

Interactive comment on “ Seasonal variation of CCN concentrations and aerosol activation properties in boreal forest” by S.-L. Sihto et al.

S.-L. Sihto et al.

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We thank the reviewer for valuable comments and feel that the paper improved significantly.

Both reviewer 2 and 3 pointed out that the methodology and description of (κ)Köhler theory was on one hand too detailed concerning methods and simplifications that were not used in the paper, and on the other hand not detailed enough concerning the D_{crit} calculation from the HTDMA data. Both also pointed out inaccuracies in the method description. Section 3 (Theoretical framework) was almost completely rewritten to provide a more clarified picture of the methods that were actually used, leaving

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the other theory to the relevant citations.

The other comments are answered point-by-point in the text below. The referee comments are presented in boldface whereas the replies are as normal text.

Anonymous Referee 2

The authors present cloud condensation nucleus counter (CCNC) data from one year of measurement. The CCN data is combined with size distribution data to calculate corresponding “critical diameters”, d-critical, the diameter above which all particles activate at a specific supersaturation assuming an internally mixed aerosol. This critical diameter is compared to critical diameters calculated from H-TDMA data, and the methods derive similar d-critical. The authors also investigate the effect of nucleation of CCN number concentration as well as the fraction of activated particles. The paper presents much needed long term CCNC data, and is generally well written. I recommend this paper to be published. However - some modifications and clarifications are needed, especially regarding the method which at times is hard to follow.

General remarks / questions 1) In 3.1. - Theoretical framework, you state that equation (2) is the “usual” way of presenting the Köhler equation, which I do not fully agree with. There are many different kinds of simplifications and static models, which lead to differences in the formulation. Rissler et al. (2010) very recently published a paper comparing differences between different approaches. I suggest you have a look at this. Overall this chapter is confusing. First you present Köhler theory from a non-ideal point of view, with an activity coefficient. Then you use simplifications from Seinfeld and Pandis to get to equation (3). However, this equation assumes that the particle volume is negligible compared to the water volume, which may not be the case when you have as low kappa values as 0.18 (again, see Rissler et al. 2010). Then you present a salt model and introduce epsilon (with ammonium sulfate) and say that the number of dissoci-

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ating ions is 3 (equation 4), which is correct, but now the solution is suddenly ideal (in reality the van't Hoff factor of ammonium sulfate is around 2). All this is rather confusing, and if I understand it correctly you end up using equation (9) in your paper. If you do not use the equations 1-5 I suggest you skip these equations and instead discuss the assumptions included in the paper from Peters and Kreidenweis (2007). The basic point is that this is an ideal approach assuming that the hygroscopicity of the particles do not change with water activity. I have a few minor comments on this chapter later on, but I suggest that you rewrite this subchapter so that it clear what model assumptions you have actually used.

As indicated earlier, this section was completely rewritten taking into account the referee comments.

2) All through the paper you have made two assumptions that needs further discussion. Firstly the assumption that the aerosol is internally mixed. Although your final result (both approaches give roughly the same d-crit) indicate that the assumption may be reasonable, to me this still sounds like a very big assumption that has to be validated with H-TDMA data. If I interpret fig. 5 correctly, both CCNC and HTDMA data suggest a higher hygroscopicity of the larger particle sizes. There must be plenty of H-TDMA measurements from Hyytiälä that you can use for reference. I recall that Pallas data is mostly internally mixed, and I would not be surprised if it was true also for Hyytiälä, but it needs further discussion in the paper. If the aerosol is externally mixed after all, this indicates that we do not have to bother about external mixture when it comes to estimating CCN concentrations. If it is internally mixed, then it is no big surprise that the methods give the same results. Possible it could then be concluded that an ideal description of the particle hygroscopicity is OK for this type of aerosol. Secondly, in equation (13) you assume that there is no insoluble core. If there is one, it would affect your deduced kappa-org value. This may be related to the

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assumption of internal mixture, but maybe you can also back this up with e.g. PSAP or MAAP data references. As a reader I wonder how big of an error these two assumptions can lead to. Please elaborate on these two points.

Both points are now discussed and clarified in the text. Kammermann et al., 2010 found that assuming an internal mixture did not have a noticeable impact on the estimated CCN number.

