

Response to Reviewers

Ms. Ref. No.: EGUSPHERE-2024-1599

Changes in Aerosol/Gas-Phase Distribution Ratio of Semi-Volatile Products
Affect Secondary Organic Aerosol Formation with NO_x from α -Pinene
Photooxidation

Dear Editor:

We greatly appreciate the time and effort that the editor and reviewer spent in reviewing our manuscript. After reading the comments from the reviewers, we have carefully revised our manuscript. All the changes we made are marked in red. Our responses to the comments are itemized below. The referee's comments are in black, authors' responses are in blue.

Anything for our paper, please feel free to contact me via ghwang@geo.ecnu.edu.cn.

All the best

Wang Gehui

October, 2024

Reviewer #1

Liu et al. investigated the photooxidation of α -pinene using a smog chamber. They studied the SOA yields under different NO_x concentrations with low- and high-VOC concentrations. Based on the two-product model and chemical composition measurement, semi-volatile oxidation products were suggested as the main components of the α -pinene SOA particles.

The study falls into the scope of ACP and will be of interest to the aerosol community. However, the use of atmospherically irrelevant VOC concentrations and the use of the language have significantly weakened the quality of the work. The manuscript will require major revisions. The comments below need to be considered and addressed before the manuscript can be considered for final publication.

Major Comments

The reported mass concentrations were claimed to be corrected with wall losses. Was it corrected for particle wall loss and/or vapor wall loss? However, there is no detailed information about the correction procedure. It is unclear to me, but also to general readers, how the mass concentration was corrected. Was the α -pinene corrected for vapor loss?

Author reply:

We are very grateful to the reviewer for this comment.

Based on our previous studies, the VOCs concentration was almost unchanged when let it stand for 5 hours in the chamber. Therefore, the wall loss of α -pinene is negligible.

All the particle mass concentration was corrected with the same way of Jiang et al. (2020) and Pathak et al. (2007) to constrained the influence of wall losses of different SOA formed with different experiment conditions. For each experiment, we continued to monitor the particle concentration in the dark condition for 1 hour, and recalculated the particle wall loss constant according to the variation of particle concentration. After the wall loss correction, the particle mass concentration was almost constant (New Fig.S1), we believe that our results are reliable and credible.

To clarify the statement, we added the sentences in line 139 of the revised manuscript as : “The particle wall loss rates were detected at the end of the chamber experiment after the UV-lamps were turned off, and the mass concentration was

corrected with the same way of Jiang et al. (2020) and Pathak et al. (2007). After the wall loss correction, the particle mass concentration was almost constant (Fig.S1), the different wall loss effect caused by gaseous oxidation products formed in the different experiment conditions have been remedied.”

Did the SOA mass concentration remain constant at the end of each experiment? How was the SOA yield defined in this study? Was the maximum or final SOA mass concentration used for the SOA yield calculation?

Author reply:

The SOA yield was calculated based on the maximum SOA mass concentration. The photooxidation time for each group of experiments is 3 h in this study. For the low NO_x condition of Exp. 1, 2, 7, 8, and 9, the α -pinene was not fully consumed in the end of the photooxidation, and the SOA mass concentration still increase in the end of the photooxidation. For the other experiments, the SOA mass concentration remain constant at the end of each experiment after the SOA wall loss corrected. But it should be noted that the maximum SOA mass concentration is equal to the final SOA mass concentration in the end of each experiment.

The SOA yield was defined in Line 160-161 “Here, SOA yield was calculated as the SOA mass concentration divided by the reacted VOCs.” To clarify the statement, it is fixed as “Here, SOA yield was defined as the ratio of the maximum SOA mass concentration ($\mu\text{g m}^{-3}$) to the concentration of reacted α -pinene ($\mu\text{g m}^{-3}$) in the end of each experiment.”, and it was moved to the section of Experimental method in line 144 of the revised manuscript. word 中复制的文字保存在一边 随时用

Lines 163 and 166: How were the low- and high-VOC experiments defined? Did Exp. 1 – Exp. 6 belong to low-VOC experiments? And the Exp. 7 - Exp. 14 belonged to high-VOC ones, didn't they?

