

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

Anonymous Referee #3

Received and published: 9 December 2010

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
C10888

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) 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.

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 ν_s .
- Instead, ν_s has to be included in Eq. (2): B should be defined as $B = (6 n_s M_w i_s)/(\pi \rho_w)$; i_s is the van't Hoff factor with $i_s \approx \nu_s \phi_s$; ν_s is the stoichiometric dissociation number of the solute and ϕ_s the osmotic coefficient.
- Note, that i_s is not necessary equal to ν_s , since $\phi_s = 1$ only for ideal solutions. E.g. for ammonium sulfate $\nu_s = 3$, but i_s 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.

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.

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 values by solving

C10890

Eq. (11) for κ and applying RH, d_{dry} , g_a and T . Then you calculate the d_{crit} for each of the 5 different κ values by searching the d_{dry} for which Eq. (11) exhibits a maximum. This calculation, however, you have to do 5 times since you want to know the d_{crit} 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.

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 d_{crit} I suggest to compare κ . For every measured CCN concentration at a certain SS and particle number size distribution you calculate d_{crit} via Eq. (7) and κ from Eq. (11) by searching the κ for which Eq. (11) exhibits a maximum when inserting $d_{dry} = d_{crit}(SS)$ 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 g_a , $S = RH$, and d_{dry} . 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 $d_{dry} = 110$ nm, $SS = 0.4\%$ and $d_{dry} = 75$ nm, and $SS = 1.0\%$ and $d_{dry} = 50$ nm.

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

C10891

of the soluble substance.

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.

6. Panel numbers

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

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 investigation in the abstract, namely that particle nucleation indeed affected the diurnal variation of the CCN properties.
2. p. 28233, l. 29: This should read: "(ii) how are CCN concentrations affected...".
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.
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 were of course in a size-resolved mode.
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)."

C10892

6. p. 28235, l. 25-26: Please mention what the measurement accuracy and precision of the temperature and the resulting RH are.
7. p. 28236, l. 8-9: Instead of writing for "small" and "bigger" particles you can just give the respective size range.
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.
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).
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".
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 ~ 40 nm ($SS = 0.1\%$) and ~ 18 nm ($SS = 1.0\%$). 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.

C10893

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).
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.
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 respective 2-day average value; a value of one would then represent the 2-day average.
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 $SS = 0.4\%$.

References:

- Juranyi, Z., Gysel, M., Weingartner, E., DeCarlo, P. F., Kammermann, L., and Baltensperger, U.: Measured and modelled cloud condensation nuclei number concentration at the high alpine site Jungfraujoch, *Atmos. Chem. Phys.*, 10, 7891–7906, doi:10.5194/acp-10-7891-2010, 2010.
- Kuwata, M., Kondo, Y., Miyazaki, Y., Komazaki, Y., Kim, J. H., Yum, S. S., Tanimoto, H., and Matsueda, H.: Cloud condensation nuclei activity at Jeju Island, Korea in spring 2005, *Atmos. Chem. Phys.*, 8, 2933–2948, doi:10.5194/acp-8-2933-2008, 2008.
- Low, R. D. H.: A theoretical study of nineteen condensation nuclei, *Journal de Recherches Atmospheriques*, 4, 65–78, 1969.

C10894

Rose, D., Gunthe, S. S., Mikhailov, E., Frank, G. P., Dusek, U., Andreae, M. O., and Pöschl, U.: Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment, *Atmos. Chem. Phys.*, 8, 1153–1179, doi:10.5194/acp-8-1153-2008, 2008.

Rose, D., Nowak, A., Achtert, P., Wiedensohler, A., Hu, M., Shao, M., Zhang, Y., Andreae, M. O., and Pöschl, U.: Cloud condensation nuclei in polluted air and biomass burning smoke near the mega-city Guangzhou, China – Part 1: Size-resolved measurements and implications for the modeling of aerosol particle hygroscopicity and CCN activity, *Atmos. Chem. Phys.*, 10, 3365–3383, doi:10.5194/acp-10-3365-2010, 2010.

Wiedensohler, A., Cheng, Y. F., Nowak, A., Wehner, B., Achtert, P., Berghof, M., Birmili, W., Wu, Z. J., Hu, M., Zhu, T., Takegawa, N., Kita, K., Kondo, Y., Lou, S. R., Hofzumahaus, A., Holland, F., Wahner, A., Gunthe, S. S., Rose, D., Su, H., and Pöschl, U.: Rapid aerosol particle growth and increase of cloud condensation nucleus activity by secondary aerosol formation and condensation: A case study for regional air pollution in northeastern China, *J. Geophys. Res.*, 114, D00G08, doi:10.1029/2008JD010884, 2009.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 10, 28231, 2010.

C10895