Atmos. Chem. Phys. Discuss., 8, S8346–S8357, 2008
www.atmos-chem-phys-discuss.net/8/S8346/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "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" *by* D. Rose et al.

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Received and published: 18 October 2008

Monodisperse CCN efficiency spectra and particle number size distributions have been measured near the mega-city Guangzhou. Measurements and data analyses have been conducted with care using state of the art techniques. The observed CCN properties are presented in a suitable form, followed by a sensitivity analysis to various simplifying assumptions for the prediction of total CCN number concentrations. These data and questions are of scientific relevance. However, the discussion of the results does sometimes not correctly reflect the simplifying assumptions of the approaches tested in the sensitivity analyses, not all sensitivity tests have been done in an appropriate way, and some figures are misleading. For the reasons detailed below this manuscript needs substantial improvement to make it suitable for publication in ACP. This review came out very long. However, it hopefully also demonstrates - besides critics - how the authors might get more out of their solid experimental data.

Major comments:

1) Spectral parameters D_t (-> kappa_t), sigma_t describing the "averaged" CCN properties: The observed CCN efficiency spectra showed that a significant fraction of externally mixed, less CCN active particles are sometimes present at larger diameters / higher supersaturations. For this reason the CCN efficiency spectra have been fitted in two ways. A three-parameter error function with spectral parameters D_a (-> kappa_a), sigma_a and MAF_f is used to retain the information on the mixing state. MAF_f gives the number fraction of more CCN active particles and D_a and sigma_a describe their properties. 1-MAF_f gives the number fraction of externally mixed less CCN active particles at diameter ˜D_a. These fit parameters provide relevant information and shall remain in the paper as is. A two-parameter error function (MAF fixed at 1) with spectral parameters D_t (-> kappa_t), sigma_t aims to provide the "average" CCN properties for each investigated supersaturation. However, D_t and sigma_t provide very subjective information without consistent meaning across the investigated supersaturations:

a) The CCN efficiency spectra have been measured to an upper limit diameter of D=270 nm for all investigated supersaturations. Insoluble, wettable particles (kappa=0) need a minimum diameter of ˜ 167, 243, 315, 449, 781 or 3000 nm in order to activate as CCN at supersaturations of 1.27, 0.87, 0.67, 0.47, 0.27, or 0.07%, respectively. This means that the scanned diameter range only covers kappa values down to zero for the highest two supersaturations, whereas at the lower supersaturations the "cut-off" of the

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measurement is always at kappa>0. The supersaturation dependence of this cut-off introduces an inconsistent meaning of the "_t". As a consequence only the 3-parameter fits should be reported for every supersaturation along with the corresponding upper limit kappa value for the observed fraction of less CCN active particles.

b) The diameter values covered with the measurements are irregularly distributed on the CCN efficiency curves. This introduces a diameter dependent weighting in the 2-parameter fit curves, which biases the fit result. Fortunately this doesn"t really matter for the 3-parameter fits, because it describes the shape of the observed spectrum well.

c) CCN efficiency spectra as a function of particle diameter for a given supersaturation, also referred to as D-scans, have been recorded in this study. Unfortunately it is not at all straight forward how to retrieve an "average" critical diameter from a D-scan. Let us assume that a full CCN efficiency spectrum of an externally mixed sample consisting two particle populations with two distinct but well defined critical diameters was available. Such a spectrum could be fitted with a superposition of two error functions centered at the respective critical diameters (D_a1, D_a2) thus also providing the relative number fractions of each mode (MAF_f1, MAF_f2). Corresponding kappa_a1 and kappa_a2 can easily be calculated. Everything straight forward so far. How to determine an "average" critical diameter from D_a1, D_a2, sigma_a1, sigma_a2, MAF_1 and MAF_2 is less clear. Is it to be done in diameter space, kappa space or any other space? Furthermore, the authors correctly state that "kappa_a calculated from the data pairs of S and D_a characterizes the CCN-active particles in the size range around D_a". This means for our hypothetical example that we get to know the properties of the less and the more CCN active particles at two significantly different diameters. Normally the chemical composition is size dependent, particularly for externally mixed aerosols, thus further complicating to find a meaningful definition of an "average" kappa value derived from a D-scan.

