) ^a ppb	initial HC/NO _x ppbC/ppb	Δ HC ppb	[SOA] _{max} ^b $\mu\text{g}/\text{m}^3$	γ %	Mid- collection time ^c	RH ^d %	Temp ^d K	Chemical assay ^e
<i>Toluene</i>										
13 Feb 2016	641	525 (193)	9	403	229	15.1	13:40	22–63	281–303	DTT
01 May 2016	935	766 (133)	9	631	348	14.6	14:20	18–46	294–316	DTT, PAN
01 May 2016	938	301 (73)	22	542	292	14.3	12:10	21–48	294–315	DTT, PAN
23 May 2016	691	906 (250)	5	546	148	7.1	13:20	18–60	288–315	DTT, Enhance
23 May 2016	735	313 (86)	16	421	147	9.3	15:40	15–22	307–316	DTT, Enhance
18 Aug 2016	640	783 (179)	6	517	178	9.1	12:30	24–61	297–319	DTT, OHP
06 Aug 2016	610	240 (55)	18	216	75	9.2	12:30	43–59	297–305	DTT
18 Aug 2016	342	107 (24)	22	227	44	5.2	14:20	20–38	303–321	OHP
17 Nov 2016	622	179 (43)	24	452	139	8.1	13:20	12–56	282–309	DTT ^f
<i>TMB</i>										
04 Oct 2015	613	920	6	613	201	6.7	14:40	20–43	290–310	DTT
04 Oct 2015	657	310	19	542	207	7.8	13:20	24–46	290–306	DTT
20 Feb 2016	589	1024	5	548	150	5.6	13:00	14–60	282–311	DTT
20 Feb 2016	583	156	34	455	128	5.7	14:40	16–61	282–311	DTT
11 Jan 2016	595	256	21	414	114	5.6	15:50	23–81	274–298	Enhance
<i>Isoprene</i>										
23 Apr 2016	2693	2680	5	2693	352	4.7	12:00	18–48	290–314	DTT
23 Apr 2016	2755	430	32	2755	93	1.2	13:30	23–51	290–312	DTT
14 May 2016	2928	2800	5	2928	406	5.0	14:20	17–47	292–315	DTT, Enhance
14 May 2016	2858	423	34	2858	107	1.3	12:00	25–55	293–312	DTT
22 Jul 2016	2525	2423	5	2525	246	3.5	13:20	20–55	297–320	PAN (gas) ^g
22 Jul 2016	2718	473	29	2718	70	0.9	12:50	23–58	297–320	PAN (gas) ^g
20 Aug 2016	3060	3300	5	3060	279	3.3	12:30	20–58	296–321	DTT, OHP, PAN
20 Aug 2016	3173	583	27	3173	125	1.4	11:50	25–61	297–318	DTT, OHP, PAN
<i>α-Pinene</i>										
25 Feb 2016	319	639	5	319	257	14.5	15:00	21–63	278–299	DTT
25 Feb 2016	323	91	36	323	650	36.1	13:30	25–67	278–298	DTT
18 Jan 2016	257	144	18	257	223	15.6	15:50	25–78	275–297	Enhance

^a For toluene experiments, NO_x was contributed by NO, NO₂ and HONO. The concentration of HONO was estimated using the difference in the NO₂ signal with and without the base denuder (1 % Na₂CO₃+1 % glucose).

^b The maximum SOA concentration during the experiment.

^c This column is the mid-collection time (local time) of SOA sampling.

^d The RH and temperature conditions shown in the Table 1 were recorded from the beginning of photooxidation (sunrise) until the ending of PILS sampling.

^e The SOA samples were applied to a series of chemical assays, namely DTT assay (DTT), DTT enhancement (Enhance), organic hydroperoxides analysis (OHP), and PAN analysis (PAN)

^f For DTT measurement of toluene SOA sample collected on 17 Nov. 2016, the concentration of potassium phosphate buffer (0.8 mM) in the first step of DTT assay was two times higher than the typical buffer concentration (0.4 mM). The DTT_m of the toluene SOA sample (17 Nov. 2016) is shown in Fig. 3.

^g The concentration of gaseous PAN products (collected by an impinger) was measured by the Griess assay.

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 NO_x/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. Mo (Odum equation) space, the SOA yields under this specific NO_x/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.

Response: Thanks for point out this comparison.

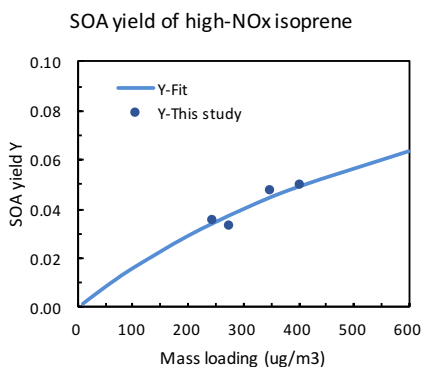
Low NO_x: The SOA yields of low-NO_x isoprene in this study were lower than the values reported by Kroll et al. (2006) or Xu et al. (2014) by several reasons. The HC ppbC/NO_x ratio of our study (low NO_x: 27-34) was much different from the study by Kroll and Xu (NO_x-free). The maximum temperature of the experiments in this study (312-320 K) was higher than the temperature condition in the study of Kroll (around 298 K) or Xu (around 298 K). The temperature effect on SOA yields were discussed in the revised manuscript (Section S3.1) and reads now, “Our SOA yields for isoprene SOA were lower than those reported in previous studies (Carlton et al., 2009; Xu et al., 2014) because the temperatures in our studies were higher than those sourced from indoor chambers.”

