Review on the Manuscript entitled: "Optimizing CCN predictions through inferred modal aerosol composition – a boreal forest case study"

Aerosol hygroscopicity and CCN activity, both depending on particle size and chemical composition, play a key role in the aerosol indirect climate effects. Aerosol hygroscopicity and CCN activity can be probed by specialized instrumentation, which can also offer size resolved measurements, like for instance the Hygroscopic Tandem Differential Mobility Analyzer (HTDMA) or the Differential Mobility CCN counter (DMA-CCNc). However, such instrumentation is not widely used due to various issues (e.g., bulkiness, purchasing and operating costs). By exploiting the dependence of aerosol hygroscopicity/CCN activity on particle size and chemical composition (both measured at higher spatial resolution), one can in principle overcome this limitation. Aerosol chemical composition and size distribution are also used in atmospheric/climate models for estimating aerosol hygroscopicity/CCN activity and for deriving potential cloud droplet number concentration and cloud dynamics using different parameterization schemes. While particle size distributions are measured and/or modelled nowadays accurately and with adequate resolution, aerosol chemical composition is most commonly measured and/or modelled for the bulk submicron aerosol population. This can reduce the accuracy of the estimated, based on the bulk chemical composition, aerosols hygroscopicity/CCN activity, especially in complex environments where the aerosols exhibit different compositions at different sizes and/or are externally mixed. The latter refers to particles of the same size that exhibit different chemical composition. The identified by many studies discrepancies between the measured hygroscopicity/CCN activity and that estimated based on the aerosol bulk chemical composition was the main motivation of the authors of this manuscript.

In more detail, the authors exploit long-term observations of submicron particles size distributions, bulk chemical compositions and CCN activity conducted at the boreal forest site of SMEAR II (Hyytiälä, Finland) for their study. They investigate the discrepancies between the measured aerosols CCN activity and that estimated from measured particle size distributions and the bulk chemical composition derived aerosol hygroscopicity, expressed by the aerosols hygroscopic parameter κ. In addition, they study the discrepancies between the measured aerosol CCN activity and that estimated by the measured particle size distributions but assuming a time-constant aerosol hygroscopicity, expressed as a constant hygroscopic parameter κ of 0.18. Furthermore, they suggest a method for improving the estimated CCN activity by assigning different chemical compositions (and hygroscopic κ parameters) at different size ranges (i.e., modes). In order to achieve this, they made some assumptions/simplifications, like treating the whole aerosol population as internally mixed (i.e., particles of the same size, share the same chemical composition), assigning similar hygroscopicities to inorganic species and assume that Black Carbon (BC) concentration fraction is the same at all particle sizes. The authors then compare the estimated CCN activities (i.e., derived by each method described above) with those

observed with the CCNc for each season. In addition, based on their improved/optimized closure study, they discuss the possible reasons causing differences in the chemical composition at the different aerosol modes and during the different seasons.

General comments

While size-resolved aerosol hygroscopicity/CCN activity can be probed with adequate instrumentation (HTDMA, DMA-CCNc, Scanning Mobility CCN Analysis; i.e., CCNc coupled to an SMPS; Moore, Nenes and Medina, 2010), this manuscript presents the very important aspect of suggesting a method for deriving modal chemical composition from (bulk) CCN and ACSM measurements. For this reason I suggest its publication in *Atmospheric Chemistry and Physics*, after a minor revision. In more detail, by using adequate instrumentation, like for instance one CCNc downstream a DMA, one can measure the CCN activity spectrum for monodisperse particles residing in Aitken and accumulation modes. Two monodisperse sizes and 5-7 super-saturations would perhaps be adequate for performing these observations. This would result in a more accurate estimation of the aerosol hygroscopic parameter κ at these two modes (i.e., Aitken and accumulation). Adding a neutralizer and a DMA in front of an existing CCNc does not require a major effort and/or cost. In addition, the time resolution of such measurements will be still adequate for studying aerosol CCN activity/hygroscopicity at rural sites and comparable to the one used in this study. However, the authors present a method that associates the modal hygroscopic parameter κ to the modal chemical composition, using bulk chemical composition measurements (i.e., ACSM); something innovative according to my best knowledge. This aspect of their work significantly increases the importance of this manuscript. More specifically:

