Responses to Referee # 1

We thank the reviewer for the careful review of our manuscript. The comments and suggestions are greatly appreciated. All the comments have been addressed. In the following, please find our responses to the comments one by one and the corresponding revisions made to the manuscript. The original comments are shown in italics. The revised parts of the manuscript are highlighted.

Anonymous Referee #1

Received and published: 26 April 2017

This manuscript describes the competing roles of NOx and SO2 on SOA formation of a-pinene and limonene. The ability of SO2 to enhance seed aerosol surface area appears to be a dominant factor, and that enhancing seed aerosol reduces the NOx suppression of SOA yields, at least in some monoterpenes. The authors use their AMS data to determine the role of organic nitrates in SOA, and find that organic nitrates account for a substantial fraction of the SOA mass. Overall, this is an interesting piece of work, and warrants publication in the ACP following some revision.

Major Comments

The nature of the experimental design was not so much to look at the impact of SO2 – but to look at the role of a sulfate seed aerosol. From the manuscript, my interpretation is that the SO2 additions were used to nucleate (inorganic) seed aerosol. Was there any SO2 left over to impact VOC oxidation? It is not clear to me if the SO2 additions really paralleled the NOx additions, because the experimental design was different. That's not to say that these aren't valuable experiments that add to the literature! I merely question whether this was truly an 'SO2 addition' rather than a 'sulfate aerosol addition' to VOC oxidation experiments.

Response:

We thank the reviewer for the supporting remarks.

In the experiments with SO_2 added, SO_2 concentration decreased slowly and most of SO_2 was still left (typically around 8 ppb) at the end of an experiment because of the low reactivity of SO_2 with OH (~2×10^{-12} molecules^{-1} cm^{3} s^{-1} at 298 K). SO_2 time series in a typical experiment are shown in a newly added figure (Fig. S2). Therefore, the experiments with SO_2 not only included the effect of sulfate formed from SO_2 oxidation as seed but also the potential role of SO_2 on VOC oxidation, although the role on VOC oxidation turned out to be likely not significant. We have added the follow sentence in the revised manuscript to clarify this point.

"SO_2 concentration decayed slowly in the experiments with SO_2 added and most of the SO_2 was still left (typically around 8 ppb from initial 15 ppb) at the end of an experiment due to its low reactivity with OH. Typical SO_2 time series in high SO_2 experiments are shown in Fig S2."

Although the SO_2 addition did not exactly parallel NO_x addition, by adding SO_2 and inducing nucleation first, we can make sure that in high SO_2 conditions enough nucleated particles were represent for the oxidation products to condense on once VOC oxidation started. Otherwise, it would be unclear whether the low SOA yield at high NO_x was due to missing nucleation or lack of condensable products. In this way, we can somewhat differentiate the role of promoting nucleation from the role of affecting the condensable products from VOC oxidation.

In the revised manuscript, we have added the following sentence.

"Adding SO_2 first and initializing nucleation by SO_2 photooxidation ensured that enough nucleating particles were present when VOC oxidation started."

The effect of SO_2 on VOC oxidation is provided in the response to one similar comment below (Pg. 7, lines 205-209).

SOA yield is influenced strongly by OA mass. The authors plot SOA yield versus OH dose, which is certainly a useful figure to see – but it is hard to compare the SOA yields if the SOA mass has not been accounted for. The authors need to also show SOA yield versus OA mass so that the readers can contrast the relationships to other studies. It would be useful to compare the SOA yields to other studies: how do the yield values compare to other measurements of OH oxidation of a-pinene? This will allow readers to place the studies in context.

Response:

We have accepted the reviewer's suggestion. In the revised manuscript, we have added a figure of SOA yield versus OA mass concentration (Fig. S8 and S9) and compared the SOA yield in this study to previous studies. We have also discussed other factors influencing SOA yield.

The results of SO2 and NOx effects on SOA yield are consistent with the Sarrafzadeh and Eddingsaas studies, which found that the presence of seed aerosol suppresses the 'NOx effect' on SOA yield. However, they contradict previous studies (e.g. Ng et al. 2007, Presto et al. 2005). The authors need to do a better job of contrasting their studies – they attribute the difference to a vague collection of parameters (e.g. NO:NO2 ratio, OH concentrations, etc.). It would be extremely helpful if the authors could synthesize the information (i.e. put numbers on those parameters) to help readers understand the differences in experimental conditions across the studies. A table would be particularly helpful.

Response:

We have accepted the reviewer's suggestions. In the revised manuscript, we have added one table summarizing the reaction conditions of previous studies (Table. S2) and elaborated the discussion related to the difference between our study and previous studies.

"…The reaction conditions of this study often differ from those described in the literature (see Table S2).

The difference in these conditions can result in both different apparent dependence on specific parameters and the varied SOA yield. For example, SOA yield from α-pinene photooxidation at low NO_x in this study appeared to be much lower than that in Eddingsaas et al. (2012a). The difference between the SOA yield in this study and some of previous studies and between the values in the literature can be attributed to several reasons: 1) RO_2 fates may be different. For example, in our study at low NO_x, RO_2+NO account for a large fraction of RO_2 loss while in Eddingsaas et al. (2012a) RO_2+HO_2 is the dominant pathway of RO_2 loss. This difference in RO_2 fates may affect oxidation products distribution. 2) The organic aerosol loading of this study is much lower than that some of previous studies (e.g., Eddingsaas et al. (2012a)) (see Fig. S9). SOA yields in this study were also plotted versus organic aerosol loading to better compare with previous studies (Fig. S8 and S9). 3) The total particle surface area in this study may also differ from previous studies, which may influence the apparent SOA yield due to vapor wall loss (the total particle surface area is often not reported in many previous studies to compare with). 4) RH of this study is different from many previous studies, which often used very low RH (<10%). It is important to emphasize that reaction conditions including the NO_x as well as SO_2 concentration range and RH in this study were chosen to be relevant to the anthropogenic-biogenic interactions in the ambient atmosphere. In addition, difference in the organic aerosol density used in yield calculation should be taken into account. In this study, SOA yield was derived using a density of 1 g cm^{-3} to better compare with many previous studies (e.g., (Henry et al., 2012)), while in some other studies SOA yield was derived using different density (e.g., 1.32 g cm^{-3} in Eddingsaas et al. (2012a))."

Lines 118: the use of the HR-ToF-AMS to derive elemental ratios uses the older Aiken method. However, as the authors note, the newer 2015 approach corrects some underestimation. Because readers may wish to compare results across studies in the future, it is appropriate and prudent to update the results to the newer calculations.

Response:

We have calculated the H/C and O/C data using the newer approach by Canagaratna et al. (2015) and compared them with the data derived from the older method (Aiken et al., 2007) (Fig. S1). The H/C derived using the newer method strongly correlated with that derived using older method and just increased by 27%. Similarly, O/C just increased by 11%. In the revised manuscript, we have discussed this difference.

"The H/C and O/C were also derived using the newer approach by Canagaratna et al. (2015) and compared with the data derived from the Aiken et al. (2007) method. The H/C values derived using the Canagaratna et al. (2015) method strongly correlated with the values derived using Aiken et al.

(2007) method (Fig. S1) and just increased by 27% as suggested by Canagaratna et al. (2015). Similar results were found for O/C and there was just a difference of 11% in O/C. Since only relative difference in elemental composition of SOA is studied here, only the data derived using Aiken et al. (2007) method are shown as the conclusion was not affected by the methods chosen."

Line 128: the authors note that they account for particle wall loss and dilution loss, but not for vapor wall loss. Recent papers have shown this to be a chemically-dependent and substantial effect on SOA yields, and most rigorous SOA yield work now accounts for these effects. How will ignoring vapor wall loss influence the results – and the interpretation thereof?

Response:

The wall loss of vapors causes an under-estimate of the SOA yield. In the revised manuscript, we have estimated the influence of the vapor wall loss on SOA yield using the measured wall loss rate of vapors. And we have added a section to address the influence of vapor wall loss.

"Wall loss of organic vapors

The loss of organic vapors on chamber walls can influence SOA yield (Kroll et al., 2007; Zhang et al., 2014; Ehn et al., 2014; Sarrafzadeh et al., 2016; McVay et al., 2016; Nah et al., 2016; Matsunaga and Ziemann, 2010; Ye et al., 2016; Loza et al., 2010). The wall loss rate of organic vapors in our chamber was estimated by following the decay of organic vapor concentrations after photooxidation was stopped in the experiments with low particle surface area (~5×10^{-8} cm^2 cm^{-3}) and thus low condensational sink on particles. Such method is similar to the method used in previous studies (Ehn et al., 2014; Sarrafzadeh et al., 2016; Krechmer et al., 2016; Zhang et al., 2015). A high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS, Aerodyne Research Inc.) with nitrate ion source ($^{15}NO_3^-$) was used to measure semi/low-volatile organic vapors. The details of the instrument were described in our previous studies (Ehn et al., 2014; Sarrafzadeh et al., 2016). The decay of vapors started from the time when the roof of the chamber was closed. The data were acquired at a time resolution of 4 s. A typical decay of low-volatile organics is shown in Fig. S3 and the first-order wall loss rate was determined to be around 6×10^{-4} s^{-1}.

The SOA yield was not directly corrected for the vapor wall loss, but the influence of vapor wall loss on SOA yield was estimated using the method in the study of Sarrafzadeh et al. (2016) and the details of the method are described therein. Briefly, particle surface and chamber walls competed for the vapor loss (condensation) and the condensation on particles led to particle growth. The fraction of organic vapor loss to particles in the sum of the vapor loss to chamber walls and to particles (F_p) was calculated. The vapor loss to chamber walls was derived using the wall loss rate. The vapor loss to particles was derived using particle surface area concentration, molecular velocity and an accommodation coefficient α_p (Sarrafzadeh et al., 2016). $1/F_p$ (f_{corr}) provides the correction factor to obtain the “real” SOA yield. f_{corr} is a function of particle surface area concentration and accommodation coefficient as shown in Fig. S4. Here a range of 0.1-1 for α_p was used, which is generally in line with the ranges of α_p found by Nah et al. (2016) by fitting a vapor-particle dynamic model to experimental data. At a given α_p, the higher particle surface area, the lower f_{corr} and the lower the influence of vapor wall loss are because most vapors condense on particle surface and vice versa. At a given particle surface area, f_{corr} decreases with α_p because at higher α_p a larger fraction of vapors condenses on particles. An average molecular weight of 200 g/mol was used to estimate the influence of vapor wall loss. For the aerosol surface area range in most of the experiments in this study, the influence of vapor wall loss on SOA yield was relatively small (<~40% for particle surface area larger than 3×10^{-6} cm^2 cm^{-3}, Fig. S4). Yet, for the experiments at high NO_x and low SO_2 for α-pinene and limonene, the influence of vapor wall loss on SOA can be high due to the low particle surface area, especially at lower α_p.”

In the Introduction, the authors do a good job of summarizing the reasons why such a study would be interesting. Much of the discussion focuses on the role of NOx on SOA yields – this is reasonable as most of the literature has focused on that problem! However, there is some relatively recent literature regarding the role of SO2 in affecting SOA chemistry and monoterpene OH oxidation that the authors should consider. In particular:

Photooxidation of cyclohexene in the presence of SO2: SOA yield and chemical composition.

Shijie Liu, Long Jia, Yongfu Xu, Narcisse T. Tsona, Shuangshuang Ge, and Lin Du. Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-30, 2017

Synergetic formation of secondary inorganic and organic aerosol: effect of SO2 and NH3 on particle formation and growth. Biwu Chu, Xiao Zhang, Yongchun Liu, Hong He, Yele Sun, Jingkun Jiang, Junhua Li, and Jiming Hao. Atmos. Chem. Phys., 16, 14219-14230, doi:10.5194/acp-16-14219-2016, 2016

Formation of secondary aerosols from gasoline vehicle exhaust when mixing with SO2. T. Liu, X. Wang, Q. Hu, W. Deng, Y. Zhang, X. Ding, X. Fu, F. Bernard, Z. Zhang, S. Lü, Q. He, X. Bi, J. Chen, Y. Sun, J. Yu, P. Peng, G. Sheng, and J. Fu. Atmos. Chem. Phys., 16, 675-689, doi:10.5194/acp-16-675-2016, 2016

Anthropogenic Sulfur Perturbations on Biogenic Oxidation: SO2 Additions Impact Gas- Phase OH Oxidation Products of _- and _-Pinene. Beth Friedman, Patrick Brophy, William H. Brune, and Delphine K. Farmer. Environmental Science & Technology 2016 50 (3), 1269-1279. DOI: 10.1021/acs.est.5b05010

Is there any evidence for organic sulfates in the SOA from the AMS data? This has been a subject of some debate in the literature, and an additional datapoint would be useful. This may also clarify the role of acid catalysis, as I believe that has been linked to the formation of organic sulfates.

Response:

We thank the reviewer for raising these papers. In the revised manuscript, we have enriched the discussion on the role of SO_2 by including some of the papers.

From our AMS data, we did not find evidence of organic sulfate. For SOA formed at high SO_2, we found no significant organic fragments containing sulfur. Also the fragment $CH_3SO_2^+$ from organic sulfate suggested by Farmer et al. (2010) was not detectable in our data. We found that the pattern of sulfate in mass spectra had no significant difference from the pattern of pure ammonium sulfate. However, we would like to note that AMS has very limited capability to differentiate organic sulfate and inorganic sulfate (Farmer et al., 2010).

Moreover, according to the literature, organic sulfate is mainly formed by aqueous reaction of sulfate with organics. In the conditions of our study, there was no aqueous phase as we stated based on the AIM model. Therefore, experimental conditions in our study did not favor the formation organic sulfate.

In the revised manuscript, we have clarified these results.

"In addition, from the AMS data of SOA formed at high SO_2 no significant organic fragments containing sulfur were found. Also the fragment $CH_3SO_2^+$ from organic sulfate suggested by Farmer et al. (2010) was not detected in our data. The absence of organic sulfate tracers is likely due to the lack of aqueous phase in aerosol particles in this study. Therefore, the influence of SO_2 on gas phase chemistry of organics and further on SOA yield via affecting gas phase chemistry is not important in this study."

Minor Comments

Line 136. The authors note an average RH of 28-42% for the experiments. This seems like a relatively large range: will this affect the SOA yields, or interpretation of the data?

Response:

The average RH was in the range of 28-42% taking into account all experiments. Actually, except one experiment, the average RH was in the range of 28-34%. For particle phase reactions, the particle water content absorbed by organic aerosol in the range of 28-42% RH is low and the difference of water content between 28% and 42 % is very minor (typically <~2% of the particle volume based on our hygroscopic growth measurement). The RH variations are not expected to significantly change the particle phase chemistry. Moreover, since water vapor is abundant and in excess in the gas phase, the

RH variations are not expected to significant change gas phase chemistry either. Therefore, we do not expect that would significantly change the SOA yield. In the revised manuscript, we have clarified this point.

"The average RH for the period of monoterpene photooxidation was 28-34% except for one experiment with average RH of 42% RH."

Re: Discussion of SO2 effects. The authors dominantly attribute the enhancement of SOA by SO2 to increased particle surface area, or perhaps to acid catalysis. These seem like extremely likely reasons; however, there is one study that suggests that SO2 will influence gas-phase oxidation products (Friedman et al.), which could also be a confounding factor unless all of the SO2 is in the particle phase before VOC oxidation commences… This would be a useful clarification.

Response:

The influence of SO_2 on gas phase oxidation is likely to be trivial in this study for two reasons. Firstly, the reactivity of SO_2 with OH is very low (2×10^{-12} vs. 5.3×10^{-11} molecules^{-1} cm^{3} s^{-1} for α-pinene with OH) and SO_2 only accounts for a very small fraction of the OH loss (typically ~2% in the beginning of an experiment). Secondly, the OH concentration is 2-3 orders of magnitude lower than those in the PAM chamber used by Friedman et al. (2016). Therefore, either the change in OH/HO_2 ratio or SO_3 concentration, which is attributed to the reason of changed oxidation products by Friedman et al. (2016), is much lower in our experiments. In the revised manuscript, we have added a brief discussion of the effect of SO_2 on gas phase oxidation of monoterpenes in this study as follows.

