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Interactive comment on "Nanoparticle formation by ozonolysis of inducible plant volatiles" *by* J. Joutsensaari et al.

B. Bonn (Referee)

Boris.bonn@helsinki.fi

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General comments

This study on new particle formation as a consequence of the ozone reaction with plant emitted reactive VOCs focuses on the investigation of nucleation and growth rates under controlled laboratory conditions in order to intercompare the results obtained with nucleation events observed in boreal forests at a more complex chemical and physical situation. This situation usually does not allow to determine the chemical composition and thus the compounds responsible for nucleation and early growth (up to 6 nm) because of the low aerosol mass. The general aim of this study is ambitious and is of course needed. Nevertheless, the authors need to put more efforts on the exact

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conditions applied in the laboratory in order to be able to intercompare with ambient conditions and need to use published results correctly as pointed out in an earlier comment.

Specific comments

These points are:

1. The emission pattern of ambient boreal forest plants is much different from the one of white cabbage. E.g. Hakola et al. [2003] determined the major emittants from Scots pine in Finland to be Δ^3-carene and α-pinene (together about 80 % of the monoterpenes) and smaller amounts of β-pinene and camphene and sabinene and limonene only during summertime up to the start of autumn. Therefore, the large quantity of endocyclic (double bond inside the ring structure) monoterpenes (Δ^3-carene and α-pinene) determined the chemistry as well as the particle formation by contrast to the mainly exocyclic (double bond outside the ring structure) monoterpenes determined in the present study, which were β-pinene and sabinene with remarkably less endocyclic compounds like α-thujene. This implies a strong feedback on the nucleating compounds, since exocyclic compounds split of parts of the parent hydrocarbon leading to mainly smaller and more volatile ketones such as nopinone with an estimated vapour pressure of about 50 Pa at room temperature [Jenkin, 2004]. This is remarkably higher than the aldehydes formed in endocyclic monoterpene reactions such as pinonaldehyde in the case of α-pinene with a saturation vapour pressure of about 6 Pa. Please note that the endocyclic and exocyclic compounds provide different ways of forming nucleating species as shown by Bonn et al. [2002]. The exocyclic ones are much more affected by the presence of sufficient water vapour forming more volatile compounds only to be able to condense as observed in the present study.
2. The second point to be made focuses on the sesquiterpenes: Hakola et al. [2003] found β-caryophyllene a mainly endocyclic reacting compound, at the boreal forest investigated. This compound provides a remarkable advantage. A it is less affected by the present water vapour and since the cyclic double bond breaks first, its molecular

structure remains nearly identically forming first stage oxidation products with 14 to 15 carbon atoms, which are able to either nucleate or to condense on pre-existing aerosol surfaces. By contrast, in this study the sequiterpenoid α-farnesene with a linear structure and four double bonds is found. Therefore, its largest oxidation product will contain 5 carbon atoms (see structure for this), close to an isoprene unit, which is not able to form particles even at the most promising conditions. Similar conclusions can be done for (E)-4,8-Dimethyl-1,3,7-nonatriene.

3. Please check once again the conclusions made by Bonn and Moortgat [2003] concerning the effect of water vapour concentration (NOT relative humidity) on the nucleation threshold. Since atmospheric nucleation events such as observed in Hyytiälä are usually not found during summertime with elevated temperatures and water vapour concentrations (saturation vapour pressure increases exponentially with temperature, relative humidity certainly not !). This is caused by the scavenging of nucleating compounds precursors by the present water vapour, which then forms more volatile condensable compounds such as hydroperoxides but suppresses the nucleating species to be formed in sufficient concentrations. Therefore the conclusion to contradict the theory of sesquiterpene ozonolysis products induced nucleation can not be hold in my opinion, since the temperature used was 22 degree Celsius much higher than about the freezing point or somewhat above at ambient nucleation.

4. Moreover please provide more details about the experimental materials used. E.g. which kind of material was used to build the growth chamber? If Teflon foil, plastic or usual glass have been used this causes doubts on the statement about the ionization, since the UV light does not penetrate. Only quartz glass is still able not to absorb the whole range of UV, but even some. Consequently, ionization can be nearly excluded in my point of view after reading the publication. Secondly, a quite intense ozone concentration is used in the experiment. This causes several problems. First, the concentration of compounds partitioning in the aerosol formation process (nucleation as well as growth) increases rapidly, much faster than in the real atmosphere, where further OH reactions, deposition or even mixing inside the boundary layer will

lower the concentration of even the condensing compounds and thus drastically reduce the growth rate. What about the Teflon lines for sampling? They provide a remarkable facility for absorption, which was always found during earlier smog chamber studies. Processes going on at the surface are not known yet and usually these compounds are released later on either at decreased gas phase concentrations or at increased temperature. Especially sesquiterpenes with their short e-folding lifetime for the presented conditions of about 10 s or even less will never make their way to the analyzer. More likely they will stick to the next wall and oxidize further enhanced by the higher wall temperature caused by the incoming radiation. This is actually the most problematic point of detecting them at ambient conditions. What are the loss rates to the chamber walls? For usual smog chamber conditions one would expect a value of about 20

Please note, that the purpose of this study is well focused and the conclusion with respect to the high growth rate of organics is drawn correctly for the chamber conditions, but remind the ambient conditions in detail for intercomparison and for formulating such strong conclusions. There are incredibly large differences between different plant types, their emissions and the subsequent reactions as well as processes in the atmosphere. Although e.g. isoprene is not (or at least nearly not) contributing to organic aerosol mass, it will influence the chemistry remarkably, if present, as it is e.g. at the Finnish Hyytiälä during summertime [Hakola et al., 2003].

Therefore, I would suggest to skip this final conclusion with respect to atmospheric nucleation events.

References

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