

Interactive comment on “Secondary organic aerosol formation from toluene photooxidation under various NO_x conditions and particle acidity” by G. Cao and M. Jang

G. Cao and M. Jang

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We would like to thank the reviewer for the thoughtful comments.

Response to reviewer # 1:

Comment 1. "How is wall loss corrected for and how much aerosol growth is "added back"(compare to the amount of aerosol growth reported)?"

Response: As mentioned in the paper (Page 14471, Line 20), we assume that the size- dependent particle lost to the chamber wall is controlled under a first order decay (McMurry and Grosjean, 1985). The data for the particle loss to the chamber wall is obtained from (NH₄)₂SO₄ aerosol atomized into the chamber by monitoring its decay

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over time for each particle size bin. All SOA data are corrected empirically for the wall loss using the first order rate constant for each particle size bin. On average, 15% SOA mass of this study increases after wall loss correction.

Comment 2. "The authors should specify the concentrations of the solutions used."

Response: The concentration of the solution has been added in the revised manuscript (line 27 of Page 14471): "atomizing 0.005 mol/L inorganic aqueous solution (various combinations of ammonium sulfate, ammonium bisulfate and sulfuric acid) with a Constant Output Atomizer (TSI, Model 3076, Shoreview, MN)."

Comment 3. "How does one define "proton concentration" in a solid seed?"

Response: All proton concentrations of the inorganic seed (either neutral or acidic seed) are calculated based on the output of the ISORROPIA at a given RH, temperature and seed composition. The ISORROPIA calculation shows that the proton concentrations of the neutral seed (ammonia sulfate) at both high RH level and low RH level equal to $0.01 \mu\text{g}/\text{m}^3$ which is near zero. Line 25 of Page 14472 already addressed how the proton concentrations are calculated in this study. The resulting proton concentrations are listed in Table 1.

Comment 4. The reviewer comments on the paragraph: "Channels A and B are the dominant pathways under low NO_x conditions, while channels C and D are significant under the intermediate and high NO_x conditions....for the intermediate NO_x conditions, channel C is likely the dominant pathway to convert NO to NO_2 and generate carbonyls". (1) Under low NO_x condition, the reviewer thinks "only $\text{RO}_2 + \text{HO}_2$ is significant given the high concentration of H_2O_2 used".(2) Under the intermediate NO_x conditions, the reviewer questions whether $\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2$ dominates over $\text{RO}_2 + \text{NO} \rightarrow \text{RONO}_2$ and suggests "authors should at least make a quick estimate on the relative importance of different channels based on the reactive rate constants of RO_2 with $\text{RO}_2/\text{HO}_2/\text{NO}$."

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Response: For the first question, we agree that RO_2+HO_2 should be dominant over $\text{RO}_2 + \text{RO}_2$ under our low NO_x experimental conditions. However, the statement that "Channels A and B are the dominant pathways under low NO_x conditions" are made specifically in the comparison against Channels C and D. For the second question, according to the Master Chemical Mechanism (MCM) (<http://www.chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html>) of gas phase toluene oxidation, the reaction rate constant of $\text{RO}_2+\text{NO}\rightarrow\text{RO}+\text{NO}_2$ is at least 8 times greater than that of $\text{RO}_2+\text{NO}\rightarrow\text{RONO}_2$.

A sentence has been made in line 24 of Page 14473: "According to the Master Chemical Mechanism (MCM) (Jenkin et al., 2003), the ratio of the rate constants of RO_2 reacting with RO_2 , HO_2 and NO is 1.0: 21.3: 1.1(producing RONO_2): 8.6 (producing $\text{RO} + \text{NO}_2$)."

Comment 5a. "Do the authors have any suggestion on what type of heterogeneous reaction may be in play here and result in the enhanced yield?"