A) I suggest that the authors emphasize more on this aspect of their work (i.e., deriving the modal chemical composition from CCN activation spectra).
B) The authors should comment (and perhaps describe/mention in the discussion/conclusion sections) if their method for deriving the modal aerosol chemical composition can be used in the case(s) where modal (or even size resolved) hygroscopic parameters κ are available.
C) Their methodology, assumptions/simplifications/limitations should be more clearly described in order to be more understandable by other aerosol scientists and to be easier to replicate in other sites/studies.

Please see more specific comments below.

Specific comments:

1) Abstract (lines 33-35): “Our study demonstrates the potential for utilizing CCN measurements for inferring information on the parts of the aerosol size distribution that are beyond the reach of traditional online composition measurements.”

This sentence needs to be better written in a way to more clearly convey the important message that bulk CCN and (perhaps; see my comment #22) size resolved hygrscopicity/CCN activity together with bulk chemical composition measurements can be used for estimating the modal chemical composition. In addition, the term "traditional online composition measurements" can be replaced by the more accurate "online bulk chemical composition measurements".

2) Introduction (line 57): "N_{CCN} and CDNC are primarily determined by aerosol properties and the drivers of SS_{max} fluctuations…"

Please define the abbreviation SS_{max} prior of its first use in the manuscript. While this abbreviation is well known to aerosol scientists studying aerosol – cloud interactions, the authors should not assume that other aerosol scientists are familiar with this abbreviation.

3) Introduction (lines 96-97): "Importantly, some organic aerosol properties beyond hygroscopicity may enhance the likelihood of an Aitken mode aerosol particle to serve as CCN (Lowe et al., 2019)."

The authors could elaborate a bit more on which properties of Aitken-mode organic aerosols, besides their hygroscopicity, can enhance their CCN activation.

4) Introduction (lines 101-103): "Studies incorporating organic aerosol effects demonstrated significant improvements in closure as compared with attempts considering inorganics alone (e.g., Broekhuizen et al., 2006; Rose et al., 2008; Ervens et al., 2009; Guenther et al., 2009; Bougiatioti et al., 2009; Jurányi et al., 2010)."

To which "organic aerosol effects" are the authors pointing at? Surface tension changes to organic compounds, solubility effects or just to the fact that by omitting the organic component particle hygroscopicity and CCN activity are overestimated? Please be more specific here.

5) Introduction (line 161): "…using a constant hygroscopicity value of 0.18 throughout the study period, as recommended by Sihto 161 et al. (2011)."

Please use the more appropriate term "hygroscopic parameter κ of 0.18".

6) Section 2.1.1 (lines 213 – 214): "However during the winter time more black carbon is also observed (Luoma et al., 2019), which tends to decrease the overall hygroscopicity."

While black carbon it's a known hydrophobic species it would be better to explicitly mention it in the sentence. For example: However, during the winter time the increased contribution of black carbon, which is hydrophobic, in the particles decreases their overall hygroscopicity, or something along these lines.

7) Section 2.1.2 (line 238-239): “For the inverse closure, we used a Python version (Khadir, 2023) of the algorithm by Hussein et al. (2005) to fit two modes into the measured aerosol size distributions”.

   The way that this sentence reads seems quite misleading. The algorithm suggested and described in Hussein et al. (2005) is aimed at performing modal analysis on the particle size distributions measured with scanning mobility particle sizers (SMPSs) and can be applied on other instruments that probe particle size distributions at equivalent size ranges and with adequate resolution. This algorithm is not related to any closure studies between aerosol chemical composition and CCN activity. I understand that the authors used a similar (or perhaps the same) algorithm for performing the modal analysis, which however is only the first step for performing the inverse closure. This sentence needs to be written in a clearer way.