"SO_2 has been proposed to also affect gas phase chemistry of organics by changing the HO_2/OH or forming SO_3 (Friedman et al., 2016). In this study, the effect of SO_2 on gas phase chemistry of organics was not significant because of the much lower reactivity of SO_2 with OH compared with α-pinene and limonene (Atkinson et al., 2004, 2006; Atkinson and Arey, 2003) and the low OH concentrations (2-3 orders of magnitude lower than those in the study by Friedman et al. (2016)). Moreover, reactions of RO_2 with SO_2 was also not important because the reaction rate constant is very low ($<10^{-14}$ molecule^{-1} cm^{3} s^{-1}) (Lightfoot et al., 1992; Berndt et al., 2015). In addition, from the AMS data of SOA formed at high SO_2 no significant organic fragments containing sulfur were found. Also the fragment $CH_3SO_2^+$ from organic sulfate suggested by Farmer et al. (2010) was not detected in our data. The absence of organic sulfate tracers is likely due to the lack of aqueous phase in aerosol particles in this study. Therefore, the influence of SO_2 on gas phase chemistry of organics and further on SOA yield via affecting gas phase chemistry is not important in this study."

Technical comments.

Line 26: should read "compared to low NOx"

Response: Corrected.

Line 29: should read "SO2 can compensate for such effects"

Response: Corrected.

Introduction: line 34: sentence has repetitive 'importants': consider removing at least one (e.g. "SOA is an important class of atmospheric aerosol" seems like an unnecessary statement for the journal's audience). This adjective is used heavily throughout the introduction (lines 45, 49), and I recommend removing or replacing the adjective to improve readability.

Response: We have accepted the reviewer's suggestion. In the revised manuscript, we have removed the "as an important class of atmospheric aerosol", and removed or replaced "important" where it is necessary.

Line 56: hydroperoxides should be plural

Response: Corrected.

Line 57: need comma between 'NO' and 'forming'

Response: Corrected.

Line 87: should read "might have either counteracting or synergistic effects on SOA: : :"

Response: Corrected.

Line 126: remove the with following 'multiplied by'

Response: Done.

Line 135: should read 'there was no aqueous..'

Response: Corrected.

Line 221, remove comma between 'that' and 'high'

Response: Done.

Line 360: should read 'in the ambient atmosphere'

Response: Corrected.

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Responses to Referee # 2

We thank the reviewer for carefully reviewing our manuscript; the comments and suggestions are very helpful and greatly appreciated. All the comments have been addressed. We believe that revisions based on these comment have substantially improved our manuscript. In the following please find our responses to the comments one by one and the corresponding changes made to the manuscript. The original comments are shown in italics. The revised parts of the manuscript are highlighted.

Before we start our responses to the reviewer, we would like to briefly clarify the motivation of this manuscript. Our primary goal of this study is to investigate how and to what extent small ambient inorganic trace gases, here NO_x and SO_2, affect the SOA formation in the ambient anthropogenic-biogenic interactions. We aimed to study the more complex situation found in the ambient atmosphere instead of pure VOC reaction systems. Our main goal is not so much to provide a single absolute value of SOA yield to modelers nor to simply "improve" values of the SOA yields from previous studies because all chamber studies have operational limitations compared to the atmosphere (e.g. wall effects). Often different studies have distinct physical and chemical regimes due to the different operational limitations and diverse experimental conditions e.g. chamber size, radical generation, and photolysis rates. We as well as the community are in the course of addressing the influence of wall loss of vapors. We believe that, rather denying the findings from previous studies, our study provided additional knowledge and insights to existing understanding of SOA formation in certain conditions of the real atmosphere. This is based on the fact that our experiments were conducted under conditions relatively close to the ambient anthropogenic-biogenic interactions, including ambient RH, concentrations of SO_2, NO_x, and VOC close to ambient levels, natural sunlight, and low surface-to-volume ratio of our large chamber.

Anonymous Referee #2

This chamber study investigated the effects of SO2 and NOx (NO) on SOA formation from photooxidation of a-pinene and limonene. It was found that SO2 enhanced SOA yield while NOx suppressed SOA yield. The suppression effect of NOx was attributed to the suppressed new particle formation and thus a lack of particle surface area for organics to condense on. The authors concluded that SO2 oxidation produced high number of particles and compensated for the suppression of SOA yield by NOx. SOA composition measured by AMS was also presented and discussed.

This is an interesting study. The gas- and particle-phase measurements are comprehensive and include several important species that have not been typically characterized in previous studies (e.g., OH, HO2 and RO2). The experiments appeared to be carefully conducted. However, I have major concerns regarding data interpretation and some conclusions in the manuscript.

One of the central themes of the manuscript is that the suppression effect of NOx on SOA formation *can be compensated by the presence of SO2. This conclusion is not accurate based on all the data presented in this manuscript. For a-pinene, it appears that under high SO2 conditions, the SOA yields under low vs. high NOx conditions are comparable. However, this is not the case for limonene, where there is still a large difference in SOA yields between low vs. high NOx conditions in the presence of high SO2. The manuscript needs to be thoroughly revised to accurately reflect what the data are showing. If one set of data is showing one thing and another set of data is showing the opposite, the authors need to discuss both datasets equally and cannot conclude that SO2 effect can compensate NOx effect.*

Response:

A key result in our study is that for both α-pinene and limonene, the difference in SOA yield between high NO_x and low NO_x was much reduced in the presence of SO_2, although for limonene the SOA yield at high NO_x and high SO_2 was still lower than the yield at low NO_x. This result indicates that the suppression of SOA yield by NO_x was compensated to a large extent by SO_2. This conclusion holds regardless the difference in the detailed results between α-pinene and limonene system.

In the revised manuscript, we have revised the conclusion to better represent the results from both α-pinene and limonene cases. The following sentence has been revised in the conclusion part:

"SO_2 oxidation produced high number concentration of particles and compensated for the suppression of SOA yield by NO_x to a large extent."

The abstract has been revised accordingly as follows.

"However, in the presence of SO_2 which induced high number concentration of particles after oxidation to H_2SO_4, the suppression of the mass yield of SOA by NO_x was completely or partly compensated."

The authors concluded that the suppression effect of NOx on SOA yields is mainly due to suppression of nucleation (absence of particle surface area as condensation sink) rather than decrease of condensable materials. If particle surface area plays a role, this will point to the importance of loss process of oxidation products via chemical reactions and/or chamber wall loss. However, the effect of loss of organic vapors on chamber walls is not considered in this study. Nevertheless, previous studies on a-pinene oxidation suggested that SOA yield is independent of particle surface area. In this regard, the interpretation that the suppression effect of NOx arises from a lack of particle surface area appears to be at odds with previous studies. All in all, it is not clear how the absence of particle surface area can explain the suppressed SOA yields under high NOx condition in this study.

Response:

In general, condensable SOA materials are chemically produced in the gas-phase and nucleation and condensation on particle surface constitute sinks for the SOA materials besides other sinks e.g. wall loss and flush out. In the case of sufficient nucleation or seeded experiments, condensation on particles is the dominant sink. In absence of nucleation and surface, the other sinks such as wall loss dominate the losses of SOA materials. Therefore, no SOA would be formed without nucleation. This *a priori* tells nothing about the importance of wall losses when SOA is formed.

The loss of organic vapors to chamber walls can be important for SOA yield, although in our manuscript we had not corrected for it because it is a challenge to quantify it. In the revised manuscript, we have added a section to estimate the influence of vapor wall loss on SOA yield (Sect. "2.3 Wall loss of organic vapors") and provided more discussion on vapor wall loss. We found that the influence of vapor wall loss on SOA yield is likely to be significant when surface area concentrations of SOA formed were low in the high NO_x and low SO_2 conditions. Yet, the influence of vapor wall loss is likely to be not significant at the higher surface area concentrations of SOA formed in the low NO_x conditions or high NO_x and high SO_2 conditions.

We respectfully disagree with the reviewer's statement that "previous studies on α-pinene oxidation suggested that SOA yield is independent of particle surface area" without considering each specific study. Although some studies showed that SOA yield from α-pinene oxidation is independent of seed particle surface area (McVay et al., 2016; Nah et al., 2016), a number of studies showed that SOA yield from α-pinene ozonolysis or photooxidation depends on particle surface area. For example, our previous studies clearly showed that SOA yields from α-pinene photooxidation depend on surface area (Sarrafzadeh et al., 2016; Ehn et al., 2014), and Eddingsaas et al. (2012) also showed that in "high NO" conditions, SOA yield from α-pinene photooxidation is much higher with neutral seed than that without seed. The discrepancy in the dependence of SOA yield on particle surface areas in the literature can be attributed to reaction conditions, surface area range and chamber setup. For example, if the reaction produces enough new particles by itself and results in fast particle growth and larger aerosol surface area as the dominant condensational sink for vapors compared to the loss on chamber walls, SOA yield would be less affected by the seed surface area. On the contrary, if VOC oxidation does not induce nucleation by itself, all vapors would be lost onto the chamber walls and SOA yield would be essentially zero.

In this study, at high NO_x and low SO_2, the particle number and surface area concentrations were low (peak surface area concentration of 6.8×10^{-7} cm^2 cm^{-3} and particle-to-chamber surface ratio of 7.7×10^{-5} for α-pinene), much lower than the aerosol surface area range in the studies by Nah et al. (2016) and McVay et al. (2016) ($\sim10^{-5}$ cm^2 cm^{-3} and particle-to-chamber surface ratio of $>4\times10^{-5}$). In addition, not only seed particle surface area but also total particle surface area formed during reaction provide condensational sinks to compete with vapor wall loss. At such low particle surface area concentrations, the condensation of vapors on particles had a much longer time scale than that of the wall loss and a large fraction of vapors condensed on chamber walls. Therefore, SOA yield was significantly suppressed due to lack of particle surface area.

In the revised manuscript, we have discussed the findings in the literature.

"Artificially added seed aerosol has been shown to enhance SOA formation from α-pinene and β-pinene oxidation (Ehn et al., 2014; Sarrafzadeh et al., 2016; Eddingsaas et al., 2012a). In some other studies, it was found that the SOA yield from α-pinene oxidation is independent of initial seed surface area (McVay et al., 2016; Nah et al., 2016). The difference in the literature may be due to the range of total surface area of particles, reaction conditions and chamber setup. For example, the peak particle-to-chamber surface ratio for α-pinene photooxidation in this study was 7.7×10^{-5} at high NO_x and low SO_2, much lower than the aerosol surface area range in the studies by Nah et al. (2016) and McVay et al. (2016). A lower particle-to-chamber surface ratio can lead to a larger fraction of organics lost on chamber walls. Hence, providing additional particle surface by adding seed particles can increase the condensation of organics on particles and thus increase SOA yield. However, once the surface area is high enough to inhibit condensation of vapors on chamber walls, further enhancement of particle surface will not significantly enhance the yield (Sarrafzadeh et al., 2016)."

The authors explained the effect of SO2 as 1) inducing new particle formation and providing surface area for vapor condensation, 2) acid-catalyzed particle-phase reactions. I have the same question regarding the first explanation, i.e., what is the role of vapor wall loss (if any), and how does one reconcile this explanation with findings from previous studies? Also, what is the effect of SO2 on gas-phase chemistry and SOA yield? This is not considered.

Response:

The role of vapor wall loss can be referred to our response to the comment above. Wall loss of vapors leads to an underestimate of SOA yield. Condensation of vapors onto aerosol particle surface competes with the loss of vapors on chamber walls. Therefore the surface area provided by nucleation and growth of particles in the presence of SO_2 enhanced the SOA yield in this study.

Only few studies have investigated the effect of SO_2 on the SOA yield from α-pinene oxidation. More studies investigated the effect of seed aerosol and particle acidity. Kleindienst et al. (2006) attributed the increase of SOA yield in the presence of SO_2 to the formation of H_2SO_4 acidic aerosol. While particle acidity may contribute to the increased SOA yield, especially at high NO_x, the effect of facilitating nucleation and further providing surface area seems to be more important in our study. The importance of the SO_2 via nucleating and providing particle surface depends on the particle surface area in the absence of SO_2 because the competition for the condensation of vapors between particles and wall depends on particle surface area. When VOC oxidation does not form enough new particles and particle surface by itself, the role of SO_2 via nucleating and providing particle surface in enhancing SOA yield is more important. In the revised manuscript, we have added more discussion on this aspect.

"Particle acidity may also play a role in affecting the SOA yield in the experiments with high SO_2. Particle acidity was found to enhance the SOA yield from α-pinene photooxidation at high NO_x (Offenberg et al., 2009) and "high NO" conditions (Eddingsaas et al., 2012a). Yet, in low NO_x condition, particle acidity was reported to have no significant effect on the SOA yield from α-pinene photooxidation (Eddingsaas et al., 2012a; Han et al., 2016). According to these findings, at low NO_x the enhancement of SOA yield in this study is attributed to the effect of facilitating nucleation and providing more particle surface by SO_2 photooxidation. At high NO_x, the effect in enhancing new particle formation by SO_2 photooxidation seems to be more important, although the effect of particle acidity resulted from SO_2 photooxidation may also play a role."

The effect of SO_2 on gas phase chemistry is not significant in this study because the reaction rate of SO_2 with OH (~2×10^{-12} molecules^{-1} cm^3 s^{-1}) and with RO_2 (<10^{-14} molecule^{-1} cm^3 s^{-1}) are very low (Lightfoot et al., 1992; Berndt et al., 2015). From the AMS data of SOA formed at high SO_2, we found no significant organic fragments containing sulfur. Also the fragment $CH_3SO_2^+$ suggested by Farmer et al. (2010) was not detected in our data. Therefore, we conclude that in our study, the effect of SO_2 on gas phase chemistry of organics and thus further on SOA yield via affecting gas phase chemistry is not important.

In the revised manuscript, we have added the following discussion about this point.

"SO_2 has been proposed to also affect gas phase chemistry of organics by changing the HO_2/OH or forming SO_3 (Friedman et al., 2016). In this study, the effect of SO_2 on gas phase chemistry of organics was not significant because of the much lower reactivity of SO_2 with OH compared with α-pinene and limonene (Atkinson et al., 2004, 2006; Atkinson and Arey, 2003) and the low OH concentrations (2-3 orders of magnitude lower than those in the study by Friedman et al. (2016)). Moreover, reactions of RO_2 with SO_2 was also not important because the reaction rate constant is very low (<10^{-14} molecule^{-1} cm^3 s^{-1}) (Lightfoot et al., 1992; Berndt et al., 2015). In addition, from the AMS data of SOA formed at high SO_2 no significant organic fragments containing sulfur were found. Also the fragment $CH_3SO_2^+$ from organic sulfate suggested by Farmer et al. (2010) was not detected in our data. The absence of organic sulfate tracers is likely due to the lack of aqueous phase in aerosol particles in this study. Therefore, the influence of SO_2 on gas phase chemistry of organics and further on SOA yield via affecting gas phase chemistry is not important in this study."

It appears that the SOA yields in high SO2 experiments might be overestimated by double counting the density of ammonium sulfate/ammonium bisulfate in the SOA mass calculation. This is not entirely clear.

Response:

The density of SOA in high SO_2 experiments was not double counted. In the revised manuscript, we have clarified this point. Please also refer to our response to the similar comment below ("detailed comment" 3).

"…and their respective density (1.32 g cm^{-3} for organic aerosol from one of our previous studies (Flores et al., 2014) and the literature (Ng et al., 2007) and ~1.77 g cm^{-3} for ammonium sulfate/ammonium bisulfate)…"

We would like to note that the SOA yield in this study was derived by adjusting the density of SOA to

1 g cm^{-3}.

Finally, the authors need to conduct a more careful and accurate comparison with previous studies. It was noted that in high SO2 conditions, their findings that SOA yields are comparable under high NOx and low NOx conditions are in line with Sarrafzadeh et al. and Eddingsaas et al. I do not think that the data in Eddingsaas et al. showed this. SOA yields are also a function of deltaMo (as well as various experimental conditions and parameters) and this could play a role, see detailed comment below. Also, the a-pinene yields in this study under comparable NOx/SO2/OH exposure are much lower than Eddingsaas et al.. This is not mentioned and discussed in the manuscript.