Author reply:

As the reviewer pointed, Exp. 1 – Exp. 6 belong to low-VOC experiments, and the Exp. 7 - Exp. 14 belonged to high-VOC. To provide a better illustration of Low and

High-VOCs conditions, the following sentences have been added in the revised manuscript in line 133-136: “Two different α -pinene concentrations were used in this study. Exp. 1 to 6 were defined as low-VOC experiments, and the others were high-VOCs experiments. The concentrations of α -pinene were kept as constant as possible across low- or high-VOC experiments to ensure the effects of NO_x were not obscured.”

Lines 167 – 173: Even though the low-VOC experiments were chosen for analysis, the concentration of α -pinene used in the experiments is still one or two orders of magnitude higher than that in the atmosphere (Li et al., 2021). I suggest that later in the manuscript, the authors should discuss the caveat of using hundreds of ppb of α -pinene in chamber studies here and what might be different from the chemistry occurring in the ambient.

Author reply:

We are very grateful to the reviewer for this comment.

We add the sentences of “Though the initial concentrations of VOCs were higher than those in the atmosphere and the SOA mass loadings were vastly overrated, this study provides new insights into the nonlinear relationship of NO_x with SOA yield, and may be informative to future studies with more atmospheric-relevant concentrations of reactants. Furthermore, according to the changes in the aerosol/gas-phase partition ratio of semi-volatile products with changing VOC concentrations, the proportion of semi-volatile oxidation products distributed in the gas phase would be much higher in the real atmosphere, while the ratio in particulate phase would be lower than observed in our study. Identifying of semi-volatile oxidation products in both the aerosol and gas phase will further enhance our understanding of SOA formation processes. Moreover, the higher ratio of semi-volatile oxidation products distributed in the gas phase in the atmosphere suggests a more pronounced influence of environmental factors, such as acid-catalyzed heterogeneous reactions and liquid-phase reactions, on SOA formation compared to the laboratory studies.” in the end of Section 3.3.

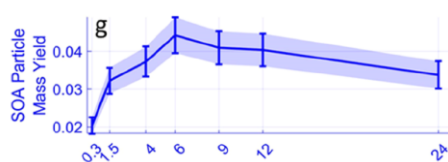
Lines 178 – 180: How was the SOA yield in this study compared to the literature data?

It will be good to include a figure for such a comparison.

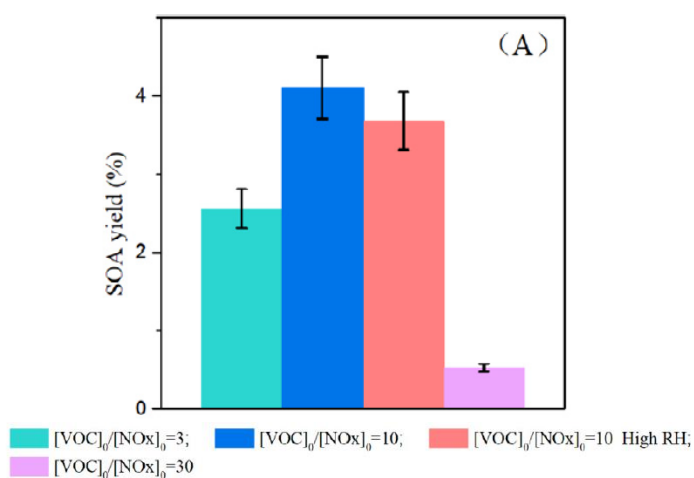
Author reply:

We are very grateful to the reviewer for this comment.

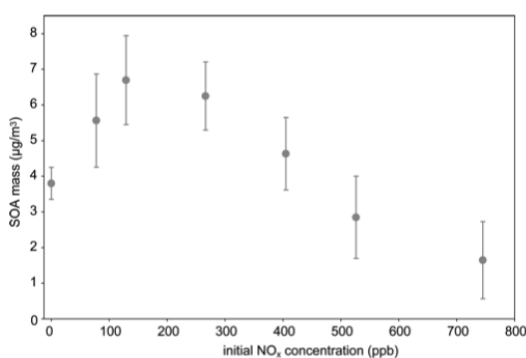
The trend of SOA yield with initial NO_x concentration is illustrated below.



