

Interactive comment on “Hygroscopic properties of ultrafine aerosol particles in the boreal forest: diurnal variation, solubility and the influence of sulfuric acid” by M. Ehn et al.

M. Ehn et al.

Received and published: 4 January 2007

We wish to thank the referees for both their scientific and technical comments. We have made most of the changes suggested, and feel that they have made the paper more clear and understandable. Detailed responses can be found below.

Response to the comments of referee 2:

It would be good to quantify your statements by citing a few numbers on your observations.

Correlation coefficient values for the GF/sulfuric acid conc. will be added to the abstract, as well as GF-values for the diurnal behavior. As the soluble fraction

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is a somewhat “artificial” quantity due to the many assumptions used in our calculations, only the major decreasing trend is important, and therefore no values will be cited in the abstract.

Page 9938, line 8: Are gases hygroscopic?

This is mostly a question of formulation. The gases might not be hygroscopic, but e.g. sulfuric acid is a hygroscopic substance, and it is found in the gas phase. In any case, we will re-phrase the sentences.

Page 9938, line 18: “during early morning” depending on what - only time for a constant size? Or depending on size?

This may indeed have been a bit confusing, and the formulation will be changed to clarify that the diurnal variation was observed for all the measured sizes independently.

Page 9938, line 19: “of condensable vapors” or on condensation processes in general taking place at night time and at day time!

We are not completely sure what “condensation processes” exactly refers to here, but the formulation was not very good, and will be changed.

Mention, that the understanding of nucleation processes is a basic issue in aerosol science independent on our focus quantifying the impact of particles on climate.

Page 9939, line 18: “high” and “low”, please give growth numbers for certain sizes and certain RHs

Please tell in general, where the systems were placed during the measurement period - air conditioned room? Also, a more detailed description about RH uncertainty during the measurement is expected.

Page 9940, line 18: “experience electrical charging” - I would rather say, they are brought into a well known equilibrium charge distribution.

Page 9941, line 1: *What was the temperature range outside, what was the temperature range inside? Please specify your conditions a bit more detailed since they are important for the operation for HTDMAs!*

The additions and changes have been made.

Page 9941, line 4: *This is the case for most species. Nobody is sure about some extraordinary species. But, in general, TDMA's are limited to what they can!*

It is true, that for example some surface coatings can influence the time it takes for a particle to reach equilibrium with surrounding water vapor. The small particles we have studied are less likely to have a thick enough surface coating to really delay this equilibrium by a significantly long time.

Page 9941, line 18: *E711; temperature of the water: Does it not depend on pressure and temperature of water outside and pressure and temperature of water vapor inside the tubing? You control one of these parameters.*

As the other parameters stay fairly constant, we can control the RH by controlling the temperature. The formulation will be changed to clarify this.

In general, you should clarify, why you use ammonium sulfate for the model. You should be able to support your decision by the data from the mass spectrometer. There could also be some good reason to use sulfuric acid or ammonium bisulfate for your calculations - at least for the smaller particles. How have no changes within air masses be monitored?

Our aim was to use a simple, size-independent model to investigate the change in hygroscopicity of the newly formed particles. This will be added to the paper. As ammonium sulfate is the most commonly used soluble compound in these kinds of studies, and since has been found to be the most common inorganic salt in aerosol particles in Hyytiälä, we chose to use it. However, our findings would be the same even if the particles contained no ammonium sulfate at all.

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Page 9943, line 8: Which system are you talking about! Specify HTDMA!

This has been added.

Page 9944, line 8: From my calculations this is about nearly 2

Yes, it indeed gives about 1.6%. The mistake was in the temperature value, which should have been 0.2 degrees, and not 0.3. This will be corrected.

Page 9944, line 10: I guess, you are talking about particle soluble volume fractions.

Basically, we are referring to the soluble mass fractions (although this will be very close to the volume fraction as well). This will be clarified in the paper.

Please discuss your results with respect to possible uncertainties. Also, this part is missing a discussion of other inorganic species that could alter the hygroscopic behavior of particles in dependence of size and time. For example, think of the presence of nitrate during daytime and nighttime. These discussions could strengthen some of your findings and assumptions.

The amount of nitrate in the particles is fairly small in Hyytiälä. A recent study concluded that ammonium sulfate made up 95% of the ions in the fine particle regime. Nitrate will partition into the aerosol phase more at lower temperatures (i.e. nighttime), but since the sample is heated to room temperature both day and night, before it is sampled in the HTDMA, the effect on the diurnal variation is believed to be small.