Response:

In the revised manuscript, we have added more discussion to compare this study with previous studies and added a table summarizing previous studies.

Please refer to our detailed responses to the specific comments below ("detailed comments" 11d, e).

Major revisions are needed before the manuscript can be published. Specific comments are listed below.

Detailed comments

1. Line 18-20. This statement is not true for limonene data presented in this study.

Response:

In the revised manuscript, we have modified this statement. Please refer to our response to a similar comment above (Pg. 1, lines 35-43).

2. Line 79 -81. This sentence seems to imply that previous studies that used higher NOx and SO2 concentrations are not atmospherically relevant. I think these sentences should be revised and clarified to more accurately reflect the experimental design and results from previous studies. For instance, the use of high levels of NOx (e.g., from HONO or CH3ONO) in some studies is to push the RO2 radical fate to the extreme (i.e., RO2+NO or RO2+NO2) to investigate SOA yields and composition under such conditions. Thus, the use of high levels of NOx do not necessarily mean that the results are not applicable to ambient conditions.

Response:

We understand that in some studies high concentration of NO_x is intentionally used to push the RO_2 radical fate to an extreme in order to study the SOA yields and composition. Nevertheless, experiments under ambient levels of high NO_x concentrations are more transferable to the ambient anthropogenic-biogenic interaction than the experiments conducted at extremely high NO_x concentrations considering the shortened lifetime of RO_2 and the potential secondary processes as well as the effect of NO_x on OH concentration at extremely high NO_x. In the revised manuscript, we have modified this sentence.

"For example, many studies used very high NO_x and SO_2 concentrations (up to several hundreds of ppb). High NO_x can make the RO_2 radical fate dominated by one single pathway (i.e., RO_2+NO or

RO_2+NO_2) to investigate SOA yields and composition under such conditions. Yet, the effects of NO_x and SO_2 at concentration ranges for ambient anthropogenic-biogenic interactions (sub ppb to several tens of ppb for NO_2 and SO_2) have seldom been directly addressed."

3. Line 132. Is the organic aerosol density 1.32 g/cm3 from Eddingsaas et al. (2012a)? If this is the case, note that this density used in Eddingsaas et al. is directly taken from the results in Ng et al. (2007), and that this density was obtained in the presence of seeds already. Therefore, it appears that there might be a double counting of the density of ammonium sulfate/ammonium bisulfate in the data presented here?

Response:

Organic aerosol density was based on our previous study (Flores et al., 2014) as well as the study of Eddingsaas et al. (2012) and thus Ng et al. (2007).

Although the density of organic aerosol in the study of Ng et al. (2007) was obtained in presence of seed, the contribution of seed aerosol (ammonium sulfate) to particle volume and thus density has been taken into account (Bahreini et al., 2005) . The value reported by Ng et al. (2007) is the density of organic aerosol instead of the density of mixed aerosol. There is no double counting of the density of ammonium sulfate/ammonium bisulfate in our study.

4. *Line 162. How were OH and O3 formed in the experiments (under each combination of NOx/SO2 condition). Please provide more info. Also, please provide typical time profiles of VOC (either a-pinene of limonene), O3, OH, NO, NO2, SO2 for each combination of NOx/SO2 condition. These are important to help the readers obtain a better idea of the reaction pathways/regimes under each condition.*

Response:

OH was formed via HONO photolysis, which was produced from a photolytic process on the Teflon chamber wall as we described in the manuscript. The details can be found in a previous study on our chamber (Rohrer et al., 2005). In the revised manuscript, we have added one more sentence to better clarify this point.

"OH was formed via HONO photolysis, which was produced from a photolytic process on the Teflon chamber wall (Rohrer et al., 2005)."

In addition, in all VOC photooxidation of our study, OH was partly contributed by the recycling reaction of HO_2 with NO. The reaction of HO_2 and RO_2 with NO also produces NO_2, whose photolysis further forms O_3. While the detailed mechanism of O_3 formation is beyond the scope of this study, we have provided a brief description in the revised manuscript.

"O_3 was formed in photochemical reactions since NO_x, even in trace amount (<~1 ppbV), was present in this study."

"In the photooxidation of VOC, OH and O_3 often co-exist and both contribute to VOC oxidation because O_3 formation in chamber studies is often unavoidable during photochemical reactions of

VOC even in the presence of trace amount of NO_x."

In the revised manuscript, we have provided time profiles of VOC, O_3, OH, NO, and NO_2 in low NO_x and high NO_x conditions for α-pinene and limonene (Fig. S5). Time profiles of these species at high SO_2 were similar to those at low SO_2 because SO_2 had little effect on gas phase chemistry due to its low reactivity of SO_2 with OH and RO_2, and thus are not further shown. SO_2 time series are shown separately (Fig. S2).

5. Line 163. Was all the VOC reacted in each experiment?

Response:

All the VOC precursor was consumed in the experiments of this study except for one experiment where small amount of VOC (~10%) was still left at the end of the reaction due to the cloudy condition and thus lower photolysis rates.

6. Lin 163. There is no "typical" experiment in this study, as each experiment was conducted under a different NOx/SO2 condition. Please clearly state that this is only for low NOx condition. Also, what about high NOx condition? Was it exclusively OH reaction? Please also specify clearly.

Response:

The relative dominance of OH oxidation over ozonolysis (as shown in Fig. 6) is similar in both the low NO_x and high NO_x conditions. At high NO_x, OH was often higher and meanwhile more O_3 was also produced.

In the revised manuscript, we have modified this sentence as follows.

"For all the experiment in this study, the VOC loss was dominated by OH oxidation over ozonolysis (see Fig. S6 as an example). The relative importance of the reaction of OH and O_3 with monoterpenes was similar in the low NO_x and high NO_x experiments. At high NO_x, OH was often higher while more O_3 was also produced."

7. Line 173 – 177. Here, under low NOx condition, RO2+NO dominates throughout the entire experiment (RO2+HO2 only contributes to 40% at most).

a. These sentences clearly demonstrate the shortcomings of classifying the experiments as low NOx vs. high NOx as discussed in Wennberg et al. (IGAC news, 2103). I suggest the authors to characterize reactions conditions by explicitly stating the RO2 fates, rather than as low vs. high NOx.

Response:

We had clearly defined our low NO_x and high NO_x conditions using the RO_2 fate in our study. Therefore, we respectfully do not think that using the terms "low NO_x" and "high NO_x" caused ambiguity as long as we define them clearly.

In the revised manuscript, we have added the following sentence to emphasize the RO_2 fates under different NO_x conditions.

"Note that the RO_2 fate in the low and high NO_x conditions quantified here are further used in the discussion below since the information of RO_2 fate is important for data interpretation of experiments conducted at different NO_x levels (Wennberg, 2013)."

b. It is stated that under low NOx conditions, in the beginning of the experiment, a trace amount of NO is formed from photolysis of HONO from the chamber wall. Is this just in the beginning of the experiment, or there is a continuous NO source from HONO photolysis throughout the entire experiment? Please specify.

Response:

There is a continuous NO source from HONO photolysis. In the revised manuscript, we have clarified this as follows.

"The trace amount of NO (up to ~0.2 ppbV) was from the photolysis of HONO, which was continuously produced from a photolytic process on chamber walls throughout an experiment (Rohrer et al., 2005)."

8. Line 189. The authors attributed the lower particle number concentration and nucleation rate at high NOx to the decreasing RO2+RO2 reaction in the presence of NOx. However, in line 182, the authors noted that RO2+RO2 reaction is negligible in this study to start with. Please reconcile these seemingly contradictory statements. Also, can be suppressed nucleation under high NOx due to the higher volatility of organic nitrates as compared to peroxides (from RO2+HO2)?

Response:

The compounds responsible for nucleation only account for a very small fraction of RO_2 reaction products. Although the contribution of RO_2+RO_2 reaction to the total RO_2 loss is negligible, it can contribute a lot to the compounds responsible for nucleation because RO_2+RO_2 reactions form dimers, which have high molecular weight and extremely low volatility (Ehn et al., 2014; Kirkby et al., 2016). Generally, organic nitrates are not expected to be the main compounds responsible for nucleation since their volatility is not low enough to nucleate, nor primary organic peroxides (from $RO_2(C_{10})$+HO_2). Therefore, although under high NO_x more organic nitrates were found, organic nitrates are unlikely to be the reason for the suppressed nucleation.

9. Line 205-206. There is nucleation (from organics) in the presence of NOx as shown in Fig. 4. In this sense, "absence of nucleation" here is a bit confusing. Perhaps would be clearer to say "absence of seed particles".

Response:

In the revised manuscript, we have modified "absence of nucleation" as follows.

"Because NO_x suppressed new particle formation, the suppression of the SOA yield could be attributed to the lack of new particles as seed and thus the lack of condensational sink, or to the decrease of condensable organic materials."

10. Line 211 and Figure 3. The author concluded that the suppression effect of NOx on SOA yields was mainly due to suppression of nucleation, i.e., to the absence of particle surface as condensation sink. Many critical aspects are not discussed, making this conclusion not well-justified and *well-supported.*

a. If the absence of seed particle surface area is the reason for the low yield under high NOx condition (at low SO2), this will point to the importance of loss of semivolatile species via chemical reactions or chamber wall loss (Kroll et al., ES&T, 2007). However, the effect of vapor wall loss in not considered in this study. Zhang et al. (PNAS, 2014) first systematically investigated the effects of particle surface area and vapor wall loss on SOA yields. For a-pinene photooxidation and ozonolysis specifically, it was found that SOA yields are largely independent of seed surface area (McVay et al., 2016, Nah et al., ACP, 2016; Nah et al., ACP, 2017). Therefore, taken all these together, it is not clear how the absence of particle surface area can explain the suppressed SOA yields under high NOx condition in this study.

Response:

Please refer to our response to a similar comment above (Pg. 2, lines 58-66).

b. The authors dismissed the "decrease of condensable organic materials" in high NOx conditions as an explanation for the observed decrease in yield. Why? If more volatile organic nitrates are formed in high NOx conditions, why can't this be an explanation for the suppressed SOA yield? For limonene data (Line 213-218), the authors appeared to embrace the role of volatility of oxidation products.

Response:

In our study, when new particle formation was already enhanced by added SO_2, the SOA yield at high NO_x was comparable to that at low NO_x for α-pinene and the difference in SOA yield between high NO_x and low NO_x was much smaller (Fig. 3a). If the organic materials such as organic nitrate formed in high NO_x conditions were more volatile, the SOA yield in high NO_x should be low regardless of SO_2 concentration unless in addition to that, SO_2 enhanced the SOA yield at high NO_x via the influence other than surface area effect, e.g., acidity effect. Organic nitrates formed at high NO_x was proposed to be more volatile (Presto et al., 2005; Kroll et al., 2006). However, many organic nitrate formed in our study is highly oxidized organic molecule (HOMs) containing multi-functional groups besides nitrate ($C_{7-10}H_{9-15}NO_{8-15}$). The compounds are expected to have low volatility and they were found to have an uptake coefficient on particles of ~1 (Pullinen et al. in preparation). A recent study also implied that organic nitrate may have low volatility (Hakkinen et al., 2012). Therefore, the suppressing effect of NO_x on SOA yield was more likely due to suppressed nucleation, i.e., to lack of particle surface as condensational sinks.

In the revised manuscript, we have elaborated our discussion.

"This finding can be attributed to two possible explanations. Firstly, NO_x did not significantly suppress the formation of low volatile condensable organic materials, although NO_x obviously suppressed the formation of products for nucleation. Secondly, NO_x did suppress the formation of low-volatility condensable organic materials via forming potentially more volatile compounds and in addition to that, the suppressed formation of condensable organic materials was compensated by the presence of SO_2, resulting in comparable SOA yield. Organic nitrates are a group of compounds formed at high NO_x, which have been proposed to be more volatile (Presto et al., 2005; Kroll et al., 2006). However, many organic nitrates formed by photooxidation in this study were highly oxidized organic molecules (HOMs) containing multi-functional groups besides nitrate group ($C_{7-10}H_{9-15}NO_{8-15}$). These compounds are expected to have low volatility and they are found to have an uptake coefficient on particles of ~1 (Pullinen et al., in preparation). Therefore, the suppressing effect of NO_x on SOA yield was mostly likely due to suppressed nucleation, i.e., the lack of particle surface as condensational sink."

For limonene data, please refer to our response to the comment below ("detailed comments" 10c).

c. Line 217. How does the different range in VOC/NOx for a-pinene and limonene experiments explain the differences in yields in high SO2 conditions? Please elaborate and explain clearly.

Response:

The cause of the difference between the α-pinene and limonene cases is unknown for the moment and it would be pure speculation when discussing reasons for this difference. Therefore, in the revised manuscript, we only state that the reason is unknown so far and as possible explanation, we note that the average volatility of limonene oxidation products may be higher at higher NO_x.

In the revised manuscript, we have revised this sentence as follows.

"The cause of this difference is currently unknown. Our data of SOA yield suggest that the products formed from limonene oxidation at high NO_x seemed to have higher average volatility than that at low NO_x."

11. Line 225-237. Comparisons with previous studies. Many critical details are not considered and discussed. I think the authors jumped to the conclusion on whether their study agree/disagree with previous studies too quickly.

a. Line 225. This sentence is only true for a-pinene data in this study, but not for limonene. Please state clearly.

Response:

In the revised manuscript, we have revised this sentence as follows.

"Our finding that the difference in SOA yield between high NO_x and low NO_x conditions was highly reduced at high SO_2 is also in line with the findings of some previous studies using seed aerosols (Sarrafzadeh et al., 2016; Eddingsaas et al., 2012a)."

b. *Seed particles were generated via SO2 oxidation in this study (for high SO2 experiments). Previous studies directly injected seeds into the chamber. In comparing SOA yields, the author should also consider the role of gas-phase chemistry and particle phase chemistry. For instance, what about the reaction of SO2 and criegee intermediates? What about the effect of particle acidity on particle-phase reactions (in this study vs. previous studies)? Please discuss.*

Response:

In our study, the reaction of SO_2 with Criegee intermediates was not important to the formation of oxidized organics and SOA formation for the following reasons. 1) The reaction of VOC with O_3 only contributed to a small fraction of VOC loss in this study and thus formation of Criegee intermediates was not significant. 2) At the water vapor concentration of this study, water may compete for Criegee intermediates with SO_2 to a large extent.

Particle acidity may affect the SOA yield via acid-catalyzed reactions, as we had discussed in our manuscript. In the revised manuscript, we have elaborated this discussion by comparing with previous studies as follows.

"Particle acidity may also play a role in affecting the SOA yield in the experiments with high SO_2. Particle acidity was found to enhance the SOA yield from α-pinene photooxidation at high NO_x (Offenberg et al., 2009) and "high NO" conditions (Eddingsaas et al., 2012a). Yet, in low NO_x condition, particle acidity was reported to have no significant effect on the SOA yield from α-pinene photooxidation (Eddingsaas et al., 2012a; Han et al., 2016). According to these findings, at low NO_x the enhancement of SOA yield in this study is attributed to the effect of facilitating nucleation and providing more particle surface by SO_2 photooxidation. At high NO_x, the effect in enhancing new particle formation by SO_2 photooxidation seems to be more important, although the effect of particle acidity resulted from SO_2 photooxidation may also play a role."

c. The experiments in this study were conducted in the presence of humidity but previous studies were mostly conducted under dry conditions. RH can affect gas-phase and particle-phase chemistry, and subsequently SOA yields.

Response:

We agree with the reviewer that RH can affect gas-phase and particle-phase chemistry and thus may also affect SOA yield. Because humidity is ubiquitous in the real atmosphere, we conducted our experiments in the presence of humidity in order to better represent ambient conditions. In the revised manuscript, we have emphasized this point.

