

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

**J. Joutsensaari et al.**

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We thank Dr. Bonn for his review and believe that the paper will be strengthened by our revisions prompted by the comments. Here we respond to the points presented in the review.

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  $\Delta$ -carene,  $\alpha$ -pinene (together about 80 % of the monoterpenes) and smaller amounts of  $\beta$ -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 ( $\Delta$ -carene and  $\alpha$ -pinene) deter-*

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*mined 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  $\beta$ -pinene and sabinene with remarkably less endocyclic compounds like  $\alpha$ -thujene. This implies a strong feedback on the nucleating compounds, since exocyclic compounds split off 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  $\alpha$ -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.*

We agree that emission spectrum of cabbage plant differ from that of Scots pine. Conifers are monoterpene storing species, while cabbage is not. In cabbage plants the synthesis of monoterpenes is strongly light dependent. We should perhaps stress that we are not drawing conclusions specific to pine forest atmosphere (although we use Scots pine emissions as an example). The point we want to make is that in any environment with VOC emitting plants there is a rich spectrum of various terpenoid species present, which may not always be the case in smog chamber experiments when using the mixtures of pure compounds. Furthermore, as shown in the review of Kulmala et al. [2004] nucleation takes place in a wide variety of boundary layer environments around the world. Everywhere, the nucleation and growth rates of the particles are on the same order. If oxidized organics are involved, this indicates that the physicochemical properties (especially vapor pressures) of the species participating in the growth are very similar, even if the species are not the same. We therefore believe that nucleation observed after oxidation of VOCs emitted by one plant species do have bearing on similar nucleation from the emissions of some other plant species.

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2. *The second point to be made focuses on the sesquiterpenes: Hakola et al. [2003] found  $\beta$ -caryophyllene a mainly endocyclic reacting compound, at the boreal forest investigated. This compound provides a remarkable advantage. As 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 sesquiterpenoid  $\alpha$ -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 drawn for (E)-4,8-Dimethyl-1,3,7-nonatriene.*

Here we agree with the referee. Atkinson and Arey [2003] gave the calculated 2 min atmospheric life time for  $\beta$ -Caryophyllene in reactions with ozone. In personal communication with Roger Atkinson, he estimated: “Based on its structure, room temperature rate constant ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for  $\text{C}_{11}$  homoterpene, 4,8-dimethyl-1,3,7 nonatriene, is estimated to be (give or take a factor of 2 or so): Reaction with  $\text{O}_3$ ,  $k = 4.1\text{E-}16 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (lifetime of 60 min for  $7\text{E}11 \text{ molecule cm}^{-3}$  of  $\text{O}_3$  (30 ppb))”. Thus in the revised paper we will point out more the possibility that the increased fine particle formation over the methyljasmonate-treated plants could be a result of drastically increased monoterpene emissions rather than novel sesquiterpene or homoterpenes emission from treated plants. Our recent unpublished results in Teflon chambers have indicated that alpha-thujene and sabinene are the monoterpenes that are most effectively destroyed by ozone. However, the unpublished volatile measurement of the indicated that  $\alpha$ -farnesene disappeared from the adsorbent samples earlier than monoterpenes after ozone pulse, suggesting higher reactivity of this compound with ozone compared to monoterpenes.

3. *Please check once again the conclusions made by Bonn and Moortgat [2003] con-*

*cerning 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.*

- We have made continuous nucleation measurements at Po Valley, Italy, for nearly three years now, and there we see the highest nucleation frequency in July, with nucleation events sometimes taking place at temperatures close to +25 centigrades (the maximum temperature we have seen at the start of nucleation was +29) [Laaksonen et al., 2005]. We will clarify in the revised paper that our conclusion regarding the homogeneous nucleation of organics in the atmosphere refers to "warm" events whereas Bonn and Moortgat (2003) discuss events occurring at somewhat colder temperatures.

