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Atmospheric Chemistry and Physics Discussions

Interactive comment on "An improved criterion for new particle formation in diverse atmospheric environments" *by* C. Kuang et al.

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(1) Γ is the ratio between GR [Measured] to GR [H2SO4]. I am very much concerned about how "practically" the authors have taken the growth due to other species, e.g. organics, into account? How the growth enhancement factor Γ is introduced in order to take into account multicomponent processes in particle nucleation and early growth. It seems that Γ is simply just a multiplier of the sulfuric acid concentration due to condensational growth? On p.499, just right after eq. 6, the authors state that "While the growth enhancement factor Γ incorporates the effects of multi-component condensation, Eqs. (5) and (6) are still based on a single-component formulation since Γ is calculated assuming a condensing molecular volume of hydrated sulfuric acid". Please explain this "main improvement point" in more detail in the revised version.

Use of the growth enhancement factor Γ allows for incorporation of measured particle growth rates (which are often the product of condensation of species other than sulfuric acid) into a single component model. Because Γ is calculated from the measured growth rate, it incorporates the contributions from the condensation of other species besides sulfuric acid, albeit as a lumped quantity. Based on the defining equations of the cluster population balance model, Γ is seen as a multiplier of the sulfuric acid concentration. But because Γ is defined as a ratio of the measured growth rate to the sulfuric acid-limited growth rate, the product of Γ*[H2SO4] is also representative of the measured particle growth rate. Incorporation of Γ therefore represents a significant improvement to the single component model. It is worth noting that previous studies have shown that ïĄĞ=1 when H2SO4 condensation is responsible for all growth [Stolzenburg et al., 2005].

(2) I really cannot understand why nano particle growth rates are that high sometimes? Could you please explain? For example, in table 1, row EUCAARI 04/15/07, the values indicate a total growth rate of about 40 nm/h. At a H2SO4 concentration of 10ˆ7 molecules cmˆ3, the nanoparticle growth rate is about 1.5 nmhˆ-1. Surely, there are several condensing vapors obviously participating in the growth process as well, however total growth rates typically do not exceed 20 nm hˆ-1. There are exceptions such as coastal areas, where oxidation of iodine-containing vapors can rapidly produce large amounts of condensable matter and also highly polluted environments, but here the explanation should be different?

For the NPF event measured on 04/15/07 during EUCAARI, the measured growth rate calculated from the time delay between profiles of [H2SO4] was 20 nm/h. Using that value and the peak [H2SO4] yielded the listed growth enhancement factor of 134. Also, the high ïĄĞ values are consistent with Jim Smith's TDCIMS measurements of nanoparticle composition, which show that sulfates are often a minor fraction of the particle mass [Smith et al., 2010]

(3) Growth enhancement factor (Γ) spans the range from 1 (ANARChE) to over 100

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(EUCAARI)? The authors claim that this might depend on the location. However, in some cases the growth enhancement factor varies in the same location by a factor of as much as 34 within the same month while the amount of measured sulfuric acid concentrations remains almost in the same range. How is this possible? I think the discussion of the variability of Gamma, as well as the related uncertainties and limitations should be discussed in more detail.

While it is true that at certain locations there is a rather wide spread in Γ (EUCAARI), it is also true that much is not known regarding other species whose condensation is contributing significantly to the measured growth rate. A more in-depth discussion of variability in Γ and reasons for such variability would be more appropriate for a subsequent study focusing on growth rates. Our plans for understanding the chemical processes that are responsible for nanoparticle growth rates are detailed in [Smith et al., 2010].

(4) I would like to see a figure, instead of a table, showing number of event days and nonevent days as a function of Γ values for each measurement sites. It was hard to make any criteria based on Γ values to distinguish between events and nonevents while Γ here is presented as a key factor for the improved dimensionless parameter. This point should be well clarified in the manuscript. (Yes, I noticed that LΓ was presented as a function frequency of NPF and non nucleation in Fig. 4, but this is a different story and we will get back to it later.)

