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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Uncertainty in global CCN concentrations from uncertain aerosol nucleation and primary emission rates" *by* J. R. Pierce and P. J. Adams

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We would like to thank this reviewer for helpful comments and recommendations that have strengthened the paper.

Major comments:

1) Although the exact nucleation mechanism(s) occurring in the atmosphere are not fully understood, it is very likely that nucleation rates and most certainly new particle and CCN formation rates depend non-linearly on vapor concentrations and other atmospheric conditions. Therefore I disagree with the authors' straightforward assumption that choosing two fairly extreme nucleation mechanisms gives meaningful bounds on the effect of nucleation on CCN. Binary mechanism is known to produce particles only in the FT and thus to severely underestimate nucleation rates in the BL. On the other hand, ternary nucleation has been shown to produce too

high particle formation rates pretty much everywhere. The problem with ternary nucleation as a CCN source is that a very high number of nucleated particles compete for a limited amount of condensable vapor and thus only a small fraction of the nucleated particles gain enough mass to become CCN. In other words, neither of these two mechanisms is optimal for CCN production (nor do they correspond well with observations).

It is therefore possible that a more realistic particle formation mechanism with a moderate nucleation rate both in the BL and FT can lead to a higher contribution of nucleation to CCN. This is because enough new particles are formed (in contrast to binary mechanism) but competition for condensation growth is not as fierce as when using the ternary mechanism.

To test this possibility, the authors should repeat at least their "basecase" run with a third nucleation mechanism that gives atmospherically realistic nucleation rates also in the BL. They can apply either recently proposed kinetic or activation mechanisms (e.g. Kuang et al., 2008, JGR; Sihto et al., 2006, ACP), or alternatively scaled down ternary nucleation rates. In my opinion this additional simulation is needed although Spracklen et al. (2008) and Wang and Penner (2008) both used activation nucleation in global models and obtained fairly similar numbers with the current study for nucleation derived CCN. Both previous studies used a model that is different in many details from the current one and thus their activation nucleation results cannot be generalized for the current model.

We have added an additional simulation using the activation-type nucleation (ACTIVATION). We use j(1 nm)=1.0E-6*[H2SO4] as the nucleation relationship in the boundary layer (Sihto et al. 2006) and Vehkamäki binary nucleation in the rest of the troposphere. Due to long simulation times were are only able to run the model for 3 months for this scenario (two months of spin up and one month of results). We find that the contribution of this scenario to CCN is in between that of BINARY and TERNARY. Below is the main discussion of this that we added to the text.

“Also shown in Table 2 is the effect of activation nucleation in the boundary layer on tropospheric CCN(0.2%). In June, the tropospheric-average nucleation in ACTIVATION is a factor of 10 higher than in BINARY causing an increase in CN10 by 17% across the troposphere. The global CCN(0.2%) increases by about 5%. As shown in Fig. 5a, the

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boundary layer CCN(0.2%) also increase by 5% as tropospheric CCN(0.2%) are dominated by boundary layer CCN(0.2%). Figure 5b shows that the increase in boundary layer CCN(0.2%) from BINARY to TERNARY is more than twice that of Fig. 5a. If the nucleation rates in the TERNARY simulation are unrealistically high, the 5% sensitivity of CCN(0.2%) to nucleation between the ACTIVATION and BINARY simulations may be a more realistic bound for the sensitivity of CCN(0.2%) to nucleation for our base case emissions and SOA.

Across the 5 simulations with present-day base-case primary emissions and SOA, the CCN(0.2%) increases monotonically with increasing global nucleation rates between the NONUC, REDBINARY, BINARY, ACTIVATION and TENARY simulations. For the reasonably comprehensive span of nucleation rates, mechanisms and distributions sampled here, the global CCN(0.2%) appears to increase monotonically with increases in global nucleation albeit with diminishing return due to a decrease in NUE with increasing nucleation rate. We found only one example in which CCN(0.2%) decreased with increasing nucleation rate: the tropical upper troposphere (Figures 4c and 4d). The reduction is modest (5-10%), localized, and in response to a strong change in nucleation rates. This occurs because the very cold temperatures in this region favor nucleation even at low H2SO4 concentrations, concentrations too low to grow the nuclei efficiently to CCN sizes. This behavior is not observed in our simulations in the planetary boundary layer."