In order to response to the reviewer, our isoprene SOA yields at high NO_x conditions (HC/NO_x = 5) were compared to the theoretically predicted SOA yields using the two-product model (Carlton et al. 2009).

$$Y_{\text{high NO}_x} = \frac{0.154}{(K_{\text{OM,high NO}_x}(T)M_0)^{-1} + 1}$$

$$K_{\text{OM,high NO}_x}(T) = K_{\text{ref}} \times \exp\left[\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right]$$

$K_{\text{ref}} = 0.0020$, $T_{\text{ref}} = 303\text{K}$, M_0 is the total aerosol concentration ($\mu\text{g}/\text{m}^3$). At $T = 313\text{K}$ (a typical temperature during our isoprene experiments), $K_{\text{OM,high NO}_x} = 0.00117$. The observed SOA yields agrees well with the predicted yields as shown below,



Reference: Carlton et al., A review of Secondary Organic Aerosol (SOA) formation from isoprene, Atmos. Chem. Phys., 9, 2009

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.

Response: Because no cellular study was conducted in this paper, we removed the comparison of our results with those of Fujitani et al. In order to response to the reviewer, a new citation was included in the revised manuscript, and reads now,

“The DTT activity of a given SOA can be applied to the assessment of SOA’s ability to oxidize cellular materials. For example, the recent study by Tuet et al. (Tuet et al., 2017a) reported a positive nonlinear correlation between DTT activities and ROS production in murine alveolar macrophages.”

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 α -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.

Response: In the previous manuscript, the DTT activity of naphthalene SOA reported by McWhinney was discussed in the Section 1. The DTT activities of SOA in this study were also further compared with other studies (Sect. 3.1, revised manuscript) and reads as:

“The DTT_t values of this study were also compared with those reported in previous studies. The DTT_t values of α -pinene SOA in this study were close to those reported by Tuet et al. (Tuet et al., 2017b). The DTT_t values of isoprene SOA was, however, higher than those observed by Tuet et al. (Tuet et al., 2017b) and Kramer et al. (Kramer et al., 2016). This difference might be caused by the degree of aerosol aging under different NO_x conditions, initial OH radical sources, humidity and temperature.”

8. Page 9, line 25. It was stated that “: : DTT_m of low-NO_x isoprene SOA was much higher than that of high-NO_x isoprene SOA”. This does not seem like it is the case from Figure 4. Some data points overlap and are within uncertainty.

Response: We re-draw this figure to make the difference of DTT_m between low-NO_x isoprene and high-NO_x isoprene clearer. As shown in Figure 3 (revised manuscript), it is obvious that the DTT_m of low-NO_x isoprene SOA was significantly higher than high-NO_x isoprene SOA after a long-time reaction (t=120 min).

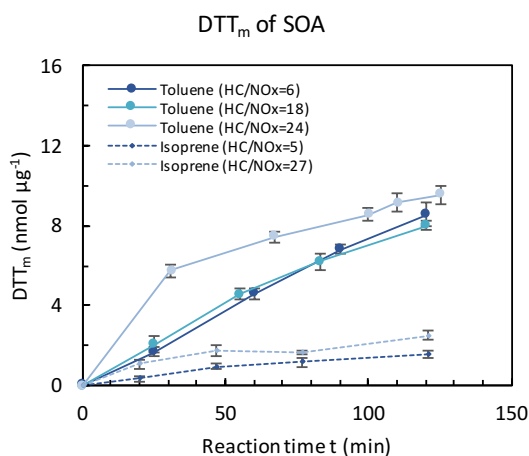


Figure 3. Time profile of DTT_m for toluene and isoprene SOA under different NO_x conditions. To achieve the completion of the reaction between DTT and SOA, the DTT_m of toluene sample (HC/NO_x=24 ppbC/ppb collected on 17 Nov. 2016) was measured with a 0.8 mM potassium phosphate buffer in the first step of DTT assay (2 times higher than the typical buffer concentration (0.4 mM)). Each error bar was calculated by $t_{0.95} \times \sigma / \sqrt{n}$ using three replicates, where $t_{0.95}$ is the t-score (4.303 for $n = 3$ replicates) with a two-tail 95 % confidence level.