While Γ is an important parameter in determining the survival probability of a nucleated particle, it is only part of the story, and does not exclusively distinguish between events and non-events. The NPF criterion also includes (along with Γ), the Fuchs surface area and the peak sulfuric acid concentration. We believe this point was clearly explained in the manuscript.

(5) As Gamma is presented in the tables, and used in the Equations following Eq. 6, please present an equation showing how it is calculated instead of just mentioning it

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inside the text. I would also be interested to see the modeled formula for N3-4nm.

The appropriate equation will be added defining Γ. The definition for N3-4nm can be found in [Kuang et al., 2008]. The appropriate citation has been added in the amended manuscript.

(6a) In the methodology: How was Nm (peak [H2SO4] during NPF event) defined for Nonevent days? To deal with the six intensive measurement campaigns similarly, the authors estimated K (pre-factor) values based on the power-law equation: J†=K[H2SO4]P and by assuming nucleation exponent (P=2; i.e assuming Kinetic nucleation mechanism for all stations) and taking the time for event days to be "times when events take place i.e during NPF event" So my question is how you get K (Kinetic coefficient) values for nonevent days while J†is missing ?. For ambient data, in which K ranges from 10ˆ-14 to 10ˆ-11 cm3 sˆ-1, have you used these ranges for K values for non-nucleation days?? Overall, a few sentences about the non-nucleation days would be very useful. (The reader necessary needs to know; how the non-nucleation data parameters were treated as well in order to be comparable with NPF days and therefore to be tested by the new criteria).

Analysis of the non-event days did not require the use of the nucleation rate pre-factor K, since the analysis of non-events focused on calculating the NPF criterion LΓ, which is a function only of scavenging and growth parameters. Use of the nucleation rate pre-factor K was limited only to model results, such as model validation (Figure 1), and the combined effects of scavenging and growth on nucleated particle survival probability (Figure 2). The peak [H2SO4] that was used to analyze non-events was determined by taking the maximum value of [H2SO4] during the period in which there was observable growth of the pre-existing aerosol. For a number of these non-events, the profile for [H2SO4] was quite noisy with no discernible diurnal profile usually observed with NPF events. A short description clarifying analysis of non-event days has been included in the revised manuscript.

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(6b) Criterion was tested against measured 77 days of new particle formation and for 19 non-nucleation days BUT so far the classification of new particle formation days has usually been based on visual examination of the temporal development of size distributions (“banana plots”) to distinguish between NPF and no nucleation days. The coauthors checked these classified days by using their criteria (calculating LΓ factor for both data sets (NPF and no nucleation days)) and plotted against the Frequency (Figure 4), so isn't it so that the authors have made an interesting *observation* about event days versus some nonevent days, and I am afraid that the word "criterion" is not rightly used here.

We have shown that this criterion is consistent with the analyzed NPF events and non-events. The analysis method that was used to calculate LΓ does not really make any a priori distinction between event and non-event prior to analysis. All that is required is a measurement of the Fuchs surface area, growth rate (applies to both events and non-events), and peak sulfuric acid concentration. For the events in this study that were classified as non-events (no observable particle production but also observable particle growth), there were no measured particle counts for particles of sizes < 30 nm. Growth rates for these non-events were determined from the time rate of change of the pre-existing aerosol mode diameter. In other words, the same analysis method for determining LΓ is consistently applied to both events and non-events.

(6c) P. 508 line 9-11: authors claimed that LΓ is a robust parameter that can be used to predict the frequency and relative strength of NPF events. However to accurately predict NPF, it is necessarily to get from the observational data i) the measured growth rate, and ii) estimate the growth rate assuming only sulfuric acid condensation ; iii) estimate activation pre-factor K, to be able to present LΓ factor correctly in the model. Please detailed discussion of this aspect in the revised version will be so much appreciated.

