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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Cloud condensation nuclei in pristine tropical rainforest air of Amazonia: size-resolved measurements and modeling of atmospheric aerosol composition and CCN activity" *by* S. S. Gunthe et al.

S. S. Gunthe et al.

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Referee Comment 10:

The penultimate paragraph in the abstract goes to the root of the main criticism I have with the manuscript. Within the current paper, I have no objective means of evaluating whether using the global mean kappa of 0.3 gives a reasonable result and, from the data that are presented, it might be independently concluded that the global average value does not represent the AMAZE data very well and only a region specific value of 0.15 should be used.

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Response:

We understand the question but we do not really understand the criticism. It was and is not the purpose and aim of our paper to resolve the question whether a kappa value of 0.3 or 0.15 should be used by the referee or other colleagues. According to our measurements and calculations and in agreement with the results of earlier studies compiled in Tab. 2, a kappa value of 0.15 is obviously better suited than a value of 0.3 for describing the hygroscopicity and CCN activity of pristine Amazonian rainforest aerosol during the wet season. If, however, somebody wants to approximate the CCN properties of continental aerosols with a single global average parameter, a kappa value of 0.3 would still yield reasonable results in the sense that the average relative deviation between calculated and actual CCN concentrations in pristine Amazonian rainforest air would can expected to be less than 50% at medium and high water vapor supersaturations (S >= 0.2%) and to exceed 100% only at low water vapor supersaturations (S <= 0.1%). Beyond that, the referee's question can only be answered with the following recommendation: If you want to approximate or predict CCN concentrations in pristine Amazonian rain forest air, please check for yourself, which approach you can and want to take, depending on your application, tools and information (cloud, atmosphere, or climate model; process, regional or global scale; aerosol particle number concentration, size distribution, chemical composition data; etc.). On our part, we have measured and characterized the average values and variability of CCN properties as detailed above and in our manuscript, and we have tested and characterized the possibilities and uncertainties of predicting CCN concentrations in different ways (including composition dependent, local average and global average values of kappa for Köhler models as well as power law parameters). In this context we would like to emphasize that we have not only provided and discussed the local and global average values of kappa (0.15 vs. 0.3). We have also presented a parameterization of kappa as a function organic and inorganic mass fractions determined by AMS. To our knowledge, this is the first publication of a parameterization of this kind, and it will be interesting to see how it performs and evolves in the course of scientific development. In the meantime,

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other studies have already followed up on this approach (Shinozuka et al., 2009).

Referee Comment 11:

p3818, line 14-17: The sentence "For the multiple charge correction we used the total aerosol particle number size distributions that were derived from the CPC measurement data and averaged over each full CCN measurement cycle as described below" is not clear. Does it mean that the multi-charge correction was applied to the distribution from each scan based on an average correction derived for the distribution measured over the entire CCN cycle? If so I am sure this is legitimate provided there is little dynamical variability in the larger size bins of the distribution. The sentence should be clarified and any such justification should be stated.

Response:

Yes, we will clarify this aspect in the revised manuscript.

Referee Comment 12:

p3819, line 3-4: The sentence "The deviation of MAFf from unity represents the fraction of externally mixed CCN-inactive particles in the diameter range of Da to Dmax" is unclear. The concept of fraction of externally-mixed particles is invalid as mixing-state is a continuum with internal and external mixtures merely end members of the continuum. This is clear in terms of hygroscopicity from HTDMA instruments where even in the most extremely externally-mixed environments, growth factors are seldom as narrow as the convolved DMA transfer functions.

Response:

We understand the referees concern, but we do not agree that the concept of externally mixed particles would be invalid. As clearly demonstrated in this study and in the preceding study of Rose et al. (2008b), CCN efficiency spectra recorded at low water vapor supersaturation can reach a plateau value well below unity. This means that a certain fraction of the aerosol particle population (MAF) does get activated at this su-

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persaturation, whereas another fraction (1 - MAF) does not get activated. By definition, this represents an external mixture of particles that are sufficiently hygroscopic to be CCN-active under the given conditions and particles that are CCN-inactive (i.e., not sufficiently hygroscopic to be CCN-active under the given conditions). Regardless of the more or less continuous or discontinuous nature of the chemical mixing state of the investigated aerosol particles, the particle population can be considered as externally mixed with regard to their CCN activity under the given conditions. Beyond that we do not fully understand the referee's comment concerning H-TDMA measurements. We are not experts in H-TDMA field measurements, but according to the papers cited in our manuscript, experts in the application of this technique report that they can discriminate externally mixed groups of particles with distinctly different hygroscopic properties (see Vestin et al., 2007, Rissler et al., 2006, Zhou et al., 2002). As described in Sect. 3.1.3 and Tab. 2 of our manuscript, closure calculations based on the assumption of externally mixed groups of particles with different hygroscopic properties as reported by other authors yield kappa parameters (kappa_t,avg) that are in good agreement with the kappa parameters derived from our CCN measurements (kappa_t).

