

Interactive comment on “Non-volatile residuals of newly formed atmospheric particles in the boreal forest” *by* M. Ehn et al.

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The authors would like to thank the referees for their comments on the manuscript. Our responses to both referees can be found below. Referee comments in *italics* and author responses in **bold** font.

Anonymous Referee 1

General comments

The article deals with atmospheric measurements of sub-micrometer aerosol size distribution preceded or not by a 280 C heating system, for the study of the volatility of newly formed particles in the boreal atmosphere. New particle formation in the boreal forest has been extensively studied for many years. However, although the technique is not new, and similar measurements have been published from data collected in another

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rural environment, this volatility measurements give additional inputs in our knowledge of nucleation in this area by focusing on ultrafine particles.

This study lies within the scope of ACP.

Generally the paper is well written, easy to understand and well structured. However, I have a few general remarks that should be addressed before the paper can be published: Only six nucleation events have been explicitly studied, although three months of measurements are apparently available. It is not really clear how representative these dates are, relative to the whole of the nucleation events occurring at the site (which I believe are much more numerous). Are the studied dates typical of clean Northern air masses advection over the area? I would expect different condensing vapour during the growth of nucleating particle, whether the air masses studied are clean or polluted. The six cases seem to have, from the volatility point of view, similar features. Is it also the case with other basic parameters?

Firstly, the instrument was set up on 18 March, and removed 18 May, so in truth there were only two months of measurements and not three. This is mentioned in the “results” and “conclusions” sections.

The first step in event analysis in Hyytiälä is to classify days into either event or non-event days, based on the DMPS size distribution plots. Further, the event days are classified into different groups. During the measurement period, 39 days were classified as event days. 19 of these days were characterized as days when a growth rate could be calculated for the new mode of particles. The above mentioned classification is done based on one-day data, and is only stated here as a reference.

In our study, we needed to extend our analysis also to the following day to allow the mode to grow large enough to be seen also after the heating. We only used events where the mode could be followed over 10 hours. This clearly reduces the number of available days, and may partially bias the analysis, since shorter

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events might, for example, more often be related to polluted periods, whereas longer might more often happen in clean air masses. But since this kind of volatility analysis can only be done on longer lasting events, we can only use a small part of the days. We added a paragraph on possible biasing resulting from this selection into the “discussions” section.

There are currently plans to try to determine if events in Hyytiälä can be divided into different categories based on different parameters. For example the above mentioned “clean” and “polluted” events, but this work is still in future. In our study, trajectory analysis shows that the six studied days were characterized by northerly, westerly or north-westerly air masses. Based on this, and other indicators such as gases, the studied days were relatively clean. These basic parameters from SMEAR II can be very easily and quickly checked by anyone, thanks to the online service Smart-SMEAR (<http://www.atm.helsinki.fi/junninen/>).

The non volatile core of the particles is observed to grow with time during nucleation events (and with the size of the selected particles, because the size of the selected particles is growing with time). Have any tests been conducted relating the size of a particle and the time needed for its volatile fraction to evaporate in the author’s oven? In my mind, it is possible that the non-core apparent growth is simply due to a longer time needed for a larger mass fraction to evaporate.

This kind of testing has not been directly performed in the laboratory for the heating tube. But based on the comparison measurements with the Leipzig thermodenuder in the urban background air in Helsinki, both systems showed similar evaporation of large particles. For example, 400 nm particles evaporated into 300 nm particles after heating. In our study we only look at particles <60 nm, so these particles should evaporate very quickly in the heating tube since the masses involved are over 100 times smaller. The residence time in the heating tube was about 0.25 seconds, which for example is the same as used by Sakurai et al. 2003 (Atmos. Env. 37, 1199-1210)

The only “quality insurance” given by the authors is the comparison between their set-up and the “Leipzig thermodenuder”. It is difficult for the reader to be convinced of the quality of the set-up without having read the technical description of this other device in another paper. Hence it would be very helpful to have the essential information about this device presented here (i.e., residence time in the oven, evaporation efficiency as a function of size, what characteristics of the desorption section?..).

Some small additions were made to the text, but we do not feel that the technical descriptions of the system need to be quoted in this paper, since readers interested in the technical part of the paper can easily read the full, detailed description in the cited article (Wehner, 2002). The evaporation efficiency would also be a function of flow rate and temperature, and providing any numbers for all this would mean a long addition to the text.

