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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 #2 for the effort and time invested in the review of our manuscript and for the positive overall evaluation of our work. The points of criticism are also well taken, and the suggestions for improvement are welcome and will be largely implemented upon revision. Some of the referee's views and opinions, however, we do not share. Detailed responses to the individual comments are given below.

Referee Comment 1:

The paper provides thorough and very useful description and climatology of the behav-

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ior of aerosol particles as cloud condensation nuclei in the Amazon during AMAZE-08. The overall point that size and number determine CCN behavior once compositional variability is removed is well demonstrated. However, the manuscript is rather unfocussed and rather does not distill the results into a digestible body of work.

Response:

We do not understand what the referee means by the phrase "once compositional variability is removed", and we do not think that this is the main point of our paper. Our manuscript was and is meant to convey not just one but multiple key findings of our study:

1) For the pristine tropical rainforest aerosols of Amazonia investigated during AMAZE-08, the median value of the effective hygroscopicity parameter kappa that can be used to describe the influence of chemical composition on the CCN activity of aerosol particles varied in the range of ˜ 0.1-0.4 (arithmetic mean and standard deviation 0.16 ś 0.06). The overall median value of kappa ˜ 0.15 was by a factor of two lower than the values typically observed for continental aerosols in other regions of the world.

2) Aitken mode particles were less hygroscopic than accumulation mode particles (˜ 0.1 at D ˜ 50 nm; ˜ 0.2 at D ˜ 200 nm), which is in agreement with earlier hygroscopicity tandem differential mobility analyzer (H-TDMA) studies.

3) The CCN measurement results are consistent with aerosol mass spectrometry (AMS) data, showing that the organic mass fraction (Xm,org) was on average as high as ˜90% in the Aitken mode (D ˜ 100 nm) and decreased with increasing particle diameter in the accumulation mode (˜80% at D ˜ 200 nm).

4) The kappa values exhibited a close linear correlation with Xm,org (R2 = 0.81) and extrapolation yielded the following effective hygroscopicity parameters for organic and inorganic particle components: kappa_org ˜ 0.1 which can be regarded as the effective hygroscopicity of biogenic secondary organic aerosol (SOA) and kappa_inorg ˜ 0.6

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which is characteristic for ammonium sulfate and related salts.

5) Both the size dependence and the temporal variability of effective particle hygroscopicity could be parameterized as a function of AMS-based organic and inorganic mass fractions (kappa_p=X_m,org*0.1+X_m,inorg*0.6)), and the CCN number concentrations predicted with kappa_p were in fair agreement with the measurement results (˜20% average deviation).

6) The median CCN number concentrations at S = 0.1-0.82% ranged from NCCN,0.10 ˜ 35 cm-3 to NCCN,0.82 ˜ 160 cm-3, the median concentration of aerosol particles larger than 30 nm was NCN,30 ˜ 200 cm-3, and the corresponding integral CCN efficiencies were in the range of NCCN,0.10/NCN,30 ˜ 0.1 to NCCN,0.82/NCN,30 ˜ 0.8.

7) Although the number concentrations and hygroscopicity parameters were much lower, the integral CCN efficiencies observed in pristine rainforest air were similar to those in highly polluted megacity air. Moreover, model calculations of NCCN,S assuming an approximate global average value of kappa ˜ 0.3 led to systematic overpredictions, but the average deviations exceeded ˜50% only at low water vapor supersaturation (0.1%) and low particle number concentrations (<=100 cm-3). Model calculations assuming constant aerosol size distributions characteristic for the campaign or for remote continental regions led to higher average deviations (˜60-1600%). 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.

We will try to clarify these messages in the revised manuscript and abstract (using some of the above formulations).

Referee Comment 2:

I would suggest that the paper is reduced in the length, removing unnecessary discursiveness and focusing on the main scientific story. I also think the paper retains far too

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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.

Response:

Following up on the referee's suggestions we will 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. Moreover, we will try to clarify and condense the story and messages as detailed above and below. 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 3:

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.

Response:

We do not understand what the referee means by the phrase "There appears to be no independent and objective metric for the degree of skill". It was and is not the purpose of our study and manuscript to develop new types of metrics. Instead, we have experimentally characterized the CCN activity of pristine Amazonian aerosols as a function of particle size and water vapor supersaturation. From the measurement data we have derived simple and widely used hygroscopicity parameters (kappa) which

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can be applied to approximate/describe the influence of chemical composition on the CCN activity of aerosol particles. By Köhler model calculations we have shown how the determined parameters can be applied to approximate/predict CCN number concentrations as a function of water vapor supersaturation, aerosol particle number concentration, size distribution, and chemical composition. The "degree of skill" of this approach has been quantified in terms of relative deviation between approximated/predicted and measured CCN concentrations, which is a common way of characterizing the outcome of CCN closure studies. The main results of these calculations are:

1) With variable kappa values determined from CCN efficiency spectra (activation curves) measured in parallel to aerosol particle (CN) number concentrations and size distributions, the measured CCN number concentrations could be approximated with a mean relative deviation of ˜7% (˜18% at low water vapor supersaturation, i.e., S = 0.1%).

