Atmos. Chem. Phys. Discuss., 8, S12600–S12614, 2010
www.atmos-chem-phys-discuss.net/8/S12600/2010/

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.

D. Rose et al.

Received and published: 4 February 2010

We thank Martin Gysel for the very thorough review and constructive suggestions for improvement of our manuscript, which will be implemented upon revision. Detailed responses to the individual comments are given below.

Referee comment 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 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 Dscans are not meaningful quantities. Reporting them in the paper would be misleading 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).

Response

We agree that the exact meaning and precision of the two-parameter fit results are influenced and limited by the number and range of measurement data points, and we intend to clarify this in the revised manuscript. However, we do not agree that the quantities that result from the 2-parameter fitting would be meaningless and misleading.

Mathematically, the two-parameter fit and the calculation of D_t, sigma_t, and kappa_t are well defined, and we are not the only group using this approach. In fact, other recent studies have used only this approach without the complementary alternatives we have presented (e.g., Petters et al., 2009). As specified and illustrated by Gunthe et al. (2009), kappa_t and kappa_a are complementary parameters: kappa_t calculated from D_t is an approximate measure (proxy) for the effective hygroscopicity of mixtures of CCN-active and -inactive particles in the size range around D_t. Accordingly, kappa_t is better suited for comparison with average kappa values calculated from H-TDMA data and for the calculation of CCN number concentrations when CCN-active particles are externally mixed with CCN-inactive particles. On the other hand, kappa_a is better suited for comparison with kappa values predicted from AMS measurements, because kappa_a is not influenced by CCN-inactive particles consisting mostly of insoluble and refractory materials like mineral dust and soot (or biopolymers that tend to char upon heating), which are also not (or less efficiently) detected by AMS. This will also be clarified in the revised manuscript and further illustrated in the following companion paper (Part 2).

We agree that kappa_t would be a better proxy, if it were determined by two-parameter fits to CCN efficiency spectra measured with a large number of regularly spaced data points covering a large enough diameter range so that MAF effectively reaches up to 1. Accordingly, we intend to increase both the number of data points and the diameter measurement range in future studies. Note, however, that improvements on this side have to be balanced against potential deteriorations of time resolution etc. For the PRIDE-PRD2006 campaign the upper limit of particle diameter in the size-resolved CCN measurements was 290 nm. Fortunately, however, the particle number size distribution of atmospheric aerosols generally decreases steeply towards larger diameters, which was also the case during PRIDE-PRD2006. Therefore, the influence of larger particles (which are not reflected by the measurement data) on the CCN number concentration at the investigated supersaturation levels is small. Accordingly, kappa_t as determined in our study is in fact a fairly good proxy for the effective overall hygroscopicity and corresponding CCN activity of the investigated aerosol particle ensembles. This is clearly demonstrated by the good agreement of the observed CCN number concentrations, i.e., the CCN number concentrations directly calculated from the measured CCN efficiency spectra and size distributions, with the CCN number concentrations predicted with kappa_t. In any case, kappa_t is a better proxy for the effective hygroscopicity and corresponding CCN activity of the investigated aerosol particle ensembles than kappa_a (see below). As far as we can see, a better proxy than kappa_t cannot be directly obtained from the measured CCN efficiency spectra and is probably also not necessary for the prediction of CCN number concentrations when taking into account other uncertainties (see also Gunthe et al., 2009 and references therein). This will be further clarified in the revised manuscript.

Following up on your suggestion, we have calculated another parameter, kappa_cut. This parameter corresponds to an apparent cut-off diameter of CCN activation, D_cut, which is the diameter above which the integral CN number concentration equals the observed CCN concentration (N_CCN,S). Unlike D_a and D_t, the determination of D_cut requires knowledge of the CN size distribution and the assumption of a sharp cut-off (corresponding to sigma_t=0). The parameter kappa_cut calculated from the data pairs of S and D_cut characterizes the effective average hygroscopicity of CCN-active particles in the size range above D_cut. Note, that D_cut and kappa_cut can also be determined from the results of integrated CCN concentration measurements of polydisperse aerosols, and may thus be useful for comparison with studies lacking size-resolved CCN data.

kappa_cut is on average ˜15% smaller than kappa_t and ˜30% smaller than kappa_a. With regard to the prediction of CCN number concentrations, kappa_cut yields by definition the same values as observed. Calculation of N_CCN,S,p with kappa_t or kappa_a leads to an average bias of +4% or +14%, respectively.

Referee comment 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.

Response

Indeed we did not directly measure the N_CCN,S values but calculated them from directly measured CCN efficiency spectra and CN size distributions. For clarification we will change the terminology from "measured" to "observed".

Referee comment 2b:

"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 do not 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.

