

***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:

8225, P5: The authors should cite an appropriate reference for the statement “SOA can directly affect the Earth’s radiation budget by scattering and absorbing incoming solar radiation.”

Answer: Reference Kanakidou et al (2005) was cited.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and

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global climate modelling: a review, Atmos. Chem. Phys., 5, 1053–1123, 2005.

8227, P20: Activated charcoal, Purafil™ select and absolute HEPA filter were used to provide the supply of clean air required for the experiment. This setup does not include a way of cleaning Methane, do the authors have evidence that this did not interfere with the results? i.e. Methane representing a possible sink for OH.

Answer: Supposing that the methane concentration in the ambient air in Northern Finland is 1900 ppb (Aalto et al, 2007) and the average rate constant of OH with pine emissions is $80 \times 10^{12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, methane resulted OH sink accounts for 0.1~0.6% of total OH consumption in all experiments ($k_{\text{OH}+\text{methane}}=0.0064 \times 10^{12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Atkinson and Arey, 2003). So this should not interfere with the results.

8232, P1 and P10: It is not very clear to me how the authors determined the correction factors used to account for the secondary loss of OH and O₃,. This should be explained and clarified. Is this applicable only to reactions with the second generation products? did the authors consider the wall losses of O₃ and OH as possible sinks?

Answer: For the O₃- induced oxidation, the correction factors were estimated to be 1.0 (Ng. et al., 2006), 1.1 and 1.2 for the monoterpenes with one, two and three double C=C bonds, respectively. Similarly, for the OH- initiated oxidation, due to the high reaction activity of OH with hydrocarbon compounds, the correction factors are estimated to be higher than the O₃ oxidation case, with 1.1, 1.2 and 1.3 for those compounds with one, two and three double C=C bonds, respectively. These factors are applicable to all the reactions including the first-step reactions of oxidant with VOCs and subsequent reactions with products. We didn't take into account the O₃ and OH sink on the wall.

8233, P15: Section 2.6 needs to be expanded in order to explain the experimental procedures in more detail. For example, the second addition of O₃ in the experiments and its rationale should be mentioned in this section.

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Answer: Section 2.6 will be described in more detail in the MS.

8234: Section 3.1 and Table 3: A discussion of the possible effect of the large variation of the emitted species between experiments on the overall results of this work should be provided here or elsewhere in the manuscript. For example, delta3-carene represented the biggest percentage of emitted compounds in E1a and E1b (40, 31%, respectively) while it was 0% in E1c and E3 (the only OH-scavenged experiment).

Answer: We can explain that this variation in Scots pine is typical as there is Δ 3-carene type plants and non-3-carene type plants and the mean proportion of Δ 3-carene in monoterpene pool is decreasing towards northern Finland (See Fig 4. Nerg. et al, 1994). In central Finland the pine populations have both types of individuals within increasing the variation.

Aerosol nucleation and growth rates were also impacted by the amounts and molecule structures of emitted VOCs. Oxidation of compounds with different positions of unsaturated bonds and number of carbon atoms can result in different aerosol growth rate and SOA mass yields (Griffin et al, 1999; Ng et al, 2006). And the nucleation potential of one biogenic compound depends on the combination of its abundance and its efficiency for nucleation. Since Δ 3-carene compound has one double bond internal to ring structure and is more likely to form condensable products when compared to compounds with external double bonds (Griffin et al, 1999), the absence of Δ 3-carene compound in the E1c and E3 might be one possibility leading to the lower nucleation rates than other cases.

Fig 2, Panel B: The authors should comment on what appears to be a systematic difference between the model and measurements in the case of formaldehyde. Also the use of Y-axis log scales in both panels seems to be “hiding” possible large differences for some cases, as a result the comparison between the model and the measurements should be quantified and reported more clearly.

Answer: It is not well known yet what caused the modeled formaldehyde concentra-

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tion deviation from the measurements. In the revised manuscript, we will add some discussions and quantified description to the comparisons between the modeling and measurements as below: 'For the parent compounds, the measured degraded concentration shows very consistent with the modeled results. With regrading to the product of acetone, measurements show more than 90% consistence with the modelling and to formaldehyde, the modeled results have 10-40% deviation from the measured which might be due to the higher formaldehyde yield parameters used in this study than they should be.'

8257: The quality of Figure 3 is poor and it needs to be improved.

Answer: It will be improved.