2) With the constant campaign average value of kappa (˜0.15), the measured CCN number concentrations could be predicted with a mean relative deviation of ˜ 15% (˜28% at S = 0.1%).

3) With a simple parameterization of kappa as a function of aerosol chemical composition (organic and inorganic mass fraction determined by integral AMS measurements), the mean relative deviation between measured and predicted CCN number concentrations was similar as with the campaign average value of kappa (˜16% overall, ˜27% at S = 0.1%).

4) With a constant kappa value of 0.3, which is twice as high as the campaign average value and equals the average kappa value reported for other continental regions, the mean relative deviation between measured and predicted CCN number concentrations was ˜45% (˜111 % at S = 0.1%).

5) With variable kappa values and with the campaign average CN size distribution (constant), the mean relative deviations between measured and predicted CCN number

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concentrations were higher than with the approximate global average value of kappa = 0.3 and variable size distributions: ˜59% overall (˜124 % at S = 0.1%).

6) With variable kappa values and with the generic remote continental size distribution listed in Seinfeld and Pandis (2006), the mean relative deviations between measured and predicted CCN number concentrations were much higher than in all other scenarios: ˜1600 % overall (˜1400-1900% for different S).

The last two scenarios have been calculated after submission of the discussion paper and will be added to the revised version. Comparison of the various scenarios very clearly confirms the general message drawn in the abstract, discussion and conclusions sections of our manuscript:

"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."

Note that this message is not only confirmed by the model scenarios and results outlined above, but also by the fact that the integral CCN efficiencies (ratios between CCN and CN number concentrations) are usually less variable than the aerosol particle number concentrations observed at different locations and times (p. 3833, l. 28 of our discussion paper):

"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 = 10

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- 10ˆ4) going from pristine tropical rainforest air to highly polluted megacity 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)."

Referee Comment 4:

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's previous work would find it very difficult to read and pick up all the jargon.

Response:

We share the referee's appreciation for measurement data, but we do not agree with his/her concerns and suggestion. Our manuscript does already display similar amounts or more measurement or "first generation" data than most other (recent) publications on CCN field measurements that we know (e.g., Roberts et al., 2001; 2002; 2003; Dusek et al, 2006; Ervens et al., 2007; Medina et al., 2007; Kuwata et al., 2008; Sorooshian et al., 2008; Wang et al., 2008; Bugiatioti et al., 2009; Shantz et al., 2009; Shinozuka et al., 2009) In Fig. 2 we show characteristic CCN efficiency spectra (activation curves) as measured by our instrument, and in Fig 4 we show time series of the primary parameters describing these efficiency spectra (midpoint diameter, width and amplitude of standard CDF fit). In Fig. 7 we show average measured CCN size distributions, and in Fig. 8 we show time series of measured CCN number concentrations (N_CCN,S) and integral CCN efficiencies (N_CCN,S/N_CN,30). In the online supplement we show box plots characterizing the statistical distributions of all these "first generation data". Due to the physical principles of CCN activation, all of the above parameters ("first

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generation data") depend strongly on the level of water vapor supersaturation applied in the reported experiments/measurements. Thus the "first generation data" cannot be directly and efficiently compared with measurements performed at different conditions (supersaturation levels), neither within the same study nor across different studies. Accordingly, they are also of limited use for model studies of CCN activation and cloud droplet formation, which usually require parameters that describe the number concentration of CCN as a function of water vapor supersaturation or updraft velocity, (e.g., Feingold et al., 2001; Feingold, 2003; Roberts et al., 2001;2003; Andreae and Rosenfeld, 2008; Heintzenberg and Charlson, 2009; Kreidenweis et al., 2009; Reutter et al., 2009; and references therein). For this reason, characteristic parameters such as the effective hygroscopicity parameter kappa and analogous parameters (e.g., equivalent soluble fractions or ion densities as specified on in Sect. 3.1.3, Eq. 1) have been developed and used for efficient comparison of the results of CCN measurements or H-TDMA measurements performed under different conditions. The conversion of the hygroscopicity parameter kappa into other parameters and/or into a pair of supersaturation and activation diameter ("first generation data") is very straightforward. In fact, our manuscript goes one step beyond most other related we know, by explicitly converting and tabulating different types of hygroscopicity parameters reported from earlier studies (Tab. 2). We understand and respect that the referee seems to prefer the use of raw data and/or different parameters/terms ("jargon") 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 (for example, see Andreae and Rosenfeld, 2008; Kreidenweis et al, 2008,2009; Shantz et al., 2009; Shinozuka et al., 2009; and references therein). Nevertheless, we will try to refine/clarify the description of our approach in the revised

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manuscript.