(Aruffo et al., 2022)



(Liu et al., 2019)



(Kroll et al., 2006)

Because the experiment conditions are different among these studies, it is hard to include a figure for such a comparison. To clarify the statement, we changed the sentence in line 208-210 of the revised manuscript as “**Like our study, similar trend of SOA yields first increase and then gradually decreasing with initial NO_x concentrations have been widely observed in previous studies (Aruffo et al., 2022;Liu et al., 2019b;Kroll et al., 2006)**”

Line 186 – 189: Was the suppressed autooxidation of RO₂ and reduction in HOMs observed in this study?

Author reply:

The suppressed autooxidation of RO₂ and reduction in HOMs were not observed in this study. This was referenced in previous studies. This sentence was fixed as “Additionally, numerous other studies have indicated that the autooxidation of RO₂ can be effectively suppressed through the RO₂ + NO / NO₂ reaction, which results in the reduction of HOMs formation and subsequently contributes to decreased SOA yields under high-NO_x conditions (Yu et al., 2022;Laskin et al., 2018)” in the revised manuscript in line 216-219.

Lines 190 - 212: The atmospheric oxidizing capacity (AOC) describes the apparent decay rate of VOCs. AOC is not a term widely used in the atmospheric science community. To help readers understand AOC, the authors are encouraged to give detailed explanations of both the mathematical and physical meanings of AOC. In the context of the work presented here, AOC describes how OH and O₃ together reacted with α -pinene under different NO_x levels. Instead of using AOC here, using a simple box model to determine how much α -pinene was consumed by individual oxidants (i.e., OH and O₃) under different NO_x conditions would be more beneficial.

Author reply:

We are very grateful to the reviewer for this comment.

A substantial amount of research on AOC studies have been reported, i.e. Dai et al.(2023); Feng et al. (2021a); Feng et al. (2021b); Pawar et al. (2024); Zhao et al. (2020); Feng et al. (2019); Ma et al. (2024) (Dai et al., 2023;Feng et al., 2021a;Feng et al., 2021b;Pawar et al., 2024;Zhao et al., 2020;Feng et al., 2019;Ma et al., 2024).

VOCs in the atmosphere are removed through atmospheric oxidation reactions. The removal rate is related to the oxidizing ability of the atmosphere, and it is apparently the strength of atmospheric oxidation. AOC determines the removal rate of trace gases and also the production rates of secondary pollutants (Prinn, 2003), is the essential driving force of atmospheric chemistry in forming complex air pollution in

the troposphere and the near-surface atmosphere (Cheng et al., 2007; Lin and Zhao, 2009).

The consumption ratio of VOCs by OH was calculated by the online data of O₃ and VOCs concentrations. The consumption ratio of VOCs by OH was increased with the initial NO_x concentration. However, there is no clear connection between our analysis of SOA yield and consumption ratio of VOCs by OH or O₃. When we analyzed the combined oxidizing capacity of O₃ and OH as a whole, which represents the amount of VOCs consumption is more reasonable to analyze the effect of the aerosol/gas-phase distribution ratio of the semi-volatile products on SOA yield.

In order to express the meanings of AOC more clearly, the following sentence of “The atmospheric oxidizing capacity (AOC), which indicates the oxidizing ability of the atmosphere, is significantly influenced by NO_x (Wang et al., 2023).” is fixed as: “Atmospheric oxidizing capacity (AOC) is an essential driving force of the oxidizing ability of the atmosphere, which determines the removal rate of trace gases and also the production rates of secondary pollutants (Lin et al., 2009;Ma et al., 2024). It has been shown that increases in AOC are essential drivers of increases in SOA mass concentration in the troposphere (Li et al., 2023;Feng et al., 2019). The strength of AOC is significantly influenced by NO_x (Wang et al., 2023).” in the revised manuscript in line 224-230.

Eq 1 and Table 2: What boundaries were set for the starting points of K_{om} and α ? Why is the value of $K_{om,1}$ always equal to 0.19? Did the author put any constraint on the $K_{om,1}$? Uncertainties need to be provided for the fitting parameters in two product models in Table 2.