"RH of this study is different from many previous studies, which often used very low RH (<10%)."

d. The authors noted that the finding that SOA yields at high NOx is comparable to that at low NOx in high SO2 conditions is in line with findings in Sarrafzadeh et al. (2016) and Eddingsaas et al. (2012a). I do not think that the data in Eddingsaas et al. showed that "in presence of seed aerosol, the difference in the SOA yield between low and high NOx is much reduced". SOA yield is also a function of deltaMo. Considering the data in Table 1 of Eddingsaas et al., the difference in yields between low and high NO experiments for nucleation is 19%, and for seeded experiments are 15% and 10%. However, the difference in deltaMo for the nucleation experiments is also the largest and this will play a role in the yield difference.

Response:

As the reviewer noticed, the data in Eddingsaas et al. (2012) showed that in the absence of seed aerosol SOA yield at low NO_x is 2.5 times higher than that at high NO_x, while in the presence of seed aerosol SOA yield at low NO_x is only 1 and 0.6 times higher than that at high NO_x for neutral seed and acid seed, respectively. Therefore, the data in Eddingsaas et al. (2012) did show that "in presence of seed aerosol, the difference in the SOA yield between low and high NO_x is much reduced".

We noticed that in the data given by Eddingsaas et al. (2012) the difference in deltaM_o for nucleation experiments is the largest, which plays a role in SOA yield. However, the large difference in deltaM_o between high NO_x and low NO_x cases is because the deltaM_o at high NO_x is the lowest in absence of seed, much lower than deltaM_o in presence of seed when other conditions are largely the same. The higher deltaM_o and the smaller difference in deltaM_o between low NO_x and high NO_x in presence of seed also originated from the seed aerosol since other conditions were kept constant. This result agrees with our finding that "in presence of seed aerosol, the difference in the SOA yield between low and high NO_x is much reduced".

e. The SOA yields in this study are much lower than previous studies, why? Consid-ering the low NOx low SO2 experiment, with OH dose of 1e11 molecules cm-3 s, the yield in this study is 7%. However, the corresponding yield in Eddingsaas et al. is > 30% (Figure 3 of Eddingsaas et al.).

Response:

The difference in SOA yield between this study and the study by Eddingsaas et al. (2012) can be explained by several reasons. Firstly, SOA yield in this study was calculated using a density of 1 g cm^{-3} while in Eddingsaas et al. (2012) SOA yield was calculated using a density of 1.32 g cm^{-3}. Secondly, reaction conditions such as VOC concentrations, NO_x concentrations, and OH source and concentrations of our study at low NO_x are different from those in Eddingsaas et al. (2012). For example, in our study at low NO_x, RO_2+NO account for a large fraction of RO_2 loss while in Eddingsaas et al. (2012) RO_2+HO_2 is the dominant pathway of RO_2 loss. These differences in reaction conditions may affect SOA yield. Thirdly, the organic aerosol concentration of this study is much lower than that in Eddingsaas et al. (2012). Fourthly, the total particle surface area may be different from Eddingsaas et al. (2012) (the data are not available to compare with), which can also affect the measured SOA yield. Also note that the exceptionally high SOA yield at lower α-pinene concentration is an "outlier" to other data in Eddingsaas et al. (2012) and could not be explained by the authors.

In the revised manuscript, we have added the following discussion regarding the comparison of SOA yield from α-pinene photooxidation with the literature.

"The reaction conditions of this study often differ from those described in the literature (see Table S2).

The difference in these conditions can result in both different apparent dependence on specific parameters and the varied SOA yield. For example, SOA yield from α-pinene photooxidation at low NO_x in this study appeared to be much lower than that in Eddingsaas et al. (2012a). The difference between the SOA yield in this study and some of previous studies and between the values in the literature can be attributed to several reasons: 1) RO_2 fates may be different. For example, in our study at low NO_x, RO_2+NO account for a large fraction of RO_2 loss while in Eddingsaas et al. (2012a) RO_2+HO_2 is the dominant pathway of RO_2 loss. This difference in RO_2 fates may affect oxidation products distribution. 2) The organic aerosol loading of this study is much lower than that some of previous studies (e.g., Eddingsaas et al. (2012a)) (see Fig. S9). SOA yields in this study were also plotted versus organic aerosol loading to better compare with previous studies (Fig. S8 and S9). 3) The total particle surface area in this study may also differ from previous studies, which may influence the apparent SOA yield due to vapor wall loss (the total particle surface area is often not reported in many previous studies to compare with). 4) RH of this study is different from many previous studies, which often used very low RH (<10%). It is important to emphasize that reaction conditions including the NO_x as well as SO_2 concentration range and RH in this study were chosen to be relevant to the anthropogenic-biogenic interactions in the ambient atmosphere. In addition, difference in the organic aerosol density used in yield calculation should be taken into account. In this study, SOA yield was derived using a density of 1 g cm^{-3} to better compare with many previous studies (e.g., (Henry et al., 2012)), while in some other studies SOA yield was derived using different density (e.g., 1.32 g cm^{-3} in Eddingsaas et al. (2012a))."

In the revised manuscript, we have also added a figure plotting SOA yield as a function of organic aerosol mass loading (Fig. S8).

12. Line 238 onwards, effect of SO2.

a. One of the proposed reasons to explain the effect of SO2 is that it induces nucleation and provides more particle surface area for condensation. Again, if this is the case, it will point to the importance of loss of organic vapors to chamber walls, though previous studies suggested that this process does not effect SOA yields from a-pinene oxidations to a large extent. With this, it is not clear if this is indeed a reason for the observed SO2 effect. Please explain.

Response:

Please refer to our response to the similar comments above (Pg. 2, lines 58-66; Pg. 4, lines 119-123) and corresponding revisions to the manuscript.

b. Line 258. Is "counterbalance" the appropriate word? If the suppression effect of NOx is counterbalanced by the enhancement effect SO2, in going from "low NOx low SO2" to "high NOx high SO2" one shall not observe change in SOA yields? Also, note that the limonene data showed very different trends comparing to the a-pinene data. This needs to be accurately and clearly stated.

Response:

We have changed "counterbalance" to "compensated". The revised sentence is as follows.

"The presence of high SO_2 enhanced the SOA mass yield at high NO_x conditions, which was even comparable with the SOA yield at low NO_x for α-pinene oxidation. This finding indicates that the suppressing effect of NO_x on SOA mass formation was compensated to large extent by the presence of SO_2."

As for the difference in the limonene and α-pinene data, please refer to our response to the similar comments above (Pg. 1, lines 35-43) and our corresponding revisions to the manuscript.

13. Line 315-318. This explanation is a stretch and not well-justified. There is extensive fragmentation in the AMS and so the H/C ratios of oxidation product molecules do not necessarily translate to the H/C ratios measured. As shown in Chhabra et al., not all experiments conducted under low NOx condition have higher H/C ratios.

Response:

In our opinion, the reaction pathway of RO_2 at least provides a likely explanation for the difference in H/C at different NO_x. Although there is extensive fragmentation in the AMS, H/C measured generally reflects the H/C ratios of the overall compounds. In addition, as we discussed, Chhabra et al. (2011)'s data also show that for α-pinene photooxidation, SOA formed at high NO_x generally has lower H/C, consistent with our study. Admittedly, the RO_2 reaction pathway is not the only factor affecting H/C and O/C. Other factors such as VOC identity, oxidants, and reaction mechanisms, including various functionalization, fragmentation, and oligomerization in both the gas phase and particle phase also play important roles in the chemical composition and thus H/C and O/C. We did not intend to apply our explanation here to all other reaction systems.

14. Line 262 onwards. Did the ratio of nitrate mass concentration to organics mass change over time?

Response:

The ratio of nitrate mass concentration to organics gradually decreased in the beginning of the reactions (2-3 h) and then leveled off. Also, note that in the very beginning of a reaction, the data have large uncertainties due to the low concentration of nitrate and organics. In our manuscript, the average ratios were used to compare different experiments. In the revised manuscript, we have clearly described this in the captions of Fig. 4.

"The average ratios of nitrate to organics during the reaction are shown and error bars indicate the standard deviations."

Minor comments

1. Line 72. Why "in contrast"?

Response:

The finding here is different from those in the studies discussed before. In the revised manuscript, we have modified this sentence as follows.

"In constrast, Eddingsaas et al. (2012a) found that particle yield increases with aerosol acidity only in "high NO" condition (NO_x 800 ppb, α-pinene: 20-52 ppb), but is independent of the presence of seed aerosol or aerosol acidity in both "high NO_2" condition (NO_x 800 ppb)" and low NO_x (NO_x lower than the detection limit of the NO_x analyzer)."

2. Line 84 citation. There are more studies on OH oxidations of a-pinene and they should also be cited here (for example, some of the studies cited in page 2).

Response:

In the revised manuscript, we have added more studies on OH oxidation of α-pinene. However, we would like to note here that many studies on α-pinene photooxidation did not quantitatively distinguish the contributions of oxidation by OH and by O_3.

3. Line 125. "mass" should be "volume"? SMPS measures volume concentration.

Response:

We have changed the "mass" to "volume" in the revised manuscript.

4. Line 126. Delete "with".

Response:

Done.

5. Line 256. Sentence not clear.

Response:

This sentence has been revised as follows.

"The presence of high SO_2 enhanced the SOA mass yield at high NO_x conditions, which was even comparable with the SOA yield at low NO_x for α-pinene oxidation. This finding indicates that the suppressing effect of NO_x on SOA mass formation was compensated to large extent by the presence of SO_2."

6.nFigure 1 caption should specify the SO2 condition.

Response:

Done.

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Effects of NO_x and SO_2 on the Secondary Organic Aerosol Formation from Photooxidation of α-pinene and Limonene

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Abstract

Anthropogenic emissions such as NO_x and SO_2 influence the biogenic secondary organic aerosol (SOA) formation, but detailed mechanisms and effects are still elusive. We studied the effects of NO_x and SO_2 on the SOA formation from the photooxidation of α-pinene and limonene at ambient relevant NO_x and SO_2 concentrations (NO_x: < 1 ppb to 20 ppb, SO_2: <0.05 ppb to 15 ppb). In these experiments, monoterpene oxidation was dominated by OH oxidation. We found that SO_2 induced nucleation and enhanced SOA mass formation. NO_x strongly suppressed not only new particle formation but also SOA mass yield. However, in the presence of SO_2 which induced high number concentration of particles after oxidation to H_2SO_4, the suppression of the mass yield of SOA ~~at high~~by NO_x was ~~comparable to that at low NO_x~~completely or partly compensated. This indicates that the suppression of SOA yield by NO_x was ~~mainly~~largely due to the suppressed new particle formation, leading to a lack of particle surface for the organics to condense on. By compensating for the suppressing effect on nucleation of NO_x, SO_2 also compensated for the suppressing effect on SOA yield. Aerosol mass spectrometer data show that increasing NO_x enhanced nitrate formation. The majority of the nitrate was organic nitrate (57%-77%), even in low NO_x conditions (<~1 ppb). Organic nitrate contributed 7%-26% of total organics assuming a molecular weight of 200 g/mol. SOA from α-pinene photooxidation at high NO_x had generally lower hydrogen to carbon ratio (H/C), compared ~~with at~~to low NO_x. The NO_x dependence of the chemical composition can be attributed to the NO_x dependence of the branching ratio of the RO_2 loss reactions, leading to lower fraction of organic hydroperoxides and higher fractions of organic nitrates at high NO_x. While NO_x suppressed new particle formation and SOA mass formation, SO_2 can compensate for such effects, and the combining effect of SO_2 and NO_x may have important influence on SOA formation affected by interactions of biogenic volatile organic compounds (VOC) with anthropogenic emissions.

1 Introduction

Secondary organic aerosol (SOA~~), as an important class of atmospheric aerosol, have important~~) have significant impacts on air quality, human health and climate change (Hallquist et al., 2009; Kanakidou et al., 2005; Jimenez et al., 2009; Zhang et al., 2011). SOA mainly originates from biogenic volatile organic compounds (VOC) emitted by terrestrial vegetation (Hallquist et al., 2009). Once emitted into the atmosphere, biogenic VOC can undergo reactions with atmospheric oxidants including OH, O_3 and NO_3, and form SOA. When an air mass enriched in biogenic VOC is transported over an area with substantial anthropogenic emissions or vice versa, the reaction behavior of VOC and SOA formation can be altered due to the interactions of biogenic VOC with anthropogenic emissions such as NO_x, SO_2, anthropogenic aerosol and anthropogenic VOC. A number of field studies have highlighted the ~~important~~ role of the anthropogenic-biogenic interactions in SOA formation (de Gouw et al., 2005; Goldstein et al., 2009; Hoyle et al., 2011; Worton et al., 2011; Glasius et al., 2011; Xu et al., 2015a; Shilling et al., 2012), which can induce an "anthropogenic enhancement" effect on SOA formation.

Among biogenic VOC, monoterpenes are important contributors to biogenic SOA due to their high emission rates, high reactivity and relative high SOA yield compared to isoprene (Guenther et al., 1995; Guenther et al., 2012; Chung and Seinfeld, 2002; Pandis et al., 1991; Griffin et al., 1999; Hoffmann et al., 1997; Zhao et al., 2015; Carlton et al., 2009). The anthropogenic modulation of the SOA formation from monoterpene can have important impacts on regional and global biogenic SOA budget (Spracklen et al., 2011). The influence of various anthropogenic pollutants on SOA formation of monoterpene have been investigated by a number of laboratory studies (Sarrafzadeh et al., 2016; Zhao et al., 2016; Flores et al., 2014; Emanuelsson et al., 2013; Eddingsaas et al., 2012a; Offenberg et al., 2009; Kleindienst et al., 2006; Presto et al., 2005; Ng et al., 2007; Zhang et al., 1992; Pandis et al., 1991; Draper et al., 2015; Han et al., 2016). In particular, NO_x and SO_2 have been shown to affect SOA formation~~.~~ from monoterpene.

NO_x changes the fate of RO_2 radical formed in VOC oxidation and therefore can change reaction product distribution and aerosol formation. At low NO_x, RO_2 mainly react with HO_2, forming organic hydroperoxides. At high NO_x, RO_2 mainly react with NO, forming organic nitrate (Hallquist et al., 2009; Ziemann and Atkinson, 2012; Finlayson-Pitts and Pitts Jr., 1999). Some studies found that the SOA yield from α-pinene is higher at lower NO_x concentration for ozonolysis (Presto et al., 2005) and photooxidation ~~(Ng et al., 2007; Eddingsaas et al., 2012a; Han et al., 2016)~~(Ng et al., 2007; Eddingsaas et al., 2012a; Han et al., 2016; Stirnweis et al., 2017). The decrease of SOA yield with increasing NO_x was proposed to be due to the formation of more volatile products like organic nitrate under high NO_x conditions (Presto et al., 2005). In contrast, a recent study found that the suppressing effect of NO_x is in large part attributed to the effect of NO_x on OH concentration for the SOA from β-pinene oxidation, and after eliminating the effect of NO_x on OH concentration, SOA yield only varies by 20-30% (Sarrafzadeh et al., 2016). Beside the effect of NO_x on SOA yield, NO_x has been found to suppress the new particle formation from VOC directly emitted by Mediterranean trees (mainly monoterpenes) (Wildt et al., 2014) and β-pinene (Sarrafzadeh et al., 2016), thereby reducing condensational sink present during high NO_x experiments.

Regarding the effect of SO_2, the SOA yield of α-pinene photooxidation was found to increase with SO_2 concentration at high NO_x concentrations (SO_2: 0-252 ppb, NO_x: 242-543 ppb, α-pinene: 178-255 ppb)

(Kleindienst et al., 2006) and the increase is attributed to the formation of H_2SO_4 acidic aerosol. Acidity of seed aerosol was also found to enhance particle yield of α-pinene at high NO_x (Offenberg et al. (2009): NO_x 100-120 ppb, α-pinene 69-160 ppb; Han et al. (2016): initial NO ~70 ppb, α-pinene 14-18 ppb). In constrast, Eddingsaas et al. (2012a) found that particle yield increases with aerosol acidity ~~at~~only in “high NO” condition (NO_x 800 ppb, α-pinene: 20-52 ppb), but is independent of the presence of seed aerosol or aerosol acidity ~~at~~in both “high NO_2” condition (NO_x 800 ppb)” and low NO_x (NO_x lower than the detection limit of the NO_x analyzer~~) and “high NO_2” condition (NO_x 800 ppb~~). Similarly, at low NO_x (initial NO <0.3 ppb, α-pinene ~20 ppb), Han et al. (2016) found that the acidity of seed has no significant effect on SOA yield from α-pinene photooxidation. In addition, SO_2 was found to influence the gas phase oxidation products from α-pinene and β-pinene photooxidation, which is possibly due to the change in OH/HO_2 ratio caused by SO_2 oxidation or SO_3 directly reacting with organic molecules (Friedman et al., 2016).