We appreciate the referee's suggestion to include additional figures showing the time series of measured CCN efficiency spectra (activation curves) in the form of contour plots for each investigated supersaturation level. However, we do not intend to follow this suggestion for the following reasons: 1) The proposed contour plots are not needed/relevant for the scientific issues and messages addressed and conveyed in our manuscript, and time series as well as statistical distributions of the essential parameters characterizing the observed CCN efficiency spectra (midpoint activation diameter, width/standard deviation, and maximum activated fraction) are already included in the manuscript and online supplement. 2) In the review and interactive public discussion of our paper Referee #2 as well as Referee #1 and Dr. Roberts have expressed concerns that our manuscript would already contain too much information and too many plots and should be focused on the most essential aspects. 3) As described in Sect. 2.2 of our manuscript, the recording of each CCN efficiency spectrum took ˜35 min followed by a gap of ˜180 min until the next CCN efficiency spectrum could be recorded at the same supersaturation level. In addition, there are several gaps in the time series due to technical problems and maintenance work (Sect. 3.1.2, Fig. 4). As a consequence, the proposed contour plots would consist mainly of gaps ($>$ 80%) with narrow stripes of data scattered in between ($<$ 20%), or they would heavily rely on interpolation techniques rather than actual measurement data.

Referee Comment 5:

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.

Response:

Thanks. We hope and are confident that the referee's concerns are properly addressed in this interactive comment and in the revised version of our manuscript.

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Referee Comment 6:

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.

Response:

Following the referee's suggestion, we will add information about the arithmetic mean value and standard deviation in the abstract. Note, however, that this information had already been included in the manuscript (Table 1), and other referees/readers often tend to complain about cluttering abstracts with too many numbers.

Nowhere in our manuscript did we suggest that the campaign median of kappa = 0.15 would be surprisingly close to the approximate global average value of 0.3. On the contrary, we stated in the abstract, in Sect. 3.1.1 (p. 3824, l.7) and in the conclusions section (p. 3839, 1. 6) that kappa is "ONLY half the value typically observed for continental aerosols in other regions of the world." Indeed, we also consider the deviation by a factor of two as large, and to our knowledge no other study has yet reported long-term (i.e., multi-week) measurements of CCN in continental air with an average kappa value that would differ by a factor of two or more from 0.3.

What we do find remarkable - albeit not surprising in view of related earlier studies referenced in our paper - are the following points: 1) p. 3830, l.25: "Compared to highly polluted megacity regions (Rose et al., 2008b; Wiedensohler et al., 2009), the CN and CCN number concentrations observed during AMAZE-08 were two orders of magnitude lower, but the integral CCN efficiencies were still similar and consistent with the global average values reported by Andreae (2009, NCCN,0.4/NCN,10 ˜ 0.4)." 1) p.3834, l. 3: "... a constant global average effective hygroscopicity parameter of kappa

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=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 (NCCN,S ˜ 10 - 10ˆ4) going from pristine tropical rainforest air to highly polluted megacity 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)."

Thanks for addressing the statement about the range of observed kappa values - we realize that it is not really appropriate. As described in Sect. 3.1 (Tab. 1, Fig. 3, Fig. 4b), the kappa values varied indeed mostly in the range of 0.1-0.4 rather than 0.05-0.45, and we will adjust the abstract and summary accordingly.

As described in Sects. 3.1.2 and 3.3, the variations of kappa can be explained and modeled on the basis of variations in the organic mass fraction determined by AMS. As specified on p. 3826, l. 1: "The factors regulating the variation in organic mass fraction are not yet fully understood (Chen et al., 2008) but may include local emissions as well as long-range transport of sea salt, mineral dust or biomass burning particles (Martin et al., 2009b)." Additional references will be added in the revised manuscript (Chen et al., 2009; Martin et al., 2009a).

Referee Comment 7:

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.

Response:

We do not understand what the referee means by "only a 10% increase in organic mass increases k by 100". The basic relations between kappa and aerosol chemical composition have been outlined by Petters and Kreidenweis (2007) and were further addressed in numerous papers published since then (e.g., Kreidenweis et al., 2009;

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Pöschl et al., 2009a; Mikhailov et al., 2009; etc.) as well as in Sect. 3.1.3 (Eq. 1) and in Sect. 3.3 (Eqs. 2 and 3) of our study. According to our observations, the effective hygroscopicity of pristine Amazonian rainforest aerosols is close to 0.1 for purely organic particles and increases with increasing inorganic mass fraction (as determined by AMS) as described by Eq. (3) on p. 3837, i.e., kappa increases by ˜0.06 when the inorganic mass fraction increases by 10%.

Referee Comment 8:

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 the statement on p3814 line 5 is correct.

