

Response to Anonymous Referee #1

We thank the reviewer for the careful review of our manuscript; your comments and suggestions are appreciated. All the comments have been addressed and we believe they have improved our manuscript substantially. In the following please find our responses to your comments and the changes made to the manuscript.

Review of Zhao et al, "Secondary Organic Aerosol formation from hydroxyl radical oxidation and ozonolysis of monoterpenes."

General Comments

In this manuscript, the authors report SOA formation from the photochemical oxidation of monoterpenes in a large outdoor smog chamber. They directly measure OH radical concentrations and the OH reactivity of organics and utilize this data, together with measurements of the particles size distributions, mass loading, and chemical composition, to infer conclusions about the relative importance of fragmentation and functionalization of the precursor oxidation products as the reaction proceeds. Particle growth rates are examined and compared to the growth rates for SOA production from ozonolysis reactions. The topic of SOA formation from photooxidation of monoterpenes is certainly relevant and of interest to the readers of ACP. There are fewer studies of SOA formation from the photooxidation of monoterpenes than from ozonolysis, though it is somewhat difficult to discern what new information this manuscript adds to the literature. The authors claim that their manuscript is the first to link particle growth to the reaction of OH with organics and that this new metric was used to examine the role of functionalization and fragmentation as the reaction progresses. I have some concerns regarding these two claims below, but if these concerns can be addressed satisfactorily, the manuscript could be published in ACP.

Major Comments

My primary concern with this article is the derivation of the particle growth rate and the conclusions that are derived from the growth rate. I am not an expert on particle growth physics, but a simple inspection of the equations the authors use suggest the equations are, at the very least, oversimplified. It seems that the equations do not consider mass transfer at all. For example, comparison of equation 22 in the text with a standard equation for particle growth rates available in text books (for example Equation 13.3 in Seinfeld and Pandis) show that the authors are neglecting several terms (diffusion, surface accommodation, noncontinuum effects, etc.) (Seinfeld and Pandis, 1998). In addition, several recent papers have shown suggested that particles may be exist in a viscous state (e.g., (Vaden et al., 2011; Virtanen et al., 2010; Renbaum-Wolff et al., 2013) and many others), which further complicates the particle growth dynamics and impacts size dependent growth rates and potentially the mass growth rates (Shiraiwa et al., 2013). It is difficult for me as a reviewer to assess what effect these factors will have on the conclusions drawn by the manuscript because an accurate assessment would require a relatively detailed model and information about the experiments that is not available. In any case, the authors should at a minimum state the limitation and assumptions of their kinetic modeling. I also encourage the authors to discuss potential impacts on their conclusions if the particles are not in equilibrium with the gas phase and/or they are not liquids.

Response:

In our derivation of the particle mass growth rate, we assumed that the particles are in equilibrium with the gas phase (P12600 line 21-22). When the concentrations of condensing species change slowly relative to the timescale for the gas-particle equilibrium, a quasi-equilibrium between gas and

particle is assumed to be established at any moment. This quasi-equilibrium approach was used here and compounds partitioned between gas and particle phase (Pankow, 1994; Odum et al., 1996; Hallquist et al., 2009). The other factors including gas/particle phase diffusion, surface accommodation, etc., which can increase the time scale to establish gas-particle equilibrium, also affect the particle mass growth. For example, as the reviewer mentioned, several studies suggests that particles may exist in a viscous state (e.g., (Vaden et al., 2011; Virtanen et al., 2010; Renbaum-Wolff et al., 2013)) which can hinder particle phase diffusion and play a role in the particle growth kinetics. As a result, the gas-particle equilibrium may not necessarily be reached all the time. These are the limitations of the method used in this study. If the equilibrium is not reached, the mass growth rate in this case is the lower limit for the contribution from gas phase condensation. The deviation from the equilibrium would result in a higher $GE_{OH}(t)$.

In the revised manuscript, we have elaborated this assumption and limitation of the method used, and discussed the potential impact of the non-equilibrium on the results similarly as above.