Note however, that even in Hyytiälä, nucleation does sometimes occur at temperatures around +10–15 °C. Furthermore, other explanations than that of Bonn and Moortgat (2003) have been offered for the decreased nucleation event activity at Hyytiälä in the summertime. Anttila et al. [2004] pointed out that since SO<sub>2</sub> concentrations are typically three times lower in Finland in the summer compared with springtime, and because of the elevated vapor pressures of condensable organics, the growth of nucleated sub-three-nanonmeter clusters is slower in the summer than in the spring. Therefore, the clusters may more often be scavenged due to coagulation with larger particles in the summertime before growth to detectable sizes, resulting in a nucleation

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event frequency minimum.

Concerning the issue of humidity; even if the mechanism suggested by Bonn and Moortgat [2003] would not be responsible for homogeneous nucleation in the atmosphere, it may be responsible for producing condensable species participating in the nucleated cluster growth, and high specific humidity may therefore suppress the cluster growth to the measurable size range (i.e. above 3 nm). However, elevated relative humidity may have a similar effect since hygroscopic preexisting particles will take up water, thereby increasing the condensation sink and depleting the condensable species more efficiently than at drier conditions.

*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*

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*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*

- Inner walls of the growth chambers are special painted aluminium and light bulb unit was insulated from chamber air with polyacrylic plate. We did not have UV light in the growth chamber (light bulb unit was insulated from chamber air with polyacrylic plate) neither did we say that ions are from UV but from cosmic rays. However, admittedly, this is somewhat inaccurate. In ambient ground-layer air, the sources of ions are cosmic rays and radon. Indoors, the possible sources are high-energy cosmic rays able to penetrate into the building, radon, and the building materials themselves which always contain some low level of radioactivity. Some beta rays from the concrete walls may well have entered our growth chamber. Also, it is doubtful that the pressurized air filters would have removed radon. To investigate this matter, we have now made simple Geiger counter measurements outside the laboratory building and inside the growth chamber. The resulting dose rate outdoors was about 0.1 microsieverts per hour, while inside the chamber it was about 0.08 microsieverts per hour. This proves our point that ions are almost as abundant in the chamber as in ambient air. We will clarify this matter in the revised manuscript.

- The high ozone concentration does not remove the fact that for the compounds produced in our chamber, the nucleation rate was similar as the atmospheric nucleation rate whereas the growth rate was higher. If in our experiment there would have been a ten times lower concentration of the condensable compounds (corresponding to a growth rate of around 5 nm/h which is very usual in the atmosphere), we would not have observed nucleation.

*Teflon lines for sampling:* Similar Teflon tubing have been used in our earlier VOC studies and volatile terpene concentrations have been on the level as we observed

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here.

*The loss rates to the chamber walls:* We agree that probably, a considerable fraction of sesquiterpenes are lost to the walls. However, it is difficult to estimate the loss rate. We have Tenax adsorbent samples collected from the chambers before and after ozone peak (but we did not report the results in the paper, because we do not know in what extent terpene loss was due to reactions in the chamber atmosphere and due to reactions with ozone on adsorbent surface). Alpha-farnese was detectable in the chamber atmosphere in the same concentrations as monoterpenes, but it disappeared from the samples just after the first ozone peak (unlike monoterpenes). We expect that this disappearance indicated rather alpha-farnesene depletion due to atmospheric reactions than rapid adsorption to the walls. (Note that the wall temperature was not appreciably higher than the air temperature as the lights were dimmed during the experiments in order to avoid temperature increase.) In any case, even if the losses occur, it is not a key issue to the interpretation of the particle measurement results, since the particle growth rate is a direct indicator of the concentration of the condensable products in the air.

*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.*

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- As pointed out above, the characteristics (especially growth rates) of nucleation events are very similar all around the world despite of the different plant types. Of course, a lot of different experiments will be needed with different types of plants, at different temperatures etc., to *prove* that our conclusions are correct. Based on their smog chamber experiments, Bonn and Moortgat [2003] suggested that the Hyytiälä nucleation events are due to homogeneous nucleation by sesquiterpene ozonolysis products, even though sesquiterpene emissions have not been detected in Hyytiälä in the spring time [Tarvainen et al., 2004]. We believe that it is justified to conclude that our experimental results *suggest* that the ambient homogeneous nucleation is not from oxidation products of VOCs.

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