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

Referee Comment 1:

This manuscript combines measurements of CCN with size distributions and chemistry to derive hygroscopicity parameters for Amazonia aerosols and demonstrates a unique method of calculating the kappa hygroscopicity parameter using inorganic and organic

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contributions measured by an AMS. The manuscript presents a thorough analysis and the efforts to quantify the errors associated with the measurements are commendable. Nonetheless, the manuscript seems present all of the analyses instead of synthesizing the results for the reader. If my comments can be successfully addressed, I recommend the manuscript for publication.

Response:

We will try to improve the synthesis of results in the revised manuscript, although we think that the abstract and the summary and conclusions section of our discussion paper had already provided a fairly concise synthesis of our results. Following up on the suggestions given in the second interactive comment posted by Referee #1 ("addendum") and below, we will also reduce the number of figures in the manuscript and online supplement. Note, however, that we consider it good scientific practice to present all relevant data, aspects and steps of our analyses. We are aware that short papers presenting little detail tend to attract less criticism, but we prefer presenting our work in a comprehensive format on which interested colleagues can build without guessing.

Referee Comment 2:

In this work, the authors clearly show that once an average chemical effect (or hygroscopicity factor) has been determined (by the AMS, for example), then aerosol particle number and size are the major predictors for the variability. This is further corroborated by Fig. 15, which shows relatively poor agreement between effective hygroscopicity parameters determined from integral AMS measurements and those determined by the CCN measurements. Subsequently, the conclusions drawn by the authors (P3814; L5 & P3840; L24) should be reworded to reﬂect these results more accurately, rather than simply stating that particle number and size are the major predictors for the CCN variability.

Response:

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Based on the results of this study and numerous earlier studies, we are very confident that the general conclusions drawn on p. 3814, l. 5 and p. 3840, l. 24 are valid and need not be reduced to more specific statements about our measurement results (which are anyhow also included in the manuscript text). As demonstrated in our paper as well as in numerous earlier papers referenced in ours, the influence of varying chemical composition and effective hygroscopicity of aerosol particles on the number concentration of CCN in continental boundary layer air is generally smaller than the influence of varying aerosol particle number concentration and size. The conclusions drawn on p. 3814, l. 5 and p. 3840, l. 24 are based on the following statement from p. 3833, l. 28:

"Clearly, the calculation of CCN number concentrations with kappa = 0.3 cannot capture the short-term variability and leads to a systematic overprediction in the investigated tropical rainforest environment with very high proportion of organic particulate matter (Sect. 3.3) and correspondingly low effective hygroscopicity of the aerosol particles. Nevertheless, we consider it remarkable that a constant global average effective hygroscopicity parameter of kappa =0.3 (Andreae and Rosenfeld, 2008; Pöschl et al., 2009a) enables the prediction of CCN number concentrations from aerosol particle number size distributions over a range of four orders of magnitude (N_CCN,S = 10ˆ4 cm-3) going from pristine tropical rainforest air to highly polluted mega-city regions (Rose et al., 2008b) with relative deviations exceeding ˜50% only at very low water vapor supersaturations (˜0.1%) and particle number concentrations (˜100 cm-3)"

We note that Referee #1 had no objections against this statement, which is essentially equivalent to the conclusions drawn on p. 3814, l. 5 and p. 3840, l. 24. Accordingly, we will try to clarify the latter in the revised version and we will add further references to related studies supporting these general conclusions and messages (Feingold et al., 2001: Feingold, 2003; Wang et al., 2008; Feingold and Siebert, 2009; Kreidenweis et al., 2009; Reutter et al., 2009). To avoid further misunderstandings we will also add the word "approximate" whenever we assume and refer to a global average effective

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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).

With regard to the correlation between the effective hygroscopicity parameters derived from AMS measurements and determined by CCN measurements, we refer to the manuscript text on p. 3837-3838, in particular p. 3837, l. 26 and p. 3838, l. 19:

"In spite of the positive bias and low correlation of predicted vs. measured kappa, the mean relative deviations between CCN number concentrations predicted on the basis of kappa_p and the measurement values of N_CCN,S were mostly less than 20% at S=0.19-0.82% (Table 4)."

"Overall, the results of the present study confirm that integral AMS measurement data are useful for the prediction of CCN number concentrations from CN size distributions. Highly precise predictions, however, would require size-resolved AMS measurement data of high precision, which are difficult to obtain at the low aerosol concentration levels of pristine tropical rainforest air."

