Atmos. Chem. Phys. Discuss., 5, S4571–S4576, 2005
www.atmos-chem-phys.org/acpd/5/S4571/
European Geosciences Union

Atmospheric Chemistry and Physics 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.

Received and published: 17 December 2005

Answers will be given punctually to the specific comments of the referee.

1) p 8854, l 21-25: Please explain the sampling strategy in more detail. It is difficult to understand at first reading how the sampling strategy worked. Furthermore it would be important to know how many hours of sampling each of the samples experienced (e.g. add a column in Table 1 including the total hours of sampling for each sample). Did you sample during night time, too? When was the sampling shifted between event and non-event? As soon as nucleation mode particles turned up in the smallest channels? When was it switched to non-event again after a nucleation even? Reword the sentence

Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper

EGU

starting "As result...".

Authors' response: The sampling strategy adopted during the field campaign has been explained in further details in the text, clarifying all the points raised by the referee. In particular, in the manuscript, the following aspects have been clarified: i) sampling duration for event and non-event samples; ii) for both event and non-event conditions, sampling was performed during daytime; ii) for the decision on the occurrence of a nucleation event on-line DMPS data were used. In Hyytiälä, nucleation events are generally expected in the late morning hours following the highest radiation fluxes. Therefore, if during midday nucleation mode particles appeared in the smallest DMPS channels, the event sampling started and generally lasted for the following hours up to 8-9 in the evening in accordance with the persistence of new particle formation or growth of the nucleated mode. In contrast, if in the middle hours of the day no new particles were formed, the non-event sampling took place to the end of the day. In general, no shift between event and non-event sampling was performed during the same day.

2) Some of the conclusions on the observed differences in the aerosol should be put forward more carefully or at least be explained in more detail. I agree, there are some distinct differences, e.g. more than a factor 2 higher total aerosol load on the nonevent days, but other differences are not as obvious in the data as stated in the text: a) p 8864 l 5-15. The biggest change between clean and modified conditions (Table 2) for the H-C-C= functional group at 2.5-3.2ppm is only changing from 15.8+-1.8% to 20.0+-2.6%. Is this difference really significant? These slight shifts in composition are probably not as relevant for the occurrence of nucleation as the changes in aerosol surface area, temperature, relative humidity, ozone, terpene emission strength and the efficiency of the oxidation processes. How were the stated uncertainties determined? Also, the shift in H-C from 48.7+-0.5% to 44.3+-1.5% does not seem very large. Please discuss. b) Please explain in more detail what is meant by the "background" signal (e.g. p 8863, l 8 and p 8862 l 27). c) It is stated that 72% of the H-NMR spectra of the event-

ACPD

5, S4571–S4576, 2005

aerosol and only 32% of the non-event aerosol can be accounted for by α-pinene oxidation products. But can it be excluded that the oxidation products of other organics, especially those of anthropogenic origin (e.g. 1,3,5-TMB) produce similar spectra? It is also not clear why the non-event spectrum of Figure 3 could not be produced mainly from terpene oxidation products as well, maybe terpenes other than α-pinene. These points should be considered and put into perspective in the Results and the Conclusions sections.

Authors' response: 2-a. The uncertainties in the functional groups distributions reported in Table 2 are calculated as the standard deviation between the functional group percentage compositions of the samples belonging to a particular set ("clean", "slightly modified" and "modified"). The functional groups composition associated to each of the three case is very reproducible and the differences in the H-C-C= (2.5 - 3.2) and H-C contents are statistically significant. The focus of section 3.3 is to identify signature of the biogenic fraction of WSOC and its varying contribution between the clean and the modified case. We showed that differences in specific spectral regions and in the intensity of peaks attributed to biogenic species allow distinguishing between the clean and the modified case. But we do not state that the distribution of the five (one aromatic and four aliphatic) main H-NMR functionalities changed significantly from the clean respect to the modified case, nor we are saying that the organic composition for the clean case promoted nucleation while the one for the polluted case inhibited it. On the contrary, as the Referee notices, the average physico-chemical properties of WSOC (e.g., solubility, condensability) did not experience dramatic modifications following the change in the air masses, and it is plausible that the strongest factors controlling nucleation were mainly physical [e.g. condensational sink i.e. pre-existing aerosol load; condensable gaseous sources, i.e. monoterpenes photo-oxidation products; solar radiation etc.]. The new information provided by the H-NMR results is that 1) the organic compounds participating to particle formation and growth contained a dominant fraction of biogenic species, and 2) the biogenic SOA constituted a reservoir of water-soluble condensable species for pristine air masses. 2-b. The baseline of the spectra shown in Figures 3