Specific comments Abstract One main implication cited in the abstract: “newly formed particles, ..., are unlikely to consist of sulphuric acid, ammonium sulphate, and water alone”, has not been mentioned in the rest of the article. This affirmation should be mentioned or discussed somewhere if it is emphasised in the abstract.

This statement was indeed missing from the text, and was added.

2. Measurements I would suggest to move the 4.1. “Losses of sampled particles in the heating tube” in this section, because the rest of the efficiencies of the set up are discussed here. Figure 1 gives the penetration efficiency of particles in the oven at 280 C as a function of size. How was this calibration test performed (what was the nature of the particles, for example, maybe the electrometer mentioned on the figure legend should be mentioned in the text)?

This subsection was moved to section 2, as it probably fits better there. Also some more information on the measurements was added. The calibration was performed with silver particles generated with a furnace.

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4.3. *Aerosol number concentration* I understand from this section that the total number concentration of heated and nonheated particles are compared between the SMPS in the “V” mode and the DMPS. I can understand this when looking at Figure 3 where, on the night of Julian day 85, the total concentration of the VSMPS is higher (almost by a factor 2!) than the concentration of the ambient SMPS, which does not allow any calculation of the volatile fraction. In this context, I do not think it is of any relevance to discuss the difference 90

The reason for the factor-of-2 difference can be seen from figure 2. The peak of the mode of particles is roughly around 80 nm, which means that the ambient SMPS will only see the lower end of it. After volatilization, however, the mode is around 20-30 nm, and thus almost all of the particles will be detected by the heated SMPS. This is therefore not related to the measurement accuracy, but to the size range of ambient particles.

The non-volatile fractions are not calculated from the concentrations, but from the relative positions of the peaks in the DMPS and the heated SMPS spectra. The ambient SMPS data is only used for comparison of the placements of the modes between the SMPS system and the DMPS. If the DMPS and the ambient SMPS agree, then it is fair to assume that the non-volatile fractions can be calculated by comparing the heated SMPS and the DMPS.

5. *Discussion* Last paragraph of the section (lines 8 to 14 of p. 10414) would fit better to section 4.3. Technical corrections Page 10414, “from 3 to 40 nm” instead of “from 3-40 nm”

These changes were made.

Anonymous Referee 2

General comments Suitable for ACP. The paper presents interesting findings concerning the volatility of particles formed in the boreal forest. The findings provide an in-

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interesting comparison to similar work for particles formed in for example the marine boundary layer and the free troposphere.

Specific comments 10413-20 The observed variation in the ratio of the non-volatile residue to original size with temperature might be simply a result of changing relative humidity and consequent influence of hygroscopic growth on the unheated particles? Was relative humidity measured in the aerosol and sheath air entering the system when measuring the ambient particle size distribution? This question should be discussed in the paper.

Both the DMPS and SMPS measured the dry particle size distributions, and therefore changes in the ambient RH would not affect the results. As the ambient temperature was clearly below the temperature of the measurement cottage, the sample was dried already due to the heating. The sheath flows of all DMA:s contained silica gel driers to ensure complete drying. It was added to the text that also the SMPS measures the dry size distribution.

10407-15 Given that the extent of evaporation or decomposition for a given material will be dependant on the residence time in the thermodenuder, an indication of the residence time in the heating section should be given. Since the intention is to remove ammonium sulphate from the aerosol it would be helpful if the system was tested on laboratory generated ammonium sulphate aerosol at similar particle sizes using the same thermodenuder flowrate in order to verify that complete volatilisation occurs.

Most of these comments were answered above. Further testing, including a similar test to the one suggested, is planned in the future.

10407-20 The observation that the size distributions for urban background aerosol downstream of the comparison thermodenuder agreed to within 10

This analysis was not done in the same way as the calculations in this paper where we compared the peaks of a distinct mode before and after heating. In

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the Helsinki-comparison, we studied the total size distributions before and after heating. Then we compared the concentration in each size bin measured after heating by the heating tube and the Leipzig thermodenuder. These concentrations were within 10% of each other.

The degree of volatilization would be a function of particle size, and not very easy to calculate. A rough estimate is that the non-volatile diameter fractions were between 0.3 and 0.6.

Technical corrections typing errors, etc.. The graphs / figures 2, 3, 4, 5 have dates and date ranges above them. These numerical ranges should be labelled as dates or explained in the caption.

The date format was changed to be consistent with the rest of the paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 10403, 2006.

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