While the cluster population balance model requires observationally-constrained inputs for the nucleation rate pre-factor K and the growth-enhancement factor Γ, application

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of the new particle formation criterion requires only inputs for the pre-existing aerosol surface area and the nucleation mode growth rate (which is equivalent to having both the peak value of [H2SO4] and the growth enhancement factor). At a particular location, while fairly reasonable estimates of the pre-existing aerosol surface area can be used as model inputs, there are, at this point, only empirical means of determining Γ, either from measurements of nucleation mode particle composition or by comparing measured and sulfuric acid-limited growth rates. There is evidence that NPF at a particular site is characterized by a relatively narrow range of growth enhancement factors, such as in Atlanta, Boulder, and Mexico City. For those types of NPF events, application of this NPF criterion would provide a reasonable estimate for the relative strength and frequency of NPF. The predictive power of this criterion will improve as better estimates are made regarding particle growth rates. This point is emphasized in the amended manuscript.

(7) The parameters L1 and Γ1 characterize the scavenging and growth processes, respectively. Therefore these two parameters are the core of the developed "criterion" for new particle formation. Later on, these two parameters were combined as LΓ (L1= Γ1) and were used to estimate the survival probability of a nucleated particle growing to the detection limit (3 nm) i.e. J3, and as an expected result, J3 depends only on the ratio L1 and Γ1. If the new modified LΓ seems to be identical to the old L when the whole growth is caused by H2SO4 as in sulfur-rich environment, would it be more informative here for the authors to present the survival probability J3 as a function of old L and the modified Lgama respectively in order to show how sensitive the modified growth enhancement factor improve the survival probability J3 estimation? As it was mentioned by the authors that LΓ is independent of the nucleation rate pre- factor K and nucleation exponent P therefore the main KEY here is how the enhancement growth factor improves this NPF "criterion"? A figure would be useful to show how well the improved "modified L –factor theory" really worked?

The "improvement" of incorporating Γ is quite evident already in Figure 4 and in the

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accompanying discussion (p. 508, lines 22 – 29), where not including Γ (or setting Γ = 1) in the criterion dramatically underestimates survival probability and misclassifies a majority of the observed NF events.

(8) Figure 2: Identical behavior was also observed in the model results for the other measurement campaigns so was there any particular reason that authors picked MILAGRO station with 9 new particle formation days and zero non nucleation days?

The results presented in Figure 2 are model results, and selection of which campaign to use was not based on the number of measured events and non-events for that campaign. The modeled results were initialized with measured ranges in scavenging rates, growth rates, and nucleation rates appropriate to what was observed in MILAGRO.

Minor comments: (9) Page 497, line 11. k under the square root is Boltzmann constant (i.e KB)not the cluster size k, Am I right? . Please correct.

The “k” on p. 497 line 11 has been amended to read “kB” for the Boltzmann constant.

(10) Fig 3. in the figure captions LΓ was defined as L1 divided by Γ1, while in page 506 ,equation 17 , LΓ was defined as the ratio between L and Gamma ? Please unify your definitions.

Equation 17 has been amended as suggested.

(11) Fig3. was it only for NPF days or all datasets? Please clarify.

The results from Figure 3 are model results and were initialized with measured ranges in scavenging and growth rates that are consistent with both events and non-events.

(12) In the reference list, the "a" is missing from Kulmala et al., 2004a

The reference has been amended as suggested.

Kuang, C., et al. (2008), Dependence of nucleation rates on sulfuric acid vapor concentration in diverse atmospheric locations, J. Geophys. Res., 113(D10), D10209, DOI:

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10.1029/2007jd009253. Smith, J. N., et al. (2010), Observations of aminium salts in atmospheric nanoparticles and possible climatic implications, Proceedings of the National Academy of Sciences. Stolzenburg, M. R., et al. (2005), Growth rates of freshly nucleated atmospheric particles in Atlanta, J. Geophys. Res., 110(D22), D22S05, DOI: 10.1029/2005JD005935.

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