

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 and the corresponding replies as normal text below each comment.

Anonymous Referee 3

Sihto et al. present a more than one-year data set of cloud condensation nuclei (CCN) measurements recorded at the boreal forest site SMEAR II, Hyytiälä, Finland. They measured total CCN concentrations with a DMT-CCN counter and obtained the activated fractions and the critical dry diameters of activation using parallel particle size distribution measurements. In the paper, the seasonal and diurnal variations of these parameters are investigated. It is also shown that particle nucleation affects the CCN properties of the particles. Moreover, the critical activation diameters are compared with activation diameters calculated from HTDMA measurements using κ -Köhler theory. The paper is well written and structured and I recommend its publication in ACP after the following comments and suggestions for correction and improvement have been addressed.

General remarks: 1. Calibration of the CCN counter For your measurements, you used the DMT-CCN counter, which is a very good instrument to measure CCN concentrations with high time resolution and for a wide range of supersaturations. However, this instrument needs to be calibrated carefully for its supersaturation to provide accurate measurement results (see DMT-CCNC operation manual). In Sect. 2.1 you describe that you indeed calibrated the CCN counter with ammonium sulfate particles but it would be good if you could give more details about it. There are still a few open questions to me: - Were the supersaturations you selected the exact ones that were calibrated or were they obtained from interpolation of a linear calibration line? What is the resulting measurement precision of SS? - Which Köhler model calculations (equations/parameterizations)

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did you use for your calibration? The one that you also describe in Sect. 3.1 or the one in Sect. 3.2? Note, that the Köhler model largely determines the exact relation between the set temperature difference in the CCN counter and the resulting supersaturation. The use of different Köhler models can yield differences in the calibrated supersaturation of up to 20% (Rose et al., 2008). It is therefore necessary that CCN studies always report which Köhler equations and parameterizations are used to ensure that the results can be properly compared.

The calibration was done by selecting temperature difference (DeltaT) corresponding to the factory calibration for supersaturations (SS) 0.1, 0.2, 0.4, 0.6 and 1.0%. After selecting the temperature difference the D50 value was determined by measuring different size of particles size selected using a Hauke-type DMA, by using the CCNC and a reference CPC (TSI 3772). The activated fraction was determined by dividing the CCNC concentration with the CPC concentration. The D50 value was determined by fitting a sigmoidal function to the activated fraction vs. diameter. The SS was determined from the Köhler theory and a linear fit was used for SS as a function of DeltaT. The linear fit was used in the measurement program. The Köhler equation used in the calibrations is the one described in Sect. 3.1.

2. Köhler theory (Sect. 3.1) The Köhler equation you discuss in Sect. 3.1 includes a term that accounts for a possible insoluble core of the solute particle. You should explain the assumptions regarding this term a bit more in detail (e.g. volume additivity). Since you do not address this issue any further in the results section you may want to just leave this term out and use the normal Köhler equation for pure solute particles. Please revise the equations in Sect. 3.1 since some variables are not defined correctly: - Eq. (4): the number of moles of the solute in the droplet is generally defined as $n_s = m_s/M_s$, without a multiplication of vs. - Instead, vs has to be included in Eq. (2): B should be defined as $B = (6 n_s M_w i_s) / (\pi w)$; i_s is the van't Hoff factor with $i_s \approx v_s \varphi_s$; v_s is the stoichiometric dissociation number of the solute and φ_s the osmotic coefficient. - Note, that

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is is not necessary equal to v_s , since $\varphi_s = 1$ only for ideal solutions. E.g. for ammonium sulfate $v_s = 3$, but is is between 2 and 2.5 (e.g., Low, 1969). - I suggest to not define the diameter of the droplet as d_p since this variable is generally reserved for the dry particle diameter, which you also actually use in Fig. 6 ($dN/d\log(d_p)$). I would rather name it “ d_{wet} ” as you do already in Sect. 3.2. In fact, the d_{wet} in Eq. (9) is the same variable as d_p in Eq. (1). In both cases it is the diameter of the dry particle plus the uptaken water, only the amount of water is different.

See Remark at the beginning. All the above comments were taken into account.

3. Comparison between CCN and HTDMA derived activation diameters In Sect. 4.2.2 you compare the critical diameters derived from CCN and HTDMA measurements and show the average values for those data sets in Fig. 5. Instead of plotting only the average values, however, I guess it would be more illustrative to present a correlation plot of all data points, i.e. CCN derived d_{crit} plotted versus HTDMA derived d_{crit} obtained at the same time. Ideally the data points should spread along a 1:1 line and any systematic offset or outlier would be clearly visible.

