

Interactive comment on “Cloud condensation nuclei closure study on summer arctic aerosol” by M. Martin et al.

M. Martin et al.

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First of all, we would like to thank the referees for their helpful comments and remarks. We answer them in detail below and name all the changes made to the manuscript. (Answers are in italic.) Especially, we included results from HTDMA measurements, to strengthen our findings.

Anonymous Referee #1

The paper presents results of a closure study on CCN concentrations measured during ASCOS. It is shown that, for the most part, CCN concentrations were overpredicted at the two highest supersaturations. If I understood correctly,

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there was a several day period when the opposite was true, i.e., CCN concentrations were underpredicted at the two highest supersaturations (233.9 - 238.1). These results are explained by invoking either the existence of small particles that contain insoluble organics or small particles that are more hygroscopic than is assumed. The paper would be more complete if it included relevant data that could add insight to the results. For example, were there multi-stage impactor samples that could be used to assess the composition of the smallest particles? Did the HTDMA measurements extend to < 100 nm to reveal hygroscopicity information about the smallest particles? I understand that further analyses are planned (comparison with the HTDMA data, case studies considering meteorology, etc.) but I think this paper could benefit itself from these type of analysis. In particular, data that would provide further information on the composition and hygroscopicity of the aerosol as a function of diameter would greatly strengthen the paper.

Yes, there is one time period, when the CCN concentrations were underpredicted at the two highest SS. As a possible explanation for this, small particles that were more active during this time were mentioned. The not measured organic fraction is an assumption made for the whole study, as it would lead to overprediction, which was seen during the other days of the study in the highest supersaturations. We also indicate that for smaller particles, the measurement uncertainties increase.

There was a 13-stage low pressure LPI (Dekati Impactor, see <http://dekati.com/cms/>) used during the campaign, which can resolve mass between 25 to 60 nm aerodynamic diameter in the lowest size bin with a time resolution of 6-48 h. However, the organic mass fraction has not been analyzed yet. Thus, it is difficult to determine the hygroscopicity of the particles from the impactor measurements.

We understand the issue raised by the reviewer that the HTDMA data is not used in the closure, and that is wished for. However, we started with this manuscript being a

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closure from chemistry to CCN, in order to combine and check these instruments. The HTDMA data is inverted and available at ASCOS.se. But, to strengthen our findings, we include in the next version submitted to ACP the following:

Average growth factor (GF) distributions for the sizes measured (31 - 263 nm dry mobility diameter) in a new figure (new Figure 4), as also shown below (attached Figure 1).

A discussion on the effects expected from these data - especially showing the relative lack of external mixture. The following text has been included in the discussion section:

"The HTDMA data (from the Lund University unit) is shown in Fig. 4. In general a mono-modal growth factor distribution was observed. The growth factor for accumulation mode particles was measured to 1.6, data corrected to 90.0% relative humidity (RH). The RH accuracy is $\pm 1.2\%$ RH at this RH. The hygroscopicity of pure ammonium sulphate is 1.69 at this RH (at 20°C) and for dry diameter 100 nm). The measured hygroscopicity decreases with decreasing size, and an average growth factor of 1.4 was measured for dry particle diameter 31 nm, indicating an increasing fraction of less hygroscopic material. The average growth factor distributions do not represent the mixing state at a certain time; in general an internal mixture was observed. The external mix seen in Fig. 4, with a less hygroscopic mode at GF 1.0, originates mainly during the time period DoY 243.5 - 246. The two modes were equally important, i.e. an important amount of non-hygroscopic particles, for all sizes, were present during this time period. Thus, most of the time, the assumption for an internally mixture holds for bigger particles, and is less good for smaller particles. This supports the assumption made of having a different, less hygroscopic chemical composition at smaller sizes."

Section 3.5 gives a short overview of the performed HTDMA measurements, the results are also mentioned in the abstract and in the conclusions.

The current work includes using HTDMA data to perform a closure with Kohler theory as well, however, that second paper is in the early stages. It will be presented at the ACP ASCOS special issue, once accepted, which at least serves the two papers to be

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found at the same location.

Abstract, lines 24 - 25: Not sure what is meant here by "this is not unambiguous"

We wanted to express, that closure could be achieved with more than one setting. We changed the sentence to "However, several settings led to closure and ..."

p. 8809, line 11: Do you mean "if they have not grown larger than 1 μm by the time they reach the OPC"?

Yes that is what we meant. The sentence has been changed as suggested.

p. 8815, line 5: omit "exemplarily"

The sentence has been changed accordingly.

Figure 2: What are the red triangles? They don't appear in the legend. Also, what do the dark blue triangles represent? If they are "considered data", why don't they coincide with a specific supersaturation? This figure needs a more descriptive caption.

We are very sorry for this confusion, the graph had a wrong caption, we updated it and the caption should be clear now.

p. 8816, last paragraph: The aerosol was assumed to be internally mixed based, in part, on HTDMA measurements. What was the size range of these measurements? Did they extend to particle sizes < 70 nm, i.e., the size range not measured by the AMS (taking mobility vs. vacuum aerodynamic diameters into account)? If so, is there evidence of a separate organic mode at the smaller sizes as has been previously reported (e.g., Zhang et al., Environ. Sci. Tech., 39, 4938-4952, doi:10.1021/es0485681, 2005)? I am wondering if the lack of closure at the highest supersaturations is due to an externally mixed insoluble organic aerosol or if it was truly an internal mixture?

Concerning the size range and internal mixture of the particles measured by the HT-

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DMA, we refer to our answer above. As stated there, the hygroscopicity decreased with decreasing size, however, no separate organic mode has been seen and the particles at one size were mainly internally mixed. Only during one period at the end of the campaign, a smaller mode has been measured.

p. 8817, lines 14 - 23: Please add more explanation to the difference between an internal mixture with an insoluble core and the assumption by Lohmann and Leck of an activated Aitken mode with a surface active fraction.

The internal mixtures refer to aerosols in which the sulfur-containing gases condensed onto small insoluble organic particles coming from the surface microlayer. The latter are mostly chains or aggregated balls. Lohmann and Leck (2005) modeled CCN concentrations that were measured on a former ship cruise (AOE-96) in the high Arctic. For measurements in the pack ice, they needed to assume particles that are as surface active as nonanoic acid to be able to model the measured concentrations. They therefore assumed an external mixture of nonanoic acid and soluble adipic acid or an internal mixture of the measured substances and nonanoic acid, which was mainly at the surface of the particles.

