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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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Specific Referee comment 8:

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

Response

We will add that to p. 17354, l. 12.

Specific Referee comment 9:

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.

Response

According to the rho_ion values determined by Niedermeier et al. (2008), characteristic kappa values for sea salt are in the range of 0.95 to 1.0. This information will be added to the revised manuscript.

Specific Referee comment 10:

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!

Response

Yes, of course - see Petters and Kreidenweis (2007) as referenced at the beginning of that paragraph. For more information about approximating volume fractions by mass fractions see Kreidenweis et al. (2009) and Gunthe et al. (2009). We will change the respective sentence to "The effective hygroscopicity... weighted by the volume or mass fractions, respectively (Kreidenweis et al., 2009; Gunthe et al., 2009)."

Specific Referee comment 11:

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).

Response

We will remove the D_50 and kappa_50 values from the revised manuscript and include additional references.

Specific Referee comment 12:

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%.

Response

Thanks for pointing out this imprecision. The corrected values will be added to the text: "... particles as large as ˜300 nm must have an effective hygroscopicity parameter of kappa $<$ 0.1 to be not activated at S = 0.068%."

Specific Referee comment 13

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).

Response

In this paragraph we intended to estimate the hygroscopicity of those particles we refer to as "externally mixed CCN-inactive particles". The diameter range scanned at low supersaturations (i.e., 0.068%) is too small to see these particles. Since they must be larger than 300 nm in order to activate at 0.068% we conclude that their kappa must be smaller than 0.1. If we assume that these particles are wettable but

completely insoluble and non-hygroscopic (kappa = 0), we can calculate their critical supersaturation to be ˜0.7%. From our measurements, however, we see that already at S = 0.47% (almost) full activation is reached (i.e., no significant fraction of non-activated particles appears). That means that they must have a kappa with a lower limit of 0.0009. From further detailed analysis of the CCN data (MAF etc.), we obtained a best estimate of ˜0.01. As mentioned in the discussion paper, this aspect will be addressed and described in more detail in a follow-up study (companion paper, Part 2).

Specific Referee comment 14:

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).

Response

Here we disagree. The term CCN-active is inherently linked to a certain level of supersaturation at which a certain particle is either CCN-active or CCN-inactive. For more information on definitions and terminology see Andreae and Rosenfeld (2008), Pöschl et al. (2009), and references therein.

Specific Referee comment 15:

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.

Response

In this paragraph we provide a plausible explanation for the observed CCN properties of the investigated aerosol, rather than inferring a detailed chemical composition. We agree that CCN measurements alone are not sufficient to determine chemical composition. In view of common knowledge and specific campaign data about the chemical composition of aerosols in Chinese megacity regions, however, it would be difficult to come up with other plausible explanations. For more detailed information we had already pointed to a follow-up study that includes chemical data (companion paper Part 2): "These and other aspects of aerosol chemical composition and mixing state will be further explored and discussed in more detail in a follow-up study (Rose et al., 2008a)."

Specific Referee comment 16:

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?

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 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), which is within the range of relative uncertainty specified in our study (+/- 10%) Except for MAF, none of the other CCN measurement parameters exhibited a discernible systematic change after 20 July.

Specific Referee comment 17:

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.

Response

It is estimation but can be also proofed by data that is discussed in the follow-up study.

Specific Referee comment 18:

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?

Response

The change in the properties during the BBE (˜10% in D_a) is much bigger than the effect of flow rate irregularities (would translate in $<$3% in D_a). Moreover, it can be seen in the data sets of all instruments recorded during this campaign, that this period was special.

Specific Referee comment 19:

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?

Response

This is an interesting question indeed. 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).

Specific Referee comment 20:

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!

Response

Thank you for pointing out this inconsistency. The correct values would be kappa=0.28 at D = 30-70nm, but was rounded once up (˜0.3) and once down (˜0.25). We will correct that in the revised manuscript.

Specific Referee comment 21:

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.

Response

In the revised manuscript we will adjust the formulation as follows: "These findings confirm earlier studies suggesting that aerosol particle number and size are the major predictors for the variability of the CCN concentration in continental boundary layer air, followed by particle composition and hygroscopicity as relatively minor modulators." This statement will also be supported by additional test calculations specifying the influence of the variability of number concentration and size distribution (kappa-Köhler model with constant CN size distributions, see Gunthe et al., 2009).

Specific Referee comment 22:

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.

Response

We think that a table is the most efficient way of presenting and substantiating the calibration properties and uncertainties. It does not need much space and would be somewhat "lost" in the supplement.

Specific Referee comment 23:

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.

Response

We agree and will change the order of the corresponding critical diameters as suggested.

Specific Referee comment 24:

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

Response

Not really. The sentence does indeed refer to the CCN size distributions that were obtained by multiplication of the CN size distributions with the CCN efficiency spectra and integrated to determine CCN concentrations.

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