Response to Anonymous Referee #2

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 the responses to your comments and the changes made to the manuscript.

General comments:
This manuscript describes results from experiments conducted inside of the SAPHIR chamber in Jülich, Germany. Monoterpenes were oxidized with OH or ozone, and the evolution of particle size and mass concentration were reported. Main conclusions from the manuscript include that fragmentation reactions dominated through most of the duration of the experiment, based on the observation that particle mass ceased to increase while OH was still in the chamber. I have a few concerns about the analysis used to reach the main conclusions. If my comments below can be addressed appropriately, the manuscript can be published in ACP.
Specific comments:
1. The conclusions of the paper depend on accurate measurements of particle mass in the chamber. Particles and vapors can be lost to the walls of the chamber, and different methods to correct for particle losses would result in different corrected particle mass concentrations. The authors corrected for particle losses; however, they should address how uncertainties in different particle-loss correction methods would affect their corrected data and conclusions. At a minimum, an estimate of uncertainty in reported particle mass concentrations is necessary. Also, the authors should comment on the effects of vapor wall losses (which they do not correct for) on their data and conclusions.

Response:
The reviewer is right that the corrected particle mass concentration is affected by the uncertainty of different particle correction methods. In this study, we determined the particle wall loss rate using an exponential fit of the decay of the particle number concentration after the nucleation has stopped for several hours (Carter et al., 2005; Fry et al., 2011; Pierce et al., 2008). Another method that has been used to determine the particle wall loss rate is by fitting the decay particle mass concentration after the condensation has finished (Presto and Donahue, 2006; Pathak et al., 2007). In this study, we found in most of our experiments, the particle wall loss rate determined through the decay of particle mass concentration kept changing until the end of the photooxidation experiment. The decay rate for particle mass concentration was lower at the end of the photooxidation experiment than during the period right after the roof was closed and photooxidation stopped. This indicates that particle formation (condensation) was still active and had not finished in the light period. In contrast, the particle wall loss rate measured through decay of particle number concentration was constant during the later period of the photooxidation reaction and higher than that determined through the decay of particle mass concentration, which supports the condensation did not finish. Therefore, the second method, which used the mass concentration, did not apply to our study and we used the first method, determining the wall loss rate by particle number concentration. Once the wall loss coefficient was determined, the particle mass concentration was corrected in every step of the SMPS scans by the dilution rate and wall loss rate. Pierce et al. (2008) compared the results from different wall loss correction methods including both methods mentioned here and a model approach, showing that different methods agree within 10% for the faster limonene ozonolysis experiment and a factor of up to two for the slow toluene oxidation experiment. Unfortunately we cannot compare the difference of these two methods since the method using the particle mass concentration is not suitable for this

study. We estimated the uncertainty by investigating the variability of the particle wall loss rate among different experiments. The uncertainty of the particle wall loss rate determined in this way is 11% (one relative standard deviation). We did a sensitivity analysis to check the effect of uncertainty of particle wall loss rate on the corrected mass as shown in Fig. S5 now. We found the corrected aerosol mass concentration is not sensitive to the uncertainty of the particle wall loss rate. For α-pinene experiment as an example, a change of 10% and 50% only results in a change 2% and 9% of the final corrected particle mass concentration. Considering the uncertainty of our SMPS system (±10%), the uncertainty of the corrected particle mass concentration due to the particle wall loss is estimated to be 12%.

As the reviewer suggested, the wall loss of vapor affects the particle mass concentration. The wall loss of vapor 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 2.8×10^{-6} 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 pinonadehdyde in SAPHR 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%.

Without correcting the vapor wall loss, the particle mass concentration is underestimated, and so is the particle growth efficiency.