Again, our general conclusions are consistent with related studies referenced in the manuscript, and we will add further references (e.g., Kuwata et al., 2008; Sorooshian, 2008; Wang et al., 2008; Shinozuka et al, 2009).

Referee Comment 3:

In reading the manuscript, it was not clear if the inorganic and organic fractions were based solely on AMS measurements or if there were additional measurements of aerosol mass to account for the refractory contributions not measured by the AMS. Presumably if the total mass were measured (as a function of size), then k_p predictions would improve.

Response:

In several parts of the manuscript we have clearly stated that the organic and inorganic

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mass fractions used for analysis and parameterization of effective hygroscopicity parameters were determined by AMS (p. 3813, l. 20; p. 3837, l. 9; p. 3839, l. 12). In the revised manuscript we will clarify this further (also in Sect. 2.4). Electron microscopic investigations of filter samples collected during AMAZE-08 (Sinha et al., manuscript in preparation) confirm that the concentrations of (potentially) refractory particles and components like mineral dust, soot, and primary biological particles were negligibly small ($<$ 5%) in the particle size range for which the kappa values derived from AMS and CCN measurements were not in good agreement (D $<=$ 150 nm corresponding to S $>=$ 0.19%). As explained in our manuscript, the deviations between kappa values derived from AMS and CCN measurements can be attributed to the observed size dependence of aerosol chemical composition (p. 3837, l. 21):

"The positive bias of kappa_p at high S is due to the enhanced organic mass fraction in small particles and could be corrected on the basis of the average AMS size distribution data (Figs. 3 and 12b), but further processing of the AMS data would go beyond the scope of this study."

Referee Comment 4:

The authors need to clarify the statement that supersaturation values in publications by Roberts and Andreae are 50% lower than reported nominal values (P3830; L1824). This statement is likely incorrect as Roberts et al. conducted closure experiments where independent calculations of CCN spectra agree with the measured CCN values. In addition, the references to Roberts et al. should be included in the section "Comparisons with other studies"

Response:

Our statement concerning the supersaturation levels of the CCN measurements reported in Roberts et al. (2001, 2002) and Andreae et al. (2004) is based on the technical note of Frank et al. (2007), who calibrated the supersaturation in the applied CCN counter (static thermal gradient chamber). However, since this issue is not crucial for

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our study, we intend to remove the questioned statement from the revised manuscript. Moreover, we will include references to Roberts et al. (2001, 2002) in Sect. 3.1.3 of the revised manuscript.

Referee Comment 5:

Several examples of extra analyses include presentation of 2-parameter and 3parameter CDFs (and 'a' & 't' subscripts), N20 and N30 concentrations, three observation periods, and a supplementary discussion that compares various single parameter calculations. While quantifying the sensitivity of different parameters is necessary, I suggest describing the differences between the approaches (if they are relevant) and present one parameter throughout the text for consistency. The 2 & 3-parameter CDFs are in good agreement and certainly within the error of the measurements (p. 3818; L18-25 & Fig 3); so it is not necessary to present both k_a and k_t throughout the en-tire manuscript. I also suggest using N30 as the reference for number concentrations throughout the text and drop parameters using N20. As stated by the authors, smaller particles will not activate at the supersaturations measured here. It is also worth mentioning in the manuscript that 30 nm is the limiting case for a pure ammonium sulfate particle at ˜0.8% supersaturation.

Response:

Following the referee's suggestion, we will remove N_CN,20 from most of the text and tables. However, we intend to retain it in the methods section (Sect. 2.3), because it is relevant for comparison with other particle number concentration measurements. In the revised manuscript we will also note that 30 nm is the critical diameter for CCN activation of pure ammonium sulfate particles at S ˜1% (Rose et al., 2008a).

With regard to the 2- and 3-parameter CDF fits and parameters we also understand and share the referee's view that unnecessary complexity should be avoided whenever simplifications are possible/appropriate. As mentioned in our manuscript and explained below, however, the parameters are not the same (neither conceptually nor

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numerically). They are differently suited for different purposes (comparison with AMS and HTDMA data), and they lead to different results in the prediction of CCN concentrations by Köhler model calculations.