For the above reasons the D_t and corresponding kappa_t values derived from D-scans are not meaningful quantities. Reporting them in the paper would be misleading

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and they should not be used for the sensitivity analyses. This does not invalidate the D-scans in general, which are in fact exactly the data type required to make predictions of total CCN number concentrations without introducing simplifying assumptions on the mixing state when number size distribution measurements are available. My suggestion to determine an "average" critical diameter from a D-scans is:

i) Assume a flat size distribution, i.e. dN/dlogDp=const.

ii) Predict a reference total CCN number concentration for this flat size distribution taking the measured CCN efficiency spectrum into account (which still needs to be measured up to a CCN/CN ratio of unity). The influence of the mixing state on the CCN concentration is taken into account with this approach.

iii) Find the "average" critical diameter such that the corresponding predicted CCN concentration for the flat size distribution becomes equal to the value calculated in the previous step.

The ultimate aim of using an "average" critical diameter is to simplify CCN predictions without introducing a bias. The approach outlined here defines the "average" critical diameter such that this goal is fulfilled for a flat size distribution. This definition allows it to further test the sensitivity to assuming internal mixture in CCN predictions (see below).

2) Section 3.3 contains testing and discussion of several simplifying assumptions for the prediction of total CCN number concentrations. Corresponding calculations seem largely okay, except for using D_t values. However, the authors are somewhat negligent when it comes to describing and naming the simplifying assumptions that have been tested:

a) "Measurement results": They authors compare the simplified predictions with the reference case referred to as "measurement results". However, no direct measurement of the total CCN number concentration has been made. The reference case is also a calculated value, which has been obtained without applying any simplification in the prediction. This means that the measured mixing state, the size dependence and the temporal variability of the chemical composition as well as the temporal variability of the number size distribution have been carried through the prediction. I am not questioning the validity of this prediction as a reference case for testing the different simplified prediction approaches but it is not a direct measurement. A very minor caveat is that the measured CCN efficiency spectra are incomplete for the smallest supersaturations.

b) "kappa-Köhler" model with variable kappa: The authors claim that they have tested the sensitivity of CCN predictions to using the "kappa-Köhler" model. However, these predictions/approximations don"t have the "kappa-Köhler" model in them! The only approximation they made in this sensitivity test is that the aerosol is internally mixed, while temporal variability and size dependence of kappa as well as the variability of the size distribution are carried along. Assuming internal mixture is equivalent to using a sharp cut-off diameter for CCN activation, as described on p. 17363, l. 24. The critical cut-off diameter has been determined as follows:

i) Fitting error function to measured CCN efficiency spectrum delivers mean critical diameter.

ii) Kappa value is calculated from critical diameter.

iii) Critical diameter used for integrating the number size distribution is calculated back from the kappa value.

Step iii) reverses step ii) thus being obsolete for this approximation (and removing any trace of kappa from this sensitivity test). Furthermore arguments against using D_t values as cut-off diameters for this sensitivity test have been provided above. Instead the "average" critical diameters as defined in comment 1) can be used to obtain simplified predictions assuming internal mixing.

c) "kappa-Köhler" model using a single constant kappa value for all times and sizes:

Again, this sensitivity test has not much to do with the "kappa-Köhler" model for the reasons listed in the previous point. The simplifications made in this approach beyond assuming internal mixing are ignoring the temporal variability and the size dependence of the chemical composition. It might be a better idea to take these two approximations apart by testing sensitivity to the temporal variability (use supersaturation dependent temporal mean cut-off diameters) in a first step, before averaging out the size dependence in a second step (use kappa space for averaging the properties measured at different supersaturations).

d) "Classical power law": The essence of this sensitivity test is to use a fixed relationship between the supersaturation S and the ratio N_CCN,S/N_CCN,1 (P. 17362, l. 26). This means plenty of approximations regarding chemistry, mixing state, size dependence and number size distribution. The exact approximations of this approach should be mentioned in the manuscript. Fitting a power law curve is just a mathematical aid to describe the relationship easily. Using alternative fit functions would not change the nature of the approximations.

Figure 10 is misleading if not wrong. It makes the performance of this approximation look much worse than it actually is! The measurements are shown as median with error bars extending to the lower and upper quartiles. On the other hand just a single example of the power law curve is shown (calculate with the median value of N_CCN,1. However, N_CCN,1 also exhibits considerable temporal variability. There are two alternatives to solve this issue. Either adding the model curve for the upper and lower quartiles of N_CCN,1 to the existing graph or plotting N_CCN,S/N_CCN,1 against S instead. By the way, there are several different ways how the data can be fitted to obtain N_CCN,1 and k. The authors should described how exactly they performed the fit. It is also worth testing whether different fit approaches deliver significantly different fit results.

e) "Modified power law" models: The essence of this sensitivity test is to use a fixed relationship between the water saturation ratio s and the ratio N_CCN,S/N_CN,30 (P.