This information has also been included in the text. The contradiction, mentioned in our results, stems from mainly an overprediction during the ASCOS expedition and an underprediction for the northern-most pack ice stations (approximately 6 days) during the AOE-96 expeditions (Lohmann and Leck, 2005).

Figure 6: It would be helpful to color the data points by supersaturation to illustrate the outliers at the two highest supersaturations.

This graph has been changed as suggested. The number of outliers is similar at the different supersaturations. Outliers for the two highest SS were only more numerous compared to the other SS during DOY 234-238, perhaps pointing to a greater uncertainty and less reliable results during this period.

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p. 8819, first paragraph: It is stated that the period from 233.9 to 238.1 has underpredicted CCN concentrations at the two highest supersaturations which is in conflict with data from other periods. Is there any evidence from the HTDMA data that the smaller particles were more soluble during this period? Can impactor data be used to probe the difference, i.e., by looking at the composition of particles on the smallest stage?

The HTDMA closure, that has recently been conducted, does not show anything unusual for this time period and also the growth factors are similar than on other days. The underprediction might be caused by the pronounced Aitken mode that is seen during this time in the DMPS data (see attached Figure 4), if the measured chemistry for particles > 70 nm is not appropriate for this Aitken mode. Furthermore, as detailed in the answer for referee 3, there are more outliers found for the smallest two SS during this time period than during others, which also points to a larger uncertainty in the closure. This information has been included in the manuscript.

The organic fraction measured by the impactors has not been analyzed yet. The inorganic mass fractions for the lowest bin of the LPI (see above) do not show any unusual behavior.

Anonymous Referee #2

This manuscript presents results of a closure study on CCN measurements conducted during the ASCOS campaign. In their analysis, the authors fitted the experimental measurements using the κ -Köhler theory to constrain values for κ_{org} . Subsequently, the authors used the best fit permutation parameters to derive κ_{tot} during the campaign. The most interesting aspect in this study is that model and measurements could not be brought into agreement for the highest supersaturations, suggesting an increase in the organic fraction composition with decreasing particle size with respect to the average composition measured by an AMS

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instrument. The paper is well written, with plenty of details on the measurements and procedures applied. To my view, this is a high quality study which provides an interesting contribution and deserves being published in ACP. I have however, some concerns, regarding the analysis conducted by the authors to constrain κ_{org} and κ_{tot} and conclusions therein derived, that should be addressed before publication in ACP. Major comments (text between " " are manuscript quotations)

-Assuming that the dissolution behaviour of marine biogenic organics deviates from non-ideality (i.e. $\kappa_{org} = \text{constant}$) variations of κ_{org} between different supersaturations (i.e. particle sizes) in this study could be attributed, as the authors postulate, to an underprediction of the organic composition with respect to the average mass fraction measured by the AMS instrument. Under this hypothesis, it is pertinent to think that the underestimation of the organic fraction in turn leads to underestimations of κ_{org} , thus explaining the decreasing value of κ_{org} required to fit model and measurements for increasing supersaturations. Because of this underestimation, the values of κ_{org} in this study would not be valid to provide a lower estimate for the hygroscopic parameter. It seems difficult to constrain a lower range for κ_{org} from these measurements without information on size-resolved particle composition. For this reason I strongly recommend the authors to state that they found an upper estimate for κ_{org} of 0.2 and that further study is needed to provide a lower estimate for this parameter. Statements in abstract and text that κ_{org} as low as 0.02 is necessary to fit the results and model would not be valid, as this is very likely to be an underestimated value. It is interesting to note that the upper range found for κ_{org} in this study is consistent with the κ_{org} range between 0.073-0.164 found for marine biogenic organics in the CCN closure by Fuentes et al. (2011). A reference to this work would certainly support the findings in this study.

We agree with the referee, that there might be mass missing, as mentioned in the paper, which would then lead to an underprediction of κ_{org} . However, we do not have

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evidence that mass was missing, especially not for the 3 lowest supersaturations investigated. It is a possibility that cannot be proven, but also not been ruled out. Thus, we still think that 0.02 can be seen as a lower limit for κ_{org} , although it is indeed likely, based on our findings, that κ_{org} is higher and as high as 0.2. Furthermore, the lower value of κ_{org} was estimated taking only the three lowest supersaturations into account. Furthermore, if the particles measured show similar behavior than marine aerosol, than missing mass should have the least effect at larger sizes, because the organic mass fraction was shown to increase with decreasing size (e.g. Facchini et al., 2008).

A reference to the results found by Fuentes et al. (2011) has been included.

-Derivation of κ_{tot} using the parameters from a particular permutation (permutation 13) leads to an overprediction and underprediction of the CCN number on different periods of the cruise (page 8819 and Figure 6). This is due to the fact that κ_{tot} needs to be constrained using the extreme values defining the uncertainty range for the fitting parameters (i.e. $\kappa_{org} = 0-0.2$ and density=1-1.6), rather than using a particular permutation case. I strongly recommend the authors to re-analyse this part of their study in this manner, as it will provide adequate upper and lower estimates of κ_{tot} that will be useful for comparison in future field studies.

As suggested by the referee, lower and upper limits of κ_{tot} have been estimated. By reevaluating the data, we found that κ_{tot} has a minimum of 0.33 ± 0.13 (Permutation 13), and a maximum of 0.50 ± 0.11 (Permutation 49), when assuming $\kappa_{org} \leq 0.2$. We included the values of the upper and lower limits in the text, but still keep the results of Permutation 13 as a best fit, as it led to the best closure for the lowest three SS.

-The abstract needs to be more concise and less ambiguous. For instance, the abstract should clearly state that findings in this study are 1) an upper range for κ_{org} of 0.2 and 2) a lack of agreement between measurements and model at high supersaturations which suggests increasing organic mass fractions for

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decreasing particle size. It would be very helpful to include information on the estimates for κ_{tot} and on the average mass organic fraction found with the AMS (i.e. 36%) in the abstract. General statements should be more consistent with the findings. For instance, the abstract should state that the upper range of κ_{org} in this study points at the organic material being from sparingly soluble to effectively insoluble. The uncertainty range for κ_{org} is too large to state that the marine organics are purely insoluble.