While these studies have provided ~~important~~valuable insights into the effects of NO_x and SO_2 on SOA formation, a number of questions still remain elusive. For example, many studies used very high NO_x and SO_2 concentrations (up to several hundreds of ppb~~),~~). High NO_x can make the RO_2 radical fate dominated by one single pathway (i.e., RO_2+NO or RO_2+NO_2) to investigate SOA yields and composition under such conditions. Yet, the effects of NO_x and SO_2 at ~~concentrations relevant to~~concentration ranges for ambient anthropogenic-biogenic interactions (sub ppb to several tens of ppb for NO_2 and SO_2) ~~are unclear~~have seldom been directly addressed. Moreover, many previous studies on the SOA formation from monoterpene oxidation focus on ozonolysis or do not distinguish ~~the~~ OH oxidation and ozonolysis in photooxidation, and only a few studies on OH oxidation have been conducted ~~(Eddingsaas et al., 2012a; Zhao et al., 2015)~~(Eddingsaas et al., 2012a; Zhao et al., 2015; McVay et al., 2016; Sarrafzadeh et al., 2016; Henry et al., 2012; Ng et al., 2007). More importantly, studies that investigated the combined effects of NO_x and SO_2 are scarce, although they are often co-emitted from anthropogenic sources. According to previous studies, NO_x ~~mainly has~~can have a suppressing effect on SOA formation while SO_2 ~~mainly has~~can have an enhancing effect. NO_x and SO_2 might have counteracting ~~effect~~ or ~~a~~ synergistic effects in SOA formation in the ambient atmosphere.

In this study, we investigated the effects of NO_x, SO_2 and their combining effects on SOA formation from the photooxidation of α-pinene and limonene. α-pinene and limonene are two important monoterpenes with high emission rates among monoterpenes (Guenther et al., 2012). OH oxidation dominated over ozonolysis in the monoterpene oxidation in this study as determined by measured OH and O_3 concentrations. The relative contributions of RO_2 loss reactions at low NO_x and high~~er~~ NO_x were ~~also~~ quantified using measured HO_2, RO_2, and NO concentrations. The effects on new particle formation, SOA yield and aerosol chemical composition were examined. We used ambient relevant NO_x and SO_2 concentrations so that the results can shed lights on the mechanisms of interactions of biogenic VOC with anthropogenic emissions in the real atmosphere.

2 Experimental

2.1 Experimental setup and instrumentation

The experiments were performed in the SAPHIR chamber (Simulation of Atmospheric PHotochemistry In a large Reaction chamber) at Forschungszentrum Jülich, Germany. The details of the chamber have been described before (Rohrer et al., 2005; Zhao et al., 2015). Briefly, it is a 270 m^3 Teflon chamber using natural sunlight for illumination. It is equipped with a louvre system to switch between light and dark conditions. The physical parameters for chamber running such as temperature and relative humidity were recorded. The solar irradiation was characterized and the photolysis frequency was derived (Bohn et al., 2005; Bohn and Zilken, 2005).

Gas and particle~~s~~ phase species were characterized using various instruments. OH, HO_2 and RO_2 concentrations were measured using a laser induced fluorescence (LIF) system with details described by Fuchs et al. (2012). OH was formed via HONO photolysis, which was produced from a photolytic process on the Teflon chamber wall (Rohrer et al., 2005). From OH concentration, OH dose, the integral of OH concentration over time, was calculated in order to better compare experiments with different OH levels. For example, experiments at high NO_x in this study generally had higher OH concentrations due to the faster OH production by recycling of HO_2• and RO_2• to OH. The VOC were characterized using a Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS) and Gas Chromatography-Mass spectrometer (GC-MS). NO_x, O_3 and SO_2 concentrations were characterized using a NO_x analyzer (ECO PHYSICS TR480), an O_3 analyzer (ANSYCO, model O341M), and an SO_2 analyzer (Thermo Systems 43i), respectively. O_3 was formed in photochemical reactions since NO_x, even in trace amount (<~1 ppbV), was present in this study. More details of these instrumentation are described before (Zhao et al., 2015).

The number and size distribution of particles were measured using a condensation particle counter (CPC, TSI, model 3786) and a scanning mobility particle sizer (SMPS, TSI, DMA 3081/CPC 3785). From particle number measurement, the nucleation rate ($J_{2.5}$) was derived from the number concentration of particles larger than 2.5 nm as measured by CPC. Particle chemical composition was measured using a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research Inc.). From the AMS data, oxygen to carbon ratio (O/C), hydrogen to carbon ratio (H/C), and nitrogen to carbon ratio (N/C) were derived using a method derived in the literature (Aiken et al., 2007; Aiken et al., 2008). An update procedure to determine the elemental composition is reported by Canagaratna et al. (2015), showing the O/C and H/C derived from the method of Aiken et al. (2008)~~ may be underestimated. Since only relative difference in elemental composition of SOA is studied here, different methods should not affect the relative trend in elemental composition. The fractional contribution of organics in the signals at *m/z*=44 and *m/z*=43 to total organics (f_{44} and f_{43}, respectively) were also derived. ~~ may be underestimated. The H/C and O/C were also derived using the newer approach by Canagaratna et al. (2015) and compared with the data derived from the Aiken et al. (2007) method. The H/C values derived using the Canagaratna et al. (2015) method strongly correlated with the values derived using Aiken et al. (2007) method (Fig. S1) and just increased by 27% as suggested by Canagaratna et al. (2015). Similar results were found for O/C and there was just a difference of 11% in O/C. Since only relative difference in elemental composition of SOA is studied here, only the data derived using Aiken et al. (2007) method are shown as the conclusion was not affected by the methods chosen. The fractional contribution of organics in the signals at *m/z*=44 and *m/z*=43 to total organics (f_{44} and f_{43}, respectively) were also derived~~SOA yields were calculated as the ratio of organic aerosol mass formed to the amount of VOC reacted. The concentration of organic aerosol was derived using the total aerosol mass concentration measured by SMPS with a density of 1 g cm^{-3} (to better compare with previous literature) multiplied by with the mass fraction of organics in total aerosol characterized by AMS. The organic aerosol concentration was corrected for the particle wall loss and dilution loss using the method described in Zhao et al. (2015). The loss of vapor on the wall was not corrected here~~.

SOA yields were calculated as the ratio of organic aerosol mass formed to the amount of VOC reacted. The mass concentration of organic aerosol was derived using the total aerosol volume concentration measured by SMPS multiplied by the volume fraction of organics with a density of 1 g cm^{-3} to better compare with previous literature. In the experiments with added SO_2, sulfuric acid was formed upon photooxidation~~. Sulfuric acid was~~ and partly neutralized by background ammonia, which was introduced into the chamber mainly due to humidification. The ~~density~~volume fraction of ~~the aerosol~~organics was derived ~~using the linear mixing of the~~based on volume additivity using the mass of organics and ammonium sulfate/ammonium bisulfate from AMS and their respective density ~~of organic aerosol (assuming~~ (1.32 g cm^{-3} for organic aerosol from one of our previous studies ~~and the literature (Flores et al., 2014; Eddingsaas et al., 2012a)~~(Flores et al., 2014)~~) and the density of ammonium sulfate/ammonium bisulfate (~~~~ and the literature (Ng et al., 2007) and ~1.77 g cm^{-3}~~).~~ for ammonium sulfate/ammonium bisulfate). According to the calculations based on the E-AIM model (Clegg et al., 1998; Wexler and Clegg, 2002) (http://www.aim.env.uea.ac.uk/aim/ aim.php), there ~~were~~was no aqueous phase formed at the relative humidity in the experiments of this study~~ (~~. The average RH ~~28-42%~~ for the period of monoterpene photooxidation~~).~~ was 28-34% except for one experiment with average RH of 42% RH. The organic aerosol concentration was corrected for the particle wall loss and dilution loss using the method described in Zhao et al. (2015).

2.2 Experimental procedure

The SOA formation from α-pinene and limonene photooxidation was investigated at different NO_x and SO_2 levels. Four types of experiments were done: with neither NO_x nor SO_2 added (referred to as "low NO_x, low SO_2"), with only NO_x added (~ 20 ppb NO, referred to as "high NO_x, low SO_2"), with only SO_2 added (~15 ppb, referred to as "low NO_x, high SO_2"), and with both NO_x and SO_2 added (~20 ppb NO and ~15 ppb SO_2, referred to as "high NO_x, high SO_2"). For low NO_x conditions, background NO concentrations were around 0.05-0.2 ppb, and NO was mainly from the background photolytic process of Teflon chamber wall (Rohrer et al., 2005). For low SO_2 conditions, background SO_2 concentrations were below the detection limit of the SO_2 analyzer (0.05 ppb). In some experiments, a lower level of SO_2 (2 ppb, referred to as "moderate SO_2") was used to test the effect of SO_2 concentration. An overview of the experiments is shown in Table 1.

In a typical experiment, the chamber was humidified to ~75% RH first, and then VOC and NO, if applicable, were added to the chamber. Then the roof was opened to start photooxidation. In the experiments with SO_2, SO_2 was added and the roof was opened to initialize nucleation first and then VOC was added. The particle number concentration caused by SO_2 oxidation typically reached several 10^4 cm^{-3} (see Fig. 2 high SO_2 cases) and after VOC addition, no further nucleation occurred. Adding SO_2 first and initializing nucleation by SO_2 photooxidation ensured that enough nucleating particles were present when VOC oxidation started. SO_2 concentration decayed slowly in the experiments with SO_2 added and most of the SO_2 was still left (typically around 8 ppb from initial 15 ppb) at the end of an experiment due to its low reactivity with OH. Typical SO_2 time series in high SO_2 experiments are shown in Fig S2. The detailed conditions of the experiments are shown in Table S1. The experiments of α-pinene and limonene photooxidation were designed to keep the initial OH reactivity and thus OH loss rate constant so that the OH concentrations of these experiments were more comparable. Therefore, the concentration of limonene was around one-third of the concentration of α-pinene due to the higher OH reactivity of limonene.

2.3 Wall loss of organic vapors

The loss of organic vapors on chamber walls can influence SOA yield (Kroll et al., 2007; Zhang et al., 2014; Ehn et al., 2014; Sarrafzadeh et al., 2016; McVay et al., 2016; Nah et al., 2016; Matsunaga and Ziemann, 2010; Ye et al., 2016; Loza et al., 2010). The wall loss rate of organic vapors in our chamber was estimated by following the decay of organic vapor concentrations after photooxidation was stopped in the experiments with low particle surface area (~5×10^{-8} cm^2 cm^{-3}) and thus low condensational sink on particles. Such method is similar to the method used in previous studies (Ehn et al., 2014; Sarrafzadeh et al., 2016; Krechmer et al., 2016; Zhang et al., 2015). A high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS, Aerodyne Research Inc.) with nitrate ion source ($^{15}NO_3^-$) was used to measure semi/low-volatile organic vapors. The details of the instrument were described in our previous studies (Ehn et al., 2014; Sarrafzadeh et al., 2016). The decay of vapors started from the time when the roof of the chamber was closed. The data were acquired at a time resolution of 4 s. A typical decay of low-volatile organics is shown in Fig. S3 and the first-order wall loss rate was determined to be around 6×10^{-4} s^{-1}.

The SOA yield was not directly corrected for the vapor wall loss, but the influence of vapor wall loss on SOA yield was estimated using the method in the study of Sarrafzadeh et al. (2016) and the details of the method are described therein. Briefly, particle surface and chamber walls competed for the vapor loss (condensation) and the condensation on particles led to particle growth. The fraction of organic vapor loss to particles in the sum of the vapor loss to chamber walls and to particles (F_p) was calculated. The vapor loss to chamber walls was derived using the wall loss rate. The vapor loss to particles was derived using particle surface area concentration, molecular velocity and an accommodation coefficient α_p (Sarrafzadeh et al., 2016). $1/F_p$ (f_{corr}) provides the correction factor to obtain the "real" SOA yield. f_{corr} is a function of particle surface area concentration and accommodation coefficient as shown in Fig. S4. Here a range of 0.1-1 for α_p was used, which is generally in line with the ranges of α_p found by Nah et al. (2016) by fitting a vapor-particle dynamic model to experimental data. At a given α_p, the higher particle surface area, the lower f_{corr} and the lower the influence of vapor wall loss are because most vapors condense on particle surface and vice versa. At a given particle surface area, f_{corr} decreases with α_p because at higher α_p a larger fraction of vapors condenses on particles. An average molecular weight of 200 g/mol was used to estimate the influence of vapor wall loss. For the aerosol surface area range in most of the experiments in this study, the influence of vapor wall loss on SOA yield was relatively small (<~40% for particle surface area larger than 3×10^{-6} cm^2 cm^{-3}, Fig. S4). Yet, for the experiments at high NO_x and low SO_2 for α-pinene and limonene, the influence of vapor wall loss on SOA can be high due to the low particle surface area, especially at lower α_p.

3 Results and discussion

3.1 Chemical scheme: VOC oxidation pathway and RO_2 fate

In the photooxidation of VOC, OH and O_3 often co-exist and both contribute to VOC oxidation~~.~~ because O_3 formation in chamber studies is often unavoidable during photochemical reactions of VOC even in the presence of trace amount of NO_x. In order to study the mechanism of SOA formation, it is helpful to isolate one oxidation pathway from the other. In this study, the reaction rates of OH and ozone with VOC are quantified using measured OH and O_3 concentrations multiplied by rate constants~~.~~ (time series of VOC, OH, and O_3 are shown in Fig. S5). Typical OH and O_3 concentrations in an experiment were around (1-15)$\times10^6$ molecules cm^{-3} and 0-50 ppb, respectively, depending on the VOC and NO_x concentrations added. For all the experiment in this study, the VOC loss was dominated by OH oxidation over ozonolysis (see Fig. S6 as an example). The relative importance of the reaction of OH and O_3 with monoterpenes ~~in a typical experiment is shown~~was similar in ~~Fig. S1. The VOC loss was dominated by OH oxidation over ozonolysis. This~~the low NO_x and high NO_x experiments. At high NO_x, OH was often higher while more O_3 was also produced. The dominant role of OH oxidation in VOC loss makes the chemical scheme simple and it is easier to interpret than cases when both OH oxidation and ozonolysis are important.