Concerning the insoluble cores, black carbon is not a major contributor to the aerosol in Hyytälä, (Carvalho et al. 2006, Saarikoski et al. 2005, O'Dowd, et al. 2000), which is now mentioned in the text. However, the paper does not deduce any kappa-org values, only makes a comparison with previously reported values. The discussion concerning this section was modified, and also discussion of insoluble material was added.

3) As I understand it you have calculated different kappa values for different dry sizes, using the 3rd moment average growth factor values from the HTDMA. Then you use this to calculate the d-crit (HTDMA). But how did you do this? Did you linearly interpolate the kappa between dry sizes to find the d-crit corresponding to a certain supersaturation ratio? Or have I misunderstood this? I think this needs clarification in the method part.

See Remark at the beginning.

4) You say that the critical diameters are in good agreement for the different methods. But I would like to know how big of an effect this has on the CCN concentration. E.g. a difference of 10 nm may not be very important for 1% supersaturation, but for 0.2% (in the middle of the size distribution) it might be more important. Please include this aspect in your discussions.

This is a very difficult task, as the influence of Dcrit on CCN number depends completely on the shape of the size distribution. The largest absolute change in CCN will always come when the aerosol concentrations are the highest, whereas

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the largest relative change occurs when Dcrit is at the upper edge of a sharp mode. However, these changes do not relate to the comparisons in this paper, and therefore we do not think that this type of discussion is warranted.

5) Since you have done AMS measurements at the site before, you may have investigated e.g. O:C ratio of the organics, which would give an indication of the k-value of the organics, or PMF or some similar technique which would further strengthen your results. If you have something like this available I suggest you include this in the text.

This has already been done previously, but was not adequately referenced in the paper. In the paper by Raatikainen et al. (2010), AMS data and hygroscopicity data were compared, and it was found that hygroscopicity of the aerosol particles could be modeled successfully by using constant hygroscopicities for inorganics, OOA1 and OOA2. These modeled values were also used to calculate the kappa-org values used by Jimenez et al. The kappa of OOA1 and OOA2 were 0.20 and 0.00, respectively. This was added to the paper.

6) Regarding the diurnal variation, I would like you to elaborate a little bit, especially on non-event days: Why does the d-crit follow a diurnal pattern, but not the CCN concentration? For non event days the total number of particles would be rather stable, which means that the CCNC concentration should be higher around 15:00. I guess you have dry deposition and coagulation, but still, I do not understand how figures 7 and 8 are connected. As I see it you have three effects on hygroscopicity: 1) Photo-oxidation of the particle. From AMS measurements we know that as the particle hygroscopicity increase with particle age. However, this would not lead to a decrease when the sun sets. 2) Surface-to-bulk partitioning. My guess is that the most volatile stuff follows the temperature cycle of the day, so that the less hygroscopic organics condense during night time (since volatility is connected to hygroscopicity). 3) Down mixing of older particles, related to boundary layer evolution, but if you have an internally mixed aerosol,

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this is not important. Do you have any idea on which of these effects is most important?

All the three factors mentioned by reviewer may contribute to this effect but, with the available measurement data, is very difficult to pinpoint the actual reason for such diurnal connection between the different quantities.

There is also a technical reason for variations being visible in Fig. 9 (Dcrit) but not in Fig. 7 (CCN conc.): the scales are very different, with the Dcrit values zoomed in more. The diurnal variation is perhaps $\pm 5\%$ in Dcrit. This variation does of course not directly translate to a similar variation in CCN concentration, but is likely smaller. And even with a variation of this magnitude, the changes would be hard to see in Fig. 7 due to the larger scales.

7) How do your critical diameters correspond to the Hoppel minimum I your size distribution data? If you have an internally mixed aerosol, the SS corresponding to the Hoppel minimum should roughly correspond to your maximum cloud SS values. Would this give a reasonable result? This discussion is not really needed in the paper, but did you think about this aspect?

This aspect was not considered, but out of the measured supersaturations, 0.2% gives a Dcrit around 110 nm, which is a fairly good estimate of the Hoppel minimum in Hyytiälä. In summer the condensation of organics that causes new particles to grow to CCN sizes also grows the older particles, producing large variability in the position of the Hoppel minimum.

