Atmos. Chem. Phys. Discuss., 8, S11973–S11977, 2009
www.atmos-chem-phys-discuss.net/8/S11973/2009/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Applying the CPCB setup to study the hygroscopicity and composition of freshly-formed 2–9 nm particles in boreal forest" *by* I. Riipinen et al.

I. Riipinen et al.

Received and published: 1 April 2009

We thank Dr. Hov for his constructive comments which we think will help to improve the manuscript. Our detailed answers to the comments are as follows:

General comments:

The study of the chemical composition of the freshly-formed nano-particles is indirect except that direct comparisons are made with the growth of pure sulphate/ammonium-sulphate particles. Organic vapours are inferred to play a role in the growth of the nano-particles under supersaturation, but as far as I can see the arguments in favour of the role of organics are indirect and are not based on chemical analysis.

Particles even as small as about 10 nm can be analysed with current mass spectrometric techniques, but unfortunately currently only indirect methods are available to infer anything about the composition of atmospheric particles as small as 2-4 nm. This is due to the very small mass of these particles, which makes their direct chemical analysis extremely challenging. The main focus of this study is on the very smallest, 2-4 nm, particles, the 7-9 nm results shown mainly for comparison and validation of the method. Although our results are indirect and subject to a significant uncertainty, we think that being the first of their kind, they do contain novel information on the properties of the vapours participating in the very first steps of atmospheric particle formation. It can be said, at least, that even the smallest particles seem to be less hydrophilic than ammonium sulphate would be - suggesting that something else in participating the early growth processes. The most plausible candidates for this "something else" are organic vapours, since they are known to be present in the boreal forest boundary layer and likely to be less hydrophilic than sulphates.

[...] As the [particle formation] process is swift (much seems to happen within a (small) fraction of a day) one would think that the exact location of the sampling inlets relative to the land surface and its vegetation, to the surrounding trees and to anthropogenic emission sources in the vicinity, can have a rather strong influence on what is actually observed.

Although the data shown in this study is based on a point measurement in the boreal forest boundary layer, we are rather confident that the new particle formation events that we observe are taking place / have similar features over a horizontal scale of typically hundreds of kilometers (see e.g. Hussein et al., 2009). This argument is based on 1) similar observations at different locations; 2) a nucleation mode growing homogeneously for hours in each of these locations, suggesting that in homogeneous air masses, also the nucleation and growth processes happen in a similar manner (see e.g. Dal Maso et al., 2005 for a review of eight years of nucleation and growth data from Hyytiala). We do, of course, see also the effect of more local particle sources in

ACPD

8, S11973–S11977, 2009

the size distribution data. The focus of this paper, however, is on the regional-scale particle formation events.

One would further think that the nano-particle formation speed could be quite different depending on the height in the surface layer or in the canopy at which the instrument inlets are located. The description of the immediate surroundings of the instrumentation could be helpful; or an argument that it is not so important if that is the case. In fact, in my view Figure 1 would be more helpful if it actually showed a physical sketch of the instrumentation and its location at the site and including where real flows of samples take place, rather than the current diagram. How certain are the authors that inlet lines do not modify the nano-particle spectrum?

It is true that the particle formation rates might vary as a function of height. Unfortunately measurements on the vertical distributions of particle formation are still quite scarce. Hot air balloon measurements by Laakso et al. (2007) indicate, however, that at least the particle concentrations seem to be quite well-mixed throughout the boundary layer during particle formation events. In-situ particle size measurements on an airplane by O'Dowd et al. (2008) show a similar homogeneous distribution of particles between 3-6 nm inside the mixed layer. Extensive descriptions of the SMEAR II measurement site and its surroundings can already be found in literature (e.g. Hari and Kulmala, 2005), so we think that it is beyond the scope of this study. However, as also suggested by the other referee, we will add a short description of the inlets used in this study to the revised manuscript. However, we tried to minimize this effect of losses by comparing the ratio of the concentrations shown by the two CPCs instead of looking at absolute numbers.

The treatment of uncertainty in the observed quantities is largely qualitative and where numbers are given for uncertainty, they are more relevant for specific aspects of the analytical process rather for its totality. It would have been helpful to know more about the integrated or accumulated uncertainties in the numbers given eg in Figures 4, 6 and 7. There seems to be a fair change in the detection efficiencies of the individual

ACPD

8, S11973–S11977, 2009

CPCs during the experiment (Figures 2 and 3), what is the implication of this for the concentrations indicated?

We agree that a more quantitative error analysis would be desirable (see also our answers to Dr. Birmili's comments), and we will add estimates on the effect of the uncertainty related to the CPC detection efficiencies and the possible errors in the size distributions measured by the DMPS and the NAIS. Particularly in the case of NAIS, however, this is very challenging since no real reference instrument for neutral particles is available. We also think that the main uncertainty in the results is actually related to the atmospheric variability and the assumptions made on the activation phenomena taking place inside the CPCs. Unfortunately this uncertainty is very difficult to assess quantitatively, as practically no reference measurements exist.

On e.g. pp 12 and 13 it is not easy for a generalist to understand when the text describes processes and mechanisms that modify the nano-particle number concentration inside the instruments, and when the text refers to ambient air. It could also be helpful if the text in the various sections is segmented more clearly into paragraphs that address the same topic, with appropriate sub headings.

We will clarify these points in the revised manuscript.

Specific comments:

line 6 from below p. 3: "preceding papers"; do the authors mean the papers by Zhang et al and Smith et al and not the paper by Allan et al? Reformulate: "The two first papers"..

We will reformulate as suggested.

line 6 from top of p. 5: "decrease the", is it meant "improve the"?

We would prefer formulating the sentence as it is (or as "improve the detection efficiency"), as decreasing detection limit would practically mean improving detection efficiencies.

ACPD

8, S11973–S11977, 2009

line 13 from top of p. 5: "this data assess", is it meant "this data to assess"?

We will clarify the sentence.

line below eq. 1 on p. 9: "nucleated inside" should be "nucleated aerosol inside"?

Yes, we will modify the revised manuscript accordingly.

line 1 top of p. 14: "modelled sulphuric acid concentrations". It would be helpful with an explanatory sentence or two on what this means.

The "modeled sulphuric acid concentrations" refer to a steady state modeling approach introduced by Boy et al. (2005) to predict ambient sulphuric acid concentrations, based mainly on ambient SO2 concentration, UVB radiation and condensation sink (CS) values. We will clarify the sentence in the revised version of the manuscript.

References:

Dal Maso, M. et al. (2005), Boreal Environ. Res., 10, 323-336.

Hari, P. and Kulmala, M. (2005), Boreal Environ. Res., 10, 315-322.

Hussein, T. et al. (2009), Atmos. Chem. Phys. Discuss., 9, 135-173.

Laakso, L. et al. (2007), Boreal Environ. Res., 12, 279-294.

O'Dowd, C. D. et al. (2008), Atmos. Chem. Phys. Discuss., 8, 2821-2848.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 14893, 2008.

ACPD

8, S11973–S11977, 2009

Interactive Comment