The abstract has been rewritten to make it more concise, especially concerning points 1) and 2) mentioned by the referee. However, concerning 2), as there is, from our point of view, no proof that mass is missing but this is just a possible explanation we did not state in the manuscript that this is the definite reason for the overprediction, but mentioned it as a likely explanation. The average organic fraction found by the AMS has been included, as well as the range for κ_{tot} . We changed the sentence about the solubility according to the suggestion from the referee.

-Can the authors provide information of the sensitivity of the CCN number calculation to variations in density and κ_{org} ? Are the calculations more sensitive to κ_{org} than to the density value?

We looked at all runs that were completed, and always compared two runs, where κ_{org} changes by 0.1 (thus from 0-0.1, 0.1-0.2, 0.2-0.3, 0.3-0.4) and all other parameters were the same. We then took the difference in the slopes of CCN_{pred} vs CCN_{meas} of these runs. This gave a mean difference in the slope of the compared fits of 0.10 ± 0.03 for the change in κ_{org} . We then did the same for runs where ρ_{org} changes by 60%, thus from 1.0 g cm^{-3} to 1.6 g cm^{-3} . This gave a similar difference in the slope of the compared fits of 0.10 ± 0.05 , although the relative change is smaller in ρ_{org} than in κ_{org} . Thus, our results are more sensitive to ρ_{org} . However, as κ_{org} was changed throughout the study in total from 0-0.4 and ρ_{org} only from 1.0 g cm^{-3} to 1.6 g cm^{-3} , κ_{org} has in total a larger influence in our study.

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-Page 8814, lines 28-29: "Surface tension of water (0.072 N m^{-1} at the given temperature in the laboratory) was assumed for all calculations." This assumption needs to be better supported. Because the organic matter could suppress the surface tension of aerosol particles, the authors should discuss why they used the surface tension of water for their calculations and how this assumption affected their conclusions. I do agree, however, with the authors that this assumption is valid, since marine organics have been shown to present low surfactancy properties, with reductions of the surface tension from 0.5-5% at the point of activation for compositions similar to those in this study (Fuentes et al., 2011). Indeed, a reduction in the surface tension would also lead to larger deviations between estimations and observations, which also support the authors' assumption.

We added more information about the assumptions made concerning the surface tension and its effects on the conclusions in the manuscript. The following sentences have been added in the text. "Marine organics have been shown before to have only low surfactant properties (Fuentes et al., 2011), which supports this assumption. Furthermore, lowering the surface tension would lead to an even higher overprediction than already found in this study when using the surface tension of water and thus is unlikely."

-Conclusions (8820, line 13). "Assuming an internally mixed aerosol and an insoluble or only slightly soluble organic volume fraction." I recommend replacing "slightly" soluble by the term "sparingly" soluble organic fraction, which is a more common term in the literature to define compounds of limited solubility (Petters and Kreidenweis, 2008). The "slightly soluble" definition may induce to think that it is nearly insoluble matter, while κ_{org} could be as high as 0.2.

The term has been changed accordingly.

-Conclusions (8820, line 18) "One way to explain this is by assuming that the

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smaller particles have a different composition than the larger ones, presumably a nonhygroscopic organic fraction." As stated above, the κ_{org} uncertainty range ($\kappa_{org} < 0.2$) is too large to state that the marine organics are purely non-hygroscopic or purely insoluble. The fact that κ_{org} needs to approach zero to bring measurements and model into agreement in some cases is due to the underestimation of the organic fraction. Rather than stating that the organic matter is non-hygroscopic it is more rigorous to state that it presents low hygroscopicity.

We agree that the κ_{org} uncertainty is too large to say the organics are non-hygroscopic. Thus, the sentence has been changed to "One way to explain this is by assuming that the smaller particles have a different composition than the larger ones, presumably a non-hygroscopic or only less hygroscopic organic fraction." However, as mentioned above, we do not see evidence that the organic fraction must be underestimated, especially for the lower supersaturations.

-(8820, line 23) "This means, that the organic fraction of the aerosols was nearly nonhygroscopic and does thus not contribute to droplet growth." As discussed above, an upper value for κ_{org} of 0.2 is certainly low but not non-hygroscopic, so there should be some contribution to the particle growth. Please, modify text accordingly.

This sentence has been changed to "This means that the organic fraction of the aerosols was non- or less hygroscopic and does not contribute significantly to droplet growth."

-(8820, line 27) κ_{tot} needs to be better constrained using the κ_{org} uncertainty range between 0-0.2 and density between 1-1.6, as described above, rather than using the parameters of a best fit permutation. This part of the conclusions needs to be updated with new upper and lower estimations of κ_{tot} .

The following sentence about the lower and upper limit of κ_{tot} , as described above,

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has been included: "When assuming that $\kappa_{org} \leq 0.2$, κ_{tot} falls in a range between 0.33 ± 0.13 to 0.50 ± 0.11 ."

-The fact that κ_{org} presents a value < 0.2 , and that the droplet surface tension at activation can be assumed equal to pure water, implies that for a given particle size, an increase in the particle organic enrichment would lead to a depression of the CCN activity and hygroscopicity of the particles. I believe this would be a relevant finding, worthy to be included in the abstract and supported with similar conclusions in Leck et al. 2002 and Fuentes et al., 2011 in the discussion section.

We added this point in the abstract ("These results suggest, together with the supposed surface tension of water, that an increase in organic mass fraction in particles of a certain size would lead to a suppression of CCN activity."). This sentence has also been added in the discussion section: "Assuming $\kappa_{org} \leq 0.2$ and assuming the surface tension of water, implies, that an increase in the organic fraction of the particles leads to a suppression of CCN activity for a given particle size. These results agree well with results by Leck et al. (2002), who found for particles measured in the high Arctic a depression in CCN activity compared to pure sulfate or sea salt particles. They concluded that this was probably caused by organics. Furthermore, Fuentes et al. (2011) found a depression in CCN activity of 5-24% in seawater enriched with marine organics compared with unenriched seawater."

Minor comments

Abstract

-"For the two highest measured supersaturations, 0.73 and 0.41%, closure could not be achieved with the investigated settings concerning hygroscopicity and density. The calculated CCN number concentration was always higher than the measured one." The last sentence may lead to confusion because it seems to refer to the whole dataset, i.e., all supersaturations.

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This sentence was changed to: "The calculated CCN number concentration was always higher than the measured one for those two supersaturations."

-"At 0.20, 0.15 and 0.10% supersaturation, the measured CCN number can be represented with different parameters for the hygroscopicity and density of the particles." This sentence is confusing. I guess the authors mean that different combinations of the hygroscopicity parameter and density allowed fitting the model to the experimental measurements?