Response: The revised sentence reads now (Line 22-25 on Page 14476) "Firstly, the role of water is more important than that of particle acidity for a certain type of reactions such as the formation of peroxyhemiacetals (Fig. 2) between a hydroperoxide and an aldehyde in the particle phase (Johnson et al., 2004), although various heterogeneous reactions in the particle phase are sensitive to particle acidity and water (WV and WP) in the system". This conclusion has been made based on the experimental observation of $\Delta Y_{\text{HRH-LRH}}$ with the neutral seed and the acidic seed. For the neutral seed, we expect no significant acidity effect on $\Delta Y_{\text{HRH-LRH}}$. Therefore, -29% reduction of the SOA yield in the neutral system should be mainly due to the WV effects. Applying the same magnitude of WV effects to the acidic conditions, WV effects on $\Delta Y_{\text{HRH-LRH}}$ (-35%) with the acidic seed would be more significant than acidity effects. This indicates that the heterogeneous reactions of ROOH and an aldehyde can occur considerably even in the absence of acidic seed. The acceleration of SOA formation through these reactions of ROOH and an aldehyde by the presence of acidic seed may

be insignificant. However acidity effects are important for some types of heterogeneous reactions: For example, organic sulfate formation can only contribute SOA formation significantly in the presence of acidic sulfate seed. The acid catalyst is necessary for some heterogeneous reactions which are combined with irreversible reaction steps such as dehydration or rearrangement.

Comment 5b. "Ng et al. (2007) studied SOA formation from aromatic hydrocarbons but the authors did not observe any significant increase in SOA formation under both high and low NO_x conditions (and $\text{RH} < 10\%$)." The reviewer asked authors to comment on the difference between the observation of this study and that of Ng et al. (2007).

Response: The finding from the studies of Ng et al has been mentioned in line 2-4 of Page 14470 of the manuscript. The calculation from ISORROPIA shows that the proton concentrations in both the neutral seed and the acidic seed (a mixture of $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4) at $\text{RH} \sim 5\%$ are near 0. Such low proton concentrations explained why no SOA yield difference was observed for the different seed types in their study. The extremely low RH level ($\text{RH} \sim 5\%$) is not relevant to the ambient atmospheric conditions.

Comment 5c. Clarify the confusion of "second" reason for the difference in yield between low and high RH experiments.

Response: The "second" reason is used to explain why SOA yield with acidic seed has additional decrease due to the increase in RH% compared to SOA yield with neutral seed. The water dilution (still the RH effects) of the acidic seed changes the particle acidity of the acidic seed, decreasing more SOA yield with acidic aerosols.

Comment 5d. The authors wrote "Thirdly, the partitioning processes may be influenced by WP particularly for hydrophilic products". How would this explain the higher aerosol yield observed in low RH experiments? "More water content in the particle at high %RH can facilitate partitioning of hydrophilic products resulting in more SOA production" - if this is true, shouldn't we expect more SOA formation in the high RH experiments?"

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Response: We attempted to propose all possible mechanisms which could take place under our experimental conditions. Various mechanisms or reaction pathways for SOA formation may respond differently to applied environmental parameters. For example in the case here, no one will deny that "More water content in the particle at high %RH can facilitate partitioning of hydrophilic products resulting in more SOA production". However, the significance of this mechanism also relies on the fraction of hydrophilic products in the total toluene oxygenated products and how water content in the particle relates to the environmental %RH.

Comment 6. The reviewer has concerns about dividing the high NO_x experiments into two NO regions and comparison of SOA yields of two NO regions against those under other NO_x conditions (Table 1).

Response: Since we agree with the reviewer, for the comparison purpose the SOA yields at high NO_x are straightforwardly determined at the end of SOA experiments (same as others at the low and the intermediate NO_x). Such SOA yields at high NO_x are listed in Table 1.

However, we think the high NO_x experiments provide very good cases to study the dynamic change of dominant chemistry mechanisms for SOA formation with NO concentration. Valuable information would be left out if we only consider the initial several SMPS data points and the final several points of the high NO_x experiments for SOA yields. We think the information from the two NO fraction of the high NO_x experiments can also potentially have implication for SOA formation in the ambient air where NO concentration is high for a certain time period (e.g., in the morning) and then decrease till NO concentration is very low (e.g., in the early afternoon). Therefore, we added a table (Table 2) to show the SOA yields for the low and the high NO fraction.

