**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "New particle formation from the oxidation of direct emissions of pine seedlings" *by* L. Q. Hao et al.

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The authors thank for the reviewer for his/her constructive and helpful comments:

First, as the authors state in the introduction and conclusions that realistic information on the dominant atmospheric process can be gained from the experiments, I would like to see some discussion on how realistic the oxidant levels are in the experiments. As the relative contribution of OH- and O3-oxidised VOC products to nucleation and growth is one of the main topics, it would be interesting to know how the relative ozone and OH levels in the experiments compare to 'realistic' ones. I also did not find a mention of the OH concentrations (except for peak concentrations in the chamber) in the article; as the abstract states that the experiments were in the 10Ë̈Ȩ6 molecules/cc regime, this should be stated somewhere in the article.

Answer: Some discussions will be added on the OH and O3 concentration levels in Sect. 3.2. Furthermore, as suggested by Referee 3, the modeled OH concentration panel will be also added to Fig. 3. The modeled peak OH concentration in this study ranged from 0.3×10^6 (E2) to 3.32×10^6 molecules cm-3(TME exists), which matches the peak daytime OH concentration of $(2\text{-}10) \times 10^6$ molecules cm-3 on the ground level in northern hemisphere during August/Spetember periods (Atkinson et al, 2000 and references cited therein). O3 concentrations inside the chamber were measured to be varying from aroud 4 ppb to 38 ppb, which is also consistent with the ozone mixing ratios ranging from several ppbs to few hunand ppbs at the background surface (Logan et al, 1985; Guicherit and Roemer, 2000).

Second, while the authors have done a good job modelling the gas phase chemistry going on in the experiments, the interpretation of the results seems to me to be on a quite qualitative level. The points that are made would carry more weight if some more quantitative analysis was presented. This could include, for example, a direct comparison (or a listing or tabulating) of the formation and growth rates (or number of particles formed) to the OH and ozone oxidation rates, maybe in some averaged form. This would help the reader to get an overview of how the change in the oxidants changes the nucleation and growth parameters.

Answer: Firstly, the argument "The modeled OH and O3 reaction rates also show good correlations with the condensational growth rates in E1-E3 experiments, suggesting that OH and O3 reactions both play roles in particle growth process. Furthermore, in E3, the highest aerosol growth rate of 74 nm h-1 was achieved where the OH reaction rate was slow, suggesting that the ozonolysis of VOCs is more efficient for aerosol growth. " will be replaced by a more qualitative discussion that "Growth rate in E1a (126 nm h-1) is 1.7-fold higher than that in E3 even if its O3 reaction rate (25.5×10^6 molecules cm-3s-1) is two-times lower than that in E3. Similarly, 5.5×10^6 molecules cm-3s-1 of O3 rate was observed in E1c, which is 9-fold lower than in E3. However, a growth rate of 25.0 nm h-1 in E1c was found, which is only 3-times lower than in E3.

These results indicate that OH and O3 both play roles in involving the particle conden-sational growth process. In E3, OH rate is at least 25-times lower (0.72×106 molecules cm-3s-1) compared to other four cases (>18.3×106 molecules cm-3s-1). However, a high growth rate of 73.8 nm h-1 was achieved, suggesting that the ozonolysis of VOCs is more efficient for aerosol growth."

Secondly, a new Table in the revised manuscript will list the comparisons of nucleation and growth rates with the OH/O3 oxidation rates. As can be seen from Table 3 and the new Table, for E1a and E1b (in these two experiments, there were roughly identi-cal initial emission spectrum distributions. Since the initial emitted VOCs distributions might impact the nucleation and growth rates and this will be discussed in the MS, so we have only compared the nucleation and growth rates to oxidation rates in these two cases), nucleation rates in E1a was 4.5 times higher than that in E1b, which is well consistent with 3.8 times faster of OH oxidation rates in E1a than E1b. Similarly, 126.0 nm h-1 of growth rate in E1a was observed, 6.6 times higher than that in E1b, which was well corresponding to the O3 oxidation rates in E1a, 6.0 times faster than in E1b. A thorough discussion will be given in the revised MS.