We mean that "At 0.20, 0.15 and 0.10% supersaturation, closure could be achieved with different combinations of hygroscopic parameters and densities within the uncertainty range of the fit." The sentence has been changed accordingly.

Introduction, results and discussion -Page 8805, lines 4-6 and page 8806, lines 3-4. "However, the hygroscopic properties, the cloud nucleating ability of these biogenic particles, and their source and sink strengths are still not well understood." The authors should also mention that some work has been done to explore the CCN properties and hygroscopic properties of particles enriched with marine biogenic organic matter (e.g. Moore et al., 2008; Fuentes et al., 2011), that shows that marine organics depress the hygroscopicity and CCN nuclei activity of particles.

In this section, we focused on particles over the pack ice, where this work is relevant and where measurements in the open ocean might not be representative. The results found for marine organics have been included in the text in the following way: "However, it has been shown that for marine particles, samples with marine organic matter were less CCN active than pure ammonium sulfate particles (Moore et al, 2008). Furthermore, seawater enriched with organic matter was found to be less CCN active than pure seawater (Fuentes et al., 2011)."

-Page 8815, lines 5-11. I do not think that Figure 2 is necessary since it does

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not provide any additional information with respect to results in Figure 3. In fact, Figure 2 is difficult to interpret, without first knowing about the calculations set presented in Figure 3.

Figure 2 was meant as an example for illustrating how closure was calculated, as starting directly with Figure 3 might be difficult to understand without an example. To clarify this, we added the following sentence: "This figure is shown as an example to illustrate how closure was calculated." and kept Figure 2 in the manuscript.

8814, lines 26-27: How are the cases of insolubility for the organic fraction implemented in the model?

The cases with 20% insoluble mass of the organic fraction were implemented in the following way, using the ZSR mixing rule:

$$\kappa_{tot} = \kappa_{org} \times \epsilon_{org} + \kappa_{sulf} \times \epsilon_{sulf} = \kappa_{org} \times V_{org}/V_{tot} + \kappa_{sulf} \times V_{sulf}/V_{tot}$$

where κ_{tot} is the total κ value of the particle, κ_{org} the κ value of the organic mass fraction, κ_{sulf} the κ value of the sulfate mass fraction, ϵ_{org} the volume fraction of the organic mass fraction, ϵ_{sulf} the volume fraction of the sulfate mass fraction, V_{org} the volume of the organic mass fraction, V_{sulf} the volume of the sulfate mass fraction and V_{tot} the total volume of the particle. Assuming that 20% of the organic mass is insoluble, this leads to:

$$\begin{aligned} \kappa_{tot} &= \kappa_{org,sol} \times \epsilon_{org,sol} + \kappa_{org,insol} \times \epsilon_{org,insol} + \kappa_{sulf} \times \epsilon_{sulf} = \\ &= \kappa_{org,sol} \times (0.8 \times V_{org})/V_{tot} + \kappa_{org,insol} \times (0.2 \times V_{org})/V_{tot} + \kappa_{sulf} \times V_{sulf}/V_{tot} \end{aligned}$$

Where $\kappa_{org,sol}$ is the κ value of the soluble organic mass fraction, $\kappa_{org,insol}$ the κ value of the insoluble organic mass fraction, $\epsilon_{org,sol}$ the volume fraction of the soluble organic mass fraction and $\epsilon_{org,insol}$ the volume fraction of the insoluble organic mass fraction.

Because $\kappa_{org,insol} = 0$ the equation reduces to:

$$\kappa_{tot} = \kappa_{org,sol} \times (0.8 \times V_{org})/V_{tot} + \kappa_{sulf} \times V_{sulf}/V_{tot}$$

-8820, line 21) "Results from counter 1 at 0.10% SS give an upper limit of $\kappa_{org} = 0.2$, since the assumption of a more hygroscopic organic fraction results

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in overpredicted CCN concentrations." What do the authors mean here by "more hygroscopic"? hygroscopicity above 0.2? please, clarify this in the text.

This sentence has been changed to: "Results from counter 1 at 0.10% SS give an upper limit of $\kappa_{org} = 0.2$, since the assumption of an organic fraction with a hygroscopicity > 0.2 results in overpredicted CCN concentrations." **Anonymous Referee #3**

1) The conclusions in the paper strongly depend on a closure concerning CCN number. It is thus very unsatisfactory that the discrepancy between total number from DMPS and CPC number is not discussed further. According to my experience, CPC numbers are much more reliable than integrating DMPS spectra. It would be interesting to see some comparison between CCN number at the highest supersaturation and DMPS number and CPC number, respectively. The maximum ratio $CCN\# : DMPS\#$ and $CCN\# : CPC\#$ should be one. This could give a hint for concluding which number to trust. I would also recommend a sensitivity test, where the DMPS concentration is increased to fit the CPC number.

As the referee points out, this is a point in this manuscript on which the results depend crucially. It is also a point which is not easy to resolve. We chose the DMPS data for several reasons. First, there were instrumental problems with the CPC. Its flow rate was below its corrected value of 1 l min^{-1} throughout the campaign. It was instead around 0.9 l min^{-1} , for which it was corrected, but it was still slightly variable, which introduces an error. Furthermore, the wick needed to be replaced during the cruise, as it was dirty, causing a miscounting for at least one certain time period during the cruise. This might have caused problems as well before we noticed it. On the other hand, the DMPS instrument agreed well with another DMPS instrument that was measuring on board in the same container (see attached Figure 2). It does, however, not fit the smaller sizes well, as the second DMPS (FMI, red curve) was not a twin system and not meant for measuring such small sizes. Furthermore, the integrated concentration of the DMPS used in this study agrees well with an UCPC which measured the total concentration in

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the same tube, located closest after the PM10 inlet, in the same container. (We define "agree well" as approximately $\pm 10\%$.)