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17363, l. 8). Again, the approximations following from this approach are to be mentioned in the manuscript. Actually, it seems that the authors haven"t really made up their mind regarding these approximations. Section 3.3.2 including Figure 11 and Table 1 comes like comparing apples with oranges. The presentation of these results makes the reader believe that the "modified power law" model performs much better for high supersaturations than for lower supersaturations. However, this is not an inherent property of this approximation but a trivial consequence of choosing a very low cut-off diameter for the reference CN concentration (N_CN,30). One simplification included in the this approach is that the ratio N_CN,Dcut/N_CN,30 remains constant in time, where Dcut is the true cut-off diameter for a given supersaturation at a certain time and N_CN,Dcut the integrated CN number concentration Dcut. Dcut varies about 32 and 187 nm for S=1.27% and 0.07%, respectively, due to variability in chemical composition (see Table 2). Temporal variability of the shape of the number size distribution will have a large effect on N_CN,187/N_CN,30 while it will hardly influence N_CN,32/N_CN,30. Therefore it is trivial that the "modified power law" performs best S=1.27% and increasingly inaccurate for decreasing supersaturation (increasing Dcut). This fact needs to be clarified in the paper.

Furthermore, the choice of N_CN,30 as a reference is worth a few extra words. The authors argue that 30 nm is chosen in order to get rid of strong interferences from the nucleation mode, which exhibits a high temporal variability and hardly acts as CCN (too small). - Agreed in so far as a smaller cut would hardly be useful. Choosing a larger reference cut diameter near Dcut at a medium supersaturation might be a better compromise towards best performance at all investigated supersaturations. Optimizing performance for the most frequent atmospheric supersaturations is another possible aim defining a suitable cut diameter. Last but not least the cut diameter may also be chosen to match available experimental data or typical model outputs.

3) The number of figures in this manuscript is rather large. Not all of them are very significant though this is always a subjective judgment. The following changes to the

figures could be considered:

a) Fig. 6 could be removed. Its content can be served in the text and tables.

b) Replace Fig. 9 in favor of a figure showing just number size distributions including statistics. Detailed information on the number size distributions is highly relevant for total CCN number concentrations because size matters a lot as the authors say.

c) The information shown in Figs. 12 and 13 is not very different and Fig. 13 is not too illustrative as is. Showing histograms of N_CCN,S,p/N_CCN,S for all supersaturations might give a clearer result.

Specific comments:

P. 17348, l. 10 and p. 17349, l. 13: How comes that the pressure inside CCNC is higher than ambient pressure?

P. 17349, l. 14-16: Yes, the supersaturation in the CCNC is generated by applying a temperature gradient along its column. This is done by controlling the columns top, middle and bottom temperature. For operational reasons the temperature gradient from the middle to the bottom is a little smaller than the gradient from the top to the middle. To my understanding the relevant temperature gradient (difference) is the gradient from the top to the middle. However, the top-middle and top-bottom temperature differences are linearly dependent - if the CCNC holds the target temperatures reasonably well - and hence it does not really matter whether the calibration curve is determined with respect to the temperature difference between top and middle or top and bottom.

P. 17351, first paragraph: It might be worth emphasizing that the activation curves in Figs. 1, 2, 3 and 6 show data which have already been corrected for multiple charge and DMA smoothing effects, just because similar graphs other publications often show CCN efficiency spectra as measured, i.e. without any correction.

P. 17352, l. 5-7: Again, it might be worth emphasizing that the corrected CCN efficiency spectra were fitted with the error function.

P. 17353, l. 3: "ideal" shape is not a good name. The authors mean: "... most efficiency spectra deviated from the shape of a completely internally mixed aerosol ...".

P. 17353, l. 25-29: It is known from TDMA applications that the effective width of a DMA"s transfer function is typically a few percent wider than the theoretical value. How would this translate into sigma_a? To what extent could it contribute to non-zero sigma_a values for pure ammonium sulphate?

P. 17354, l. 7-9: Kappa is only a parameterization for the relationship between concentration and water activity (Raoult effect). The Köhler curve and associated critical supersaturation values are only obtained by combination of the Raoult effect with the Kelvin effect. Both, kappa and a model for the concentration dependence of the surface tension of the solution are hence needed for determining critical supersaturation. Often surface tension of pure water is assumed due to lack of better knowledge of the actual surface tension. However, this does not mean that kappa is always to be used in combination with surface tension of pure water and hence kappa on its own does not define a critical supersaturation.