As mentioned above, RO_2 fate, i.e., the branching of RO_2 loss among different pathways, has an important influence on the product distribution and thus on SOA composition, physicochemical properties, and yields. RO_2 can react with NO, HO_2, RO_2, or isomerize. The fate of RO_2 mainly depends on the concentrations of NO, HO_2 and RO_2. Here, the loss rates of RO_2 via different pathways were quantified using the measured HO_2, NO and RO_2 concentrations and the rate constants based on the MCM3.3 (Jenkin et al., 1997; Saunders et al., 2003) (*http://mcm.leeds.ac.uk/MCM.*). Measured HO_2 and RO_2 concentrations ~~in a typical experiment~~ are shown in Fig. ~~S2~~S7 as an example and the relative importance of different RO_2 reaction pathways is compared in Fig. 1, which is similar for both α-pinene and limonene oxidation. In the low NO_x conditions of this study, RO_2+NO dominated the RO_2 loss rate in the beginning of an experiment (Fig. 1a~~) because a~~). The trace amount of NO (up to ~0.2 ppbV) was ~~formed~~ from the photolysis of HONO, which was continuously produced from a photolytic process on ~~the~~ chamber ~~wall~~walls throughout an experiment (Rohrer et al., 2005). But later in the experiment, RO_2+HO_2 contributed a significant fraction (up to ~40 %) to RO_2 loss because of increasing HO_2 concentration and decreasing NO concentration. In the high NO_x conditions, RO_2+NO overwhelmingly dominated the RO_2 loss rate (Fig. 1b), and with the decrease of NO in an experiment, the total RO_2 loss rate decreased substantially (Fig. 1b). Since the main products of RO_2+HO_2 are organic hydroperoxides, more organic hydroperoxides relative to organic ~~nitrate is~~nitrates are expected in the low NO_x conditions here. The loss rate of RO_2+RO_2 was estimated to be ~10^{-4} s^{-1} using a reaction rate constant of 2.5×10^{-13} $molecules^{-1}$ cm^3 s^{-1} (Ziemann and Atkinson, 2012). This contribution is negligible compared to other pathways in this study, although the reaction rate constants of

RO_2+RO_2 are highly uncertain and may depend on specific RO_2 (Ziemann and Atkinson, 2012). Note that the RO_2 fate in the low and high NO_x conditions quantified here are further used in the discussion below since the information of RO_2 fate is important for data interpretation of experiments conducted at different NO_x levels (Wennberg, 2013).

3.2 Effects of NO_x and SO_2 on new particle formation

The effects of NO_x and SO_2 on new particle formation from α-pinene oxidation are shown in Fig. 2a. In low SO_2 conditions, both the total particle number concentration and nucleation rate at high NO_x were lower than those at low NO_x, indicating NO_x suppressed the new particle formation. The suppressing effect of NO_x on new particle formation was in agreement with the findings of Wildt et al. (2014). This suppression is considered to be caused by the increased fraction of RO_2+NO reaction, decreasing the importance of RO_2+RO_2 permutation reactions. RO_2+RO_2 reaction products are believed to be involved in the new particle formation (Wildt et al., 2014; Kirkby et al., 2016) and initial growth of particles by forming higher molecular weight products such as highly oxidized multifunctional molecules (HOM) and their dimers and trimers (Ehn et al., 2014; Kirkby et al., 2016).

In high SO_2 conditions, the nucleation rate and total number concentrations were high, regardless of NO_x levels. The high concentration of particles was attributed to the new particle formation induced by H_2SO_4 alone formed by SO_2 oxidation since the new particle formation occurred before VOC addition. The role of H_2SO_4 in new particle formation has been well studied in previous studies (Berndt et al., 2005; Zhang et al., 2012; Sipila et al., 2010; Kirkby et al., 2011; Almeida et al., 2013).

Similar suppression of new particle formation by NO_x and enhancement of new particle formation by SO_2 photooxidation were found for limonene oxidation (Fig. 2b).

3.3 Effects of NO_x and SO_2 on SOA mass yield

3.3.1 Effect of NO_x

Figure 3a shows SOA yield at different NO_x for α-pinene oxidation. In order to make different experiments more comparable, the SOA yield is plotted as a function of OH dose instead of reaction time. In low SO_2 conditions, NO_x not only suppressed the new particle formation but also suppressed SOA mass yield. Because NO_x suppressed new particle formation, the suppression ~~on~~of the SOA yield could be attributed to the ~~absence~~lack of ~~nucleation~~new particles as seed and thus the ~~absence~~lack of condensational sink, or to the decrease of condensable organic materials. We further found that when new particle formation was already enhanced by added SO_2, the SOA yield at high NO_x was comparable to that at low NO_x and the difference in SOA yield between high NO_x and low NO_x was much smaller (Fig. 3a). This finding ~~indicates that NO~~ can be attributed to two possible explanations. Firstly, NO_x did not significantly suppress the formation of low volatile condensable organic materials, although NO_x obviously suppressed the formation of products for nucleation. Secondly, NO_x did suppress the formation of low-volatility condensable organic materials via forming potentially more volatile compounds and in addition to that, the suppressed formation of condensable organic materials was compensated by the presence of SO_2, resulting in comparable SOA yield. Organic nitrates are a group of compounds formed at high NO$_x$, which have been proposed to be more volatile (Presto et al., 2005; Kroll et al., 2006). However, many organic nitrates formed by photooxidation in this study were highly oxidized organic molecules (HOMs) containing multi-functional groups besides nitrate group (C$_{7-10}$H$_{9-15}$NO$_{8-15}$). These compounds are expected to have low volatility and they are found to have an uptake coefficient on particles of ~1 (Pullinen et al., in preparation). Therefore, ~~we conclude that~~ the suppressing effect of NO$_x$ on SOA yield was ~~mainly~~mostly likely due to suppress~~ing~~ed nucleation, i.e., ~~to~~ the ~~absence~~lack of particle surface as condensational sink.

For limonene oxidation, similar results of NO$_x$ suppressing the particle mass formation have been found in low SO$_2$ conditions (Fig. 3b). Yet, in high SO$_2$ conditions, the SOA yield from limonene oxidation at high NO$_x$ was still significantly lower than that at low NO$_x$, which is different from the findings for α-pinene SOA. ~~That might be caused by either the larger~~The cause of this difference ~~between the volatility of oxidation~~ is currently unknown. Our data of SOA yield suggest that the products formed ~~under different NO$_x$ conditions for~~from limonene ~~case compared to α-pinene or by the different ranges of VOC/NO$_x$ for α-pinene (VOC/NO$_x$= 1~~ oxidation at high NO$_x$~~, see Table 1) and limonene (VOC/NO$_x$=0.35,~~ seemed to have higher average volatility than that at ~~high~~low NO$_x$~~)~~.

The suppression of SOA mass formation by NO$_x$ under low SO$_2$ conditions agrees with previous studies (Eddingsaas et al., 2012a; Wildt et al., 2014; Sarrafzadeh et al., 2016; Hatakeyama et al., 1991). For example, it was found that~~,~~ high concentration of NO$_x$ (tens of ppb) suppressed mass yield of SOA formed from photooxidation of β-pinene, α-pinene and VOC emitted by Mediterranean trees (Wildt et al., 2014; Sarrafzadeh et al., 2016). And on the basis of the results by Eddingsaas et al. (2012a) , the SOA yield at high NO$_x$ (referred to as "high NO" by the authors) is lower than at low NO$_x$ in the absence of seed aerosol.

Our finding that the difference in SOA yield ~~at~~between high NO$_x$ ~~is comparable to that at~~and low NO$_x$ ~~in high SO$_2$~~ conditions was highly reduced at high SO$_2$ is also in line with the findings of some previous studies using seed aerosols (Sarrafzadeh et al., 2016; Eddingsaas et al., 2012a). For example, Sarrafzadeh et al. (2016) found that in the presence of seed aerosol, the suppressing effect of NO$_x$ on the SOA yield from β-pinene photooxidation is substantially diminished and SOA yield only ~~varies~~decreases by 20-30% in the NO$_x$ range of <1 ppb to 86 ppb at constant OH concentrations. The data by Eddingsaas et al. (2012a) also ~~found~~showed that in presence of seed aerosol, the difference in the SOA yield between low NO$_x$ and high NO$_x$ is much decreased. However, our finding is in contrast with the findings in other studies ~~(Presto et al., 2005; Ng et al., 2007; Han et al., 2016)~~(Presto et al., 2005; Ng et al., 2007; Han et al., 2016; Stirnweis et al., 2017), who reported much lower SOA yield at high NO$_x$ than at low NO$_x$ in presence of seed. The different findings in these studies from ours may be attributed to the difference in the reaction conditions such as VOC oxidation pathways (OH oxidation vs. ozonolysis), VOC and NO$_x$ concentration ranges, NO/NO$_2$ ~~ratio as well as~~, OH concentrations as well as organic aerosol loading, which all affect SOA yield. ~~Note that even at "high NO$_x$" the NO$_x$ concentration in~~ The reaction conditions of this study ~~was much lower than in many previous studies and the NO$_x$ concentration range here was more relevant to the anthropogenic-biogenic interactions in the ambient.~~often differ from those described in the literature (see Table S2).

The difference in these conditions can result in both different apparent dependence on specific parameters and the varied SOA yield. For example, SOA yield from α-pinene photooxidation at low NO$_x$ in this study appeared to be much lower than that in Eddingsaas et al. (2012a). The difference between the SOA yield in this study and some of previous studies and between the values in the literature can be attributed to several reasons: 1) RO_2 fates may be different. For example, in our study at low NO_x, RO_2+NO account for a large fraction of RO_2 loss while in Eddingsaas et al. (2012a) RO_2+HO_2 is the dominant pathway of RO_2 loss. This difference in RO_2 fates may affect oxidation products distribution. 2) The organic aerosol loading of this study is much lower than that some of previous studies (e.g., Eddingsaas et al. (2012a)) (see Fig. S9). SOA yields in this study were also plotted versus organic aerosol loading to better compare with previous studies (Fig. S8 and S9). 3) The total particle surface area in this study may also differ from previous studies, which may influence the apparent SOA yield due to vapor wall loss (the total particle surface area is often not reported in many previous studies to compare with). 4) RH of this study is different from many previous studies, which often used very low RH (<10%). It is important to emphasize that reaction conditions including the NO_x as well as SO_2 concentration range and RH in this study were chosen to be relevant to the anthropogenic-biogenic interactions in the ambient atmosphere. In addition, difference in the organic aerosol density used in yield calculation should be taken into account. In this study, SOA yield was derived using a density of 1 g cm^{-3} to better compare with many previous studies (e.g., (Henry et al., 2012)), while in some other studies SOA yield was derived using different density (e.g., 1.32 g cm^{-3} in Eddingsaas et al. (2012a)).

3.3.2 Effect of SO_2

For both α-pinene and limonene, SO_2 was found to enhance the SOA mass yield~~,~~ at given NO_x levels, especially for the high NO_x cases (Fig. 3). The enhancing effect of SO_2 on particle mass formation can be attributed to two reasons. Firstly, SO_2 oxidation induced new particle formation, which provided more surface and volume for further condensation of organic ~~vapor.~~vapors. This is consistent with the finding that the enhancement of SOA yield by SO_2 was more significant at high NO_x when the enhancement in nucleation was also more significant. Secondly, H_2SO_4 formed by photooxidation of SO_2 can enhance SOA formation via acid-catalyzed heterogeneous uptake, an important SOA formation pathway initially found from isoprene photooxidation (Jang et al., 2002; Lin et al., 2012; Surratt et al., 2007) and later also in the photooxidation of other compound such as anthropogenic VOC (Chu et al., 2016; Liu et al., 2016). For the products from monoterpene oxidation, such an acid-catalyzed effect may also occur (Northcross and Jang, 2007; Wang et al., 2012; Lal et al., 2012; Zhang et al., 2006; Ding et al., 2011; Iinuma et al., 2009) and in this study, the particles were acidic with the molar ratio of NH_4^+ to SO_4^{2-} around 1.5-1.8~~. As mentioned above, inducing new particle formation by SO_2 is especially important at high NO_x conditions, when nucleation~~, although no aqueous phase was ~~suppressed by NO_x. In addition, we~~formed.

We found that the SOA yield in the limonene oxidation at a moderate SO_2 level (2 ppb) was comparable to the yield at high SO_2 (15 ppb) when similar particle number concentrations in both cases were formed. Both yields were significantly higher than the yield at low SO_2 (<0.05 ppb, see Fig. ~~S3~~S10). This comparison suggests that the effect in enhancing new particle formation by SO_2 seems to be more important~~.~~ compared to the particle acidity effect. The role of SO_2 ~~on~~in new particle formation is similar to adding seed aerosol ~~on~~and providing particle surface for organics to condense. Artificially added seed aerosol has been shown to enhance SOA formation from α-pinene and β-pinene oxidation (Ehn et al., 2014; Sarrafzadeh et al., 2016; Eddingsaas et al., 2012a). In some other studies, it was found that the SOA yield from α-pinene oxidation is independent of initial seed surface area (McVay et al., 2016; Nah et al., 2016). The difference in the literature may be due to the range of total surface area of particles, reaction conditions and chamber setup. For example, the peak particle-to-chamber surface ratio for α-pinene photooxidation in this study was 7.7×10^{-5} at high NO_x and low SO_2, much lower than the aerosol surface area range in the studies by Nah et al. (2016) and McVay et al. (2016). A lower particle-to-chamber surface ratio can lead to a larger fraction of organics lost on chamber walls. Hence, providing additional particle surface by adding seed particles can increase the condensation of organics on particles and thus increase SOA yield. However, once the surface area is high enough to inhibit condensation of vapors on chamber walls, further enhancement of particle surface will not significantly enhance the yield (Sarrafzadeh et al., 2016).

~~The finding that in presence of high SO_2, the SOA mass yield at NO_x conditions was enhanced to the value comparable with that at low NO_x indicates that the suppressing effect of NO_x on SOA mass formation was counterbalanced by the presence of SO_2.~~Particle acidity may also play a role in affecting the SOA yield in the experiments with high SO_2. Particle acidity was found to enhance the SOA yield from α-pinene photooxidation at high NO_x (Offenberg et al., 2009) and "high NO" conditions (Eddingsaas et al., 2012a). Yet, in low NO_x condition, particle acidity was reported to have no significant effect on the SOA yield from α-pinene photooxidation (Eddingsaas et al., 2012a; Han et al., 2016). According to these findings, at low NO_x the enhancement of SOA yield in this study is attributed to the effect of facilitating nucleation and providing more particle surface by SO_2 photooxidation. At high NO_x, the effect in enhancing new particle formation by SO_2 photooxidation seems to be more important, although the effect of particle acidity resulted from SO_2 photooxidation may also play a role.

SO_2 has been proposed to also affect gas phase chemistry of organics by changing the HO_2/OH or forming SO_3 (Friedman et al., 2016). In this study, the effect of SO_2 on gas phase chemistry of organics was not significant because of the much lower reactivity of SO_2 with OH compared with α-pinene and limonene (Atkinson et al., 2004, 2006; Atkinson and Arey, 2003) and the low OH concentrations (2-3 orders of magnitude lower than those in the study by Friedman et al. (2016)). Moreover, reactions of RO_2 with SO_2 was also not important because the reaction rate constant is very low ($<10^{-14}$ $\text{molecule}^{-1}\ \text{cm}^{3}\ \text{s}^{-1}$) (Lightfoot et al., 1992; Berndt et al., 2015). In addition, from the AMS data of SOA formed at high SO_2 no significant organic fragments containing sulfur were found. Also the fragment $CH_3SO_2^+$ from organic sulfate suggested by Farmer et al. (2010) was not detected in our data. The absence of organic sulfate tracers is likely due to the lack of aqueous phase in aerosol particles in this study. Therefore, the influence of SO_2 on gas phase chemistry of organics and further on SOA yield via affecting gas phase chemistry is not important in this study.

The presence of high SO_2 enhanced the SOA mass yield at high NO_x conditions, which was even comparable with the SOA yield at low NO_x for α-pinene oxidation. This finding indicates that the suppressing effect of NO_x on SOA mass formation was compensated to large extent by the presence of SO_2. This has important implications for SOA formation affected by anthropogenic-biogenic interactions in the real atmosphere ~~as discussed below~~ when SO_2 and NO_x often co-exist in relative high concentrations as discussed below.

3.4 Effects of NO_x and SO_2 on SOA chemical composition

The effects of NO_x and SO_2 on SOA chemical composition were analyzed on the basis of AMS data. We found that NO_x enhanced nitrate formation. The ratio of the mass of nitrate to organics was higher at high NO_x than at low NO_x regardless of the SO_2 level, and similar trends were found for SOA from α-pinene and limonene oxidation (Fig. 4a). Higher nitrate to organics ratios were observed for SOA from limonene at high NO_x, which is mainly due to the lower VOC/NO_x ratio resulted from the lower concentrations of limonene (7 ppb) compared to α-pinene (20 ppb) (see Table 1). Overall, the mass ratios of nitrate to organics ranged from 0.02 to 0.11 considering all the experiments in this study.