We also attach a plot (attached Figure 3) of the ratio CCN/CN_{DMPS} and CCN/CN_{CPC} for the highest supersaturation measured, which was 0.7%. There is only one point in time, where the CCN/CN_{CPC} curve reaches 1, this is around DoY 243. If we look at the size distribution of this day (size distribution of the DMPS for the investigated time period is in attached Figure 4), it can be seen that the particle concentration was very low at this time. The main mode was around 100 nm, where all particles should activate at 0.7% SS, but there were also smaller particles (between 30 to 100 nm) measured. For 0.7% SS, pure ammonium sulfate particles should activate at 37 nm. However, as the AMS also measured organic mass (around 50%), one can assume that the critical diameter was higher during this time. For particles consisting of 50% insoluble organics and 50% ammonium sulfate, they would activate at 44 nm at 0.7% SS. And if one now assumes, as it has been shown before, that for marine particles the insoluble organic fraction increases with decreasing size (Facchini et al., 2008), and that more than 50% of the chemical composition of the smaller particles was organic material, the critical diameter would increase further and at the same time the activated fraction would decrease. Furthermore, the maximum ratio CCN/CN at 0.7% has been shown before in other measurements to be below one, i.e. Jurányi et al. (2010) have a maximum ratio reached in a one month study in Switzerland around 0.9 at 0.7% SS.

Unfortunately, as there were no size resolved measurements of the composition of these small particles at sufficient resolution, it is thus hard to decide if all particles would activate at this SS or if a higher SS would be needed and therefore to conclude, which CN device to trust. For the reasons outlined above, we prefer to base the closure on the DMPS data. We have clarified that in the revised manuscript.

Concerning the sensitivity test, the reviewer probably wants to decrease the DMPS particle number until it fits the CPC concentration, not increase. When fitting all data

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with a LTS fit, the DMPS data would have to be multiplied by 0.84 to fit the CPC concentrations. This would result in the slopes decreasing by approximately 0.15 and would thus mean that a different subset of parameters would explain the observations.

2) The conclusion that the κ value for the organics is close to one is based on the fact that this parameter setting gives smaller error than all others. But, since this parameter setting, that is really in the low hygroscopicity end, does not give a good closure one will have to consider errors or factors not included (see e.g. comment 1 above) that will change the results. When done, why could they not change enough for some of the other parameter settings to fit?

We assume that the reviewer means, that the κ value is close to 0, not 1. Choosing the parameters mentioned in the paper as best results is not based on the fact, that these results give the smallest errors but on the fact that the best closure (the slope of CCN_{pred} vs CCN_{meas} is closest to 1 for the lowest three SS) could be achieved within the error bars. Thus, we disagree that it does not give good closure. Of course, if we would increase the error bars, more results could give closure. But the best result based on our criteria would remain the same. As suggested by Referee 2, we decided to add upper and lower limits for the κ values when assuming that $\kappa_{org} \leq 0.2$.

3) Throughout the paper one is waiting for the results from the H-TDMA data to be used. It is very frustrating to know that these data are available but not used. I understand very well that the group of authors wants to get more than one paper from all the efforts to take the instruments to the high Arctic, but I think that it has to be handled in a better way. Ideally, I would have liked the two papers to be presented side by side as part 1 and part2 on the same subject. A minimum is that it is clearly stated in the introduction, that H-TDMA data are not used.

Some HTDMA results have now been included in the manuscript, as detailed in the answer to Referee 1. Furthermore, more HTDMA results will be presented in a manuscript in the same special edition, and can thus be found in the same place. We would like to

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mention, that it is of course good for researchers to have several papers, but this was not our main objective by not including the data. It has instead been a judgment from scientific as well as organizational (time and manpower) issues to start by presenting the current paper as it is.

Minor comments:

Concerning chemical composition: Wouldn't one expect the aerosol in this area to also contain NaCl? I know that the AMS cannot detect NaCl, but do you have any other analysis to support not including NaCl?

Measurements of the BCI (Berner Cascade Impactors) also carried out during the cruise show only very low NaCl mass, which was the reason for not considering it. In attached Figure 5, the mass of the lowest stages of the BCI (25 to 161 nm) is plotted against the time of the ice drift. If NaCl is present, it is assumed to be mostly in the larger sized particles (250-500 nm), as shown in Bigg and Leck (2001).

The HTDMA measured the largest dry size at 263 nm. The range of growth factors investigated with the HTDMA was set in order to be able to detect sea salt at 90% relative humidity ($GF = 2.3$). But also there only occasionally scans with counts corresponding to NaCl were detected.

P8806 I9: "Closure was achieved" sounds as a conclusion. One could use "Closure was tested".

This sentence has been changed accordingly.

P8808 I 10: "The RH of the sample flow was assumed to ". Was it just assumed or estimated based on temperature increase?

It was assumed based on experience from former expeditions (see Leck et al., 2001). However, measurements of the RH made in the laboratory close to the BCI show that the RH was between 30 to 40% (on the first stage it was $30 \pm 6\%$). As the CCN counters were situated further away from the inlet than the BCI, the RH would have been lower

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than at the BCI. However, it is more accurate to state that the RH was below 40%. This has been changed in the text and the information about the measurements has been included.

P8809 I 12-13: How do you know that there are no smaller droplets?

The CCNC counts particles in several size bins, the lowest bin is from 0.7 to 1 μm . Particles counted in there are not counted as CCN. We checked the CCN number concentrations in this size bin (and also in the next bigger ones), and as there were not many particles in the smallest size bins, we concluded that there were not many smaller particles, which did not grow sufficiently and would lead to an undercounting of CCN. We rewrote this sentence to make it clearer.

P 8810 I3: shouldn't the sheath to flow ratio be described as 13:1 and 10:1? Are the CCN numbers compensated for this flow ratio? Describe how the CCN number was calibrated. Could the numbers of CCN at the highest supersaturations be used to verify the CCNC number detection?

We thank the reviewer for pointing out this mistake, the sheath to flow ratio was 13:1 and 10:1, respectively. This has been changed accordingly in the text. The CCN numbers have been corrected for this flow ratio. The CCN number was not calibrated, but the CCN concentrations of both counters showed good agreement after this correction considering that the two counters were not running on the exact same supersaturation. The supersaturations were calibrated several times during the cruise, as described in the manuscript. Furthermore, filter measurements in the line in front of the CCNCs suggested that the noise of the instruments was as low as 0.2 cm^{-3} .

Unfortunately, as described above, the CCN number concentration at the highest SS cannot be used to verify the CCNC number detection, as smaller particles were always present that did not activate at this SS.

P 8810 I 14 Are the diameters given as vacuum aerodynamic diameters? Please

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specify the diameter measure.

We apologize for the incorrect wording. The diameter was referring to a mixture of geometric and aerodynamic diameters. We changed the wording to "100 nm to 500 nm vacuum aerodynamic diameters." The lower end of the vacuum aerodynamic diameters, 100 nm, converts to a geometric diameter of 67 nm when assuming that the particles have a density of 1.5 g cm^{-3} . This information has also been added in the text.