There is definitely a lot scatter in short term values and the amount of scatter is increasing with increasing supersaturation. Also the deviation from 1:1 line is increasing with increasing super-saturation. However the long term average is always rather close to 1:1 line. Because this is a simple one figure that can be usable for modelers we wanted to present the results this way and let the standard deviation error bars to describe the scatter in the data. Moreover, based on the comments by referee 2, we recalculated the values in Table 1 to better represent times of concurrent CCNC and HTDMA data.

Moreover, I cannot figure out how you obtain the HTDMA data points in Fig. 5. From what you write in Sect. 3.2, I understand that for every HTDMA measurement cycle (a sequence of 5 selected dry diameters) you should get 5 different κ

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values by solving Eq. (11) for κ and applying RH, ddry, ga and T. Then you calculate the dcrit for each of the 5 different κ values by searching the ddry for which Eq. (11) exhibits a maximum. This calculation, however, you have to do 5 times since you want to know the dcrit at 5 different supersaturations (Fig. 5). As far as I understand this would lead to 25 data points (5 kappas times 5 supersaturations). Since you plot only 5 data points in Fig. 5, I assume that you averaged the 5 κ -values you obtained from the 5 dry sizes via Eq. (11). If so, you would have to mention that in the text but in fact I think that averaging the κ would not be good because you lose information.

See Remark at the beginning. The Dcrit was calculated in the way suggested by the reviewer, except for the final step. Dcrit was determined from the kappa corresponding to the dry size which was closest to the Dcrit. In other words, Dcrit at SS = 0.1% and 0.2% was typically calculated from the 110 nm dry size, SS = 0.4% and 0.6% from 75nm, and SS = 1.0% from 50nm.

For this reason I recommend to compare the CCN and HTDMA measurements as follows, similar to what was done by Juranyi et al. (2010). Instead of comparing dcrit I suggest to compare κ . For every measured CCN concentration at a certain SS and particle number size distribution you calculate dcrit via Eq. (7) and κ from Eq. (11) by searching the κ for which Eq. (11) exhibits a maximum when inserting ddry = dcrit(SS) and S = 1 + SS. For every measured HTDMA spectrum at a certain dry size you calculate κ from Eq. (11) by searching the κ for which Eq. (11) exhibits a maximum when inserting ga, S = RH, and ddry. Then you can compare the CCN and HTDMA derived κ with each other. The best agreement you should get for those measurements for which the HTDMA dry size is close to the activation diameter at a certain SS, i.e., for SS = 0.2% and ddry = 110 nm, SS = 0.4% and ddry = 75 nm, and SS = 1.0% and ddry = 50 nm.

Although originally it was not stated clearly, the method we used relied on the last point of the reviewer, that the most correct results are obtained from HTDMA data where the

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dry size is close to Dcrit. The suggested comparison would have been another way to perform the comparison in this paper, but we feel that comparing Dcrit is equally good, and also gives a more concrete result.

4. Hygroscopicity and solubility In your paper, you use the term “soluble” as equivalent for “hygroscopic” (e.g., p. 28244, l. 8; p. 28247, l. 18). This is, however, misleading because the solubility and the hygroscopicity of water-soluble particle compounds are not directly proportional. In fact, compounds with higher solubility can be less hygroscopic and less CCN-active than compounds with lower solubility (e.g., NH_4NO_3 vs. NaCl). Solubility determines the deliquescence relative humidity, whereas the hygroscopic growth factor and the critical supersaturation of CCN activation are primarily governed by the hygroscopicity of the soluble substance.

The terms hygroscopicity and solubility are often used interchangeably, but the reviewer is correct, and as we discuss hygroscopicity throughout the paper, all instances of solubility were exchanged to hygroscopicity.

5. Statistical distribution In your figures and tables you present mostly only mean values. It would be more illustrative if you could add statistical uncertainties (e.g., standard deviations, percentiles). So-called box-and whisker-plots can be a nice tool for visualization.

To keep the figures more clear, we didn't include error bars (or similar) to show the variability, but instead included figures 1 and 3 to show the variation.

6. Panel numbers Please indicate the panel numbers in your figures for better reference in the text.

Done.

Specific remarks: 1. p.28232, l. 8-10: Instead of just writing that you investigated the effect of particle nucleation you should rather formulate the result of this

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investigation in the abstract, namely that particle nucleation indeed affected the diurnal variation of the CCN properties.

It already says in the abstract that “New particle formation was observed to increase the CCN concentrations by 70–110%, depending on the supersaturation level.”

2. p. 28233, l. 29: This should read: “(ii) how are CCN concentrations affected...”.