As specified on p. 3819, l. 21 (and similarly on p. 3823, l. 20), "kappa_a calculated from the data pairs of S and D_a characterizes the average hygroscopicity 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_t is better suited for comparison with average kappa values calculated from H-TDMA data (kappa_t,avg, Sect. 3.1.3). On the other hand, 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. We will try to clarify this aspect and include the above statement in the revised manuscript (Sect. 2.2).

Please note that the error bars in Fig. 3 do not represent measurement errors but the variability of effective hygroscopicity parameters as observed throughout the campaign.

As will be specified in the revised manuscript, the statistical uncertainties in the determination of midpoint activation diameters by curve fitting were on average ˜2-3 nm (standard error of the corresponding CDF fit parameters), corresponding to relative uncertainties of ˜1-5% in activation diameter and ˜5-15% in the determination of kappa, because the latter is inversely proportional to the third power of the critical diameter of CCN activation (Petters and Kreidenweis, 2007; Kreidenweis et al., 2009). At low supersaturations and large particle diameters (S ˜ 0.1 %, D_a ˜ 200 nm) the relative uncertainty of the kappa values was on average of the same magnitude as the difference between kappa_a and kappa_t (˜ 5%). Thus, the difference between kappa_a

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and kappa_t was at the edge of being statistically significant. Nevertheless, it had a noticeable systematic influence on the prediction of CCN concentrations by Köhler model calculations (p. 3823, l. 24, p. 3832, l.27): the positive bias of the calculations increased by ˜50% (relative) when using kappa_a instead of kappa_t (from ˜10% to ˜16%, Table 4). The observed differences between kappa_t and kappa_a and the implications for the prediction of CCN concentrations are less pronounced but fully consistent with earlier investigations (Rose et al., 2008b). Therefore, we do not consider the distinction of kappa_a and kappa_t as a key message of our paper and we have kept it out of the abstract and the summary and conclusions section, but we still want to keep it in the body of the text and report all parameters in the tables. We do not consider it good scientific practice to achieve conciseness of manuscripts at the expense of completeness and precision.

Referee Comment 6:

The authors also need to update their reference list and check the order of the figures. One reference is cited without a title (Chen et al.) and the manuscript cites a number of articles that are in preparation or are not easily accessible (user manual and conference abstract). The reference (Frank et al., 2007) is also incorrectly cited (APCD vs. ACP). In addition, the figures are not in sequential order in the text and some of them are not even referenced in the manuscript. Editing the manuscript's style should not be required by the reviewers, but these oversights detract from its message.

Response:

We will update the reference list as suggested. Unlike indicated above and as confirmed by a second comment of Referee #1 ("addendum"), all figures are in sequential order and are properly referenced in the manuscript.

Referee Comment 7:

P3814; L10: The authors should use caution in extrapolating results from the Amazon

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to rainforests in Africa which have different sources of aerosols (Artaxo, 1995; particularly, with respect to the much larger contribution of dust in Africa).

Response:

We will restrict our statement to "pristine tropical rainforest aerosols of Amazonia".

Referee Comment 8:

P3814; L24: replace _absorb_ with _uptake_

Response:

We will change the formulation to "ability to take up water vapor".

Referee Comment 9:

P3817; L5: Cite Rose et al., ACP, 2008 as well.

Response:

We will move the citation of Rose et al. 2008a from l. 6 to l. 4.

Referee Comment 10:

P3817; L22: Maximum difference of temperature between the optical particle counter and the temperature of the bottom of the column should be stated as this is particularly important for the measurements at low supersaturations.

Response:

The temperature difference was 2 K, which will be stated in the revised manuscript.

Referee Comment 11:

Tables 1a and 1b contain the same information and need not be repeated. I suggest condensing Table 1b (keeping the error analysis, but removing 'a' or 't' and columns related to N20) and removing Table 1a.

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Response:

Following the referee's suggestion, we will remove Table 1a from the manuscript text and delete the N_CN,20 columns. However, because the median values are statistically more robust (less affected by short events of local pollution, etc.) and thus more representative for the average conditions during the investigated periods (preferred by many colleagues for model comparison), we intend not to delete Table 1a completely but to move it to the online supplement (Table 1S). As explained above, we intend to keep both the 3 parameter and the 2 parameter fit results (subscripts a and t) in the table, because they do provide relevant complementary information.

Referee Comment 12:

P3827; L1-8: The authors should reference their choice of hygroscopic thresholds (or describe how they determined the values of these thresholds).

