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Atmospheric
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Discussions

Interactive comment on "Size-segregated aerosol chemical composition at a boreal site in southern Finland, during the QUEST project" *by* F. Cavalli et al.

F. Cavalli et al.

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Answers will be given punctually for each of the specific comment of the referee.

Specific comments There are some minor comments I have concerning some points mentioned: 1. During the first reading of the paper I was confused with the times associated with nucleation events and non-events, both given with the same date, although the authors state correctly that there are nucleation days and non-nucleation days and that the sampling took place for 7 days for each sample, with alternative sampling to the present conditions (nucleation or no nucleation). May I ask the authors to switch the names to the time scales of the samples, e.g. ne-170303-260303 instead of ne-

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170303, to provide an easier identification of the sampling period? A picture showing an example day and the splitting in both would be nice, but is not needed in this context.

Authors' response: As suggested by the referee, we have switched the name of the samples to the time scale allowing for an easier identification of the sampling period.

2. Seven day sampling is quite a long time for organic compounds to be collected while air is passing containing all ambient oxidants and with varying concentrations in the gas-phase. Certainly, I am aware of the time needed to collect sufficient amounts of mass, but I would be interested in the more short lived compounds participating in the nucleation as well. I suspect them to be converted to acids or carbonyl compounds with the longest chemical lifetime among the oxidation products available. What do the authors think about this?

Authors' response: The quite long sampling time is required to collect sufficient aerosol mass in order to perform reliable analysis; we are aware of the potential modifications that the prolonged sample exposition can cause in the chemical composition of organic species present on the quartz filter. However, we believe that this does not invalidate the evidences of our study. Short lived primary photo-oxidation products  e.g. pinonaldehyde from α-pinene  unlikely participate in nucleation due to their high vapor pressure. In contrast, longer lived oxidation products with a very low vapor pressure  as e.g. pinic acid from α-pinene photo-oxidation  are suspected to take part in the new particle formation process causing a condensation growth of newly formed thermodynamically stable cluster (e.g. Christoffersen et al., 1998). Concerning the suspects of the referee that the organic composition observed could be an artefact of long sampling time, it should be mentioned that (1) significant amount of organic acids are produced already as "first/early" oxidation products when terpenes (e.g. α -pinene) are oxidised (see also Larsen et al., 2001; Glasius et al., 2000); and (2) numerous are studies which confirm the presence of organic acids in aerosol particles with higher concentrations during nucleation event, even over shorter observation periods (e.g. Kavouras et al. Nature 1998;

Anttila et al., 2005; etc.).

3. One comment concerning the identification of oxidation products by comparing the H-NMR spectra to smog chamber results of the monoterpene α-pinene. The approach is quite valid and a reasonable idea, but the used concentration of 5 to 10 ppmv is at minimum about 20000 times higher than the ambient concentrations of monoterpenes in the boreal forest at that time. It might be that even more volatile compounds like carbonyl compounds will significantly contribute to the aerosol mass in the smog chamber while they don't under ambient conditions. Also the high NOx concentrations might overestimate nitrogen containing species for the present site. Nevertheless, this approach is reasonable.

Authors' response: The high amount of reactant, 5 to 10 ppmv of α-pinene, used in the photo-oxidation experiments, is needed, in a 480 L smog chamber, to generate enough oxidation product material (aerosols) for further chemical analyses, as HNMR. Although, these concentrations are significantly higher than the atmospheric levels of monoterpenes in a boreal forested environment, the approach can be considered reasonable, as stated by the reviewer himself. The comparison between ambient aerosol HNMR spectra and the laboratory generated SOA-HNMR spectrum showed a strong the similarity in their chemical features. This, therefore, suggests a clear biogenic fingerprint of the aerosol collected during nucleation events and allows for strong, although qualitative, evidence that oxidation products from α-pinene as well as from other monoterpenes might play a role in nucleation of new aerosol particles. The observation of the referee is correct: laboratory experiments can only simulate what occurs under the atmospheric conditions, the latter being, in general, quite different. This limits the use of laboratory results to provide estimates of the atmospheric processes, as we have done in our study.

4. A very nice result is Figure 2, indicating the important role of water soluble organic compounds at nucleation conditions and the opposite effect for non sea-salt sulfate as well as for ammonia. Interesting is the large contribution of unaccounted material

during the nucleation events. Can the authors speculate more about this? Is this probably a mixture of several group types or reactive compounds of e.g. a further VOC oxidation with several carbon double chains? I am sure that this is a risky business, but it might be of high importance for the nucleation process.

Authors' response: The chemical analyses performed in this study do not allow speculating on the nature of the water-insoluble species that can contribute to the event aerosol mass. However, other studies - i.e. Allen et al., 2005 and Shimmo et al, 2005 - performed during the same field experiment indicate much of the event aerosol mass as being long chain n-alkanes (C27-C29); these compounds are likely to have originated from leaf waxes, evaporate through the radiative heating from the tree surfaces and condense onto the particle phase.

Technical corrections Figure 6: Please switch the green colour of the 'modified' case to yellow. I guess it has become green by accident but should be correct in the final version to stick to the legend.

Authors' response: corrected.

p. 8864ff.: I would suggest to switch the expressions 'clean', 'modified' and 'slightly modified' to 'clean', 'polluted' and 'slightly polluted' probably including the word 'anthropogenic' to make it clear to the reader what is meant, since the authors didn't modify the samples but the air mass was different.

Authors' response: corrected. The text, tables and figures have been modified using the expression suggested by the referee as "clean", "slightly polluted" and "polluted". The word anthropogenic has been omitted in tables and figures for brevity; however, in text, it has been rendered clearer the anthropogenic origin of the polluted conditions encountered during the field experiment.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 8851, 2005.

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