P. 17354, l. 12: Mineral dust is another important example an aerosol compound with a kappa value close to zero.

P. 17354, l. 13-14: The kappa value of sodium chloride is of the order of 1.2-1.3 at the point of activation. Sea spray aerosol is of course not pure sodium chloride but a reference supporting the kappa value of sea spray aerosol could be added.

P. 17354, l. 16: Weighting by volume fractions or by mass fractions is not the same if the components have different densities. The correct weighting in the mixing rule for kappa can only be one of them!

P. 17355, l. 8-15: D_50 and kappa_50 values have been included by the authors "for comparison with other studies". Overall there are not too many comparisons of the results of this study with previous studies, none of which is touching "_50" values. Just one example of an earlier study which might be worth being included in this paper are the findings on the influence of the composition of individual particles on cloud droplet activation by Twohey et al. (Environ. Res. Lett. 3, doi: 10.1088/1748-9326/3/4/045002).

P. 17357, l. 7-8: I can"t get the number D=250nm, kappa=0.1 and S=0.07 to match. My back of the envelope calculation suggests that particles with D=250 nm and kappa=0.1 activate at S=0.094%.

P. 17357, l. 6-13: The message of this paragraph is not quite clear to me. Is there any indication of particles which do not activate at the critical supersaturation calculated with the assumption kappa=0 or is the diameter range scanned at lower SS too small to see such particles? In the latter case, an upper limit of the kappa value for those particles which did not activate at the largest selected diameter could be given (depends on the critical supersaturation of course).

P. 17358, l. 7: "CCN-inactive particles" is not a good term. A particle with kappa=0 is still CCN active if it is wettable. Only an upper limit of the kappa value of those particles which did not activate can be given based on the measured diameter range, if my interpretation of the data is correct. (This term is again used on p. 17367, l. 2).

P. 17358, l. 19-24: This paragraph gives the impression that the authors use the measured kappa values to infer chemical composition. This is never unambiguously possible if no supporting chemical information is available because a certain kappa value of a mixed particle can be obtained from different combinations of materials with higher and lower kappa values. The authors must provide supporting chemical information or at least refer to a paper providing this information for this study.

P. 17359, l. 14-18: The flow rate in the CCNC column is an important parameter determining the supersaturation. Did the flow rate drop after July 20 also affect the supersaturation?

P. 17359, l. 19-25: Here it is again unclear whether the statements made on the chemical composition are just speculation or based on experimental facts.

P. 17360, l. 8-21: The "biomass burning event" falls within the period were the CCNC instrument suffered from an artifact due to a flow rate drop. Is the observed change in properties much bigger than the potential effect of the flow rate drop?

P. 17361, l. 23-24: The average CN number concentration is smaller during the period with strong local influence from biomass burning. Wouldn"t one expect a higher CN number concentration if the local emissions add on top of the "background" level? Does this finding imply that the biomass burning event came along with a different "background" air mass, which could have contributed to observed changes in particle properties to some extent?

P. 17358, l. 14-17 and P. 17365, l. 11-12. The kappa values given in the conclusions section do not agree with the kappa values in the discussion section!

P. 17367, l. 6-10: The authors conclude that using a size-independent and constant kappa value allows making fair predictions of the CCN number concentration for this data set, with which I do agree. However, then they recycle the prominent (over-)simplified phrase stating that "size matters more than chemistry". That"s definitely not what they have shown. In contrary, they could show that arbitrary assumptions on the chemistry lead to substantial CCN prediction errors, if they were to calculate CCN predictions with kappa=0 and kappa=1.3 - possible limits for kappa if no chemical information is available at all. The mean value of kappa=0.3 contains already a lot of chemical information. A valid statement might be that the variability of the chemical composition is less important than the variability of the size distribution.

P. 17374, Table 1: The authors have carefully calibrated the CCNC using state of the art techniques. The summary of the calibration results shown in Table 1 is undoubtedly important. Nevertheless it might go into the supplementary material just leaving the statement about deltaS/S in the main text.

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Technical corrections:

P. 17345, l. 9-10: Higher supersaturation corresponds to smaller critical diameter. As a consequence I suggest to write "...diameters were in the range of 200-30 nm.

P. 17355, l. 26: this should read "... CN size distributions ..."

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 17343, 2008.

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