2) Nucleated particles are introduced to the model at a size of 10 nm by using Kerminen et al. (2004) formulation to relate the formation rate of particles at this size to nucleation rate at 1 nm. There are however some important assumptions behind Kerminen et al. (2004) equations that very likely are not met when they are applied to formation at 10 nm size. First is the requirement of constant growth rate of nucleated particles. As it typically takes at least several hours - and in many parts of the atmosphere more like a half a day - for particles to reach 10 nm, the concentration of condensing vapors is bound to change during this time (e.g. daily cycle of H2SO4). Second is the requirement for fixed pre-existing particle size distribution which is likely not to be the case at least in the boundary layer where particle sources and

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sinks as well as condensation growth modify the properties of the size distribution. I am also concerned how the instantaneous growth of nucleated particles to 10 nm affects the nucleation rate at subsequent time steps as the treatment lowers the concentration of nucleating vapors unrealistically fast.

All in all, I have doubts whether reliable simulations of nucleation can be made with a model using a 10 nm cut-off size. I suggest the authors try to prove me wrong by making simple box model calculations with two set-ups: 1) current set-up in 3-D model (10 nm cut-off, Kerminen et al. formulation, long time steps), and 2) detailed size distribution down to 1 nm with sufficient number of bins, explicit simulation of condensation and coagulation growth of nucleated clusters from 1 to 10 nm, fairly short time steps, varying condensable vapor concentrations.

Both of your points should cause the Kerminen parameterization generally to overestimate the growth of new particles to 10 nm. For the constant growth rate assumption, both nucleation rates and growth rates will generally be the highest when sulfuric acid production is at its peak. By assuming the growth rate at the time which nucleation occurred, the J10 rates will be biased high. For the constant fixed pre-existing particle size distribution assumption, there will generally be an increase in the condensation/coagulation sink after nucleation has started due to the increase in the number of particles. Again, by assuming the condensation/coagulation sink at the time nucleation occurred, this will bias the J10 rates high.

We have a new version of the global model that is now being tested in which the explicit aerosol size section extend down to 3 nm. We have reran the BINARY simulation and there was very little difference in J10 rates with the model presented here. We have not yet reran the TERNARY simulation. However, when we were incorporating nucleation into the global model, we did do box model tests similar to what you described above. In general, there was little error for binary nucleation cases and high bias for J10 in ternary cases during cases where the environment changed quickly.

If there is indeed a high bias in J10 rates in the TERNARY simulation, this would further reduce the sensitivity of CCN to changes in the nucleation rate. The Napari et al. (2002)

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rates are already very likely too high, so this would mean that our upper bound for the contribution of nucleation to CCN is potentially too high (for fixed primary emissions and SOA).

We have added the following sentences to the text where we describe the Kerminen parameterization. “Also, this approximation explicitly assumes that the growth rate and condensation sinks remain constant. Because nucleation rates and growth rates are generally correlated, and an increase in the condensation sink generally lags behind a nucleation event, the approximation may overpredict the 10 nm particle formation rate causing the impact of nucleation to be biased high.”

3) The model SO2 emissions seem to be from GEIA inventory for the mid-80's. However, almost all of the measurement data that the model has been compared against is from the late 90's or the current decade. SO2 emissions have decreased dramatically in the industrialized world since the 1980s (e.g. latest inventory from European Environmental Agency shows 60% decrease in Europe from 1990 to 2005). I therefore do not see any point in presenting the comparison of model output to the selected North American and European data. Furthermore, if the decision to reduce the fraction of primary sulfate emissions from 3 to 1% has been made based on a similar biased comparison, it can hardly be called an improvement in the model. One would assume a model with 80's emissions to overestimate the aerosol mass and number measured in the late 90's.