P 8810 I 14: How should we read that the AMS sample these particles with 100% efficiency? Isn't the AMS sampling efficiency much below 100% and a subject of discussion?

As written above, this was incorrect wording and has been changed to "from 100 nm to 500 nm vacuum aerodynamic diameter with near 100% efficiency." As shown in the graph below (attached Figure 6) from Liu et al. (2007), the CFD model suggests a 100% transmission efficiency for 70-700 nm vacuum aerodynamic diameter, however, the experimental data shows that this is more true for particles with a vacuum aerodynamic diameter between 100-500 nm.

P8811 I 1: This set up is normally not called a tandem DMPS (tandem: two after each other) but rather a Twin DMPS and it has two DMAs in parallel (not in tandem, I 3).

It is a Twin DMPS, the text has been changed.

P 8811 I 6-7: How well do the two DMAs agree in the overlapping channels?

We have double checked the data, and the channels agree within the expected accuracy. Furthermore, as mentioned above, the DMPS agrees well with another DMPS and an UCPC measuring in the same laboratory.

P 8814 I 24-26: Couldn't you get the ammonium to sulphate ratio from the AMS?

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The measured mass was in general very low, the ammonium measured with the AMS was 86% of the time under the detection limit (for details see Chang et al. (2011)), and thus we cannot get the ratio from ammonium to sulphate reliably from the AMS.

P 8815 I 15: The identification and excluding of outliers have to be discussed in more detail. Why are they excluded? Which are the criteria for excluding them? How big a fraction of the data is considered as outliers? Have you tested a regression including the outliers? Would that change the results?

The LTS fit minimizes the number of h smallest residuals, where h is a subset of the total number of points n (here, $h=0.75n$). This is done because then outliers cannot influence the fit. For details of the mathematical descriptions, we refer to Rousseeuw (1984) and an example for the influence of different fitting methods including the LTS fit on climate data can be found in Muhlbauer et al. (2009). Outliers are thus excluded because of a mathematical criteria, when their residual exceeds a certain threshold. The fraction of outliers varies with the supersaturation, and is between 13% to 21% of the total data. The highest fraction is found for 0.7% SS, because during the time, when the closure was underpredicted, there were a lot of outliers identified. During other times, the number of outliers is similar for the different supersaturations.

We did closure runs with simple linear fits, thus with regressions without outliers. This changed the slopes, but not the trend of the results. Higher supersaturations were still more overpredicted than lower supersaturations. However, the LTS fit was chosen because we think the results are more robust and also more relevant this way. A more detailed description on the LTS fit has been included in the manuscript.

P 8819: On line 12 a mean κ value for the whole campaign is given and on line 20, a modeled κ value is presented. How well could these κ values, taken as constant values over the campaign, explain the CCN#?

When looking at the lowest (0.1%) and at the highest (0.7%) supersaturations, a constant κ value of 0.33 as found from the best fit in the closure can represent the

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CCN number concentrations well for the lower SS with a ratio CCN_{pred}/CCN_{meas} of 1.04 ± 0.39 for the entire study. The large standard deviation is caused by the very variable κ value, as mentioned in the manuscript. For the highest SS, we find a significant overprediction with this constant value, with a ratio of 1.37 ± 0.30 . The time series for CCN_{pred}/CCN_{meas} with the constant κ from the closure is shown in attached Figure 7.

The agreement with the κ value from the model is less good for the lowest SS, the ratio CCN_{pred}/CCN_{meas} is then 0.81 ± 0.29 , but closure is still achieved within the standard deviation. The highest SS still gives an overprediction, with a ratio of 1.27 ± 0.28 , but here closure is possible within the uncertainty. The time series of CCN_{pred}/CCN_{meas} with the constant κ from the model is shown in attached Figure 8.

Table A1: An impressive table and an impressive work running all these simulations! It would be interesting to include also the slope of CCN_{pred} vs CCN_{meas} . One could also consider including the size limits for the different supersaturations.

Thanks! The slopes of CCN_{pred} vs CCN_{meas} have been included. We did not include the size limits though, because this made the table very unclear. But it could be included in a supplementary table, if the reviewer thinks it is worthwhile.

In several places a κ value of 0 for the organics is interpreted as the organics being insoluble. Still, there is a difference between parameter settings 13 and 14 where the only difference is that in 13 80 % of the organic is water soluble with κ 0 and 20% is water insoluble and in 14 all the organics is water soluble with $\kappa = 0$. How could this be?

Run 13 and 14 are the same concerning the parameters, and it can also be seen on Figure 3 in the manuscript, that the data points are the same and that only the length of the error bars differ. This difference was caused by a scripting error in calculating the error for the runs including 20% insoluble mass. The graph has been corrected, and we apologize for that mistake.

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We also mentioned the runs that lead to the same parameters in Table A1.

Fig 7. One could look at a closure on the cases dominated by ammonium sulphate (κ 0.61) (that could not be influenced by organics) and see if the closure is better. This could be a way to check the CCN vs DMPS number calibration.

There are only few data points of the closure (CCN_{pred}/CCN_{meas}), when it is dominated by sulphate. There is one time period at the end of the campaign, when there are several closure points dominated by sulphate. However, during this time the mass measured by the AMS was very low, and is thus not very reliable. And the HTDMA data shows a less hygroscopic mode during this time. Thus, the AMS does not seem to give the accurate result here. Furthermore, if organic mass was not measured by the AMS, this would also influence the results and result in an overprediction. Thus, this suggestion can unfortunately not be tested.

Spelling and language errors have also been corrected.

