

Interactive comment on “The role of VOC oxidation products in continental new particleformation” by A. Laaksonen et al.

A. Laaksonen et al.

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We thank Dr. Donahue for the useful comments.

P 2722 line 14: The statement in the introduction "It is suspected that the vapors causing the condensational growth of the clusters to observable sizes are low vapor pressure organic species ..." is too broad. Clearly low vapor pressure compounds are needed to sustain condensational growth of the TSCs. Organics can play that role, but sulfate certainly can as well; this has been convincingly demonstrated by Stanier et al and Qi Zhang et al (EST 2004) for Pittsburgh, as the authors discuss later in the article. Neither Pittsburgh nor Hyytiälä is globally representative; discovering where sulfate and where organics play this vital role in new-particle growth is a major need.

Answer: We appreciate the comment, and will stress that we refer to the Boreal forest

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environment where sulfuric acid concentrations are clearly too low to alone explain observed growth rates (e.g. Boy et al., ACP 5, 863, 2005).

P 7825 line 2: Please state the vaporiser temperature as well (600 oC?). This influences the organic mass spectra by adding a thermal pre-heat to the electron impact ionization.

Answer: Yes, indeed. Temperature included in above reply, reporting that the AMS was operated at typical 600C desorption temperature, consistent with other lab calibrations and field observations.

p 7828 line 15: I have a very hard time believing that pinonaldehyde has much to do with the growth of sub-10 nm particles at low total aerosol mass. We see pinonaldehyde in the gas phase, where it belongs, using PTRMS (Presto EST 2006; Supplemental Material). The saturation concentration of pinonaldehyde is 1000 g m³ or more. However, it can adsorb to quartz filters, leading to a positive artifact in filter sampling. This artifact would, however, be correlated with the first-generation α -pinene SOA products in the air and thus might serve as a useful surrogate for the much lower vapor pressure material that must be needed for new particle growth. The only reasonable counter argument to this point I can see would be for the pinonaldehyde to react heterogeneously on the particles to form much less volatile oligomers. However, there are two problems with this. First, once the pinonaldehyde reacts it is hard to understand how it would then be detected as the monomer (reversible oligomerization just won't do it, in my opinion). The other problem shows up in Figure 4 of our supplemental material again; at least in the chamber, the pinonaldehyde appears to be perfectly stable; if it were engaged in a heterogeneous reaction associated with particle growth we would expect loss.

Answer: Our studies have indicated that aldehydes, such as pinonaldehyde, can be found in aerosol samples in large quantities. Note that here we refer to aerosols generally, not to sub-10nm particles. The fact that the growth rate of the particles can be

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related to gas-phase MTOP (including pinonaldehyde) concentration is merely an indication that further oxidation products likely drive the growth. What, then could be the reason for the finding of pinonaldehyde in the aerosol? We are certainly not the first ones making such an observation (see e.g. Cahill et al, J.Geophys. Res. 111, D16312, doi:10.1029/2006JD007178, 2006; Boy et al, Atmos. Chem. Phys., 4, 657-678, 2004; Kavouras and Stephanou, Environ. Sci. Tech. 36, 5083, 2002; Jaoui et al., J. Geophys. Res. 106, 12541, 2001). That said, Dr. Donahue is certainly right about the vapor pressure issue. Also, partitioning of pinonaldehyde into the aerosol by an absorptive process can be discussed in terms of "dissolution" of pinonaldehyde into an organic-inorganic mixture, and an activity coefficient can be calculated that corresponds to the measured concentrations. Kavouras and Stephanou did such a calculation of pinonaldehyde activity coefficients and obtained values so low (0.000001 or lower) that they are difficult to explain without some degree of chemical bonding.

Regarding adsorption, it is certainly possible that pinonaldehyde can be adsorbed onto quartz filter, but if so, it should be evaporated from it (sample flow is $90 \text{ m}^3/\text{h}$, sampling time at least 2 h). However, if the adsorption is the fact, then the amount of corresponding acid should be larger than it is. Also, even though gas phase products are separated from the aerosol phase in many publications, the pinonaldehyde amount found is almost the same as presented in this paper. AMS ion 43 indicates that amount of aldehydes is greater than amount of acids (ion 44) in Hyytiälä, and the aldehydes can not come from the gas phase because of vacuum.