The best options would be to either compare the model output to measurements from the 80's (but sufficient data may not be available) or to switch to e.g. AEROCOM emissions for year 2000 and rerun the simulations (but this is very time consuming). If neither of these options is practical, my recommendation is that the detailed comparison to measurements (section 3.2 and figure 2) should be left out as it does not give reliable information on how well the model and the different nucleation mechanisms perform against observations.

You are correct that we use the 1985 GEIA inventory. However, the uncertainty in primary emissions in general is likely larger than the change in the emissions inventory. Recent inventory improvements certainly improve total sulfur emissions, but we are not aware of any work that has substantially improved our knowledge of the magnitude and

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size distributions of primary particles. To address this uncertainty, we also compare our reduced primary emissions simulations to the observations over Europe and North America. We have added the follow discussion to the text.

"The anthropogenic SO2 emissions for the model are taken from the 1985 GEIA emissions inventory. Because these emissions have generally decreased since 1985 in Europe and North America where most of the comparisons are located, the modeled CN10 with the base case emissions may be biased high; however, the uncertainty in primary emissions is likely as large as this change in SO2 emissions. The simulations with reduced primary emissions address this uncertainty."

4) The results are presented as annual global and zonal averages. However, changes in CCN are most relevant on local to regional spatial scales and on much shorter than annual time scales. Because of this it can be misleading to make conclusions about the significance of a process or about uncertainties related to it on the basis of large scale averages. Therefore, the authors should discuss the spatial and temporal variability in their results and preferably present some of the figures as global maps at a model level that corresponds to a typical (low-level) cloud altitude.

We now include boundary layer lat-lon maps of the enhancement of CCN when activation is included in the boundary layer or when binary nucleation is switched to ternary nucleation. This more clearly shows the surface regions where CCN may be more affected by nucleation.

We also explored the temporal variability of CCN with different nucleation schemes. To do this we outputted the CCN(0.2%) concentrations every 6 hours and plotted the cumulative distribution function of CCN(0.2%) for the Northeastern US and Finland for BINARY, ACTIVATION and TERNARY. For both locations, the enhancements in CCN(0.2%) of ACTIVATION and TERNARY over BINARY are relatively uniform across all CCN probability levels. We ultimately chose not to add these figures to the paper because they did not add enough new information.

Other remarks:

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1) A very recent paper by Wang and Penner (2008) (ACPD, 8, 13943-13998) addresses some of the same topics than the current manuscript. The authors should compare their results and conclusions with those of Wang and Penner and discuss possible differences and similarities.

We have added some discussions of Wang and Penner (2008) throughout. The most significant comparison is in regards to the recently added activation-type nucleation.

"The 5% sensitivity of CCN(0.2%) to the addition of activation nucleation in the boundary layer (with A = 1x10-6 s-1) was also seen by Wang and Penner (2008) in their simulations that also included primary sulfate particle emissions. However, when they did not include the primary sulfate particles, the sensitivity of CCN(0.2%) to nucleation increased greatly. A higher sensitivity of CCN(0.2%) to boundary layer nucleation was also seen by Makkonen et al. (2008), who had on a small number emission rate of primary sulfate. The contrast of these results shows that the sensitivity of CCN(0.2%) to nucleation may depend greatly on the primary emissions rates. This sensitivity will be explored in more detail in the next section."

2) Change Vehkamaki to Vehkamäki.

Done.

3) p. 16300, lines 24 -27: The fact that a parameterization predicts nucleation onset correctly at one measurement location does not automatically mean that it has skill in predicting nucleation rates - or even onset of nucleation events in the atmosphere in general. This is the case with e.g. activation nucleation parameterization for boreal forests (Sihto et al., 2006, ACP) which cannot be applied to a Central European site without an order of magnitude modiïň129;cation of its prefactor term (Riipinen et al., 2007, ACP).

You are correct. Our main point was not that the old ternary parameterization is the best for predicting nucleation rates everywhere (or even in Pittsburgh), but that it was far and away is the best at predicting the occurrence of nucleation events in Pittsburgh. We have changed it to "suggests that it has skill in predicting atmospheric nucleation occurrences in the Northeastern United States."