Author reply:

SOA yield has been described by a semi-empirical model based on the absorptive gas-particle partitioning of products (Ng et al., 2007b; Song et al., 2005). The SOA yield (Y) of an individual precursor is calculated via

$$Y = M_0 \sum_{i=1}^n \left(\frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_0} \right)$$

Previous studies on SOA yields from both biogenic and anthropogenic precursors suggested that a two-product model ($n = 2$) can accurately and adequately describe the experimental data with the model parameters a_1 , a_2 , $K_{om,1}$, and $K_{om,2}$. We assumed that similar low-volatility species were generated in each NO_x scenarios, as the same set in the previous study (Li et al., 2016a; Li et al., 2016b). The lower-volatility partitioning parameter ($K_{om,1}$) in all yield curve fitting are assigned to a fixed value by assuming similar lower-volatility compounds are formed during all photooxidation experiments. The experimental fitting parameters in the two-product model were determined by minimizing the sum of the squared of the residual. Each experimental yield data can be fitted well by the two-product model.

To illustrate more clearly, the following sentences have been added in the revised manuscript in line 278-283: “We assumed that similar low-volatility species were generated in each NO_x scenarios, as the same set in the previous study (Yang et al., 2020;Li et al., 2016). The lower-volatility partitioning parameter ($K_{om,1}$) was assigned a fixed value in all yield curve fittings based on the assumption that similar lower-volatility compounds are formed during all photooxidation experiments.”

As far as we know, no uncertainties for the fitting parameters were reported. But we also think the uncertainties is very important. In order to better display the reliability of fitting results, the correlations between the models and experiments data were added in Table 2.

Table 2 Parameters of the two product model for α -derived SOA under different initial NO_x concentration.

Initial NO _x conc. (ppb)	α_1	$K_{om,1}$ ($m^3 \mu g^{-1}$)	α_2	$K_{om,2}$ ($m^3 \mu g^{-1}$)	R^2
12	0.048	0.19	0.28	0.0040	0.9991
25	0.038	0.19	0.30	0.0039	0.9997
68	0.028	0.19	0.32	0.0037	0.9989
150	0.019	0.19	0.33	0.0031	0.9992
337	0.017	0.19	0.35	0.0019	0.9990
600	0.014	0.19	0.38	0.0016	0.9987

Lines 283 – 286: The assumption for the constant proportions of different volatile oxidation products is out of sense. Variations in α_1/α_2 ratios with initial NO_x concentration have been mentioned in the part associated with the two-product model.

Author reply:

This assumption is not for our study, but for the result in the study of Chen et al. (2022). The variations in α_1/α_2 ratios with initial NO_x concentration is used to evaluate the distribution of different volatile oxidation products between gas and aerosol-phase. But not for the ratio of the photooxidation products with different vapor. We are very grateful to the reviewer for this comment. The assumption was deleted from the manuscript. In addition, to clarify the statement, we changed the sentence in line 323-331 in revised manuscript as “Chen et al. (2022) categorized the photooxidation products into five classes based on their saturated vapor pressure (C*), and relative content of different classes of volatile products in both gas and particulate phase were compared. The contributions of semi-volatile oxidized products in the particulate phase were larger, but the proportion of semi-volatile oxidized products in gas-phase intermediate products was lower when experiments had higher VOC consumption and SOA yields. This result indicated that the proportion of semi-volatile organic products condensed into the particulate phase relative to the total formation of semi-volatile organic products was larger when more VOCs were consumed.”

Minor Comments

Line 33: Unless more contexts are provided, it is unclear why “low- and high-volatility” are used here.

Author reply:

As the reviewer pointed, we give a description of “low- and high-volatility” in the revised manuscript in line 133 as “Two different α -pinene concentrations were used in this study. Exp. 1 to 6 were defined as low-VOC experiments, and the others were high-VOCs experiments.”

Lines 36 – 38:” ... and the change in the aerosol/gas... with increasing NO_x” is too long to read and understand. Please rephrase the sentence.

Author reply:

This sentence is change to “The enhanced SOA yields with increasing NO_x were primarily attributed to the change in the aerosol/gas-phase partition ratio, resulting from the increased formation of α -pinene photooxidation products.” in the revised manuscript in line 36-38.

Lines 77 – 78: What are the other experimental conditions? Please provide examples.

Author reply:

The experimental conditions include oxidation conditions, NO_x concentration, RH, temperature and so on. For instance, in the research conducted by Takeuchi et al., the typical seed number and volume concentrations were maintaining consistency. The initially ratio of N₂O₅ to α -pinene was 4. The chamber was conditioned to 5 °C and low humidity (RH < 5%).