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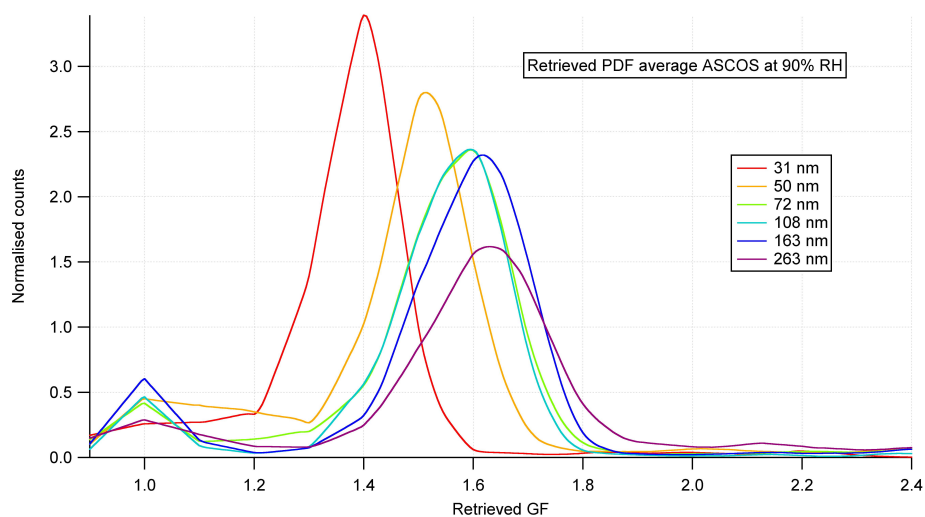


Fig. 1. Average probability density functions for the hygroscopic growth factor (GF, at 90\% relative humidity) during the pack ice drift period. Dry particle diameters investigated are indicated in legend.

C9367

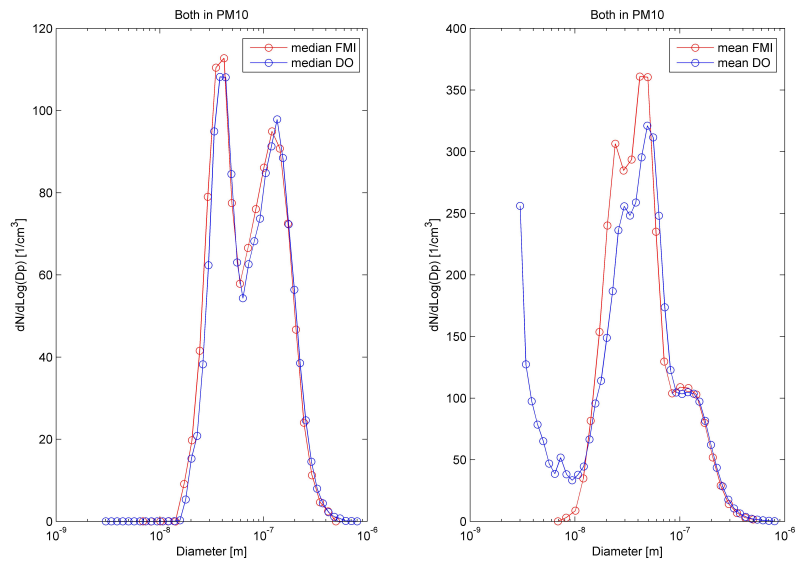


Fig. 2. Median and mean size distribution measurements of both DMPS systems on board ship.

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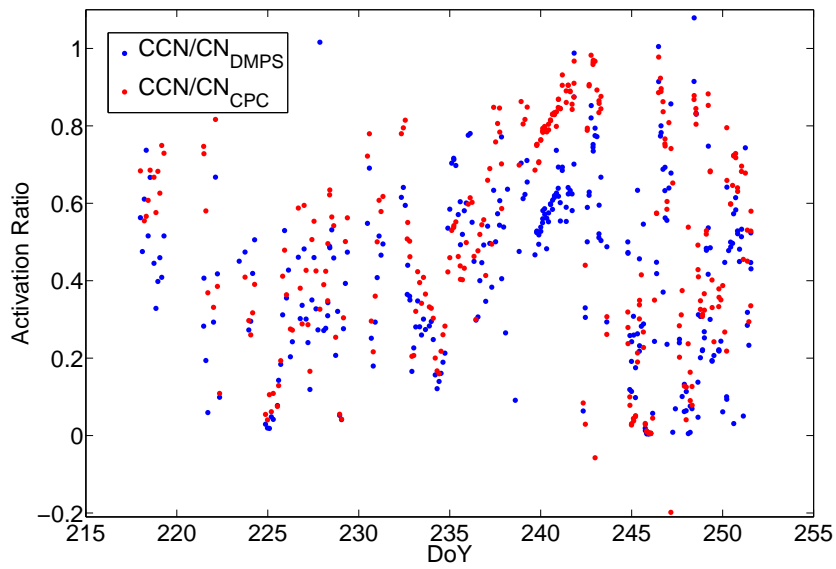


Fig. 3. Time series of CCN/CN for CN measurements made with the DMPS and the CPC, respectively.

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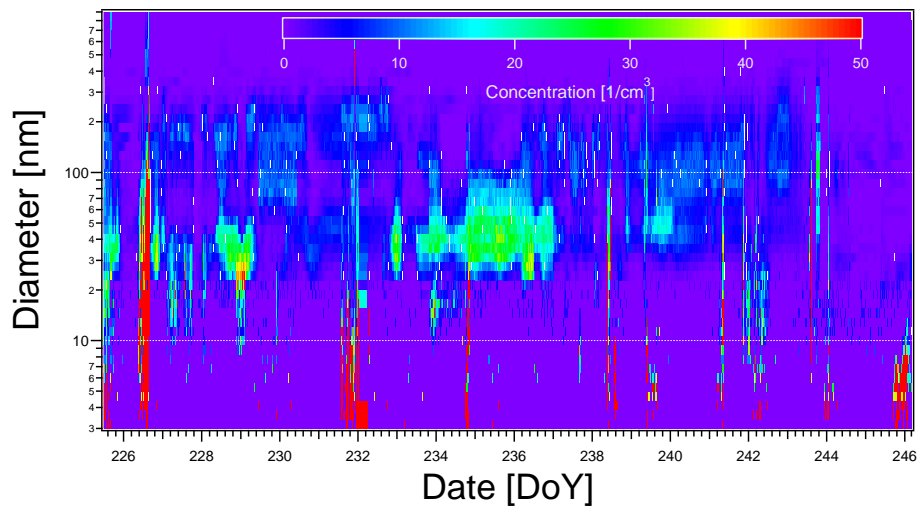


Fig. 4. Time series of the size distribution measured with the DMPS system.