The effect of the amount of VOCs added to the chamber, as well as the changing VOC mixture is not discussed enough, in my opinion. For example, looking at table 3, one can see that the two experiments with the lowest nucleation rates are experiments E1c and E3; these have also no contribution from delta-3-carene. Of course it is evident that the OH reaction clearly plays a role here, as the nucleation rate decrases siginificantly when OH is removed. While this topic is touched upon on page 8237 for the case of b-pinene, a somewhat more thorough discussion would not go amiss.

Answer: Thanks for the comment. The amount and species of VOCs are believed to affect the new particle formation. Positions of unsaturated bonds and number of carbon atoms in the VOC molecules have been observed to affect the aerosol growth rate and SOA yield in previous studies (Griffin et al, 1999; Ng et al, 2006). Δ3-carene compound has one double bond internal to ring structure and is more likely to form con-

densable products when compared to compounds with external double bonds (Griffin et al, 1999). So in this study, in E1C and E3, the absence of Δ3-carene compound might be one possibility leading to the lower nucleation rates than other cases. We have made discussions in the revised MS.

Also, regarding the point of OH contributing to nucleation, some explanation, or for the absence or weakness of nucleation at the second OH reaction peak in eg. Experiments should be given or discussed.

Answer: At the second OH reaction peak, OH oxidation reactions appeared to have weak influence on aerosol nucleation activities during the secondary ozone addition period (second OH concentration peak, see in E1a and E1c), its major role is to par-ticipate in the particle condensational growth process. This can be explained that to achieve strong nucleation, a high supersaturation of the nucleating vapor must build up. This is possible in the beginning of the experiment when there are no particles present in the chamber, i.e. there's no surface for the vapor to condense on. However, at the second OH peak, there is a lot of particle surface in the chamber, and the reaction products will start condensing as soon as they have reached supersaturation. Thus, a high supersaturation level cannot build up, and only weak nucleation pulse (or even no nucleation) occurs.

In addition to these points, which I think should be addressed, I have some minor detailed comments below. * page 8228, line 27: I think one should be careful with stating that the sulphuric acid effect is negligible; in an empty chamber with no sinks a quite low source could cause the concentration to become significant on a timescale of a few hours, if OH is present.

Answer: It is well known that contribution of sulphuric acid to the aerosol nucleation is significant (e.g. Boy et al, 2005). So in the MS, we deleted the state that 'The low level of SO2 concentration would make the potential influence of H2SO4 on the new particle nucleation to be negligible.'.

* page 8229, line 3: Add 'For off-line analysis,' in front of 'VOCs were...', otherwise this is confusing.

Answer: will be fixed.

* page 8235, line 8 onwared: The gas-phase model indeed shows a good agreement at least on a qualitative level, but there are some deviations from the measurements, visible for example in figure 2 for formaldehyde. Is the reason for this known, or can the authors speculate what it could be? Also, I don't think that the sentence' is justified by the findings in this manuscript.

Answer: Possible contributions to formaldehyde are from process of OH and O3 reactions with parent precursors and products as shown in Eq. (16). The deviation of modeled results from the measurements is still unknown. It might be due to the higher formaldehyde yield parameters used in this study than they should be. We deleted the statements 'degraded products of these ten VOCs will contribute to new particle formation' in the MS.

page 8236, line 24: The figure does not show correlations, but time series of several parameters.

Answer: Will be fixed.

page 8236, line 26: I think 'nucleation event' is usually used for the whole process of particle formation and growth, while here it seems to refer only to the period of intense nucleation. A rewording could be good.

Answer: 'nucleation event' will be replaced by 'intense nucleation'.

page 8237, line 16: 'nucleation rates were lower even under...'; to what are the rates being compared to?

Answer: The nucleation rates in E1c were compared to that in E1b.

Is the language fluent and precise? - The english is easily understandable, but con-

tains a significant amount of errors. The manuscript could benefit from being read and corrected by a native speaker.

Answer: language will be improved by a native speaker.

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