Referee Comment 13:

p3819, line 11: How were the DMA transfer functions corrected for? I am not aware of any available DMA that exhibits an ideal transfer function. If the measured transfer function was used, the authors should describe how it was determined. Since it is not clear how this was done, it is difficult to evaluate whether the heterogeneity parameter is attributable to the water supersaturation or particle shape effects or at least partly to instrumental broadening.

Response:

As mentioned in the manuscript, the exact procedure of how we correct for transfer function effects is described in Rose et al. (2008b). In this correction procedure we assume an ideal transfer function and we are aware that this is a simplifying assumption,

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but we think that the uncertainties introduced by this simplification are minor relative other uncertainties involved in the reported measurements and data analyses. As mentioned in our manuscript, we attribute the small residual broadening that we obtain after transfer function correction of calibration measurements (sigma/D ˜ 3%) to non-idealities of various kinds, including imperfections of the transfer function correction. The latter has not been explicitly mentioned in our discussion but we intend to add this point in the revised manuscript (p. 3819, l. 14): "...or other non-idealities such as DMA transfer function or particle shape effects."

Referee Comment 14:

p3820, line 26: The reasons for only "fair agreement" are difficult to assess -particularly the explanation for the disagreement in the sizing of the accumulation mode. Assuming the counting is correct, the absolute quantification of the activation behaviour is still very dependent on accurate sizing.

Response:

We agree, but we have already reported all available information. Based on our calibration experiments we are confident that our instrument was performing as well as specified in our manuscript and in related earlier publications (Rose et al., 200a,b).

Referee Comment 15:

p3821, line 13: The CCN measures activated number in a given size bin. It should be straightforward to describe a fitted dNCCN /dlogD directly from the measurements rather than fitting a CDF to the activated fraction and multiplying by the dNCN /dlogD. Would the errors associated with the latter approach be greater or lower than those propagated through multiplying the number distribution by a fitted CDF? It is obvious that a fitted CDF will give a tidier representation, but does it retain the accuracy of the measurements?

Response:

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Due to low number concentrations and counting statistics the AMAZE-08 data set is not well suited for analyses involving individual data points of the measured CCN efficiency spectra. The measurement uncertainties related to the scatter of individual data points are efficiently reduced by the applied CDF fitting procedure as established and described by Frank et al. (2006). As will be specified in the revised manuscript, the average standard error of the midpoint activation diameters were 2-3 nm (corresponding to relative uncertainties of 5-15 % in kappa). We think that the overall precision and accuracy of the CDF fitting approach is likely to be higher than alternative approaches propagating the statistical uncertainty of individual measurement data points, especially under measurement conditions as experienced during AMAZE-08. Detailed investigations of alternative data processing techniques go beyond the scope of this study, but we agree that it may be worthwhile to explore this aspect in follow-up studies.

Referee Comment 16:

Table 2. There is a difficulty in describing hygroscopicity data from HTDMA as e.g. VLH and LH modes. Such descriptions are necessarily arbitrary (and there is no reason to suspect that growth factor will fall into "modes" of given form -normally distributed, for example) and should be attributed instead to their growth factor bins. The use of mode descriptions such as VLH and LH are also cautioned against because their definition will change from study to study, whereas a defined growth factor bin at a given RH is fixed. Similarly, defining a mode in terms of a kappa is also ambiguous given the often found difference in derived kappa from HTDMA and CCNc instruments (resulting from the kappa dependence on RH).

Response:

As mentioned above, we are not experts in H-TDMA field measurements. According to the papers cited in our manuscript, however, experts in the application of this technique report that they can discriminate externally mixed groups of particles with distinctly dif-

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ferent hygroscopic properties (see Vestin et al., 2007, Rissler et al., 2006, Zhou et al., 2002). As detailed in Sect. 3.1.3 and Tab. 2 of our manuscript, closure calculations based on the assumption and averaging of externally mixed groups of particles with different hygroscopic properties as reported by other authors yield kappa parameters (kappa_t,avg) that are in good agreement with the kappa parameters derived from our CCN measurements (kappa_t). The referee's caveat is well taken. As explained on p. 3828 of our discussion paper, however, our results indicate that the simple averaging approach taken for the comparison of hygroscopicity parameters derived from HTDMA and CCNC measurements is suitable for (approximately) describing the CCN activity of atmospheric aerosols - at least in Amazonia during the wet season. Thus, we suggest that the applicability of kappa_t and kappa_t,avg for efficient comparison and description of the CCN activity of atmospheric aerosol particles should be tested by further investigations combining size-resolved CCNC, HTDMA and particle composition measurements at different locations and conditions.