It reads now:

“Note that in Eq. (1) we assumed that the particle is in equilibrium with the gas phase. When the concentrations of condensing species changes slowly relative to the timescale for the gas-particle equilibrium, gas-particle equilibrium is assumed to be established at any moment (Zhang et al., 2012). This quasi-equilibrium approach was used here and compounds partition between gas and particle phase (Pankow, 1994; Odum et al., 1996). Theoretically many factors such as diffusion, surface accommodation etc. can affect the timescale for gas-particle equilibrium (Shiraiwa and Seinfeld, 2012) and hence affect the particle mass growth. For example, several recent studies suggests that particles may exist in a viscous state (e.g., (Vaden et al., 2011; Virtanen et al., 2010; Renbaum-Wolff et al., 2013) and particle phase diffusion could play a role in the particle growth kinetics. In addition, the particle-phase photolysis is not included in this derivation, which could also potentially affect the gas-particle equilibrium. As a result, the gas-particle equilibrium may not necessarily be reached all the time. These are the limitations of the method used in this study. If the equilibrium is not reached, the mass growth rate in this case is the lower limit for the contribution from gas phase condensation. The deviation from the equilibrium would result in a higher $GE_{OH}(t)$.”

I'm not completely convinced by the authors' interpretation of the role of functionalization and fragmentation through the use of their growth efficiency metric. Fundamentally, their argument is that the particle growth stops while there is still OH available in the chamber to oxidize reactions products; therefore, fragmentation must dominate. It seem like this is an oversimplification that will be extremely sensitive to accurately determining both the particle wall loss rate and the gas wall loss rate. In fact, from Figure 2, the particles only shrink in one of the experiments and are in fact still growing rapidly at the end of another experiment. Have the authors done any sensitivity studies to determine how errors in the particle wall loss rates would affect their conclusions? How can the authors rule out that higher generation oxidation products are not simply lost to the chamber walls (Matsunaga and Ziemann, 2010) or simply too volatile to condense? Can the authors provide any additional evidence to demonstrate that fragmentation dominated over functionalization when they say it did? The authors have a PTR-MS attached to the chamber. Do they see any evidence for the increased formation of lighter VOC's from the PTR-MS data as the reaction proceeds?

Response:

Firstly, we made a mistake by using the word “dominant” on page 12592, line 20: “It shows that functionalization of organics was dominant in the beginning of the reaction (within two lifetimes of the monoterpene) and fragmentation started to be dominant after that.” We meant the fragmentation

played an important role in the later period of the reaction. In the revised manuscript, we corrected this and now it reads:

“It shows that functionalization of organics was dominant in the beginning of the reaction (within two lifetimes of the monoterpene) and fragmentation started to play an important role after that.”

For all OH oxidation of monoterpene, a dramatic decrease in the size growth rate and particle growth efficiency $GE_{OH}(t)$ was observed in the later period of the reaction (as shown in Fig. 4). In the case of limonene, particle shrink and negative particle growth efficiency $GE_{OH}(t)$ was observed indicating the increase of volatility and the dominance of the fragmentation over functionalization.

From Fig. 3 A, B and C, one can notice that the particle mass increase rate became slower as reaction proceeded, and so did for the particle size (Fig. 4 A, B, C). This indicates a decreased formation of condensing compounds. In Fig.3 the particle growth efficiency $GE_{OH}(t)$ decreased dramatically in the later period of the reaction, although it is still positive for α -pinene and β -pinene system. The dramatic decrease of $GE_{OH}(t)$ indicates that the reaction of organic with OH to reduce the volatility became much less efficiently. This is caused by the increasing role of fragmentation relative to functionalization.

In the revised manuscript, we have improved the discussion on the functionalization and fragmentation. Now it reads:

“Moreover, time series of $GE_{OH}(t)$, the metric of particle growth efficiency due to reaction with OH, shed light on the role of functionalization and fragmentation in the reaction process. Figure 3 shows that the $GE_{OH}(t)$ time series and the particle mass concentration as well as total OH reactivity of organics for comparison. The change of $GE_{OH}(t)$ reflects the evolution of the overall volatility of organics undergoing reaction with OH and the relative role of functionalization and fragmentation. $GE_{OH}(t)$ was positive and increased fast in the beginning of the reaction. This indicates that the reaction products had a lower volatility than the reactants, i.e., lower saturation concentration (refer to Eq. (21)). As the volatility decreased, $GE_{OH}(t)$ increased. The decreased volatility was caused by functionalization, which played a dominant role in the beginning. Afterwards, $GE_{OH}(t)$ gradually decreased, which indicates the decrease of overall volatility of the organics slowed down. This indicates an increasing role of fragmentation since fragmentation cleaved the carbon frame and formed some smaller molecules with higher volatility. As the reaction proceeded, the products got more oxidized and O/C ratio of products increased, the fragmentation of the compounds became more and more significant (cf. Kroll et al., 2009; Chacon-Madrid and Donahue, 2011; Chacon-Madrid et al., 2010). After the continuous decrease, $GE_{OH}(t)$ decreased to almost zero or even negative for the limonene case (Fig. 3C). This indicates that overall volatility of organics almost stopped decreasing and even increased after further reactions of the functionalized intermediates with OH (see limonene case in Fig. 3C). When the overall volatility of the reactants is equal to that of the products, $GE_{OH}(t)$ is equal to zero. From Fig. 3 one can recognize that $GE_{OH}(t)$ had decreased dramatically in the relatively early period of the reaction (within approximate two lifetimes) when the mass concentration was still low, indicating the fragmentation started to play an important role.”