8) Section 2.1.2 (lines 239 – 242): “The algorithm takes size distribution as input and returns the lognormal parameters (number concentration, geometric standard deviation, geometric mean diameter) of different modes as output. While the algorithm would allow fitting up to four modes, bimodal fits (Aitken and accumulation mode, respectively; Fig. S1a) were selected to avoid overfitting.”

   According to my opinion, this part of the procedure should be described in more detail (perhaps in the supplement, before figure S1). When reading it, some questions arise. For example, is the number of fitted modes (e.g., unimodal, bimodal, trimodal) decided by the user (as an input parameter) in the algorithm employed by the authors or is it an automated process? In Hussein et al. (2005) a number of criteria for reducing the number of fitted modes (e.g., from a trimodal to a bimodal fitting) are described. Did the authors use those criteria or they choose the bimodal fittings due to improved Pearson’s *r* correlation in respect to a unimodal fitting? Was the bimodal fitting optimum for all the measured size distributions or there were cases when a unimodal or even a trimodal fitting would be preferable? For instance, during a new particle formation (NPF) event, particles residing in the size range <25 nm would exhibit increased number concentrations, thus making necessary a trimodal fitting (i.e., nucleation, Aitken and accumulation modes) to better describe the measured particle size distribution.

9) Section 2.1.3 (lines 253 – 256): “The CCNc consists of a saturator unit and an Optical Particle Counter (OPC). The saturator includes a vertical flow tube where aerosol samples are introduced alongside filtered sheath air under laminar flow conditions, creating a central flow path. The tube’s inner surface is kept moist to generate a supersaturation gradient.”

   The sentences describing the operating principles of the CCNc can be better and more clearly written. For instance the sheath air flow is saturated at the inlet temperature. A

positive temperature gradient is maintained at the saturator column, inducing a quasi constant supersaturation profile for a specific temperature difference.

10) Section 2.1.4 (lines 278 -280): “An Aerosol Chemical Speciation Monitor (ACSM; Ng et al., 2011) was used to retrieve long-term observations of the non-refractory sub-micron particulate matter (NR-PM1; i.e., organics, sulfate, nitrate, ammonium and chloride) at SMEAR II. “

    This sentence can be written in a clearer way that better describes what the ACSM is measuring. For example, the ACSM measures the mass concentrations of ions originating from non-refractory organic and inorganic atmospheric species. The results are provided as mass concentrations of ammonium, sulfate, nitrate and chloride ions, as well as a total organic mass.

11) Section 2.1.4 (Data Coverage and seasonal classification): This should be section 2.1.5.

12) In the same section (lines 321 - 322): “As mentioned earlier, SOA formation and NPF events lead to higher particle number concentrations during spring and summer.”

    During these observed NPF events did the authors still use a bimodal fitting? Would a trimodal fitting (i.e., including nucleation, Aitken and accumulation modes) be more appropriate during the cases that NPF events were observed (see also my comment #8)? Would a trimodal fitting during NPF events affect the inverted closure (CCN-ACSM) procedure described in the manuscript? The authors should clarify these aspects. In addition, in the case that they have used bimodal fittings for all the measured particle size distributions they should justify that by omitting the nucleation mode during NPF events the inverted closure procedure is not significantly affected. They can add briefly this justification to the manuscript.

13) Section 2.2.2 (lines 390 – 392): “We acknowledge that the assumption that sulfate is present solely as AS can cause underestimations of aerosol hygroscopicity at SMEAR II, because aerosols can be more acidic at the site (e.g., Riva et al., 2019).”

    What do the authors mean by more acidic aerosols? Do they mean that perhaps there are cases that particles may contain ammonium bisulfate or sulfuric acid as well? Please be more specific here. In addition, why did the authors not employed a simplified ion-pairing algorithm, similar to the one described in Gysel et al. (2007)? They could employ this simplified ion-pairing scheme, after calculating the organic nitrate content (as they have already done).