"Note, however, that the simple averaging approach and effective hygroscopicity parameters/proxies presented above are not meant to replace other more detailed approaches that attempt to resolve externally mixed groups of particles with different hygroscopic properties by more elaborate measurements and models. In fact, more detailed investigations should help to corroborate and/or improve the presented approximations." (p.3828, l.23).

Referee Comment 17:

Figure 2 is good for representiong the campaign averaged behaviour, but does not give a very good indication of the variability in mixing-state at all supersaturations. The mixing-state argument made in the paragraph starting line 8 p3823 must apply to some degree at all supersaturations for various periods in the project since the maximum activated fraction was below 1 for periods at all supersaturations.

Response:

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As specified in our manuscript (Sect. 2.2, p. 3817, l. 14) and illustrated in Figs. 2, 4d and S1 (percentiles and data points reaching up to physically unrealistic CCN efficiency values near ˜1.2), the estimated relative uncertainties of the reported measurement results are $<$20% for individual measurements and $<$10% for the reported average values. At medium and high supersaturations, MAF exhibited only random positive and negative deviations from unity that were generally smaller than the relative uncertainty estimates specified above (Figs. 2, 4d, and S1). Thus we do not consider these deviations as significant (p. 3823, l. 4). Only at S = 0.1 did the average and individual deviations of MAF from unity reach or exceed the estimated uncertainty limits (Figs. 2, 4d, and S1) and have been discussed accordingly (p. 3823, l. 8).

Referee Comment 18:

p3823 line 13 onwards: the strong reliance on kappa to represent the CCN behaviour is curious. It is a 2nd order product. The CCN does not measure kappa. Kappa from an HTDMA is not the same as kappa from a CCNc owing to the RH dependence and change in non-ideality and probably surface tension approaching saturation. There is recent evidence to believe that kappa is not straightforwardly capable of linking sub-and supersaturated water uptake. It is much more past-and future-proof to use a measurement which has a demonstrably physically-meaningful interpretation. This also clearly allows for comparison with other works. Kappa can always be introduced later and used to frame the conclusions of the work.

Response:

We fully understand the concentration and RH dependence of kappa (see Mikhailov et al., 2009, Sect. 3.5 and Fig. 7; Reutter et al., 2009 and interactive comment by Su et al., Atmos. Chem. Phys. Discuss., 9, C3272 - C3273, 2009, Fig. 2 on p. 12 of supplement). Nevertheless, we consider kappa to be (one of) the best suited parameters for reporting and discussing the results of CCN field measurements. As explained above (Response to Referee Comment 3), we understand and respect that

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the referee seems to prefer the use of raw data and/or different parameters/terms than the ones that we and many colleagues in the scientific community are using (including Referee #1 and Dr. Roberts in the interactive public discussion of our paper). At the same time, we hope and expect that the referee will also respect our choice of data analysis and presentation format, which is by no means unusual. Again, we would like to emphasize that our exchange with Referee #1, with Dr. Roberts and with many other colleagues confirms that the kappa-Köhler model approach applied in our work is understandable, useful, and widely used.

Referee Comment 19:

p3829, line 10: again, in agreement with the other reviewer, the reference to remote sensing to derive CCN behaviour using an assumed kappa should be removed. It is a step too far.

Response:

We understand the referee's concern, but we intend to retain this exploratory statement outlining the potential relevance of highly simplified formalisms for the description of aerosol particle hygroscopicity and CCN activity in with regard to remote sensing and related long-term/large-scale atmospheric research. To confirm the appropriateness of this statement we intend to add references to recent studies and ongoing research activities addressing these issues (Andreae, 2009; Kinne, 2009; Shinozuka et al., 2009).

Referee Comment 20:

p3834, line 3: why is this considered remarkable? The reason is not stated. Where is the validation and what is the weighting of the global average value to get the best agreement (and with what)?

Response:

We consider this finding remarkable because it demonstrates that the influence of aerosol chemical composition on the atmospheric abundance of CCN can be effi-

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ciently approximated with a single parameter value over a wide range of conditions. At the same time we also specify the limitations of this simplified approach (deviations $>$ 50% at low particle concentrations and water vapor supersaturations). To our knowledge, the applicability and limitations of this approach have not been quantified before. Further validation and refinement go beyond the scope of the present study. To avoid further misunderstandings we will also add the word "approximate" whenever we assume and refer to a global average effective hygroscopicity parameter of kappa ~ 0.3, which is and was of course always meant to be a simple first-order approximation based on the currently available data (see Andreae and Rosenfeld, 2008; Kreidenweis et al, 2009; and references therein).

Referee Comment 21:

Figure 11. I am not sure what this shows. Obviously a straight line will be achieved.