ACPD

5, S4571–S4576, 2005

and 4 is almost horizontal, therefore the rising of the signal between 0.9 and 5 ppm and between 7 and 8.5 ppm must be attributed to the sample. Most probably, they are unresolved envelops of a large number of resonances from organic compounds showing a similar but not coincident chemical structure. A few resonances attributable to individual compounds present in relatively high concentrations appears superimposed to the broad bands of the unresolved mixture, which are therefore labelled as “background”. 2-c. H-NMR data for anthropogenic SOA were collected within the frame of the laboratory experiments discussed in section 3.3 for α-pinene. Toluene was oxidised with OH and the aerosol produced in the smog chamber was collected on Teflon filters and extracted for H-NMR analysis. The results are not discussed in this study, which focuses on particle formation and growth in the boreal forest. However, we include a H-NMR spectrum of a SOA sample collected in a reaction chamber where toluene was oxidised by the OH radical, as supplementary material. These spectra are very different from those obtained by the reaction of α-pinene. They also lack the individual peaks which were found in the Hyytiala samples (and particularly in clean conditions): the singlets of pinonic acid (H = 0.85, 1.32 and 2.13) and the other intense unidentified signals (e.g., those with H = 1.57, 1.60). The contribution of biogenic reactive VOCs other than α-pinene to the spectra in Figure 3 cannot be assessed on the basis of the available data. On the other hand, we found an increasing contribution of the “background” signal in the more polluted samples (see Table 2). The distribution of the bands of the “background” is consistent with that in the spectra in European polluted countries (e.g., Decesari et al., Atmos. Environ., 2001).

Technical corrections: p 8858, l 6: "...transported polluted air from the Kola peninsula in Russia to the measurement site ...". Authors’ response: corrected.

p 8858, l 7:"...supermicron mode is measured..." (no comma) Authors’ response: corrected.

p 8858, l 16: correct to "n-e310303" and clarify the sentence "the n-e310303 collects, however, the only non-event day in that week". Authors’ response: corrected and

ACPD

5, S4571–S4576, 2005

clarified.

p 8858, l 18: "precipitation" Authors' response: corrected.

p 8859, l 8: "as it typically occurs" Authors' response: corrected.

p 8859, l 28: "In contrast, " Authors' response: corrected.

p 8860, l 4: "occurred when air masses, ..." Authors' response: corrected.

p 8860, l 5: "coming from an east to south-east direction" Authors' response: corrected.

p 8860, l 23: please reword/clarify: "as the northerly air flow increasingly arrives from the west" Authors' response: reworded.

p 8861, l 2: explain, in how far the NO3- could also be influenced by temperature effects, changing the gas-particle partitioning of nitrate. Authors' response: As described in the experimental section, event and corresponding non-event samples were collected at daytime during the same week. Meteorological data show, on average, no significant differences in temperature between event sampling periods and non event sampling periods. Those differences and, thus, temperature effects can not, in any case, account for the large differences found in the NO3- concentrations between event and non-event aerosols.

p 8862, l 5: "resemble any other H-NMR spectra collected so far" Authors' response: corrected

p 8863, l 8: clarify what is meant by "background signals" Authors' response: the meaning of background signals has been clarified.

p 8863, l 8: "in contrast" and "n-e070403" Authors' response: corrected.

p 8863, l 29: "n-e070403" Authors' response: corrected.

p 8864, l 12: "in contrast" Authors' response: corrected.

p 8864, l 12: "Hyytiälä" Authors' response: corrected.

ACPD

5, S4571–S4576, 2005

p 8865, l 21: "never" - never within the one month of measurements Authors' response: not corrected. The meaning of the sentence is more general and not confined to the only results of this field campaign. The authors state that, under HNMR analysis, the occurrence of aldehydic functional groups in atmospheric aerosol samples has never been observed.

Figure 7: green bar should be yellow Authors' response: corrected.

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