8238 and Fig 6: A massive decrease in the contribution of m/z 44 to total mass in the second hour averaged mass spectrum compared to the first hour is evident in experiments E1b (~ 20 to 5%) and E1c (~ 14 to 5%). The second hour data in E1a is also similar ($\sim 6\%$). This should be discussed and explained in the light of fact that m/z 44 is generally considered as a marker for highly oxygenated organic compounds.

Answer: Thanks for the comment. It can be explained that in the first hour, terpenes react with OH and O₃, leading to the gas-phase nucleating and condensing species. Before reaching their vapor saturation, these products can be reactive with the oxidants and get further oxidized. The most highly oxidized material generally has the lowest vapor pressure; therefore, it condenses earlier. This might be the reasons that highly oxidized nature of aerosol was observed in the first hour duration in E1. Once new particle formed, increased precursors oxidations produces the condensing species with condensing on the formed particles and just simply increase the total aerosol volume. The products of chemical compositions do not evolve too much since they are no longer reactive towards the oxidants.

The above assumption further confirmed our conclusion that OH is more responsible for the more oxidized aerosol products because OH oxidation reactions dominate in

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E1.

8240, P1: The statement about the similarities of the measurements and the ambient mass spectra needs to be quantified. It is certainly not enough to “see” the same fragments, the overall mass spectral fragmentation pattern and the contribution of each fragment to the total mass spectral signal need to be taken into account for such claim to be valid.

Answer: In the revised manuscript, Fig. 7 will show the comparison of the fragmentation patterns of aerosol products in the chamber simulations in this work with those in the field campaign. The mass spectra in this work are averaged in the first hour in E2 and ambient measurement is from two-hour averaged mass spectra during one nucleation event from 9:30AM to 11:30AM on June 1st, 2007, in Hyytiälä forest in Finland. Good correlation ($R^2 = 0.89$) of our measurements with the ambient mass spectra indicate that the experimental results are able to reproduce the products distributions of SOA formed in the real atmosphere.

8241, P15: Isoprene should not be stated as a major emitted VOC from Scot pine given that it accounted for a maximum of 3.9% to the pine emissions (Table 3)

Answer: We agree.

Minor Corrections:

8225, P10: replace “low volatile products” with “low volatility products”

8225, P20: Remove “etc.”

8226, P10: replace “was” with “were”

8227, P20: “. . .for over night” this sentence should be rewritten as “. . .the chamber was continuously flushed overnight by compressed laboratory clean air.”

8230, P1: “flight of time” should be replaced with “time of flight”

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8230, P5: “the interested particle” should be replaced with “the particle of interest”

8230, P10: “FMPS instead” should be rewritten as “The FMPS, on the other hand, provides...”

8233, P15: “in the presence OH” should be “in the presence of OH”

8235, P15: It should be “modelled and measured” instead of “modelled and modeled”

8256: Delete the word “be” in the last line of the fig caption. It should read “.. are not shown here.”

8237, P1, line 4: Delete “and” from the beginning of the sentence.

8238, P5: “..are in strong agreement...” instead of “..are strong agreement.”

8240, P5: “calculated following the...” instead of “calculated followed the...”

8241, P1: “larger than 1.25.” instead of “larger 1.25...”

A mixture of “modelled” and “modeled” are used in the manuscript, use a consistent spelling.

Answer: All above comments are accepted and will be fixed in the MS.

Reference: Aalto, T., Hatakka, J. and Lallo, M.: Tropospheric methane in northern Finland: seasonal variations, transport patterns and correlations with other trace gases, *Tellus*, 59B, 251–259, 2007.

Atkinson, R., and Arey, J.: Atmospheric degradation of volatile organic compounds, *Chem. Rev.*, 103, 4605-4638, 2003.

Nerg, B. A., Kainulainen, P., Vuorinen, M., Hanso, M., Holopainen, J.K. and Kurkela, T.: Seasonal and geographical variation of terpenes, resin acids and total phenolics in nursery grown seedlings of Scots pine (*Pinus sylvestris* L.), *New Phytol.*, 128, 703-713, 1994.

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Ng, N. L., Kroll, J. H., Keywood, M. D., Bahreini, R., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Contribution of first- versus second-generation products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons, *Environ. Sci. Technol.*, 40, 2283-2297, 2006.

Griffin, R. J., Cocker III, D. R., Flagan, R.C., and Seinfeld, J. H.: Organic aerosol formation from the oxidation of biogenic hydrocarbons, *J. Geophys. Res.*, 104, 3555–3567, 1999.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 9, 8223, 2009.

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