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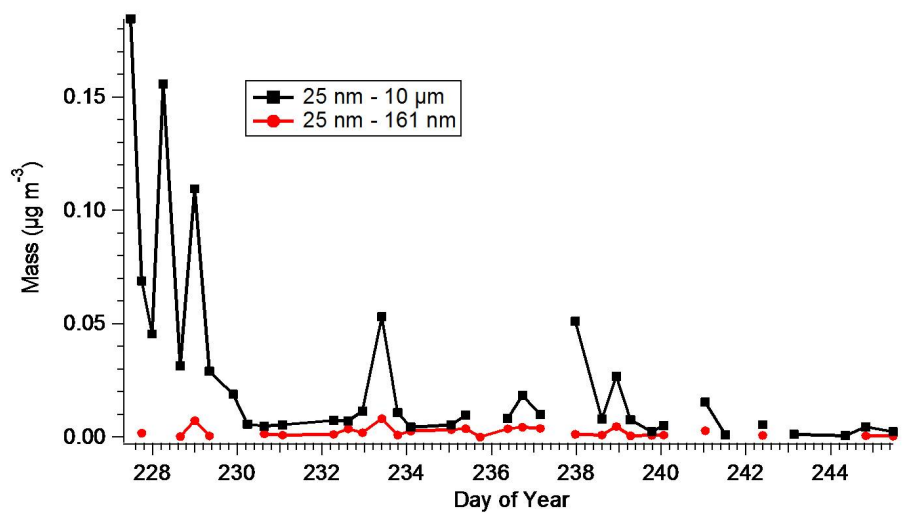


Fig. 5. Time series of the Cl^- measurements made with the Berner Cascade Impactors.

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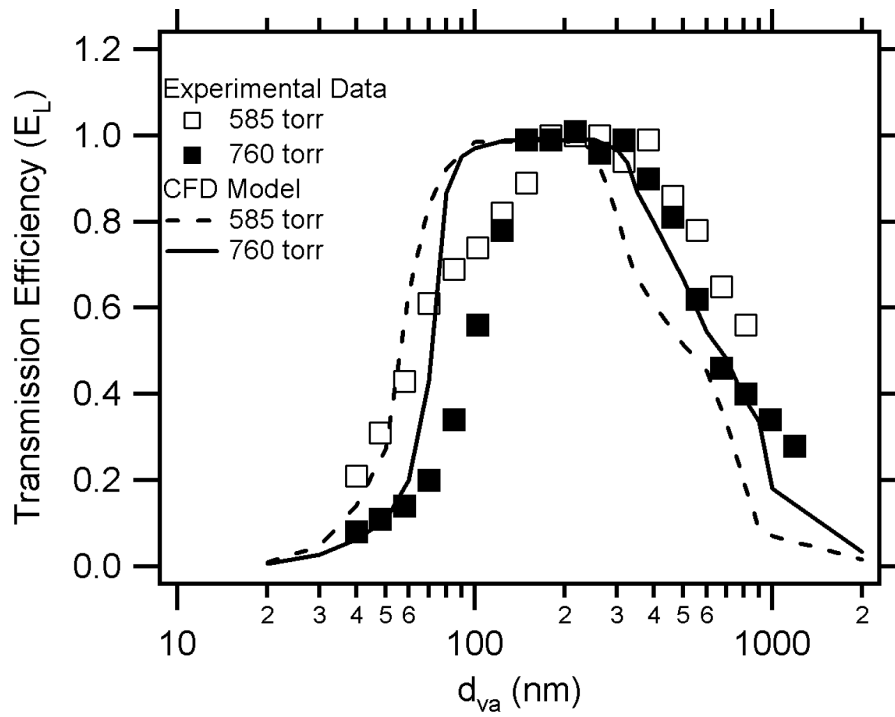


Fig. 6. Transmission efficiency of the AMS (Liu et al., 2007).

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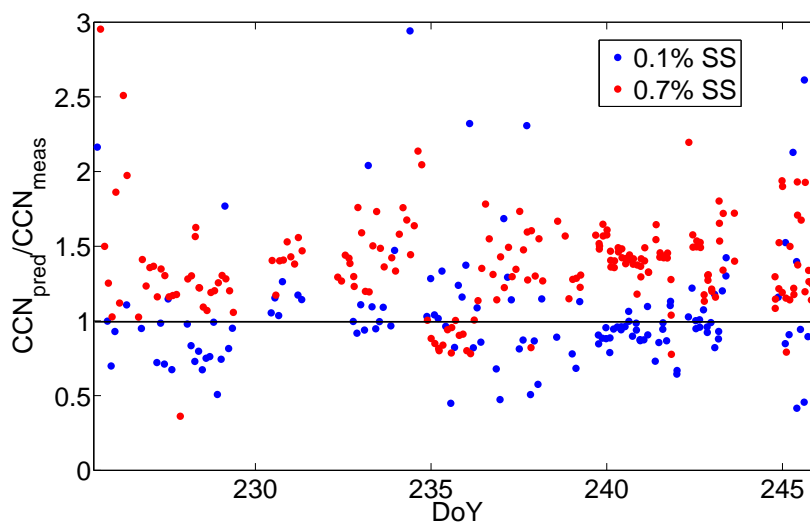


Fig. 7. Time series of CCN_{pred}/CCN_{meas} with the mean constant κ value from Permutation 13.

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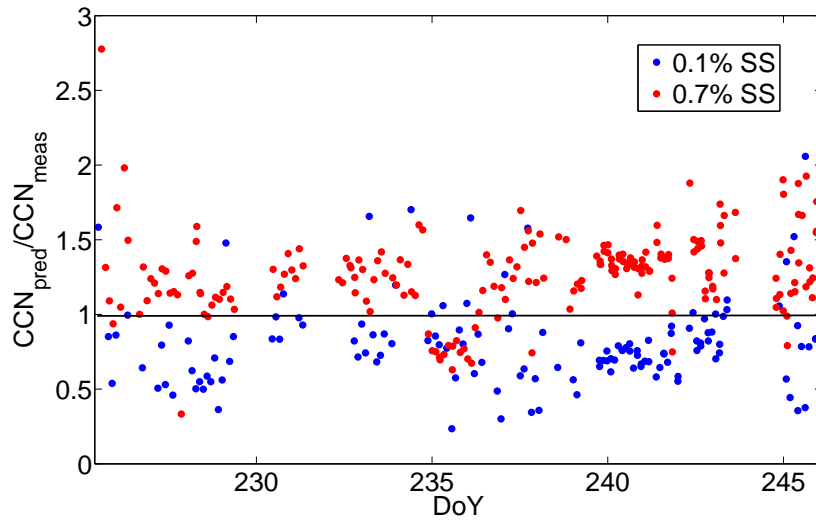


Fig. 8. Time series of CCN_{pred}/CCN_{meas} with the mean constant, modeled κ value.