Response:

As explained in our manuscript (Sect. 3.2.2, p. 3832, l. 13), Fig. 11 illustrates the degree of agreement achieved with different approaches of approximating/predicting CCN concentrations. We do not understand what the referee meant with the phrase "Obviously a straight line will be achieved." Rather than speculating about the meaning/motivation of this statement, we would like to invite the referee and interested readers to consider the differences between the different panels (in particular between panels a and d) in combination with the manuscript text.

Referee Comment 22:

Figure 14. Why does the integral AMS composition give a better R2 value?

Response:

The answer to this question is explicitly given in our manuscript (p. 3835, l. 20): "The lower correlation coefficient obtained with the size-resolved AMS data (R2=0.66, Fig. 14b) is a result of the lower signal-to-noise of these data under the very low

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concentration conditions of this campaign."

Referee Comment 23:

p3838 and figure 15: this is an important result. In showing that size-resolved composition is required to fully explain the kappa and hence CCN behaviour, it provides a pointer to future field quantification of CCN behaviour. This should be used within the discussion and conclusion. There is, however, a slight difficulty with the interpretation here. Whilst there is probably some truth in the fact that the composition at around 200nm (corresponding to the lowest supersaturation) is at the mass modal diameter and hence gives the better agreement with kappa, it was also stated earlier that larger particles appear in an external mixture probably containing material which the AMS does not measure. How is this reconciled?

Response:

As mentioned in our manuscript (p. 3838, l. 4), we attribute the observed deviations to a combination of effects caused by the shape of the size distribution and by externally mixed CCN-inactive particles: "This re-confirms that the prediction of N_CCN,S is less robust at low S (Rose et al., 2008b), which is due to the enhanced error sensitivity caused by the steep slope of the aerosol size distribution typically observed at the large activation diameters corresponding to low supersaturations (Ervens et al., 2007) and also to the stronger influence of externally mixed CCN-inactive particles at large D and low S (Figs. 2 - 3, Rose et al., 2008b, 2009)."

The close correlation of kappa_p and kappa_a does not contradict the proposed influence of externally mixed CCN-inactive particles on the observed overprediction of N_CCN,S. It just highlights the importance of clear distinction between different types of kappa parameters.

As specified on p. 3819, l. 21 of our manuscript (and similarly on p. 3823, l. 20), "kappa_a calculated from the data pairs of S and D_a characterizes the average hy-

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groscopicity of CCN-active particles in the size range around D_a. 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 (Rose et al., 2008b)."

Accordingly, kappa_a is better suited for comparison with kappa values predicted from AMS measurements (kappa_p, Sect. 3.3), 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. On the other hand, kappa_t is better suited for comparison with average kappa values calculated from H-TDMA data (kappa_t,avg, Sect. 3.1.3) and for the calculation of CCN number concentrations when CCN-active particles are externally mixed with CCN-inactive particles (Sect. 3.2.2, p.3832, l. 25).

We will clarify these aspects in the revised manuscript by adding the above information in the revised manuscript (Sect. 2.2).

Referee Comment 24:

The supplementary material provides useful additional material but, for brevity, I agree with the other reviewer that an informed choice be made between 2 and 3 parameter CDF fits early in the paper and only one used thereafter. Likewise N30 only should be used, eliminating the need for N20. In providing useful statistical metrics, I feel that Figure S1 and S6, once these choices are made, might be usefully included in the main manuscript at the expense of less informative figures in the paper.

Response:

As mentioned in our response to Referee #1, we understand and share the referees' view that unnecessary complexity and superfluous information should be avoided. As explained above, however, the kappa values from the 2- and 3- parameter fits parameters are not the same (neither conceptually nor numerically). They are differently suited for different purposes (comparison with AMS vs. HTDMA data; prediction of CCN num-

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ber concentrations for internally mixed CCN-active particles vs. external mixtures of CCN-active and inactive particles).

Thus, we intend to report the values of both parameters in our manuscript, because we do not consider it good scientific practice to achieve conciseness of manuscripts at the expense of completeness and precision. Nevertheless, we intend to reduce the number of figures both in the manuscript and in the online supplement, and we will remove N_CN,20 from most of the text and tables. For comparison with other particle number concentration measurements, however, we intend to retain information about N_CN,20 in the methods section (Sect. 2.3).

As mentioned above, we will also reduce the number of figures in our manuscript and online supplement as follows: merge and simplify Figs. 3 and 5; omit Figs. S8, S9, S12; and delete panels S6b and S7b. We appreciate the suggestion to include Figs. S1 and S6 (box plots illustrating the statistical distribution of various CCN parameters) in the main manuscript. In view of the comments from Referee #1 and Dr. Roberts, however, and because we do not explicitly comment/discuss the statistical distribution as such in the text (unlike the content of the other figures), we prefer to leave these figures in the online supplement, where they are also freely available for all interested readers.

To be continued (Part 3: References)

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 3811, 2009.