Nitrate formed can be either inorganic (such as HNO_3 from the reaction of NO_2 with OH) or organic (from the reaction of RO_2 with NO). The ratio of NO_2^+ (*m/z*=46) to NO^+ (*m/z*=30) in the mass spectra detected by AMS can be used to differentiate whether nitrate is organic or inorganic (Fry et al., 2009; Rollins et al., 2009; Farmer et al., 2010; Kiendler-Scharr et al., 2016). Organic nitrate was considered to have a NO_2^+/NO^+ of ~0.1 and inorganic NH_4NO_3 had a NO_2^+/NO^+ of ~0.31 with the instrument used in this study as determined from calibration measurements. In this study, NO_2^+/NO^+ ratios ranged from 0.14 to 0.18, closer to the ratio of organic nitrate. The organic nitrate was estimated to account for 57%-77% (molar fraction) of total nitrate considering both the low NO_x and high NO_x conditions. This indicates that nitrate was mostly organic nitrate, even at low NO_x in this study.

In order to determine the contribution of organic nitrate to total organics, we estimated the molecular weight of organic nitrates formed by α-pinene and limonene oxidation to be 200-300 g/mol, based on reaction mechanisms ((Eddingsaas et al., 2012b) and MCM v3.3, via website: http://mcm.leeds.ac.uk/MCM.). We assumed a molecular weight of 200 g/mol in order to make our results comparable to the field studies which used similar molecular weight (Kiendler-Scharr et al., 2016). For this value, the organic nitrate compounds were estimated to account for 7-26% of the total organics mass as measured by AMS in SOA. Organic nitrate fraction in total organics was within the range of values found in a field observation in southeast US (5-12% in summer and 9-25% in winter depending on the molecular weight of organic nitrate) using AMS (Xu et al., 2015b) and particle organic nitrate content derived from the sum of speciated organic nitrates (around 1-17% considering observed variability and 3% and 8% on average in the afternoon and at night, respectively) (Lee et al., 2016). Note that the organic nitrate fraction observed in this study was lower than the mean value (42%) for a number of European observation stations when organic nitrate is mainly formed by the reaction of VOC with NO_3 (Kiendler-Scharr et al., 2016).

Moreover, we found that the contribution of organic nitrate to total organics (calculated using a molecular weight of 200 g/mol for organic nitrate) was higher at high NO_x (Fig. 4b), although in some experiments the ratios of NO_2^+ to NO^+ were too noisy to derive a reliable fraction of organic nitrate. This result is consistent with the reaction scheme that at high NO_x, almost all RO_2 loss was switched to the reaction with NO, which is expected to enhance the organic nitrate formation. Besides organic nitrate, the ratio of nitrogen to carbon atoms (N/C) was also found to be higher at high NO_x (Fig. ~~S4~~S11). But after considering nitrate functional group separately, N/C ratio was very low, generally <0.01, which indicates majority of the organic nitrogen existed in the form of organic nitrate.

The chemical composition of organic components of SOA in terms of H/C and O/C ratios at different NO_x and SO_2 levels was further compared. For SOA from α-pinene photooxidation, in low SO_2 conditions, no significant difference in H/C and O/C was found between SOA formed at low NO_x and at high NO_x within the experimental uncertainties (Fig. 5). The variability of H/C and O/C at high NO_x is large, mainly due to the low particle mass and small particle size. In high SO_2 conditions, SOA formed at high NO_x had the higher O/C and lower H/C, which indicates that SOA components had higher oxidation state. The higher O/C at high NO_x than at low NO_x is partly due to the higher OH dose at high NO_x, although even at same OH dose O/C at high NO_x was still slightly higher than at low NO_x in high SO_2 conditions.

For the SOA formed from limonene photooxidation, no significant difference in the H/C and O/C was found between different NO_x and SO_2 conditions (Fig. ~~S5~~S12), which is partly due to the low signal resulting from low particle mass and small particle size in high NO_x conditions.

Due to the high uncertainties for some of the H/C and O/C data, the chemical composition was further analyzed using f_{44} and f_{43} since f_{44} and f_{43} are less noisy (Fig. 6). For both α-pinene and limonene, SOA formed at high NO_x generally ha~~s~~d lower f_{43}. Because f_{43} generally correlates with H/C in organic aerosol (Ng et al., 2011), lower f_{43} is indicative of lower H/C, which is consistent with the lower H/C at high NO_x observed for SOA from α-pinene oxidation in ~~presence of~~ high ~~concentrations of~~ SO_2 conditions (Fig. 5). The lower f_{43} at high NO_x was evidenced in the oxidation of α-pinene based on the data in a previous study (Chhabra et al., 2011). The lower H/C and f_{43} are likely to be related to the reaction pathways. According to the reaction mechanism mentioned above, at low NO_x a significant fraction of RO_2 reacted with HO_2 forming hydroperoxides, while at high NO_x almost all RO_2 reacted with NO forming organic nitrates. Compared with organic ~~nitrate, hydroperoxide~~nitrates, hydroperoxides have higher H/C ratio. The same mechanism also caused higher organic nitrate fraction at high NO_x, as discussed above.

Detailed mass spectra of SOA were compared, shown in Fig 7. For α-pinene, in high SO_2 conditions, mass spectra of SOA formed at high NO_x generally had higher intensity for CHOgt1 ("gt1" means greater than 1) family ions, such as CO_2^+ (*m/z* 44), but lower intensity for CH family ions, such as $C_2H_3^+$ (*m/z* 15), $C_3H_3^+$ (*m/z* 39) (Fig. 7b) than at low NO_x. In low SO_2 conditions, such difference is not apparent (Fig. 7a), partly due to the low signal from AMS for SOA formed at high NO_x as discussed above. For both the high SO_2 and low SO_2 cases, mass spectra of SOA at high NO_x show higher intensity of CHN1 family ions. This is also consistent with the higher N/C ratio shown above. For SOA from limonene oxidation, SOA formed at high NO_x had lower mass fraction at *m/z* 15 ($C_2H_3^+$), 28 (CO^+), 43 ($C_2H_3O^+$), 44 (CO_2^+), and higher mass fraction at *m/z* 27 (CHN^+, $C_2H_3^+$), 41 ($C_3H_5^+$), 55 ($C_4H_7^+$), 64 (C_4O^+) than at low NO_x (Fig. ~~S6~~S13). It seems that overall mass spectra of the SOA from limonene formed at high NO_x had higher intensity for CH family ions, but lower intensity for CHO1 family ions than at low NO_x. Note that the differences in these *m/z* were based on the average spectra during the whole reaction period and may not reflect the chemical composition at a certain time.

4 Conclusion and implications

We investigated the SOA formation from the photooxidation of α-pinene and limonene under different NO$_x$ and SO$_2$ conditions, when OH oxidation was the dominant oxidation pathway of monoterpenes. The fate of RO$_2$ was regulated by varying NO$_x$ concentrations. We confirmed that NO$_x$ suppressed new particle formation. NO$_x$ also suppressed SOA mass yield in the absence of SO$_2$. The suppression of SOA yield by NO$_x$ was ~~mainly~~likely due to the suppressed new particle formation, i.e., absence of sufficient particle surfaces for organic vapor to condense on at high NO$_x$. ~~NO$_x$ did not significantly suppress the formation of condensable organics from α-pinene oxidation as evidenced by the similar SOA yield at high and low NO$_x$ in the presence of SO$_2$.~~

SO$_2$ enhanced SOA yield from α-pinene and limonene photooxidation. SO$_2$ oxidation produced high number concentration of particles and compensated for the suppression of SOA yield by NO$_x$~~.~~ to a large extent. The enhancement of SOA yield by SO$_2$ is likely to be mainly caused by facilitating nucleation by H$_2$SO$_4$, although the contribution of acid-catalyzed heterogeneous uptake cannot be excluded.

NO$_x$ promoted nitrate formation. The majority (57-77%) of nitrate was organic nitrate at both low NO$_x$ and high NO$_x$, based on the estimate using the NO$_2^+$/NO$^+$ ratios from AMS data. The significant contribution of organic nitrate to nitrate may have important implications for deriving the hygroscopicity from chemical composition. For example, a number of studies derived the hygroscopicity parameter by linear combination of the hygroscopicity parameters of various components such as sulfate, nitrate, and organics, assuming all nitrates are inorganic nitrate (Wu et al., 2013; Cubison et al., 2008; Yeung et al., 2014; Bhattu and Tripathi, 2015; Jaatinen et al., 2014; Moore et al., 2012; Gysel et al., 2007). Because the hygroscopicity parameter of organic nitrate may be much lower than inorganic nitrate (Suda et al., 2014), such derivation may overestimate hygroscopicity.

Organic nitrate compounds are estimated to contribute 7-26% of the total organics using an average molecular weight of 200 g/mol for organic nitrate compounds and a higher contribution of organic nitrate was found at high NO$_x$. Generally, SOA formed at high NO$_x$ has a lower H/C compared to that at low NO$_x$. The higher contribution of organic nitrate to total organics and lower H/C at high NO$_x$ than at low NO$_x$ is attributed to the reaction of RO$_2$ with NO, which produced more organic nitrates relative to organic hydroperoxides formed via the reaction of RO$_2$ with HO$_2$. The different chemical composition of SOA between high and low NO$_x$ conditions may affect the physicochemical properties of SOA such as volatility, hygroscopicity, and optical properties and thus change the impact of SOA on environment and climate.

The different effects of NO$_x$ and SO$_2$ on new particle formation and SOA mass yields have important implications for SOA formation affected by anthropogenic-biogenic interactions in the ambient atmosphere. When an air mass of anthropogenic origin is transported to an area enriched in biogenic VOC emissions or vice versa, anthropogenic-biogenic interactions occur. Such scenarios are common in the ambient atmosphere in many areas. For example, Kiendler-Scharr et al. (2016) shows that the organic nitrate concentrations are high in all the rural sites all over Europe, indicating the important influence of anthropogenic emissions in rural areas which are often enriched in biogenic emissions. ^{14}C analysis in several studies show that modern source carbon, from biogenic emission or biomass burning, account for large fractions of organic aerosol even in urban areas (Szidat et al., 2009; Weber et al., 2007; Sun et al., 2012), indicating the potential interactions of biogenic emissions with anthropogenic emissions in urban areas. In such cases, anthropogenic NO$_x$ alone may suppress the new particle formation and SOA mass from biogenic VOC oxidation, as we found in this study. However, due to the co-existence of NO_x with SO_2, H_2SO_4 formed by SO_2 oxidation can counteract such suppression of particle mass because regardless of NO_x levels, H_2SO_4 can induce new particle formation especially in the presence of water, ammonia or amine (Berndt et al., 2005; Zhang et al., 2012; Sipila et al., 2010; Almeida et al., 2013; Kirkby et al., 2011; Chen et al., 2012). The overall effects on SOA mass depend on specific NO_x, SO_2 and VOC concentrations and VOC types as well as anthropogenic aerosol concentrations and can be a net suppressing, neutral, or enhancing effect. Such scheme is depicted in Fig. 8. Other anthropogenic emissions, such as primary anthropogenic aerosol and precursors of anthropogenic secondary aerosol, can have similar roles as SO_2. By affecting the concentrations of SO_2, NO_x, and anthropogenic aerosol, anthropogenic emissions may have important mediating impacts on biogenic SOA formation. Considering the effects of these factors in isolation may cause bias in predicting biogenic SOA concentrations. The combined impacts of SO_2, NO_x, and anthropogenic aerosol are also important to the estimate on how much organic aerosol concentrations will change with the ongoing and future reduction of anthropogenic emissions (Carlton et al., 2010).

Acknowledgements

We thank the SAPHIR team, especially Rolf Häseler, Florian Rubach, Dieter Klemp for supporting our measurements and providing helpful data. M. J. Wang would like to thank China Scholarship Council for funding the joint PhD program.

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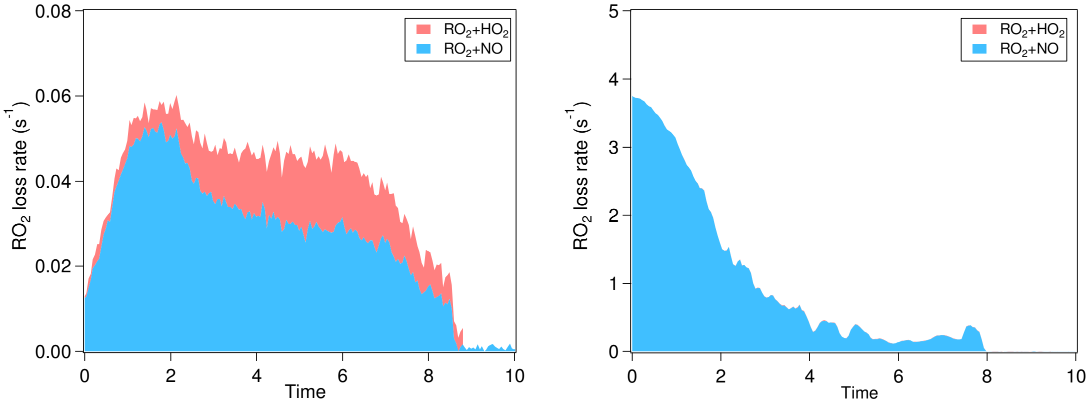
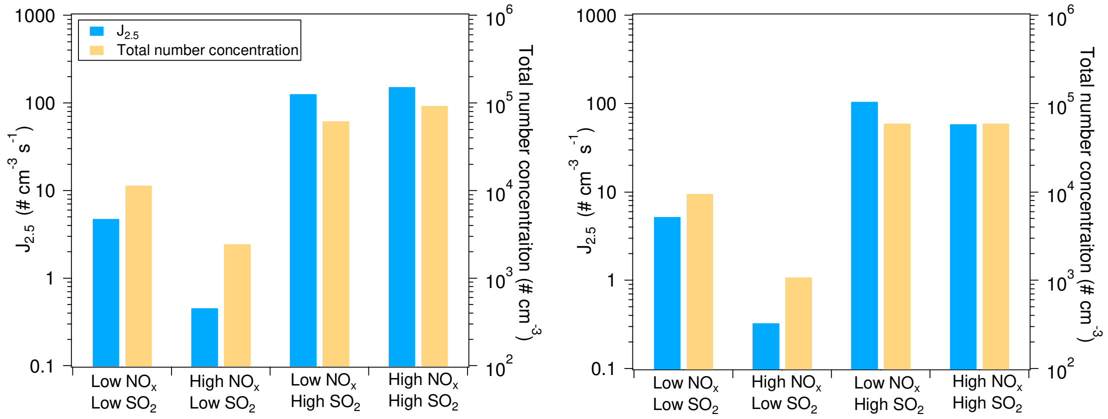
Table 1 Overview of the experiments in this study

Precursor	**SO_2**	**NO_x**	**NO (ppb)**	**SO_2 (ppb)**
α-pinene (~20 ppb)	Low SO_2	Low NO_x	0.05-0.2	<0.05
		High NO_x	~20	<0.05
	High SO_2	Low NO_x	0.05-0.2	~15
		High NO_x	~20	~15
Limonene (~7 ppb)	Low SO_2	Low NO_x	0.05-0.2	<0.05
		High NO_x	~20	<0.05
	High SO_2	Low NO_x	0.05-0.2	~15
		High NO_x	~20	~15
	Moderate SO_2	High NO_x	~20	~2



(a) (b)

Figure 1. Typical loss rate of RO_2 by RO_2+NO and RO_2+HO_2 in the low NO_x (a) and the high NO_x (b) conditions of this study. The experiments at low SO_2 are shown. The RO_2+HO_2 rate is stacked on the RO_2+NO rate. Note the different scales for RO_2 loss rate in panel a and b. In panel b, the contribution of RO_2+HO_2 is very low and barely noticeable.



(a) (b)

Figure 2. Nucleation rates ($J_{2.5}$) and maximum total particle number concentrations under different NO_x and SO_2 conditions for the SOA from α-pinene oxidation (a) and from limonene oxidation (b).