9. Page 9, line 27. (and page 10) But for the “toluene LNO_x-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.

Response: We re-draw figure 4 by adding lines for each case. The DTT_m of toluene LNO_x (collected on 17 Nov 2016, HC/NO_x=24 ppbC/ppb) is not linear with reaction time and eventually reached to a plateau (Figure 3, revised manuscript). Please find Figure 3 in response to question 8.

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.

Response: In the previous manuscript (Section 1), we discussed the difference in compositions between SOA and typical combustion particulates. Combustion particles contain a small amount of metals, PAHs and oxy-PAHs, which can be redox catalyzers. Such compounds in SOA are negligible.

11. Page 11, NO_x conditions.

a. Line 5 onwards. The authors noted that under low NO_x conditions, RO₂ predominately reacts with HO₂, producing hydroperoxides (among other products). This accuracy of this statement will depend on what precisely the “low NO_x conditions” are, as “low NO_x 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 NO_x (even under “low NO_x” 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” NO_x conditions.

Response: Please find the definition of low-NO_x and high-NO_x in response to question 1. We clarified the NO_x condition in Figures 2 and 5. As suggested by the reviewer, we simulated the relative significance of RO₂+NO and RO₂+HO₂ at two different HC ppbC/NO_x ratios (6 and 25) for toluene. Based on integrated reaction rate (IRR) analysis for several RO₂ species, the reaction of RO₂+NO is very sensitive to NO_x condition: i.e., the IRR at the high NO_x level is 5 times higher than that at the low NO_x. The IRR of RO₂+HO₂ is higher at the low NO_x level but relatively less sensitive than the reaction of RO₂+NO. However, our IRR analysis is for the gas phase oxidation. The composition of aerosol is complex due to the involvement of aerosol phase reactions of various multifunctional organic compounds.

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-NO_x conditions produce SOA that is more oxidizing compared low-NO_x conditions. This results 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.

Response: Please find the response to question 7(b).

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.

Response: The DTTt values reported in this study should be compared to those with denuder in our previous study (Jiang et al. AE, 2016), because the carbon denuder was also applied in this study (Section 2.1). The effect of denuder on DTTt has been explained in our previous study. Overall, there was no difference between the DTTt reported in this study and the values reported by our previous study (Jiang et al. 2016). For example, the DTTt of isoprene SOA (low NO_x) was about 50-60 pmol min⁻¹ μg⁻¹ in this study, which was the same to the values reported before. The DTTt of toluene SOA (with denuder, collected during 13:30-14:50) was reported to be 43 min⁻¹ μg⁻¹ in the previous study, and was lower than the DTTt of toluene SOA (collected in the morning or early afternoon) due to the aging effect. The influence of aging on DTT response was consistent with that reported in this study (Section 3.1).

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 in each experiment. Is this the case? The authors simply explained the difference in [OHP]_m between low and high NO_x toluene SOA as the low-NO_x SOA being collected at a later time and resulted in a lower level of [OHP]_m due to further reactions/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?

Response: The x-axis is based on local time (EST). In Figure 6, the RH conditions of high-NO_x and low-NO_x experiments for toluene SOA are similar because two experiments were conducted in the same day. As pointed by the reviewer, other factors, like organic mass loading, may also influence the SOA compositions. Overall, we think that the major factors to affect SOA compositions are the NO_x condition and the aging process.

12. Table 1. Was ozone present in these experiments? If so, please include some information 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.

Response: Ozone was not introduced to chamber but was formed during the photooxidation of biogenic HCs (i.e. isoprene and α-pinene). The additional sentences were added to the 1st paragraph in section 3.1 and read now,

“Aromatic hydrocarbons (toluene and 1,3,5-trimethylbenzene) are mainly oxidized by OH radicals while biogenic hydrocarbons (isoprene or α-pinene) by both OH radicals and ozone. Based on the IRR (integrated reaction rate) analysis, the oxidation of isoprene by OH radicals is at least 3 times higher than that by ozone at the low NO_x condition. The oxidation of biogenic hydrocarbons is dominated by OH radicals, particularly, in the morning.

Minor Comments:

1. Page 1, line 26. Clearly state in the abstract under what NO_x conditions the sentence “The amount of organic hydroperoxide was substantial, while PANs were found to be insignificant for both SOA.”

Response: This sentence was modified as follows

“Under the NO_x conditions (HC/NO_x ratio: 5-36 ppbC/ppb) applied in this study, 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.

Response: This sentence was modified as follows,

“The DTT assay results of the model compounds study suggest that electron-deficient alkenes, which are abundant in toluene SOA, could also modulate DTTm”

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).

Response: These references were included in the revised manuscript (Section 1).

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.

Response: This sentence was modified as follows

“Selected toluene and isoprene SOA samples were immediately applied to the DTT assay and the quantification of particulate oxidizers.”

5. Page 5, line 16. Was 23 May 2016 a typo? Should it be July 22? (based on Table 1)

Response: The date of experiment was corrected as below: “To measure the concentration of PANs in the gas phase, gaseous photooxidation products (22 Jul 2016) were collected using an impinger (filled with 5 mL DI water) at a flow rate of 0.8 L min⁻¹.”