To avoid misunderstandings, the sentence of “Based on the semi-volatile partitioning theory in SOA formation, it has been established that SOA yield is a function of SOA mass concentration when other experimental conditions are held constant (Odum et al., 1996;Takeuchi et al., 2022).” is changed as “Based on the semi-volatile partitioning theory in SOA formation, SOA yield is strongly dependent on the SOA mass concentration present in the system (M_0) (Odum et al., 1996;Takeuchi et al., 2022).” in the revised manuscript in line 76-79.

Line 80: “the SOA yield is often discussed as a constant” lacks clarity.

Author reply:

We are very grateful to the reviewer for this comment.

The sentence of “However, the SOA yield is often discussed as a constant, and the nonlinear relationships between SOA yield and initial NO_x concentration reported in chamber studies do not account for the consumption of VOCs.” is fixed as “However, the nonlinear relationships between SOA yield and initial NO_x concentration reported in chamber studies do not account for the consumption of VOCs” in the revised manuscript in line 80-82.

Lines 92 -94: Please provide more descriptions of chemical processes and physical processes.

Author reply:

We are very grateful to the reviewer for this comment.

The sentence of “The roles of chemical processes are often considered due to the impacts of NO_x on SOA yields, but physical processes in SOA formation are equally significant and should be given more attention.” is fixed as “The roles of chemical processes (the branching of RO₂ reacts with RO₂/HO₂ or NO) are often considered due to their impacts of NO_x on SOA yields, but physical processes (aerosol/gas-phase partition) in SOA formation are equally significant and should be given more attention.” in the revised manuscript in line 91-94.

Lines 110 – 111: What is the volume of the chamber? What was the experimental temperature?

Author reply:

The volume of the chamber is 5 m³. The sentence in Line 120 have shown that 5 m³ zero air was added into the chamber. For clarify, the volume of the chamber was added in the revised manuscript in Line 110-111 as “A series of α -pinene photooxidation experiments initiated by NO_x were performed in a temperature controlled 5 m³ photooxidation chamber.”

We added the sentence of “The temperature during the photooxidation process was 25 ± 3 °C.” in the revised manuscript in Line 128.

Line 128: What were the sources of OH and O₃? Did the authors inject H₂O₂?

Author reply:

No H₂O₂ was added into the chamber.

Both of the O₃ and OH are the coexisting oxidants in the photooxidation (Sarrafzadeh et al., 2016; Liu et al., 2017; Wang et al., 2017) . The O₃ are formed from the photooxidation of NO₂, and OH was formed from the photolysis of O₃ (O₃+h ν →O(₁D)+O₂, O(₁D)+H₂O→OH+OH) and the recycle of HO₂ radicals (NO + HO₂ → NO₂ + OH) .

For clarify, the references of Liu et al. (2017); Wang et al. (2017); Sarrafzadeh et

al. (2016) were added in the revised manuscript in Line 130.

Was the chamber operated in a batch mode or continuous mode? How long did one experiment last?

Author reply:

The chamber was operated in a batch mode. Each experiment last 180 min as shown in Fig.2.

We added the sentences of “The photooxidation was operated in a batch mode, and each experiment lasted 180 min.” in the revised manuscript in Line 131-132.

What was the background level of NO_x before any experiment?

Author reply:

Normally, the background level of NO_x before each experiment is lower than the detect limitation (1 ppb) of NO_x analyzer.

We added the background level of NO_x in the revised manuscript in Line 118-120 as “This filling-purging cycle was repeated 5 times between experiments to ensure the residual particulate, α -pinene and NO_x concentrations were less than 5 cm⁻³, 0.5 ppb, and 1 ppb, respectively.”

Figure 1: Please include error bars for the SOA yield. In addition, using different marker shapes is redundant.

Author reply:

We are very grateful to the reviewer for this comment.

The error bars were added, and the Fig. 1 is fixed as below.