Response:

Our choice of threshold values follows from the externally mixed particle groups and corresponding effective hygroscopicity parameters reported by the referenced H-TDMA studies as detailed in Table 2. The average effective hygroscopicity parameters were generally $<$ 0.1 for the lowest hygroscopicity group (VLH), and for the next higher groups they were $<$ 0.2 (LH) and $<$ 0.4 (MH), respectively. Thus, the choice of the threshold values 0.1 and 0.2 was very straightforward - it is the only possibility to represent the reported groups with simple (single decimal place) threshold numbers. The preliminary choice of an upper threshold value for the MH group was based on the observation that kappa values determined by CCN measurements at other continental locations exceed the value of 0.4 much more frequently than the value of 0.5 (Rose et al., 2008b). Upon re-considering this choice in view of the referee's question, however, we conclude that it may be more reasonable to set the approximate upper limit of the MH fraction 0.4 (corresponding to an ammonium sulfate equivalent soluble volume fraction of ˜ 67%). As indicated above, the value of 0.4 follows directly from earlier

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studies of Amazonian aerosols. Higher threshold values such as 0.5 may eventually turn out to be equally or more suitable, but for now we have no solid basis to propose such values. Thus, we will revise definition of the kappa range for the MH particle group in our study to ~ 0.2-0.4, suggesting that it may be worthwhile for future studies to check and develop this or alternative classifications further. Key aspects of the above paragraph will be included in the revised manuscript.

Referee Comment 13:

P3829; L9: The statement that coupling remote sensing measurements and kappa values to predict CCN concentrations is tenuous as the size distributions from satellite measurements are not detailed enough to predict CCN concentrations within the range presented in this manuscript. This sentence should be removed.

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 14:

P3831; L13+: This classical power law approximation is not physically-based and should in general be avoided. I suggest simply reporting the values for comparison to older literature rather expanding a new section to include a modified power law approach.

Response:

We agree that reporting classical power law parameters serves mainly for comparison with older literature data. With regard to the relatively uniform integral CCN ef-

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ficiency N_CCN,S/N_CN,30 found in this and earlier studies and discussed in Sect. 3.2.1 (p3830, l. 25), however, we consider it relevant to explore and characterize also the applicability and limitations of the modified power law approach based on N_CN,30.

Referee Comment 15:

P3833; L12: replace _little higher_ with a quantitative value

Response:

Following the referee's suggestion, we will add quantitative values based on Table 4 into the text of the revised manuscript.

Referee Comment 16:

P3852; Table 3: What is significant about the time period 'Rest of the campaign'? It does not seem to present any new information here.

Response:

We agree that these parameters and other information concerning the "rest of the campaign" (not only in Tab. 3 but also in Tab. 1 and in Fig. 7) are not among the key results and main messages of our manuscript. However, we consider this information as a natural complement to the parameters and information provided for the entire campaign and for the focus period. We would like to remind the referee that our manuscript is part of a fairly large field measurement campaign, and that other studies and collaborators will most likely want to use and refer not only to the entire campaign and to the (pristine) focus period selected in our study but also to the (less pristine) "rest of the campaign". We consider it easy and natural to provide quantitative information about the average aerosol particle size distributions measured during the different measurement periods investigated and characterized in our study, and it would be fairly difficult for readers to retrieve such information just from comparison of the entire campaign and pristine period data. With all due respect for the referee's intention of helping us and future readers and users of our results to stay focused on the main messages, we

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do not understand why a couple of lines in a table reporting complementary information rather than exciting new research highlights would do more harm than good. To our knowledge, (Amazonian) aerosol particle size distribution data are fairly scarce in the scientific literature but essential for any kind of atmospheric aerosol (model) study.

P3853; Table 4:

The differences between k=0.147 and k=0.149 are insignificant; both columns are not necessary.

Response:

We will replace the two columns by one column with a rounded overall median value of kappa = 0.15.

P3860; Fig. 5:

Figure 5 is not referenced. Remove figure or combine with Figure 3.

Response:

Unlike indicated by the referee, Fig. 5 was referenced and discussed at the end of Sect. 3.1.2 (p. 3825, l. 14). Nevertheless, we will follow the referee's suggestion and include the data from Fig. 5 in Fig. 3.

P3865; Fig 10:

Remove figure (not referenced). Verify order and reference for all figures.

Response:

Unlike indicated by the referee, Fig. 10 was referenced and discussed in Sect. 3.2.2 (p. 3832, l. 2).

To be continued (Part 2: References)

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