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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.

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We thank Referee #1 for the review of our manuscript. Detailed responses to the individual comments are given below.

Major Referee comment:

p. 17535, p. 17 ff: I have a serious difficulty to accept the two-parameter fitting (indexed t) and all resulting conclusions. You observe a portion of particles which can be activated and characterized by the CCN efficiency spectra. In addition you observe an

offset of non activated particles, of which you know nothing more than that they are not activated at the given conditions. The latter shifts the 50Or you have to extend the measurement conditions such that you can measure the CCN efficiency spectra of the presently non-activated fraction. The two parameter fit is meaningless and arbitrary since it is not the correct model to describe an external mixture of particles which can be only partly activated. Is a mixture with a MAF = 80 percent less homogeneous than a mixture with MAF = 20 percent? As a logical consequence of the "wrong premise" all conclusions based on it are arbitrary. Including your analysis of kappa t. You have to find here another way to describe and to present the problem of external mixtures.

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 arbitrary.

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

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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 the suggestion of M. Gysel (Referee 2), we have calculated another

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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.

Minor Referee comments:

Comment 1:

p. 17349, line 23: The timing for the measurement seems tight. How much time was allowed to adjust to the next particle size? How much time was allowed to adjust the next supersaturation level?

Response

To adjust to the next particle size 50s were allowed. To adjust to the next supersaturation level more than 4 min were allowed. Note that the supersaturation was increased within one cycle of measurements. When switching from the highest to the lowest S we allowed additional 5 min for adjustment. Note, that there was a typing error in the manuscript (p.17349, l. 23): The integration time for each measurement data point was 30 s rather than 50 s. All these details will be changed/added to the revised version of

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this manuscript.

Comment 2:

p.17351, line20 and Fig. 1: Shouldn’t the correction function (red line in Fig. 1) follow the top of the sigmoidal curves)? It does for 20nm $<$ D $<$ 40nm, but not for 60nm $<$ D $<$ 100nm. Are there more reasons for size dependence of the CCN counting efficiency than loss inside the CCN counter?

Response

As specified in our paper, the correction function (red line in Fig. 1) had been fitted to the data points of all calibration experiments. Thus, the line shall and does go through the bulk of the data rather than following the top. There might be other effects in addition to wall losses in the CCN counter, but we are not aware of any.

Comment 3:

p.17351, line 25 f: "The deviation...". I don’t understand this sentence. Do you refer to the scattering of the observations around your correction function?

Response

Yes, we do. We will clarify the sentence accordingly. "The scattering of the N_CCN/N_CN measurement values around the counting efficiency correction function..."

Comment 4:

p.17351, line 28 f: "For the period...". How serious is that? Please, you need to explain more, or to discard the affected data.

Response

We have no indication that the supersaturation would have been affected significantly. Only MAF decreased by 5%, which can be explained by a 5% decrease of flow in the

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CCNC relative to the flow of the CPC. We are not sure which of the flow rates was actually offset. An offset of the CPC flow rate would not affect S, while a 5 % offset of the CCNC would affect S by less than 4% (Rose et al., 2008). Except for MAF, none of the other CCN measurement parameters exhibited a discernible systematic change after 20 July.

Comment 5:

p.17353, line 6 ff.: I would expect that for an external mixed aerosol, the fractions of the components are themselves size dependent. In the chosen measurement scheme this could lead to a falling or a rising top of the sigmoidal curves. The latter seems to be the case for ss=0.27.

Response

We agree that the chemical composition of the externally mixed non-activated particles may be size-dependent, and that this can influence the shape of the CCN efficiency spectra. A detailed discussion of such effects, however, would go beyond the scope of our manuscript.

Comment 6:

p. 17355: R = 8.134 J mol-1 K-1

Response

Thank you for pointing out this typing error.

Comment 7:

p.17355, line 20: Physically, the MAF cannot be larger than 1. Within your errors it can well be larger than 1. By suppressing this fact you bias your errors.

Response

We agree that limiting the MAF to a maximum value of 1 introduces a bias in the

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calculation of N_CCN,S. Additional test calculations with MAF not limited to 1, however, led to total CCN concentrations that were on average less than 1% higher.

Comment 8:

p.17356, line 24 and p. 1757, line 4: "...a substantial portion..." and "...high portion..."?

Response

Yes, you are right. We will change that in the revised manuscript.

Comment 9:

p.17359, line 11, Fig. 5: The diurnal cycles are difficult to recognize. It could make sense to present average diurnal cycles, maybe for a few typical periods (see next comment).

Response

As mentioned already in the discussion paper (p. 17359, l.13-15) the detailed analysis of the diurnal cycles will be part of the follow-up study of this paper (Rose et al., 2010). To present them already in this paper would go beyond the scope of this manuscript (it is anyhow already quite long).

Comment 10:

p. 17359, line 19 ff, Fig. 5: What happened in the period 15.7. and 20.7.? Please, comment.

Response

In the period of 15 to 24 July we performed measurements at a higher supersaturation level (1.27% instead of 0.67%). Otherwise the measurement results were not distinctly different from the average of the campaign.

Comment 11:

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Interactive Comment

p.17359, line 26 ff: "...the burning of plant waste by local farmers was visible in the vicinity of the surrounding..." Despite the vicinity of (strong?) sources the particle concentration was lower than on average, there were less small particles, but the non-activated fraction did not change. The single observations seem not match, please explain.

Response

You are right that there were less small particles during the BBE. The non-activated fraction, however, still did not change significantly (for S>=0.47%) because at the same time the activation diameters increased. Moreover, the particle concentration was lower than on average. We are not sure whether the lower particle number concentrations are due to a different background air mass or to enhanced coagulation of small particles with the large surface area of the relatively large biomass burning particles (see Fig. 8). As discussed by Garland et al. (2008), the BBE was characterized by particularly low wind speeds (stagnation) indicating little influence of particles from other than the local sources. A detailed investigation and full explanation of these observations would require highly resolved regional air quality model investigation with detailed aerosol dynamics (particle sources and sinks).

Comment 12:

p. 17363, line 3: Andreae et al. 2008?

Response

The reference was correct (Andreae, 2008), but by now the ACP version of this paper has become available (Andreae, 2009).

Comment 13:

p. 17364, line 9, Fig. 13: Why are almost all deviations positive?

Response

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Interactive Comment

The majority of the deviations are positive because kappa_t does partially but not fully account for the effects of externally mixed CCN-inactive particles. Fig. 13 simply reflects the average positive bias specified in Table 3: +4% for N_CCN,S,p calculated with kappa_t. Note that the positive bias of N_CCN,S,p calculated with kappa_a is considerably larger (+14%). This confirms that kappa_t (2-parameter fit) is a better proxy for the CCN activity of the investigated aerosols than kappa_a (3-parameter fit).

Comment 14:

Figures: It would be helpful, if you could shade the BBE period in all relevant plots.

Response

We appreciate the suggestion but we prefer not to implement it because it would tend to decrease the readability of several figures.

References:

Andreae, M. O.: Correlation between cloud condensation nuclei concentration and aerosol optical thickness in remote and polluted regions, Atmos. Chem. Phys., 9, 543–556, 2009.

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