14) Section 2.2.3 (“Inverse closure”): This section can be complemented with additional information (and perhaps equations) in order for the inverse closure procedure to be clearer and easier to reproduce or even being improved. The authors may use the supplement for including the additional information (and perhaps explanatory figures) for this scope, if they want to avoid “overloading” the manuscript.

i) Lines 412 – 413: "This makes κ_{opt} variable in time as well as a function of particle size."

Was κ_{opt} variable as a function of particle size, or two κ_{opt} values were assigned (i.e., one for the Aitken and one for the accumulation modes)? This needs to be clarified.

ii) The equation(s) relating κ_{opt} to the measured CCN activation spectra is missing. The authors in section 2.2.1 provide the generalized equation of the κ-Köhler theory only (see equation 2 in the manuscript). Did they use this equation, during the inverted closure? If yes, what was the value(s) assigned in D_{p},wet ?

iii) In section 2.2.1, equation 3, the authors (correctly) provide the equation for the volume fraction of each species, accounting for the mass and the density of each species. However, in section 2.2.3, they use the bulk density (derived by the bulk chemical composition measurements). While this is perhaps a necessary simplification, I wonder if they could further optimize this aspect. If the system of equations solved for the inverted closure procedure was provided, it would be clearer if this assumption (and potential limitation) is indeed necessary or if two different apparent densities (i.e., one for the particles residing in the Aitken mode and one for those residing in the accumulation mode) could be estimated, further improving the results.

iv) It would be easier for the reader to deeply understand the inverse closure procedure if some explanatory images were added in the supplement. For instance, figure S6 helps a lot in understanding the scaling process of the fitted lognormal distributions. Similar figures could be added below figure S6, showcasing the process step by step (e.g., converting the scaled fitted size distributions to mass distributions and then to fractional volume distributions, which in turn will be used for estimating modal hygroscopic parameters, etc).

15) Section 3.1 (lines 467 – 469) : "The activation diameters decrease with increasing supersaturation and when all seasons are taken into account median D_{act} (see Table S1) being generally higher than reported in earlier studies using similar methodology (e.g., Sihto et al., 2011; Paramonov et al., 2015)."

It is not very clear what the authors refer to as the median D_{act} when all seasons are taken into account. Do they mean the yearly median $D_{act,}$ which is not depicted in Table S1 or that D_{act} for every season is generally higher than that reported in earlier studies? In addition, it would be better to report the median D_{act} from those earlier studies for comparison reasons.

16) Section 3.1 (lines 475 – 476): "While the median activation diameters show almost no seasonality, looking in more detail (see Fig. S4), an increase in the D_{act} is observed during the transition from winter to spring. "

Figure S4 does not depict D_{act} values. Please correct accordingly (figure S3 seems to be the correct one). In addition, the increase in D_{act} is more pronounced for the lower supersaturations (0.1 and 0.2%).

17) Section 3.1 (lines 478 – 481) : "After autumn, there is an increase in D_{act} toward winter, despite a decrease in BVOC emissions and the resulting lower organic mass fraction alongside a higher inorganic fraction (see Fig. S9). This suggests the influence of another factor, possibly the higher eBC fraction observed during winter (see Sect. 3.3)."

    From figure S3 it seems the opposite (i.e., D_{act}) decreasing for the lowest supersaturation (i.e., 0.1%) from November and until April (i.e., last month of autumn and the whole winter). For all the other supersaturations a clear trend for autumn and winter months cannot be seen, with the exception perhaps of 0.5% supersaturation. For the lowest supersaturation (0.1%) the decrease of D_{act} during the winter period is consistent with the lower contribution of the organics, observed during the same period from the bulk chemical composition (figure S9). That said, D_{act} for 0.1% supersaturation is well within the accumulation mode and in the size range where the chemical composition measured by the ACSM should match that of these particles. On the other hand, for the higher supersaturations (0.5 and 1.0%), where D_{act} resides well within the Aitken mode, the differences in the median D_{act} values between autumn and winter do not seem significant to justify a higher contribution of BC in this mode.