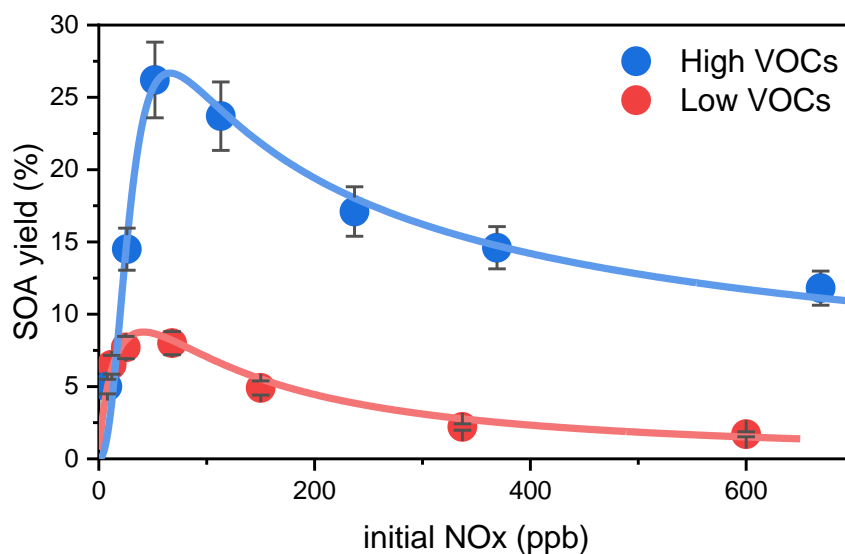


Figure 1. SOA yield from α -pinene photooxidation with different initial NO_x concentrations under two levels of VOCs. The error bars were determined on the system error of AMS.

Lines 231 and 232: What concentrations? Please clarify it.

Author reply:

This sentence is fixed as “the distribution coefficients of semi-volatile substances into the particulate phase are larger the higher their concentrations are” in the revised manuscript in Line 266.

Lines 337 -341: Falling into the lower area of SV-OOA does not necessarily mean that the semi-volatile products were the main components of α -pinene SOA (Paciga et al., 2016; Kang et al., 2022).

Author reply:

We are very grateful to the reviewer for this comment.

Both of the study of Paciga et al. and Kang et al. assess the volatility of SOA based on the C^* value. However, the C^* cannot be obtained from our current experimental conditions.

This method for the assessment of organic aerosol volatility based on F_{43} vs. F_{44}

has been used in many studies, i.e. (Ng et al., 2010;Hao et al., 2014;Reyes-Villegas et al., 2016;Singh et al., 2019), and these references are added into the manuscript.

For clarify, the sentence of “The AMS results provided direct evidence that semi-volatile products were the main components of α -pinene SOA formed through NO_x photooxidation.” is fixed as “The AMS results suggested that the α -pinene SOA formed through NO_x photooxidation exhibited semi-volatile characteristics.” in the revised manuscript in Line 385-386.

Lines 359 – 377: How would the method of estimating NOC used here differ from that of Kiendler - Scharr et al. (2016)?

Author reply:

Our study estimated the concentration of NO₂⁺ fragmentated from the organic nitrate, and calculated NO⁺ from the organic nitrate based on the R_{ON}. In the study of Kiendler-Scharr et al. (2016), they first determine the fraction of particulate organic nitrate (pOrgNO_{3frac}) in the measured total nitrate, and then calculated the mass concentration of organic nitrate by multiplying the measured total nitrate (NO_{3total}) with the fraction of pOrgNO₃

The R_{AN}, R_{ON}, and R_{means} in our studies is expressed as pInNO₃, pOrgNO₃, and R_{measured} in the study of Kiendler - Scharr et al. (2016), respectively. In the review of Ng et al. (2017), both methods were mentioned simultaneously for the calculation of NOCs. The method used in our study and Kiendler - Scharr et al. (2016) for the estimation of NOC through AMS is in agreement with each other.

Technical Comments

Line 26: “Atmospheric α -pinene” sounds very odd. Please just use “ α -pinene”.

Author reply:

Fixed.

In many places, I found there are two terms for nitrogen oxides, i.e., NO_x and NO_x.

Please make it consistent throughout the manuscript.

Author reply:

We are very grateful to the reviewer for this comment, and all the “NO_x” is fixed as “NO_x”

Line 50: Wang et al., 2016 investigated the mechanism behind the sulfate formation. I don't know why this paper is cited here.

Author reply:

We are very grateful to the reviewer for this comment.

This reference is deleted, and the references of Wei et al. (2021); Matsui and Liu (2022) were added here.

Line 52: Lv et al., 2022 is about the gas-to-particle partitioning of WSOC. This paper seems irrelevant to be cited here.

Author reply:

We are very grateful to the reviewer for this comment. This reference is deleted.