Details Page 28232. In the abstract, I suggest that you mention somewhere that you have assumed an internally mixed aerosol.

Done.

Page 28232 Row 3: “a HTDMA” should be “an HTDMA”.

We chose to write the article in front as though one would pronounce the entire instru-

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ment name and not the abbreviation.

Page 28233 row 29: “how CCN concentrations are affected by...” should be “how are CCN concentrations affected by...”, since you state before that you are listing questions. **Page 28235 row 4:** “correct” should be “corresponding”. **Page 28236 row 20:** “Usually Köhler: : :” should be “Usually the Köhler: : :”, but I think you should reformulate this altogether according to the general remarks. **Page 28237 row 8:** No paranthesis needed around wet. **Page 28237 row 11-13:** This sentence is confusing, what do you mean by expand? And the parenthesis makes the sentence a bit strange, please rephrase this. **P 28238 row 2.”** Note that this diameter is different than the point corresponding to the maximum of the Köhler curve, which is given by Eq 3.” Yes it is, this is the dry diameter and the other is the wet diameter, but they correspond to the same Köhler curve. Could be an idea to make this a bit clearer. I had to think for a bit before I got it.

Done or rewritten.

Page 28239: row 14 ZSR is not needed for this equation as far as I can see. It is only used for multicomponent systems, and you have no such assumptions here.

The statement is that ZSR is used for multicomponent solutions. Naturally, if the system is single componenet then ZSR need not be used.

P. 28240 row 19: “to be larger” should be “to be a larger”

Done.

p. 28240 row 21: ”This might be related to: : :” Please explain, I do not understand why this should lead to larger CCN differences during spring and summer.

We agree. The sentence was deleted.

Page 29242 row 12: “note that the linear scale: : :”. If you think that you have

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relevant changes that are hidden - use another scale. Otherwise you can delete this comment, since as far as I can see it does not really clarify anything.

The comment was deleted.

P 28244 Equation 13. Here you assume that the ZSR rule is applicable, so maybe the ZSR reference should be here instead.

Since we left the previous reference, this is not needed.

Page 28242 row 18: “Fig. 3 does not reveal any clear difference in the critical diameter between new particle formation days and other days.” Maybe not, but even if there were it would hardly be possible to see. I suggest separating nucleation days and other days and make e.g. monthly averages in subplots. Then it would be possible to see. I suggest you either make a more detailed analysis of this or delete the comment.

The comment was deleted.

P. 28244 row 20: “it takes into account the average deviation of aerosol particles.” This sentence is somehow strangely formulated, please rephrase.

This part was rewritten.

P 28245: You refer to AMS data to compare the organic fraction, but I guess this is PM1 data? Again you assume internal mixture, but do you have size resolved AMS measurements that support this? I would expect that there is more organics in the Aitken mode than in the accumulation mode.

This section was rewritten and the different composition of Aitken and accumulation mode aerosol is now discussed in more detail. Fig. 5 also shows that the hygroscopicity of the Aitken mode is typically lower.

P 28245 row 28: “of this and previous study” should be “of this and the previous study”. P 28248 row 1: “smallest” should be “lowest”. P 28248 row 16 “Fig.

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??A1” should be “Fig A1” P 28249 row 16: “smallest” should be “lowest”.

Done.

P 28252 row 27 “By extrapolating the data,..” What do you mean by “extrapolating” in this case?

“Extrapolating” was removed.

P 28262 Table 1: Why you did not compare the times when both the HTDMA and the CCNC were running? This would make it much easier to compare the numbers. Since you do not state data coverage for the different instruments, it is not possible to draw any conclusions from this. I would like a number on the correlation between d-crit from HTDMA and CCNC based on periods when both instruments were running. Also – as it is now, the ratio seems to be season dependent, can you comment on this?

The referee has a good point. Unfortunately, the amount of good simultaneous data points (mainly HTDMA data missing) was quite low in few months that comparing only these points wouldn't be any more representative. Thus, we decided to show both averages from CCNC and HTDMA based on simultaneous data as well as all monthly averages of all available CCNC data.

***) On four places you write out “kappa” instead of using the symbol. Be consistent.**

All instances ok “kappa” were changed to κ .

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