We have done the sensitivity analysis to check the effect of uncertainty of the particle wall loss rate on the particle mass concentration as shown in Fig. S5. From the figure, we can see that the corrected mass concentration is not sensitive to the particle wall loss rate. A change of 10% and 50% of particle wall loss rate only result in a change 2% and 9% in the particle mass concentration. The wall loss of vapor can also affect the particle concentration as higher oxidation products may also be lost to the

walls, which can result in an underestimate of the particle concentration. But in presence of pre-existing particles, condensation on them will be able to compete with wall loss, depending on the S/V of the chamber which is very favorable in our large chamber and surface density of the particles. The wall loss of vapor was investigated in our SAPHIR chamber using experiments in which pinonaldehyde, one important first generation product from α -pinene oxidation, was injected into the chamber. The concentration was monitored over several hours. Constant first-order decay with a rate constant of $2.8 \times 10^{-6} \text{ s}^{-1}$ was observed over a period of 14 h and no equilibrium was observed. It was not possible to detect rapid initial losses of pinonaldehyde in SAPHIR chamber due to the chamber setup and injection procedures. The vapor wall loss rate is on the same order of magnitude as described by Loza et al. (2014) but lower than that given by Matsunaga and Ziemann (2010) and Zhang et al. (2014). Different vapor wall loss rates in different chambers are expectable since vapor wall loss rates depend on the mixing in the respective chamber, the thickness of the diffusive boundary layer and penetration into the chamber wall (Zhang et al., 2014). Matsunaga and Ziemann (2010) found that vapor wall loss depends on structure and compound vapor pressure in contrast to Zhang et al. (2014) who used one vapor wall loss rate for all compounds in the whole reaction system. It will result in uncertainties to extrapolate wall-loss rates of pinonaldehyde to all products from monoterpene oxidation. However as a first approach, we estimate the effect on the particle mass concentration, assuming the wall loss rate of pinonaldehyde and same particle yields for all lost vapors (the same as in the reaction system). The particle mass concentration would then be underestimated by approximately 17%. Combining the particle wall loss and vapor loss by wall loss and dilution, the uncertainty of the particle mass concentration is estimated to be approximately 30%.

We have difficulty to understand why higher oxidation products (containing more O atoms) formed from condensing precursors should be too volatile to condense, unless fragmentation is involved.

In the revised manuscript, we have added the discussion similarly as above and Figure S5.

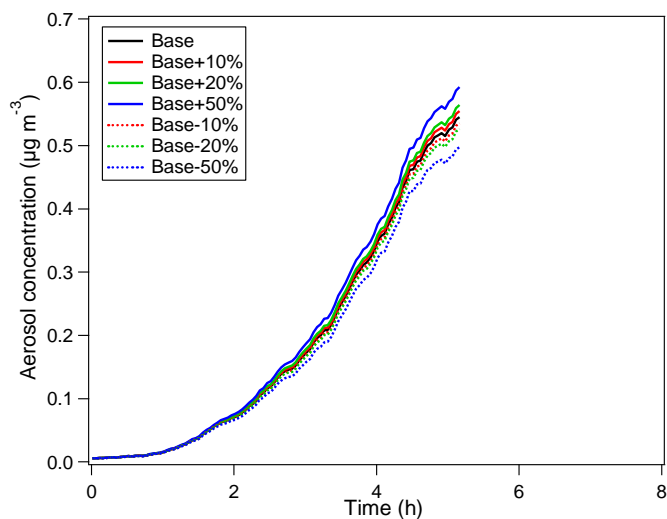


Figure S5. Sensitivity of the corrected aerosol mass concentration to the uncertainty of the particle wall loss rate. Base is obtained using the particle wall loss rate determined in this study. Aerosol mass concentration is investigated by varying particle wall loss rate by 10%, 20%, 50%.