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4) top of p. 16301: It is true that strong self-coagulation grows the nucleation mode particles and this decreases their coagulation coefiñ129;cients with larger particles. But simultaneously particle number is lost in self-coagulation. Coagulation coefficient for self-coagulation is of course very low but coagulation loss depends also strongly on the particle number of both colliding particle sizes. Therefore, I don't think it is self-evident that neglecting self-coagulation in Kerminen et al. (2004) causes underprediction of 10 nm formation rate.

It is true that it is not guaranteed that neglecting self coagulation will cause J10 to be too small; however, Kerminen et al. (2004) suggests that the larger particle formation rates will be underpredicted when nucleation is occurring quickly.

For a fixed condensation/coagulation sink from particles larger than 10 nm, at low nucleation rates the primary growth of particles to 10 nm will be from condensation. As the nucleation rate increases, the condensational growth rate decreases (more particles competing for condensate) and the coagulational growth rate increases (accompanied by a loss of nucleation mode number). As the nucleation mode further increases, the coagulational growth rate will at some point become the primary method of growth of these particles because the particles will essentially stagnate at small sizes if only condensational growth is considered. Only 1 in one million nucleated particles in the TERNARY simulation are predicted to grow to 10 nm. This shows that the particles are often stagnating at small sizes due to only having condensational growth.

There may certainly be cases where the coagulation sink of particles larger than 10 nm is very low and self coagulation of nucleation mode particles will be the primary sink of nucleation mode particles. In these cases, ignoring self-coagulation will cause an overprediction of J10. This behavior would be characteristic of cases where the fraction of nucleated particles growing to 10 nm is very high, which is definitely not that case for TERNARY globally (again, only 1/1E6 particles grow to 10 nm in this simulation).

To make the point more clear, we have modified to text to read, "The nucleation-mode parameterization of Kerminen et al. (2004) does not take into account self coagulation, so the new particle formation rate at 10 nm diameter may be underpredicted in cases

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where self coagulation is the primary growth mechanism for nucleation-mode particles."

5) p. 16306, lines 11-18: One could get an estimate of the relative importance of these factors by making quick box model calculations.

I am guessing that you are referring to p 16305, lines 11-18, the factors that contribute to the reduction of the fraction of nucleated particles growing 10 nm. It would be interesting to explore this methodically using a box model; however, it would take an extensive suite of box model simulations to cover all possible atmospheric behaviors and seems out of the scope of this paper. This may end up being a paper in its own right.

6) What is the motivation for including REDBINARY simulation? The standard binary mechanism produces particles only in the FT and doesn't severely overestimate the concentrations there.

The purpose was to give an intermediate nucleation particle source between no nucleation and the Vehkamäki binary nucleation. In hind sight, an intermediate nucleation between binary and ternary may have been a better choice. We have added the ACTIVATION simulation to do this. Here is the sentence that describes their purpose.

"The REDBINARY and ACTIVATION simulations give further insight into how sensitive CCN predictions are due to more modest changes in nucleation rate."

7) Figures 6e and 6f should be discussed in the text.

Fixed. Figs. 6e,f are now 7e,f and are mentioned... "To explore the sensitivity of pre-industrial CCN(0.2%) to the nucleation rate, Fig. 7e shows the CCN(0.2%) for the BINARY-PI case, Fig. 7f shows the CCN(0.2%) for the TERNARY-PI case, Figs. 8a and 8b show the changes in CCN(0.2%) between preindustial times and today for binary and ternary nucleation, respectively, and Fig. 8c shows the ratio of CCN(0.2%) in the TERNARY-PI simulation to that in the BINARY-PI simulation."

8) Figure 2: some of the run labels do not match the run names given in table 1 (however, see major comment 3)

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Fixed.

9) Figure 7: Change either the order of the panels or the sentences in the text. The text discusses first panel 7c.

Fixed. Figure 7 is now Figure 8, and Figures 8a and 8b are now mentioned before 8c.

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