Line 54: It should be “many” instead of “much”.

Author reply:

We are very grateful to the reviewer for this comment. We think "much" is more reasonable here. We fixed this sentence to “**much research is still needed to fully understand the formation mechanisms of SOA**” to make the language clearer.

Line 141: What was the E/N value used for the PTR? How long was the sampling line of PTR connected to the chamber outlet?

Author reply:

The E/N is 135 Td. The sampling line of PTR connected to the chamber outlet is

1.2 m.

The operation of PTR-MS is fixed as: “The drift tube of the PTR-tof-MS was operated at 60.0 °C (T_{drift}), 2.30 mbar (P_{drift}), and 600V (U_{drift}), which resulted in an EN value of 135 Td.”

Line 151: Please provide more information about the scanning mobility particle sizer.

Author reply:

The SMPS information is added as: “The SOA mass concentrations obtained from AMS measurements were compared and corrected through a scanning mobility particle sizer (SMPS, TSI Inc., USA). The sheath and aerosol flow rate used in the SMPS were set to 3 and 0.3 L min⁻¹, respectively. Each scan lasted 240 s and the scanning range of aerodynamic equivalent diameter of SOA was 13.8–749.9 nm. For the calculation of SOA mass concentration in this study, an assumed density of 1.2 g cm⁻³ for α -pinene SOA was taken into account (Aruffo et al., 2022).” in the revised manuscript in Line 163-169.

Line 164: Is the word “defend” a typo?

Author reply:

Fixed as “defined”

Figure 3: What do the lines' colors stand for? It is very hard to follow the order of the markers without carefully reading the legend.

Author reply:

Fig. 3 is fixed as below.

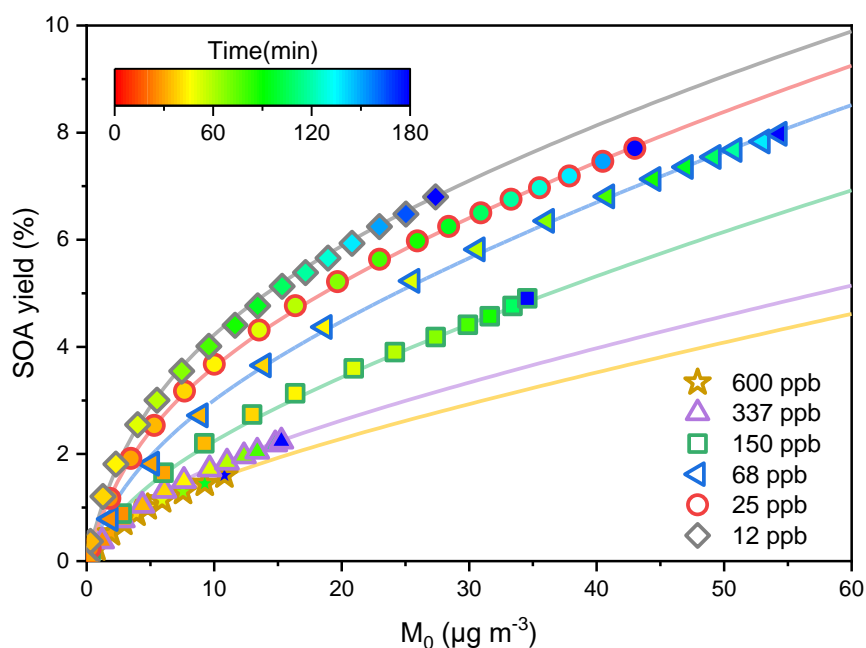


Figure 3. SOA yields as a function of organic aerosol mass concentration M_0 of α -pinene at different initial NO_x concentrations. The simulated SOA yields based on the two-product model are shown by the solid lines.

Line 406: Is it supposed to be "...under low-VOC conditions was only $54.3 \mu\text{g m}^{-3}$..."?

Author reply:

We are very grateful to the reviewer for this comment and fixed.

Line 430: Is it VOC ratio or VOC/ NO_x ratio?

Author reply:

The VOCs ratio is correct.

For clarify, we fixed this sentence as "The ratio of SOA yield from high-VOC experiments was about 3–8 times higher than that from the low-VOC experiments, which surpassed the VOC ratio (~2.2 times) between different low- and high-VOC conditions." in the revised manuscript in Line 460-462.

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