Many of the products in the α -pinene oxidation cannot be detected and/or quantified by PTR-MS or GC-MS due to the loss in the sampling line or degradation in the instrument. From the PTR-MS data, we found the increasing concentration of the acetone in the reaction, which a product of monoterpene

oxidation due to fragmentation. The following figure (Fig. S4) shows acetone concentration increases during the OH oxidation of α -pinene as an example, indicating the ongoing fragmentation in the reaction. The acetone concentration was corrected for the dilution loss. However, we did not observe a significantly faster acetone formation rate in the later period of the reaction compared to the early period of the reaction because acetone formation depends on its precursor concentrations and OH concentration, which were not monotonic in our study.

In the revised manuscript we have added this figure and related discussion similar as above.

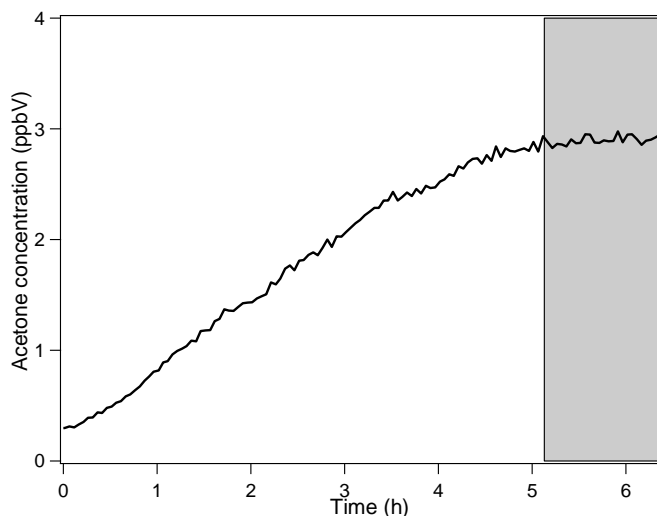


Figure S4. Acetone concentration time series during OH oxidation of α -pinene. The grey shaded area shows the dark period.

Related to the issue of functionalization vs fragmentation, the O:C and H:C of the particles remain largely unchanged once a sufficient amount of SOA is present in the chamber for the measurements to be significant. Wouldn't one expect to see some evolution in O:C and H:C in time if later generation oxidation products were contributing to the aerosol growth?

Response:

The change of O:C and H:C was quite minor in the later period of the reaction. Actually even a slight decrease of O:C was observed for β -pinene and limonene photooxidation in the later period of the reaction (Fig. 3B and 3C). We attribute the relative stability of the O/C and H/C to the following process: In the early period of the reaction (before O/C reached the maximum value) low concentrations of multi-generation products were generated via functionalization and had already condensed on the particle phase. As the reaction proceeded, more of these similar multi-generation products were formed and continued to condense on the particle. Further oxidation of the multi-generation products may cause the fragmentation resulting in the formation of high volatility oxidation products, which did not condense significantly on the particle. As a result, the O/C ratio did not manifest significant increase in the particle phase. This is consistent with the analysis of functionalization and fragmentation via the evolution of $GE_{OH}(t)$.

In the revised manuscript, a similar explanation has been added.

P 12597, lines 23 – 30. P 12599, lines 4-11. Please clarify whether an OH radical generator such as HONO or H2O2 was added to the chamber. The manuscript seems to indicate that no OH radical

generator was added. The authors state that photolysis of HONO generated most of the OH radicals and the OH radical concentrations are quite high; however, they also state that NO_x was below 1 ppbv. I'm having trouble reconciling these observations. Photolysis of HONO produces NO_x and a sizeable amount of NO_x must have photolyzed in order to supply OH concentrations of 6×10^6 and oxidize multiple generations of the 4 ppbv concentrations of VOCs. The authors should explain how the high OH radical concentrations can be generated and sustained in their experiments without NO_x exceeding 1 ppbv or ozone exceeding 20 ppbv.

Response:

In our SAPHIR chamber, the primary OH comes from the photolysis of HONO which originates from the photolytic emission from the Teflon wall. This OH source in our chamber has been well characterized by Rohrer et al. (2005), and more details can be found in that paper. No additional OH generator was added to the SAPHIR. The HONO from the chamber wall sustained the high OH concentration in the photooxidation experiment. We have clarified this in the revised manuscript.

All figures are extremely small and hard to read in the printed version. Figures 3, 4, and 5 are particularly difficult to read. I could not distinguish the traces at all in Figure 5 in the printed versions. The H:C trace is almost invisible in Figure 3. I strongly suggest resizing the figures so they are legible before publication.