Done.

3. p. 28234, l. 21: As far as I know the inner wall of the supersaturation column of the CCN counter is covered with a porous alumina bisque liner (cf. DMT- CCNC operation manual) instead of filter paper.

The referee is absolutely correct. Corrected.

4. p. 28234, l. 16: Mention in the experimental section explicitly that you measured total CCN concentrations (not size-resolved). It is not obvious from your experimental section, especially since you also write about the calibration measurements that where of course in a size-resolved mode.

Done.

5. p. 28235, l. 23: I suggest writing the sentence as “Finally the humidified aerosol passes through another DMA and a CPC, which are used as a differential mobility particle sizer (DMPS).”

This was rewritten.

6. p. 28235, l. 25-26: Please mention what the measurement accuracy and precision of the temperature and the resulting RH are.

Uncertainty ranges were added.

7. p. 28236, l. 8-9: Instead of writing for “small” and “bigger” particles you can just give the respective size range.

Done.

8. p. 28241, l. 8-9: This statement is not fully correct. As far as I can see from the plots the activated fraction exhibits large variation for ALL supersaturations. For every supersaturation the maximum in the activated fraction is about twice as high as the minimum value.

The reviewer is correct that the relative variation is similar, but the absolute variations are clearly largest for three highest SS. The reason for this remark is to note that the new particles are also activated at higher SS.

9. p. 28241, l. 12-19: How well does the parameterization in Eq. (12) represent your data set? Is it possible to reproduce the measured CCN concentrations with this parameterization? This might not be the case especially at low supersaturations (e.g., Rose et al., 2010).

The simple parameterization does not work well for the data, in particularly in the lowest supersaturations. We added the following to the discussion:

“However, the parameterized CCN-concentration does not reproduce the measured CCN data and the mismatch is the worst in the lowest supersaturations as the correlation coefficients are 0.34, 0.22, 0.16, 0.08 and 0.02 for SS= 1, 0.6, 0.4, 0.2 and 0.1 %, respectively. Clearly the simple parameterization does not capture the temporal variability of the CCN population and should be applied only at the highest supersaturation and even then with caution.”

10. p. 28242, l. 9-10: Could you please mention here again according to which equation the critical diameters were estimated. 11. p. 28243, l. 5-6: Could you please mention here again according to which equation the critical diameters were estimated. 12. p. 28246, l. 11: This should read “July 2008”. 13. p. 28247, l. 9: Please write “during” instead of “inside”.

Done.

14. p. 28247, l. 13-22: I believe that your measurement results on 20 April are not realistic. Either your CCN or your DMPS measurements (or even both) might be biased probably due to the very low particle concentrations. From the lowest panel in Fig. 6 one can see that d_{crit} reached values as low as 40nm (SS = 0.1%) and 18nm (SS = 1.0%). This would correspond to a κ -value of 20 (!) and 2.4, respectively, which is certainly not possible even for marine air masses. Please verify your measurement data for this day. There might be also other days in your one-year data set with the same feature (e.g., on 23 April), which you should check too.

The referee is correct, we now clearly state that the unrealistically low D_{crit} values were due to incorrect particle counting during this extremely clean period.

15. p. 28247, l. 23 to p. 28248, l. 3: Please compare your results with Wiedensohler et al. (2009) and Kuwata et al. (2008), who also measured CCN properties during nucleation events. They observed also that the nucleation particles can grow very rapidly into the size range that is relevant for CCN activation and that these particles become more hygroscopic with time (only Wiedensohler et al., 2009).

A paragraph was added to the end of section 4.3.1, in which these two investigations are mentioned and briefly compared with our results.

16. p. 28248, l. 18: Something seems to be wrong with the reference of Fig. A1.

17. p. 28250, l. 25-26: I would suggest to write just “... with a minimum in the afternoon” since the minimum not necessarily occurs at 3 pm.

Done.

18. p. 28251, l. 9-12: To get rid of the seasonal variation of d_{crit} , which may affect the diurnal cycles in Fig. 9, you should try plotting the normalized activation diameter instead. The normalized d_{crit} would be each data point divided by its

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respective 2-day average value; a value of one would then represent the 2-day average.

As presented in Table 1, d-crit seems to have seasonal variability. We made an attempt to normalize the d-crit with a respective 2-day average value and made a corresponding figure. However, this treatment did not change the conclusion that the new particle formation was able to produce CCN active particles during the second day after the initial formation. Thus, we decided to keep the original Figure 7.

19. Tab. 1: You do not need to write the footnote since you mention already in the table caption that the values are measured at SS = 0.4%.

Removed.

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