One possible explanation could be collection "artifact" from gas phase species deposited on the filter. During aerosol collection on filters, large vapor artifacts can occur because the aerosol on the filter accumulates. The effective aerosol loading for air passing through the filter is thus enhanced, so that vapor/condensed phase partitioning can be shifted toward the condensed phase. However, our recent experiments in which the gas phase was removed prior to the sampling of particles, yielded similar high levels of pinonaldehyde in the particle phase. Therefore, we do not think artifact

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formation is the (main) reason for high levels of pinonaldehyde found in particle phase. Another possibility is that the observed pinonaldehyde is a degradation product of the extraction/analysis procedure. This is particularly a problem in conventional GC, due to the high temperatures required for transport through the column. The "total" secondary organic aerosol is an extremely complex mixture of oxidized organics - which are inherently thermally unstable. It is very possible that the low volatility species that actually condense in the ambient aerosol are more complex (larger) compounds that evolve pinonaldehyde during the analysis. On the other hand, we have used very "gentle" extraction method, with no heating of the sample. Also our GC method is gentle: we are using cool on-column injection. Thus, alteration of sample during sample introduction is very unlikely.

Taken together, at this point we are not able to give a definitive reason for the appearance of pinonaldehyde in the aerosol sample analysis. However, having said all this, the origin of the pinonaldehyde doesn't really change the arguments in this manuscript. The pinonaldehyde functionality is real - whether as molecular pinonaldehyde in the vapor phase or as a degradation product of the aerosol analysis. Therefore the correlation of the aerosol growth behavior with observed pinonaldehyde still is a strong argument for biogenic, terpene source of the condensing vapors under these conditions. We will add the above discussion to the revised manuscript.

p 7828 line 22: 23.5%?? That is awfully precise. I think one significant digit, and not three, is in order here.

Answer: Will be fixed.

p 7830 line 5: If the size range of the total particle measurements was indicated, I missed it and can't find it easily again. Please state it here.

Answer: 3 nm - approx. 1 micron. We added this in the caption of Fig. 5.

Table 1: There is an extra word ("and") in the caption. It would be useful to know the

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total organic aerosol mass (OA) in these samples too in order to get an idea of the expected partitioning.

Answer: "And"; will be removed. Unfortunately, due to short collection times, we were not able to determine the total mass on the filters, and we did not have extra filters for performing TOC analysis. We therefore do not know the total OA mass.

Fig 2: I find the linear fit here misleading. It is clearly correct to assert that the periods of highest MTOP are all associated with high EtOH growth factors, but there are plenty of high-growth points at low MTOP too - it appears that high MTOP leads to high EtOH growth, but that other things can too.

Answer: Indeed, assuming that two major types of species, sulfates and organics, constitute most of the mass of the 10 nm particles, and accounting for the fact that sulfate does not take up ethanol in 10 nm particles, then it could be possible to have high growth factors at low MTOP provided that the sulfuric acid concentration is low also. The linear fits were only made in order to check the statistical significance of the correlations. The most important thing to notice is of course that the correlations only appear during nucleation and growth events. We will improve the writing in the revised ms.

Fig 4: Please resort the legend so that high Theta is at the top - this confused me for a second! Also, virtual potential temperature (including water vapor buoyancy) is typically a better measure of boundary layer stability. I doubt that influences the qualitative point here, though.

Answer: Will be corrected

Fig 5: It would be interesting to reproduce the turbulent mixing height line here - the correlation (aside from the general sign of the trend) is not obvious to me

Answer: Prompted by Dr. Donahue's comment, we looked into this matter more carefully. We re-estimated the ABL dynamics using observed data of potential temperature

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profile in the free atmosphere (O'Dowd et al. ACPD 8, 2821, 2008). The geostrophical wind was approximated as 5 m/s whereas the original Fig. 4 was derived with $G = 10$ m/s. The resulting mixing height line is now somewhat steeper, and we have redrawn Fig. 4 accordingly. As the surface above which the flights took place is not homogeneous, we calculated the ABL dynamics assuming different types of vegetation, which resulted in some variance (will also be shown in new Fig. 4).

Regarding reproduction of the mixing lines in Fig. 5, we are afraid that this would lead to misunderstandings. The composite and interpolated contour distribution of particle concentration height evolution derived from two aircraft datasets covering a large spatial area gives a general picture of the nature of the aerosol evolution and when compared with modeled boundary layer growth from a single point, it appears to suggest that the new particle plume grows above the mixing line height at 1100am. This is, however, not the case: The individual profiles shown in O'Dowd et al., 2008, confirm that always the particle plume is within the mixed layer. O'Dowd et al., 2008, illustrated a large degree of horizontal variability in boundary layer structure in the region (due to, presumably, different heat fluxes over lake and canopy surfaces). The aircraft sampling through this inhomogeneous structure cannot therefore be compared directly or quantitatively with the model predicted evolution of the (homogeneous) boundary layer structure. We will change the manuscript text to reflect this discussion.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 7819, 2007.

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