Response:

We apologize for the difficulty in reading caused by the small figures. In the revised manuscript, we have enlarged figures, including the curves and symbols, to make it clear.

Specific Comments and Technical Corrections

The growth rates in Figure 4, particularly in panels A, B E, and F look to be either very noisy or have a very complicated non-monotonic dependence in time. It is difficult to imagine any processes (other than noise) creating such “jagged” growth rates. Can the authors comment on this?

Response:

Primarily, the “noisy” change in the growth rate was caused some fluctuations in the particle mass or size. Moreover, more fluctuations were introduced when the growth rate was derived from fitting the particle mass or particle size as a function of time. In addition, some non-monotonic change in the growth rate in the photooxidation experiments was caused by the fast change of OH concentration due to presence of the clouds (Fig. 4A, B, C).

This is elaborated in the revised manuscript as follows.

“These variations in the reaction rates as well as the growth rates were mostly caused by sudden changes of the OH concentration due to variations of solar radiation affected by cloud coverage. In addition, the fluctuations in the growth rate were partly attributed to the fluctuations in the particle mass or size and deriving the growth rate from fitting the particle mass or particle size as a function of time.”

How reproducible are the growth rates in the experiment? Only one experiment was carried out for each condition. Since no seed particles were used, particles had to nucleate. I can imagine the growth rates being very dependent on the nucleation conditions, which it typically very hard to reproduce in a chamber, particularly in one as large as this one.

Response:

For the photooxidation experiments, we carried out two duplicates for each monoterpene. The experiments in the SAPHIR chamber are quite resource and labor intensive and somewhat also dependent on the weather conditions. Therefore the time limited us to do more repetitions.

The average growth rates in each experiment are 12.9 and 11.1 nm/h for α -pinene, 9.7 and 7.4 nm/h for β -pinene, and 29.0 and 28.7 nm/h for limonene, respectively. Actually the growth rates reproduce relatively well from these two duplicates considering the not exactly same environmental conditions such as solar radiation and cloud coverage. (Since the growth rate became much lower in the later period of the reaction, it took a long time to reach the maximum size. Therefore, the average growth rate was calculated from the growth starting time to the time when 95% of particle size rather than maximum size reached in order to make different experiments more comparable.). At the same time, as the reviewer expected, the nucleation events are not well reproducible in our large chamber. The peak number concentrations are 2.4×10^3 and 2.3×10^3 #/cm³ for α -pinene, 7.9×10^3 and 4.2×10^3 #/cm³ for β -pinene, 5.9×10^3 and 2.7×10^3 #/cm³ for limonene. The variations in the nucleation are strongly affected by the environmental conditions, especially the solar radiation, which directly affects OH concentrations.

Many experiments appear to start with relatively large particles present in the chamber. See for example Figure 5 in the α -pinene experiment appears to start with 40 nm particles in the chamber. The number concentrations are impossible to read, though I imagine from the mass loading that the numbers are relatively low. Please correct the scale on the number concentration on these figures and comment on the source of the relatively large particles.

Response:

The scale of particle number concentration for Fig.5 A-C (OH oxidation) was intentionally adjusted to be same as the ozonolysis case for a better comparison. In the revised manuscript we have changed the scale. The large particles were introduced after humidification, which produced the background particles in our experiments with a typical concentration of one to several hundred #/cm³. We have tried our best to take all measures to reduce this including using high purity MilliQ water (18 M Ω , TOC ~3 ppb) and stainless steel container as water container, and bubbling high purity nitrogen (99.9999%) through the water before use. Note that the mass concentration was fairly low as shown in Table 1. These background particles had relatively large diameter (median diameter 40-60 nm) without an obvious distribution. In the revised manuscript, we have omitted the size data of the background particle and only shown the diameter of the particles after nucleation in order to avoid misleading the readers. We have explained this data processing as follows.

“Before nucleation there were some background particles present introduced after humidification which had relatively large diameter (median diameter 40-60 nm) but with fairly low concentration (refer to Table 1). Particle size before nucleation was not shown in order to avoid confusion.”

P12594 lines 26-29. In chamber studies, it is very likely that oxidation products of VOC are indeed the nucleating agents because they dominate the gas-phase in these experiments and SO₂ is low in clean chambers. So this line should be corrected. Whether they are involved in nucleation in the atmosphere is a different question.

