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Atmospheric
Chemistry
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Discussions

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

Anonymous Referee #2

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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 equationn (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 dissociating 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 Petters 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.

2) All through the paper you have made two assumtions 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 hygroscopcicity 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 hygroscopcicity 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 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.

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.

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.

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.

6) Regarding the diurnal variation, I would like you to elaborate a little bit, especially

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

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?

Details

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

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

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.

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.

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

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.

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

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

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.

P. 28244 row 20: “it takes into account the average deviation of aerosol particles..” This

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sentence it somehow strangely formulated, please rephrase.

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.

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. ??A1” should be “Fig A1”

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

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

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?

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

References:

Petters and Kreidenweis: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, ACP, 7, 1961-1971, 2007.

Rissler, J. et al.: An evaluation and comparison of cloud condensation nucleus activity models: Predicting particle critical saturation from growth at subsaturation, JGR, vol 115, D22208, 2010.

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