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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.

Anonymous Referee #2

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The paper provides a thorough and very useful description and climatology of the behaviour of aerosol particles as cloud condensation nuclei in the Amazon during AMAZE'08. The overall point that size and number determine CCN behaviour once compositional variability is removed is well demonstrated. However, the manuscript is rather unfocussed and does not distill the results into a digestible body of work. I would suggest that the paper is reduced in length, removing unneccesary discursiveness and focussing on the main scientific story. I also think the paper retains far too many figures. In accord with the other reviewer I would suggest that the main focus of the work

may be represented in a smaller number of figures.

There are also two primary scientific concerns I have with the paper:
1) There appears to be no independent and objective metric for the degree of skill which is judged as adequate for large (or indeed process level) modelling in the simplification approach that is presented. There is very little context presented when making statements such as close, well-correlated, low, high - all references to such comparative assessments must be put into objective context or replaced with a statistical quantification of the goodness of fit / degree of reconciliation.
2) the metrics for the results are presented in the simplified parameterised form such that they are not readily comparable with other data which have not been subjected to this second generation processing. The instrumentation does not directly produce a kappa value and I think it is necessary to provide more actual data (contour plotted time series of activated fraction as a function of particle size at a given supersaturation etc.) rather than the overemphasis on a 2nd generation derived parameter. A reader unfamiliar with the author&8217;s previous work would find it very difficult to read and pick up all the jargon.

If these broad areas are addressed throughout the manuscript shortening process, in addition to the following specific criticisms (mostly relating to the above points), I recommend that this comprehensive manuscript is published.

Specific points:

Abstract: Given that theoretically kappa varies between about 1.2 and 0.01 for most pure component inorganic and organic compounds, 0.05 to 0.45 is a rather broad range under what appear to be fairly settled atmospheric conditions. Can the authors comment?
The standard deviation as well as the mean kappa should be stated.
If k=1/2 global value is considered surprisingly close, it should be put in context - a 100% error might seem large to a non-specialist.

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It is interesting that only a 10% increase in organic mass increases k by 100%
"Close linear correlation with Xm,org" - how close is close - such a statement should be quantified.
How variable was the aerosol size? i.e. would the difference between a constant normalised size distribution and the actual size distribution lead to variability in predicted ccn number greater than 50%. This must be the case if if the statement on p3814 line 5 is correct.
Fully consistent CCN and AMS results - this needs to be qualified stating the differences in consistency between using integral and size-resolved AMS composition.
How does a 50% relative deviation in N_{CCN} resulting from assuming a global mean in kappa propagate into radiative forcing estimates? If statements are to be made such as this in an abstract, the inference that these are low must be justified.
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.

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'm 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.

p3819, line 3-4: The sentence "The deviation of MAFf from unity represents the frac-

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tion 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.

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.

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.

p3821, line 13: The CCN measures activated number in a given size bin. It should be straightforward to describe a fitted $dN_{CCN}/dlogD$ directly from the measurements rather than fitting a CDF to the activated fraction and multiplying by the $dN_{CN}/dlogD$. 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?

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

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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).

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.

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.

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.

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)?

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

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Figure 14. Why does the integral AMS composition give a better R^2 value?

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?

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 N_{30} only should be used, eliminating the need for N_{20}. 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.

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