Response:

We modified these lines and now it reads:

“One reason of the controversy on particle nucleation and growth is that the OH oxidation and ozonolysis have seldom been separated when comparing the SOA formation from both pathways.”

Can the authors show the measured decay rate of the parent VOC's from the PTR-MS data? How does the observed lifetime of the parent hydrocarbon compare to the lifetime inferred from the OH measurements? Is the data shown in Figure 1 calculated from the measured decay of the VOC precursor or from the decay rate that would be calculate from the rate constant and the measured OH concentration?

Response:

In the revised manuscript, we show the decay of measured monoterpene concentration with time (as in Fig. S3).

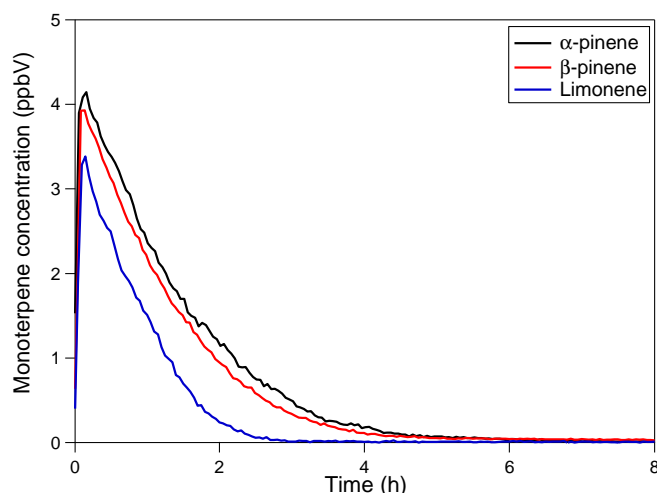


Figure S3. Monoterpene concentration time series during the OH oxidation of each monoterpene measured by PTR-MS

The observed the decay of the parent hydrocarbon agrees with that inferred from the OH measurements within measurement uncertainty (PTR-MS: $\pm 15\%$, OH concentration: $\pm 10\%$) and uncertainty of reaction rate constant of monoterpene (Atkinson et al., 2006; Atkinson and Arey, 2003; Gill and Hites, 2002). Figure S6 shows the data of the time series of the measured monoterpene concentration (taking α -pinene as an example) as well as monoterpene concentration calculated using the initial monoterpene concentration and OH concentration (Fig. S6).

In the revised manuscript, we have added this comment similarly as above and Figure S6.

The data shown in Figure 1 is calculated from the measured decay of VOC precursor.

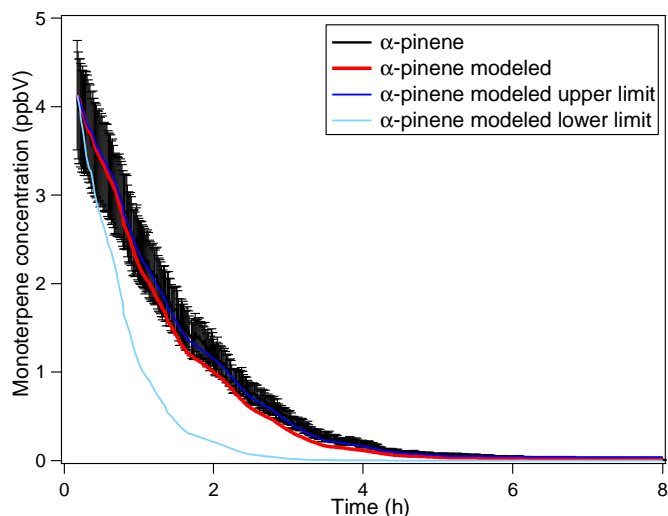


Figure S6. Measured monoterpene concentration time series and modeled monoterpene concentration calculated using the initial monoterpene concentration and the loss by the reaction with OH (reaction rate is product of monoterpene concentration, measured OH concentration and rate constant) and dilution. The limits are defined by the uncertainty of monoterpene data, OH data and the reaction rate constant of the monoterpene with OH.

P12595, line 18 “of whole the reaction system” is a typo.

Response:

Corrected.

P12596, line 16 and 17 – missing “the” before light and louvre

Response:

Corrected.

P12597, line 25. The OH reactivity measurements should also be briefly described since they are a key part of the manuscript.

Response:

Accepted. In the revised manuscript, we have added the brief description of the OH reactivity measurements.

P12600 Equation 1 and throughout. The superscripts are sometimes written with a capital P and sometimes with a lower case p.

Response:

We corrected this typo in the equations throughout the manuscript to make it consistent.

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