Response:

The shape of the aerosol size distribution was fairly stable (Aitken and accumulation mode, Fig. 7) but the number concentrations varied substantially (Fig. 8, Tab. 1). Indeed, CCN prediction using a constant average size distribution as observed during AMAZE-08 led to a mean relative deviation of ˜60% (we had intended but did not manage to include this information already in the discussion paper). Note, however, that this scenario should be compared to the scenario with constant average kappa of 0.15 (mean relative deviation ˜15%). The scenario with a global average value of kappa = 0.3 (mean relative deviation ˜45%) should be compared to a scenario using a constant size distribution that can be taken as a proxy for the global average aerosol size distribution in continental air. With the generic remote continental size distribution listed in Seinfeld and Pandis (2006), the mean relative deviations between measured and predicted CCN number concentrations were much higher than in all other scenarios: ˜1600 % overall (˜1400-1900% for different S; see point 6 under Referee comment 3 above). On top of that, the approximate global average value of 0.3 holds also in highly polluted megacity air (Rose et al., 2008b; Wiedensohler et al., 2009) where the concen-

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trations of aerosol particles and CCN increase up to 10ˆ4 and higher. Together with the similar integral CCN efficiencies reported from highly polluted and pristine air masses (˜0.4 +/- 0.1 at S ˜ 0.4%), the above scenarios clearly confirm the general conclusion drawn from our results in relation to the results of earlier studies (p. 3840, l. 20). "The similar integral CCN efficiencies observed in pristine tropical rainforest and in highly polluted megacities and the relatively small errors in predicting NCCN,S with constant kappa=0.3 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 (Dusek et al., 2006; Ervens et al., 2007; Andreae and Rosenfeld, 2008; Rose et al., 2008b; Andreae, 2009; Kreidenweis et al., 2009; Pöschl et al., 2009a). At low supersaturtion level, however, N_CCN,S remains difficult to predict with high accuracy."

In the revised manuscript we intend to add the additional scenarios of CCN prediction outlined above, to clarify the interpretation, and to add more references to other studies conveying the same or similar messages as follows (end of section 3.2.2):

"With the constant campaign average size distribution (Fig. 6a, Tab. 3) and variable kappa, the mean relative deviation between measured and predicted CCN concentrations (˜60%) was by a factor of ˜4 higher than with the constant campaign average value of kappa ˜ 0.15 and variable size distribution (˜15%, Tab. 4). Assuming a constant generic size distribution for remote continental areas with variable kappa, the mean relative deviation between measured and predicted CCN concentrations (˜1600%) was by a factor of ˜27 higher than under the assumption of an approximate global average value of kappa ˜ 0.3 with variable size distribution (˜1600%, Tab. 4). The comparison of measured and modeled CCN concentrations clearly demonstrates that the variability of CCN concentrations is much stronger influenced by the variability of aerosol particle number concentration and size distribution than by the variability of aerosol chemical composition and hygroscopicity. This applies for the temporal variations during the

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AMAZE-08 campaign (factor ˜4) as well as for spatial/geographic variations between central Amazonia during the wet season and other remote continental regions (factor ˜27). The above sensitivity studies and the similar integral CCN efficiencies observed in pristine rainforest, highly polluted megacities and other remote and polluted regions around the world (Sect. 3.2.1, Andreae, 2009) 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 (Feingold et al., 2001; Feingold, 2003; Dusek et al., 2006; Ervens et al., 2007; Andreae and Rosenfeld, 2008; Rose et al., 2008b; Anderson et al., 2009; Feingold and Siebert, 2009; Kreidenweis et al, 2009; Pöschl et al, 2009a).”

Referee Comment 9:

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 NCCN 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.

Response:

To accommodate the referee's concern, we intend to change the formulation from "fully consistent" to "consistent". However, we would like to point out that the degree of closure between CCN concentrations measured and modeled on the basis of chemical composition data is similar to other recent studies (e.g., Ervens et al., 2007; Kuwata et al., 2008; Sorooshian et al, 2008; Wang et al., 2008; Shinozuka et al., 2009). We do not agree that the inference of consistency between CCN and AMS measurements would need to be justified by radiative forcing estimates. The consistency of CCN and AMS measurement has been clearly demonstrated in the manuscript: 1) linear correlation between kappa and organic mass fraction; 2) description of size dependence and

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temporal variability of kappa based on AMS data (good agreement for large accumulation mode particles around 200 nm; decreasing agreement with decreasing particle size due to decreasing precision of AMS data); 3) ability to predict hygroscopicity parameters and CCN concentrations based on AMS data as discussed above and in Sects. 3.2.2 (p. 3833, l.13) and 3.3 (p. 3837, l. 17), respectively. The determination of radiative forcing estimates goes beyond the scope of the present paper.

To be continued (Part 2)

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