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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A numerical comparison of different methods for determining the particle formation rate" *by* H. Vuollekoski et al.

Anonymous Referee #2

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In this manuscript, Vuollekoski et al., present an improved method to calculate the formation rate of new particle formation (J3) by using the aerosol dynamics model (UHMA). Formation rate is always a focal point in new particle formation analysis. Increase the accuracy of the calculated/predicted J3 is likely to increase the accuracy of the nucleation rate (J1.5) estimation as well. Therefore, this will significantly improve our insight of new particle formation analysis. The study is definitely in the scope of ACP journal. I believe that this idea has the potential to make a good piece of work, however, the current form of the manuscript does not present enough new scientific information and it needs further significant improvement to make it acceptable for publication in the ACP journal. Proof read the paper is very much needed here as well.

Referee 1 suggested many improvements to the manuscript about which I agree completely. For this reason I will not start all over again but concentrate on some issues.

General comments

A first main point of this paper is to show that the improved version of J3 calculations (presented by Eqn.8) is taken over the J3 calculated by Eqn. 3 and Eqn.5. Therefore, authors suggested using Eqn. 8 rather than Eqns. 3 and 5 in further analysis. The authors have put considerable effort into this version of this manuscript. However, the logic argumentation regarding the preference of this modified way for calculating the J3 rather than the calculating the J3 by the earlier traditional methods seems to be off the mark. The simulated data used to address this preference of Eqn. 8 remains tainted with high uncertainties, provided numbers (presented as comparative ratios between different equations used for J3 calculations) seem sometimes inconsistent and with that the conclusions become rather speculative. Significant details appear to be missing, and the comparisons, which the conclusions are based on, are not rigorously analyzed and not clearly significant. Logically authors should have, at least, presented one example of the modelled (made-up events) nucleation events by UHMA using the improved formula for J3, together with the other two traditional methods of calculating J3 (eqns. 3 and 5) and additionally compare these all simulated event cases with one real (actual) measured event day - This would have given a good support to their suggested formula for J3 to be applied to the real life situation. Unfortunately, this has not been done satisfactorily as described below. However, the authors were claiming that "Since we treat our simulation data as it were traditional field measurement data, our results should be valid for analyses of experimental data as well". In my opinion, this concluded statement sounds awkward. Further treatment and discussion will be needed to support this conclusion.

A second main topic of this paper is to highlight the connection between the particle formation rate and the precursor vapor concentrations and applied it to UHMA. Authors showed that time-shift analysis and the related simple power-law (i.e. the dependence

between [H2SO4] concentration and formation rate) are inaccurate. I completely agree with them about the reasons they gave to explain this inaccuracy. I was concerned to see how the method described by Vuollekoski et al. (2010) to calculate the temporal behaviour of the time delay did improve the simulations when they took it into account? Would be nice to give more information how this estimation has been done and rewrite this paragraph in a way to make this point clear. And how in practice this could be done in atmospheric conditions?

The obtained time delay is interpreted as the time it takes for the newly formed clusters (1-1.5 nm) to grow to the detectable size of 3 nm. How much variation in the time delay values were seen for different event simulations? Were the values of the time shift as same as in atmospheric conditions (e.g. Sihto et al, 2006; Riipinen et al, 2007) ?. Kuang et al (2008) claimed that time delay – time delay was calculated in their study by making the fitting only over the duration of the nucleation event (i.e. the increasing part of N3-6 curve) – was very sensitive to the length of the fitting time interval. Has the time interval of the estimated time delay was tested in this study?

In our current understanding of nucleation and new particle formation, sulphuric acid is a key compound in atmospheric nucleation, but its ambient concentrations seem not to be enough to explain observations of particle growth. In the atmosphere there may be several others (e.g., amines, several organic compounds with different properties) contributing to the early stages of cluster growth (e.g., Smith et al., 2010). To what degree your prescribed model organic vapor influences the results?

The vapour concentrations used in the simulation are presented in Fig. 1, does this mean that the authors simulate only sulphuric acid and one condensing organic compound? Have the authors tried to vary the organic saturation pressures?

The slower the clusters grow, the larger fraction of them is scavenged by coagulation before reaching the detectable size range and vice verse and as a result of this, the formation rate calculations will be underestimated/over estimated. Please clarify, how

this point (if at all) has been tested in this study?

How is the sensitivity of the results to the assumptions of the procedures authors have taken into account while they modelled the events? Yes, I have noticed the last paragraph in page 18789, was mainly about the sensitivity checks. I would suggest to the authors to add some statistical tests in order to show the accuracy of each setup that are used in the UHMA model.

How the estimates of the J3 by these different methods affect the estimates of the actual nucleation rate e.g. J1.5 at critical cluster size 1.5 nm?

All in all, here, the presented analysis consisted of 2 steps. First step is to estimate accurately the time delay (using Eqn.7) and the second step is to calculate the particle formation rate at 3 nm (J3) from the DMPS-gridded distribution using different equations (Eqn. 3, 5 and 8). After the authors achieved these two steps, what are the recommendations needed to be taken in to account then when researchers analyze the new particle formation data from atmospheric conditions? How large are the uncertainties compared to other errors, such as those from measurements?

Minor comments

(1) In Fig.2. The authors present an example of the simulated burst. Please clarify in the figure caption, the J3 equation that was used (was it Eqn.5?). How the figure will look like if it was the modified eqn.8 that used instead of Eqn. 5?

(2) How many numerical nucleation events have been used in the simulations to test the J3 calculations by different methods?

(3) Ratios presented in tables 1 and 2; apparently, they are for individual modelled events simulated by UHMA and not overall the numbers of simulations. What was the degree of variations of these ratios for different runs?

(4) About the nucleation mechanisms, here for all analysis, authors used only the activation mechanisms (i.e. one sulphuric acid molecule in a critical cluster), is there any

reason for this choice? Although, many recent studies from field measurements, lab experiments and modeling establish that kinetic mechanics seem to be more favourable.

(5) In Fig.4 caption, Please correct that different terms contributing to the Eqn. 5 for formation rate, not Eqn. 3.

(6) In the recent article presented by Korhonen et al, ACP, 2011, Korhonen and coauthors made it clear that using this Eqn. 8 improves their predictions of mean J3 with 2.8 % of events. However, here in Fig.3, where the formation rates were calculated by different methods and are plotted as functions of time, the theoretical formation rate (i.e formation rate that was calculated by Eqn. 3) gives the closest values to the modified formation rate Eqn.8 while the most traditional formation rate formula that is given by Eqn.5 is overestimated. Can authors give more discussion on that?

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