The sentences in Line 11-13 on Page 14473 has been changed to: "The SOA yields (Table 1) were 0.2-0.38 at low NO_x; 0.13-0.28 at intermediate NO_x; 0.12-0.13 at high NO_x. Within the high NO_x experiments, the SOA yields (Table 2) were 0.17-0.21 at low

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NO fraction of high NO_x conditions and 0.027-0.031 at high NO fraction of high NO_x conditions".

Comment 7. The reviewer questions the explanation of this manuscript for the change in the shape of growth curves (Figure 5C) and suggests the authors adding the time profiles for the NO and NO₂ concentration at high NO_x levels.

Response: We added the time profiles of NO and NO₂ for a typical high NO_x experiment in Figure 5C in the revised manuscript. We also changed the sentence (Line 1-3 on Page 14481) "this is likely because large amounts of nitro products existed in the system at high NO₂ concentrations and the gas-particle partitioning of nitro products act as the dominant pathways for SOA formation" to "This is likely because reactions of RO₂ with HO₂ become the main channels to form less volatile compounds or more reactive compounds for heterogeneous reactions when NO concentration is low. Some nitro-containing compounds, which are possibly produced at high NO₂ concentrations, can contribute SOA formation through gas-particle partitioning. However, the study of Koch et al. (2007) shows that the production of nitro-containing compounds from aromatic-OH adducts is insignificant even at high NO_x conditions."

Comment 8a. "How do the time-dependent growth curves for the two atmospherically relevant experiments look like? The difference in yield (12.5%) seems pretty small compared to the uncertainties in yield. The authors need to make sure that such a difference is observed throughout the experiment."

Response: The time-dependent growth curves of our atmospherically relevant experiments (intermediate NO_x level) show the same pattern as illustrated in Figure 5B. Several experiments under the same conditions have been done before reported in the paper to ensure the resulting SOA yield difference due to particle acidity at high %RH is repeatable. The scattered data have never been used for the calculation of the SOA yields for all our experiments. To show the repeatability of our experimental data, we added two more experiments performed under the similar atmospheric relevant condi-

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tions. In addition, we added two experiments done at low %RH with low concentrations of toluene and seed under different acidity to show the greater difference due to particle acidity compared to those at high %RH.

Comment 8b. "Why are the majority of the experiments conducted with high initial seed volumes (and extremely acidic seed) and high toluene concentrations (Table 1)? What is the initial concentration of toluene in the chamber and how much is left at the end of the experiment?"

Response: There are two main purposes to perform the SOA experiments with relative high toluene concentrations: one is to understand SOA formation mechanisms at different NO_x levels, humidity and particle acidity as addressed in this manuscript. The other is to provide the data for the development of a predictive SOA model. Developing a SOA model that includes heterogeneous reactions and gas-particle partitioning requires accurate experimental data to determine model parameters.

For the reviewer's second question, the initial toluene concentration ranged from 0.4–0.6 ppm. About 33%–40% of initial toluene was reacted.

Comment 8c. "With the relative high initial toluene concentrations, the first generation products may have a difficult time competing with toluene for the OH and further oxidations would be suppressed. How would this affect the SOA formation in these systems and the conclusions of this study?"

Response: In this study, due to the high initial concentration of toluene, the first generation products could be the major contributor for SOA formation. According to the interpretation of the observations in the study of Ng et al. (2007), SOA formation with high initial toluene concentration should be lower than that with the lower initial toluene concentration. The comparison of SOA yields at intermediate NO_x level between the experiments in Table 1 (high initial toluene concentration) and the experiments in Table 4 (low initial toluene concentration) shows the experiments with low initial toluene concentration led to the higher SOA yields, which is in the agreement of Ng et al.'s

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findings. The conclusion in this paper is particularly useful for the case where high concentration of VOC are present in the air, if we consider toluene as the representative of VOC. In reality, VOC are abundant particularly in the polluted urban air. Most VOC are more competitive for OH radicals than toluene. How far the degree of toluene oxidation can go really depends on the real environmental conditions (e.g., the abundance of OH radical, the reactivity and concentration of coexisting VOC in the air, and the sun light). From this perspective, the SOA studies with high initial toluene concentration are necessary and are very valuable to imitate the certain real situations in ambient atmosphere.