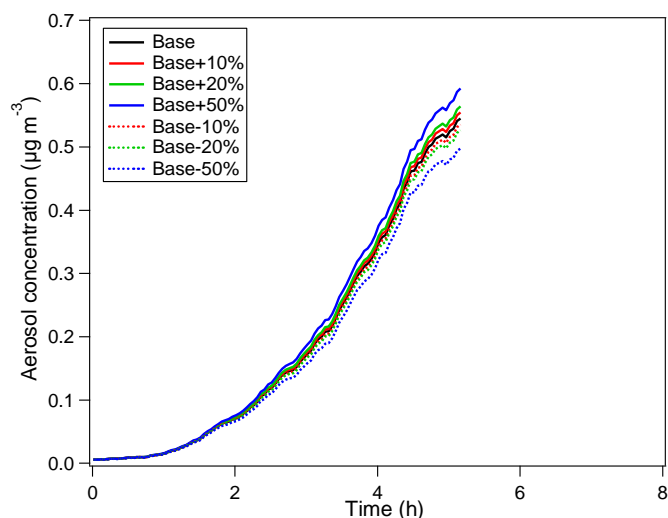In the revised manuscript, we have discussed this point similarly as above and added the figure.

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%.

2. Measurements of the total reactivity (kOH) are essential to the conclusions of this paper and should therefore be discussed. Also, the authors presumably have measurements of the VOC concentrations from the PTR-MS data. Are the decays of the VOCs consistent with measured OH concentrations?
Response:
In the revised manuscript, a more detailed description of the measurement of the total OH reactivity is provided.

The decays of monoterpenes are consistent with those calculated using initial monoterpene concentrations, the measured OH concentrations and rate constants of the reaction of monopterpene with OH within measurement uncertainty (PTR-MS: ±15%, OH concentration: ±10%) and uncertainty of reaction rate constant of monoterpene. In the revised manuscript, we have shown the measured monoterpene concentrations as well as monoterpene concentrations calculated using OH concentrations and rate constants taking α-pinene as an example (in Fig. S6).

In the revised manuscript, we have discussed this consistence similarly as above (see also our comments to the remarks of referee # 1).
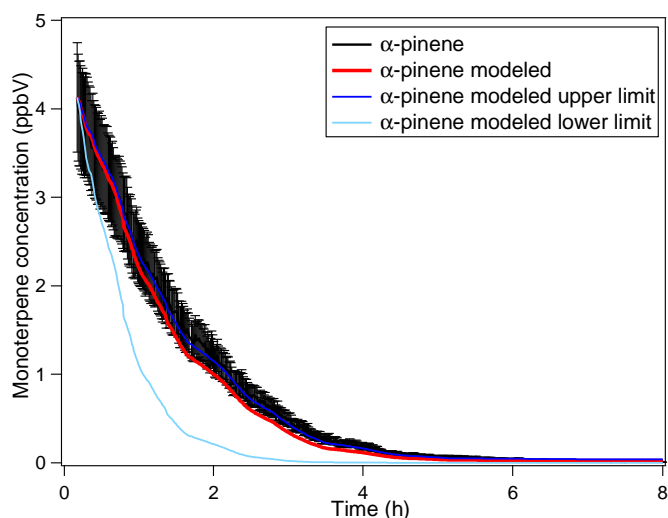
Figure S6. Measured monoterpene concentration time series and modeled monoterpene concentration calculated using the initial monoterpene concentration and the loss by the reaction with OH (reaction rate is product of monoterpene concentration, measured OH concentration and rate constant) and dilution. The limits are defined by the uncertainty of monoterpene data, OH data and the reaction rate constant of the monoterpene with OH.

3. If fragmentation was dominant during the later part of the experiments we would expect the particles to shrink (decrease in diameter). A decrease in diameter is only apparent in the limonene experiments; this should be addressed in the revised manuscript.

Response:
Firstly, we made a mistake on using the word "dominant" in (p. 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 induced oxidation of monoterpenes, 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 about this point similarly as above.

4. p. 15, line 19: The authors state that the overall OH reactivity of organics was determined by subtracting the OH reactivity with inorganic species. The listed inorganic species do not include HONO, which is present in these experiments as it is cited as the source of OH. This should be addressed in the revised manuscript.

Response:

The reviewer is right that HONO also works as OH sink although it is mainly an OH source. However, the HONO concentrations are fairly low in these experiments. The maximum peak HONO concentration measured by a LOng-Path-Absorption-Photometer(LOPAP) (Häseler et al., 2009) is approximately 300 pptV. The maximum contribution to the total OH reactivity is 0.04 s^{-1}, which only account for less than 1% of the total OH reactivity. Therefore, it was not neglected in the calculation of overall OH reactivity of organics. In the revised manuscript, we have added explanation of this data processing.

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