Page 9946, line 19: Here, better give a relative increase in terms of percent, when you have discussed uncertainties in percent at an earlier stage.

The uncertainties in RH have been expressed in %, but the uncertainty in GF was given as ± 0.05 .

Page 9950, line 14: Excuse me, but I cannot find this tendency. Please show it for some events by giving numbers for different cases.

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The 4 days which are mentioned in the text are the only ones that start with soluble fractions below 0.6, and are also the only days when the mode could be followed above 30 nm (they all reached 40+ nm). Further, during 3 of these days the modes can be followed 6 hours longer than any other days. We feel that all this can be seen in Fig. 8.

Page 9950, line 16: My guess is, this is because the model assuming ammonium sulfate fits better for larger particles. At 10 nm in diameter you may have sulfuric acid particles. With respect to sulfuric acid in the model, you would come up with smaller values in soluble volume fractions, but your tendencies in changes would lead to the same conclusions.

Whatever substance we would have chosen, the soluble fraction would have been highest for 10 nm. As mentioned earlier, we will clarify that the use of the soluble fraction is only for comparison between different sized particles.

Page 9951, line 10: I guess, you mean the soluble mass flux.

Page 9951, line 13: You mean there may be additional organic compounds causing the growth, but how many species could be involved in this process is fairly well unknown.

Page 9951, line 17: ... in concentration of condensable gases ...

Page 9952, line 6: Here, better give a relative growth in percent or say from ... to

Page 9952, line 9: For clearness, repeat once more, which pattern you mean.

Please use expressions at all times the same way. Say hygroscopic growth factor and never growth factor. So, you never will exchange formation growth rates and hygroscopic growth. I would encourage the authors to check the whole manuscript for used times. Please write in past or in presence.

Page 9939, line 1: better: ... in the atmosphere

Page 9941, line 13: better: ... chemical composition

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Page 9941, line 16: better: ... the sample flow is conducted

Page 9941, line 21: better: ... the RH in the sheath flow

Page 9941, line 24: better: In the excess flow line ... is operated.

Page 9942, line 11: better: ... particle number size distribution

Page 9942, line 18: better: ... in dry particle size

Page 9943, line 13: This is not a complete sentence.

Page 9943, line 15: better: ... were inverted

Page 9943, line 16: better: ... transfer function

Page 9946, line 6: better: ... presenting instead of containing

Page 9949, line 3: better: ... growth factors

Page 9949, line 4: better: ... values were

Page 9951, line 9: better: ... this contribution accounted on average for ...

All the above additions and changes have been made

Page 9945, line 2, 5, 22, 25: better: ... soluble volume fraction

Page 9950, line 4, 8, 10, 12 16, 17, 19, 23, 26, 28: better: ... soluble volume fraction

Page 9951, line 15: better: ... soluble volume fraction

Page 9952, line 7, 8, 9, 10: better: ... soluble volume fraction

Page 9956, Table 1 caption: better: ... soluble volume fraction

Page 9964, Figure 8 caption: better: ... soluble volume fraction

Page 9965, Figure 9 caption: better: ... soluble volume fraction

It will be clarified in the text that the soluble fraction refers to the soluble mass

fraction.

Response to the comments of referee 2:

(1) I am concerned about a possible systematic error associated with the method of drying particles within the first DMA. On page 9940, line 24, the authors state that the water in the particles evaporates very quickly once they enter the DMA. I doubt that this is so. Water will certainly evaporate quickly once the particles enter dry air, but when they first enter the DMA they are still surrounded by moist air. They only encounter dry air after they are transported some distance radially in the DMA. Furthermore, because of the diffusion of water vapor, the transition to dry air will not be sharp. So the particles will be changing size as they pass through the DMA and the average particle size, determined by the DMA voltage, will be somewhat greater than the size of the dry particles exiting the DMA. This would cause the growth factors to be systematically somewhat small. One might hope that the effect is not significant, but the authors provide no evidence of that.

If this systematic error were always the same, it would not be of much concern since it would have no effect on the major results of the paper. But variations in the RH of the aerosol flow could lead to variations in the magnitude of this effect. I am especially concerned that this might produce a diurnal variation as the humidity increases under the nocturnal inversion and decreases during boundary layer growth. That would directly impact one of the most interesting results: the diurnal variation in growth factor. The authors might have the data needed to address this point. Figure 1 shows a humidity sensor on the excess air output of DMA1. How constant were those readings? Did they show a diurnal variation? Of course, any variation in sample air humidity would be greatly damped at that point.