18) Section 3.2 (paragraph starting from line 536 ending in line 553): In this paragraph the authors provide some plausible explanations for the discrepancies between the estimated (based on the different closure methods) and measured CCN number concentrations. According to my opinion, they should include in addition some sentences discussing the implication(s) of particles mixing state. In section 2.2.3, the authors correctly point out that for performing the closure studies they had to assume internally mixed particles. However, what would be the effects of sampling externally mixed particles? In addition, the authors could perhaps use the HTDMA measurements (Hämeri et al., 2001; cited in the manuscript; or other more recent HTDMA measurements if available) for qualitatively investigating if the particles residing in the Aitken mode are externally mixed and if yes, if this happens in most of the cases or just in some.

19) Section 4 (lines 641 - 642): "However, all of the applied methods tend to overpredict CCN concentrations to varying degrees."

    A more clear "take home" message can be conveyed to the reader if the authors could be more specific. For instance, they may add some percentages, in order for the reader to better understand the magnitude of the overprediction.

20) Section 4 (lines 657 – 659):" The Aitken mode has the lowest κ values in winter while summer features higher Aitken mode hygroscopicity (lowest accumulation mode κ) possibly due to decreasing BC content which was not accounted for in the calculations."

This sentence can be written in a clearer way. I suggest that the authors should conclude separately for the κ values of the Aitken and of accumulation mode particles, since the reasons for the observed seasonal variability in their hygroscopicities are most probably different, based on the discussion in the previous sections. In addition, if I understood correctly, BC content was accounted during the estimation of the particle hygroscopicities and in the different closure methods. What was not accounted for, was a size-dependent BC content. The authors need to describe this in more clear way.

21) Section 4 (lines 678 – 680): "Our study uses this approach, leveraging routine monitoring instruments to estimate size-dependent composition; with the inverse closure method it takes only a few seconds to determine the composition of Aitken and accumulation mode particles for a given time."

Do the authors refer here to the computation time of the inverse closure method or to the necessary measuring time by the ACSM, CCNc and DMPS? To my understanding, the time resolution of these instruments is in the order of an hour or longer, especially when accounting for the time that the CCNc needs in order to step 5 supersaturations. Considering this, the estimation of size-dependent composition by combining these instruments would take far more than few seconds. The authors should distinguish and more clearly report the necessary time resolution of the measurements from the computational time of their software routine(s).

22) Section 4 (lines 682 – 684): "Moreover, the aerosol particle size distribution should remain relatively stable during a CCN measurement cycle, as the accuracy of predicting CCN spectra is more sensitive to variations in size distribution than to changes in chemical composition (see e.g. Lowe et al., 2016)."

The combination of the instruments described in this work for estimating one data point of size-segregated chemical composition results to time resolution in the order of one hour or more (see my comment above). However, perhaps the same (or similar) instruments with a different mode of operation can be employed for reducing the necessary measuring time. For example, could a Scanning Flow CCN Analysis (SFCA, Moore and Nenes, 2009) or a scanning mobility CCNc Analysis (SMCA, Moore, Nenes and Medina, 2010) be used for significantly reducing the necessary measuring period? Can the above two CCN methods be used with the inverse closure method and software routine(s) developed by the authors?

References:

Gysel, M., Crosier, J., Topping, D. O., Whitehead, J. D., Bower, K. N., Cubison, M. J., Williams, P. I., Flynn, M. J., McFiggans, G. B., and Coe, H.: Closure study between chemical composition and hygroscopic growth of aerosol particles during TORCH2, *Atmos. Chem. Phys*., 7, 6131–6144, 2007

Moore, R. H., & Nenes, A. (2009). Scanning Flow CCN Analysis—A Method for Fast Measurements of CCN Spectra. *Aerosol Science and Technology*, *43*(12), 1192–1207, 2009

Moore, R. H., Nenes, A., & Medina, J. (2010). Scanning Mobility CCN Analysis—A Method for Fast Measurements of Size-Resolved CCN Distributions and Activation Kinetics. *Aerosol Science and Technology*, *44*(10), 861–871, 2010