Comment 8d. "Under similar conditions (intermediate NO_x , high RH), the difference in yield between the acid and neutral seed in Table 3 is 44%, yet the difference is only 12.5% when more realistic concentrations are used. What does this imply about the other experiments that are conducted at high toluene and seed concentrations (and seed acidity)?" The reviewer has concerns that "one can assume the results in Table 3 can be extended to atmospherically realistic conditions."

Response: The mass ratio of organic to inorganic of the SOA generated from the high concentration experiments are within 0.3-0.6 that is the range of ratios measured in the realistic ambient aerosols (Drewnick et al., 2004; Russell et al., 2004). Compared to the high concentration experiments, the mass ratios of organic to inorganic compounds for the low concentration experiments are larger resulting in less acidity effects on SOA formation. The actual particle acidity effects in the ambient air are probably toward the observations from our high concentration experiments (Table 3), because the mass ratios of organic to inorganic compounds are the most important factor to determine the degree and the rates of heterogeneous acid-catalyzed reactions of organic species in aerosol.

For experiments at low NO_x level, about 25% was observed at high %RH, which implies that the upper bounds of the toluene SOA increase due to particle acidity are about 25%. This is consistent with the observations of our previous study (Cao and

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Jang, 2007). For experiments at high NO_x level, acidity effect on SOA formation is not significant in the ambient atmosphere.

Comment 9. "Table 1. The author should not divide the high NO_x experiments into "high NO fraction" and "low NO fraction"."

Response: Table 1 has been changed by removing the SOA yields for different NO regions of high NO_x experiments and adding the SOA yields for the two combined sections of the high NO_x experiments.

Comment 10. "Table 2. When calculating the percentage difference, it is better if the authors use the SOA yield at low NO_x as the denominator in all cases."

Response: In this paper, there are two percentage differences: ΔY_{A-NA} and $\Delta Y_{HRH-LRH}$. Both have been well defined in Eq. (1) and Eq. (2) of this paper. ΔY_{A-NA} is used to study the particle acidity. Therefore, the difference of SOA yields is normalized by the SOA yield with neutral seed. $\Delta Y_{HRH-LRH}$ is used to estimate the humidity effects. Hence, the difference of SOA yields is normalized by the SOA yield at low %RH. We don't see why the difference normalized by SOA yield at low NO_x will be better than those defined in Eq. (1) and Eq. (2).

Comment 11. "Table 3. How did the authors determine the relative magnitude (the number of arrows) of each specific effect (WV, WP, acid)?" The reviewer suggests "the authors should either include some calculations to show the relative importance of each effect, or they should simply omit the last 3 columns in the table."

Response: The relative magnitude (strong, medium and weak) of each effect of WV, WP and acidity has been qualitatively described based on the ΔY_{A-NA} and $\Delta Y_{HRH-LRH}$ for each NO_x level as we mentioned in the paper. The quantitative estimation of these effects is very challenging, because various complex chemical and physical processes are compounded. To quantify the contribution from each effect, further great research efforts in both experiments and the predictive SOA model are needed in future stud-

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ies. A study using an SOA model to quantify the effects of WV, WP and acidity is in progress. We think relative estimation is the best we can have in the current study and is valuable to be shown for the clear conceptual understanding of the magnitude of the effects.

Comment 12. "Figure 1. Same as Table 1, I do not think that the authors can divide the high NO_x experiments into two different periods and compare their yields with other experiments."

Response: Figure 1 has been changed by replacing the columns that represent the SOA yields of low NO and high NO regions with the columns for the final combined SOA yields at high NO_x level.

Comment 13. "Figure 5. It would be clearer if the time-dependent growth curves for different experiments are colored. Also, the authors should include the time-dependent growth curves for the two atmospherically relevant experiments for comparison."

Response: Figure 5 has been replaced with the colored one. Because the time-dependent growth curves for the experiments with relative high concentrations of toluene and seed concentration represent the typical pattern for all experiments at the same NO_x level as we mentioned in Response to Comments 8a, we think that the growth curves for the atmospheric relevant conditions are not necessary to be shown in this paper. But we added the sentence in the section 3.3 (line 11 of Page 14481) as follows: "The time-dependent growth curves for these experiments showed the similar pattern as those in Fig. 5B."

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