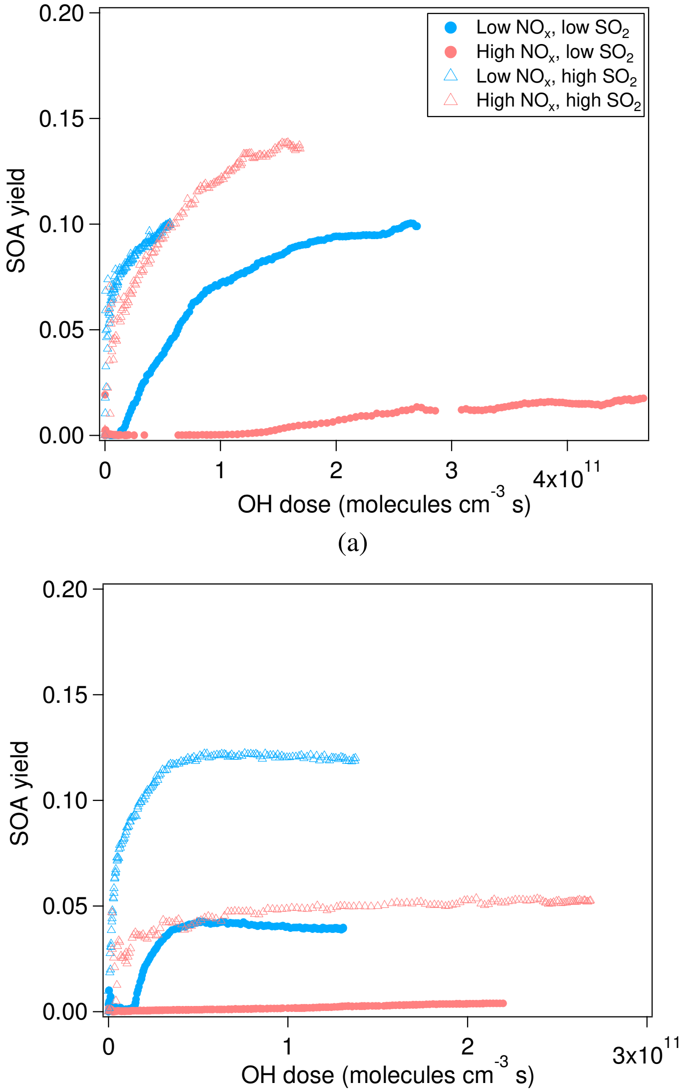
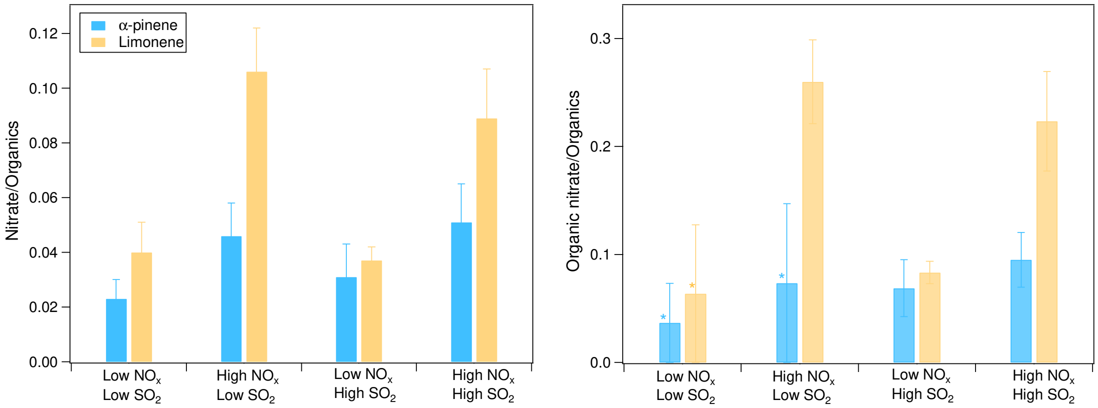


Figure 3. SOA yield of the photooxidation of α-pinene (a) and limonene (b) in different NO_x and SO_2 conditions.



(a) (b)

Figure 4. (a) The ratio of nitrate mass concentration to organics mass in different NO_x and SO_2 conditions~~;~~. The average ratios of nitrate to organics during the reaction are shown and error bars indicate the standard deviations. (b) ~~t~~The fraction of organic nitrate to total organics in different NO_x and SO_2 conditions calculated using a molecular weight of 200 g/mol for organic nitrate. The average fractions during the reaction are shown and error bars indicate the standard deviations. In panel b, * indicate the experiments where the ratios of NO_2^+ to NO^+ were too noisy to derive a reliable fraction of organic nitrate. For these experiments, 50% of total nitrate was assumed to be organic nitrate and the error bars show the range when 0 to 100% of nitrate are assumed to be organic nitrate.

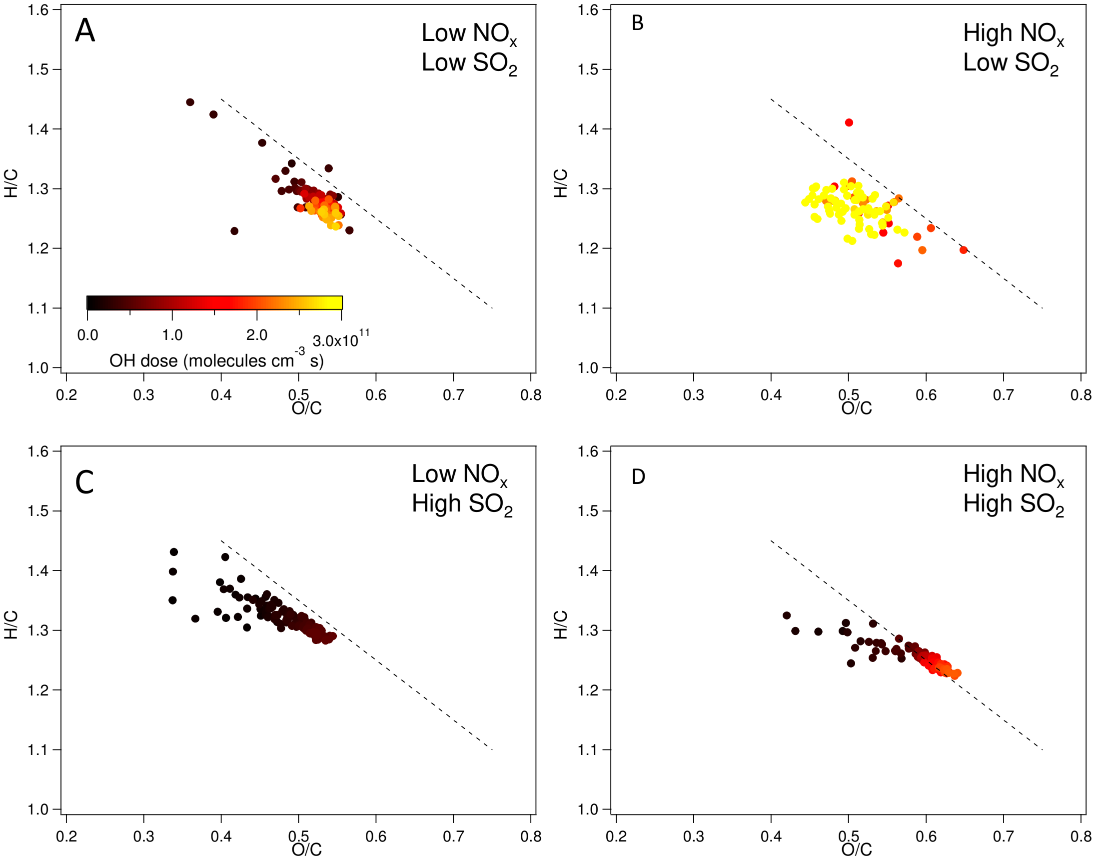


Figure 5. H/C and O/C ratio of SOA from photooxidation of α-pinene in different NO$_x$ and SO$_2$ conditions. A: low NO$_x$, low SO$_2$, B: high NO$_x$, low SO$_2$, C: low NO$_x$, high SO$_2$, D: high NO$_x$, high SO$_2$. The black dashed line corresponds to the slope of -1.

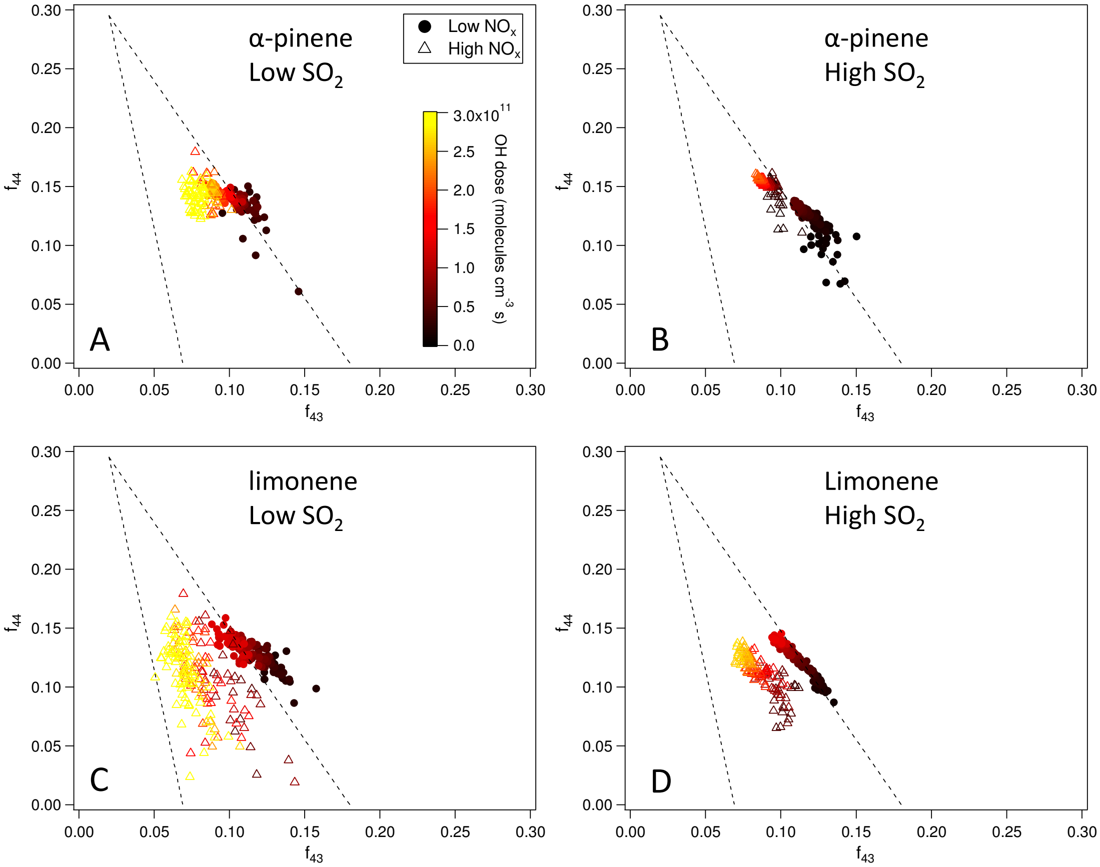


Figure 6. f_{44} and f_{43} of SOA from the photooxidation of α-pinene and limonene in different NO_x and SO_2 conditions. A: α-pinene, low SO_2, B: α-pinene, high SO_2, C: limonene, low SO_2, D: limonene, high SO_2. Note that in the low SO_2, high NO_x condition (panel C), the AMS signal of SOA from limonene oxidation was too low to derive reliable information due to the low particle mass concentration and small particle size. Therefore, the data for high NO_x in panel C show an experiment with moderate SO_2 (2 ppb) and high NO_x instead.

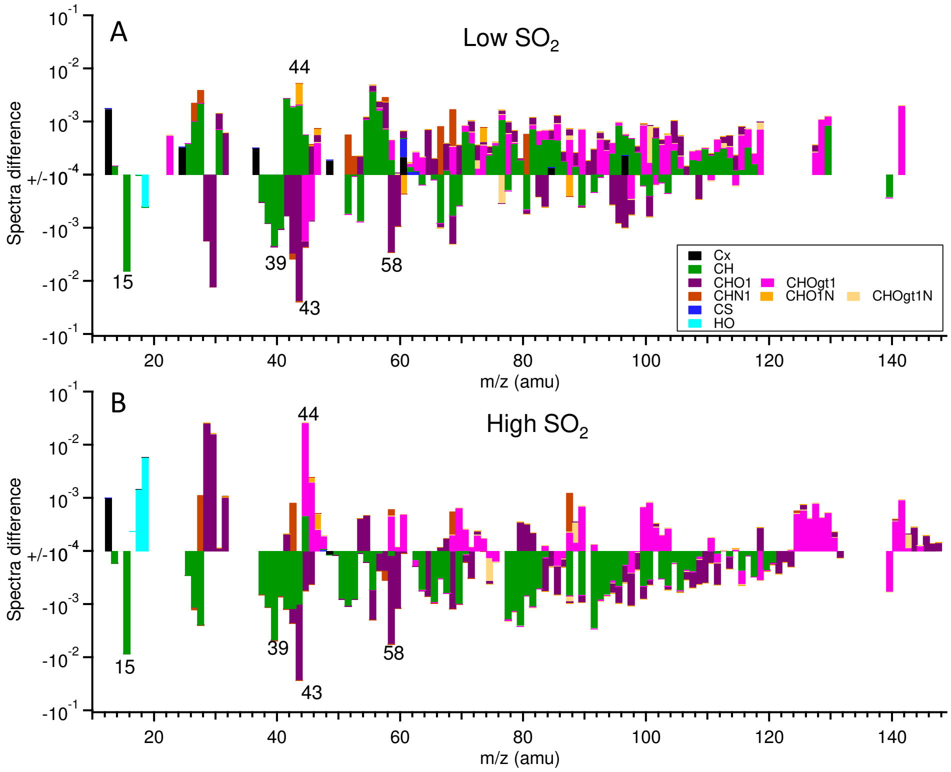


Figure 7. The difference in the mass spectra of organics of SOA from α-pinene photooxidation between high NO_x and low NO_x conditions (high NO_x-low NO_x). SOA was formed at low SO_2 (a) and high SO_2 (b). The different chemical family of high resolution mass peaks are stacked at each unit mass *m/z* ("gt1" means greater than 1). The mass spectra were normalized to the total organic signals. Note the log scale of y-axis and only the data with absolute values large than 10^{-4} are shown.

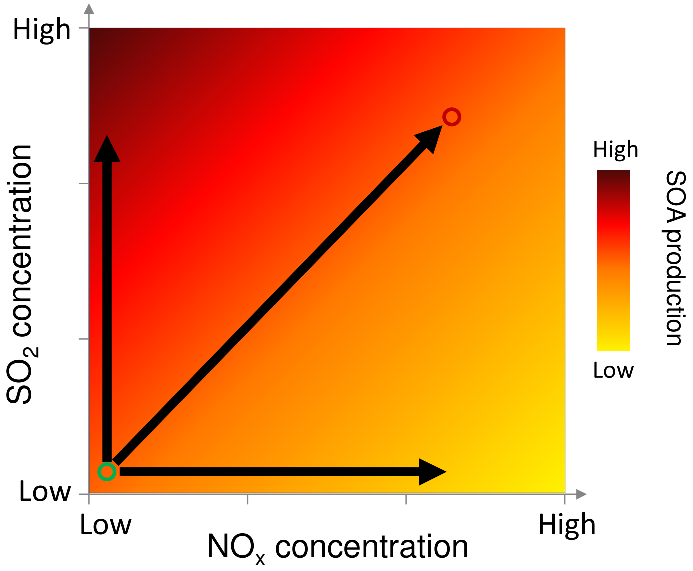


Figure 8. Conceptual schematic showing how NO_x and SO_2 concentrations affect biogenic SOA mass production. The darker colors indicate higher SOA production. The circle on the bottom left corner indicates biogenic cases and the circle on the right top corner indicates the anthropogenic cases. And the horizontal and vertical arrows indicate the effect of NO_x and SO_2 alone. The overall effects on SOA production depend on specific NO_x, SO_2 concentrations and VOC concentrations and speciation.