Response

We have used the kappa formalism assuming internally mixed aerosol. It is true that we could have done this prediction with just using D_t (or D_a), but the kappa formalism is much more handy because it is not related to a supersaturation. Also in the next step of prediction (assuming a constant kappa of 0.3), the aim was to reduce the hygroscopicity parameterization to a minimum level. It is thus much easier to work in kappa space because other scientists can compare their results easily with ours. The activation diameters, however, would be only easily comparable if they were measured at the exact same supersaturations.

Referee comment 2c:

"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).

Response

We have used the kappa formalism assuming internally mixed aerosol without temporal variation or size-dependence of the chemical composition. The kappa-Köhler model is used to calculate the respective activation diameters from kappa=0.3 and S.

Referee comment 2d:

"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.

Response

We agree that this approach provides only a mathematical relationship between S and the number concentration of CCN including two constant parameters (N_CCN,1 and k), which are derived for this campaign. This fixed relationship has no physical meaning which means that no assumptions on particle number concentration or chemical composition are included. However, it provides an estimate on the order of magnitude of N_CCN,S, which makes it possible to guess N_CCN,S for this campaign reasonably well (at least for S>=0.27%). We would therefore keep this sensitivity test as a part of this paper.

Referee comment 2d continued:

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 describe how exactly they performed the fit. It is also worth testing whether different fit approaches deliver significantly different fit results.

Response

The fit to the data points (median values) was performed with a standard non-linear least squares algorithm (Origin Software), as will be clarified in the revised manuscript. The power law method is a standard text book and CCN modeling approach (Andreae and Rosenfeld, 2008; Pruppacher and Klett, 1997). Further testing and discussion of this approach would go beyond the scope of our study.

Referee comment 2e:

"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. 17363, l. 8). Again, the approximations following from this approach are to be men-

tioned 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.

Response

The cut point of 30 nm is well-suited and widely used for distinction between nucleation and Aitken mode particles (e.g., Seinfeld and Pandis, 2006; Gunthe et al., 2009). We find it self-evident that the modified power law using NCN,30 fits best for (high) supersaturations where the activation diameter is close to 30 nm. The intention of our power law calculations was to quantify the deviations rather than discussing and emphasizing certain aspects. We also agree and consider it self-evident that different cut point diameters may be useful for different applications (measurement or model supersaturation ranges). We encourage future investigators to select this. Further exploration goes beyond the scope of this study (this paper is anyhow quite long).

Referee comment 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.

Response

We agree and will remove Fig. 6.

Referee comment 3b:

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.

Response

We will remove Fig. 9 and give more information (parameters of a lognormal fitting) on the CN size distribution in the revised version of this manuscript.

Referee comment 3c:

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.

Response

We agree that showing the time series in Fig. 13 is not too illustrative and will remove this figure in the revised version. Detailed information on N_CCN,S,p/N_CCN,S can be also obtained from Fig. 12 and Tab. 3.

Specific Referee comment 1:

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

Response

Thanks for pointing out this inconsistency. We have checked the values and compared them with other instruments measuring pressure during this campaign. It seems that there was an offset in the data we got for the meteorological conditions during the campaign. Also, laboratory tests indicate that the uncertainty of the pressure reading of our CCNC is on the order of +/-5 hPa. Thus the outside pressure value recorded during PRD is within the range of uncertainty of the CCNC pressure gauge. The uncertainty does not affect the CCN measurements, because the CCNC was calibrated in-situ and the pressure data were not used for any calculations.

Specific Referee comment 2:

P. 17349, l. 14-16: Yes, the supersaturation in the CCNC is generated by applying a temperaturegradient 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.

Response

Our instrument version requires the difference between T_1 and T_3 as an input parameter. For more details about the actual temperature profile in the DMT CCNC column see Snider et al. (2010).

Specific Referee comment 3:

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.

Response

We will emphasize that as follows: "Note that all CCN efficiency spectra presented in the figures of this paper show the corrected ones."

Specific Referee comment 4:

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

Response

This has been done already a few lines before (see p. 17351, l.23-24).

Specific Referee comment 5:

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 ...".

Response

We will change this sentence to: "At low supersaturation (S = 0.07-0.27%), however, most CCN efficiency spectra deviated from the ideal shape of a completely internally mixed aerosol and looked like the exemplary spectrum displayed in Fig. 2b, which is characteristic for externally mixed aerosols."

Specific Referee comment 6:

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?

Response

In the revised manuscript we will add this aspect to the already mentioned non-idealities (particle shape effects). A detailed investigation of these effects would go beyond the scope of this paper.

Specific Referee comment 7:

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.

Response

Kappa values derived from CCN measurement data through Köhler model calculations assuming the surface tension of pure water have to be regarded as "effective hygroscopicity parameters"; that account not only for the reduction of water activity by the solute ("effective Raoult parameters") but also for surface tension effects. For more information see Petters and Kreidenweis (2007), Rose et al. (2008), Gunthe et al.

(2009), Mikhailov et al. (2009), Pöschl et al. (2009).

To be continued (Part 2).

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