The temperature range outside during the measurement period fluctuated between -7 and +16 degrees. The dewpoint temperature was measured at the SMEAR station nearby, and the maximum dewpoint was +9 degrees, and at this

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time the temperature inside the measurement cottage was close to +25. We calculated the RH based on this, and concluded that the maximum sample flow RH entering DMA1 was 40%, but normally the values were around 20%. The DMA1 excess flow RH was between 8 and 14% during the first 10 days, and after that always below 10%. Based on this data, we can be fairly certain the particles had dried sufficiently before and in DMA1. Any small difference in dry size would in any case not influence our major results, since the dewpoint temperature did not have any clear diurnal variation.

An addition clarifying this will be added to the text.

(2) Although the authors state that the sheath air in DMA1 was dried, they do not give the range of RH values. This data is essential to assess whether drying was complete.

The values will be added to the text.

(3) With respect to equation 2 (page 9944), I think there now is quite a bit of data showing that the organic component of atmospheric particles does pick up water. This should at least be acknowledged since it would alter the calculated soluble fractions. It would not alter the major conclusions, which are based on trends in the soluble fraction.

It will be added to the text, that the soluble fractions should not be viewed as absolute numbers, but rather as values comparable between each other. We have to make a lot of assumptions to get a value for the soluble fraction, and if we want a simple two-component model, the clearest way to do it is to assume a soluble and a non-soluble part. Assuming a two-component model with soluble and a slightly soluble material would mean that we never could explain a GF of 1.0.

(4) A frustrating shortcoming in the paper is the lack of any error estimates.

The error in GF was estimated to ± 0.05 . We decided that inserting a constant error in every figure would only make them harder to understand. However, the

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variance in GF from day to day could be fairly large, but again, adding these to the plots would have taken a lot of attention away from the main findings.

Are the differences in growth factors discussed on page 9948, lines 3-12, actually significant?

This text refers to figure 5. Each plot is a mean of 9-15 two-day periods, and we would of course wish for a much longer data set when doing an analysis like this, but we were limited to what we had. The lower GF:s preceding event-days can be seen for both days and has been seen also in previous studies. So if this data set is enough to see this feature, then it is fair to assume that also other features can be distinguished.

Although the scatter in figure 8 gives some idea of uncertainty, error bars would be helpful in figure 9. On page 9950, line 10, the authors refer to soluble fractions greater than 1. Are they really greater than 1, or just near 1 with some scatter? The latter seems more likely to me.

The value 1 is not of significance when viewing the soluble fractions here, since it is an artificial quantity. If the new particles contained much sulfuric acid, they would have a GF in excess of that of ammonium sulfate, and therefore we would get a soluble fraction higher than 1. This may be the case here, or some of the other assumptions we have made might give rise to a soluble fraction above 1. Or it might just be scatter in the data, as suggested by the referee.

(5) Are the trends in Figure 6 statistically significant? Are the correlation coefficients R , or RL^2 ?

They are R , and the trends are statistically significant ($p < .00002$ for all sizes). This will be added into the text.

(1) The first three sentences of the abstract would be appropriate for an introduction, or perhaps a conference abstract, but they don't belong in the abstract to a paper.

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(2) *The size range of sampled particles should be given in the abstract.*

These changes have been made.

(3) *In figures 24, I found the top panels illegible when viewed on screen. The black and white printed versions were actually much more readable. I don't know if this a problem is somehow specific to my computer. But Figure 7 is fine.*

Perhaps this is due to the usage of the letter ä in the headings. On all the computers I have checked it on, everything seems fine.

(4) *In discussing Figure 8, the text refers to specific particle sizes but not to the deviations from the mode. So in the figure, different symbols should be used for the former with the different colors for the later. Then the text could be followed with printed black and white figures.*

(5) *Different symbols should be used in Figure 9 so that they may be distinguished when printed in black and white.*

In figure 8, the different symbols are of less importance than the different sizes, as the former can be fairly well deduced from the figure even without the different symbols. As ACPD/ACP allow the use of colored pictures, our aim is to make use of this and different colorings are the easiest way to distinguish between plots in a figure. Most of the other pictures would need to be changed as well, to make them clear also in black and white.

(6) *Page 9945, lines 20-22. It would be helpful to the reader to say explicitly that the purpose is to ensure that the samples are near the mode maximum.*

To be added.

(7) *Page 9950, line 8. "The large variations ...". This caused me some confusion since all sizes seem to have similar variations. Also, it is not clear if the variations referred to are the trends during each day or the differences from one day to another (I think it is*

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the latter).

The variations indeed referred to the variations between different days. This will be clarified in the text.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 9937, 2006.

ACPD

6, S5931–S5941, 2007

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