

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

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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

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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 reasoning for Eq. 6 (previously Eq. 8) is now partly rephrased to make it more intuitive: "... a better solution would be estimating  $n_6$  from a size range closer to 6 nm, for example...".

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.

The preference of using equation 6, compared to equation 5, arises mainly from the fact that when approximating a derivative, central difference is more accurate than backward difference, i.e.  $n(dp = 6) = dN/ddp (dp = 6) \approx (N(7)-N(5))/(7-5)$  is a better approximation than  $\approx (N(6)-N(3))/(6-3)$ . This is now more clearly stated right before equation 6. The improvement can be clearly seen from both table 2 and figure 3.

Logically authors should have, at least, presented one example of the modelled (made-

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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.

Analyzing a real measured event-day will not tell us which method performs best – since we do not know the ‘correct answer’. However, the suggestion by the referee is still very good! Not to give additional info on which method is best, but just to illustrate what kind of differences they can give when applied to real measured data. Thus, we have added a section to the end of our manuscript where the methods for J3 estimation are compared when applied to a real atmospheric particle formation event.

However, the authors were claiming that “Since we treat our simulation data as it were traditional 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.

See first reply to reviewer 1.

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 [H<sub>2</sub>SO<sub>4</sub>] 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?

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Since the original submission of the article the research of this topic has advanced to the point that we decided to remove the time shift analysis from this article.

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?

Please see the answer to previous question.

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?

Since the organic vapor was set to be non-volatile, it increases the growth rate of particles of all sizes. And because its concentration is over a magnitude higher than that of sulphuric acid, the organic vapor definitely affects the formation rates. However, from the perspective of Chapter 4.1, the simulations were equal, except for the varied parameter in Table 1, and hence the effect of the organic vapor on the general trends (calculated as means for 11:00 – 13:00) can be neglected. The effect of changing the growth rate, i.e. varying the vapor concentrations, is included in Table 1.

The reference to Figure 1 states now: “The vapour concentrations used in the simulation are presented in Figure 1: the particles grow due to condensation of sulphuric acid, and a non-volatile organic vapour with significantly higher concentration. These cause

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growth of particles of all sizes, and most of this growth can be attributed to the organic vapour. The only organic vapour considered was set non-volatile, because otherwise the Kelvin effect would significantly hinder its condensation on particles around the 3 nm size.”

A notion on the importance of the organic vapor was added in the caption of Fig. 1:” The concentrations of sulphuric acid and a non-volatile organic vapour used in the simulations. Note that as the concentration of the organic vapor is significantly higher than that of sulphuric acid, the organic vapor will cause most of the growth in particles.”

Additionally, the part explaining the effect of changing particle growth rate was changed to: “...if the concentration of the organic vapour was increased, the growth rate would be higher and more particles would grow to 3–6 nm before being coagulated...”

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?

Yes, only two vapors were present. If the organic vapor had any significant vapor pressure, the Kelvin effect would practically stop it from condensing on the particles, thereby lowering the growth rate. The effect of lowering the growth rate is presented in Table 1. For changes in the manuscript, please see the answer to the previous comment.

The slower the clusters grow, the larger fraction of them is scavenged by coagulation before reaching the detectable size range and vice versa 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?

The effect of varying the growth rate is presented in Table 1, and the text states:” ...if the concentration of the organic vapour was increased, the growth rate would be higher and more particles would grow to 3–6 nm before being coagulated. Because the loss

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due to coagulation is most significant for particles below 3 nm, this would decrease the importance of the coagulation term, which would then again bring the ratio between formation rates closer to unity.”

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.

For sensitivity checks of the UHMA model in general, please see the original model description paper by Korhonen et al. (2004). Regarding our J3 estimation method the results of the sensitivity studies are presented in tables 1 and 2.

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?

Although a very good question, this is not within the scope of this study.

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?

We recommend the simple modification in Eq. 6 over Eq. 5 due to its simplicity. However, we agree that the accuracy gain from this step is likely minimal as compared to general uncertainties related to measurements. The Conclusions state: “It can therefore be concluded that the general uncertainties related to experimental measurements greatly exceed the error caused by using approximative expressions for formation rate,

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and both methods are accurate enough in atmospheric applications. Nevertheless, since a partial solution to the error caused by coagulation is easily applied in data analysis, the presented modification (Equation 6) is recommended.”

#### 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?

The UHMA simulation was done with full aerosol microphysics, starting from nucleation, so that no J3 parameterization was needed.

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

This is the number of entries in Table 1, i.e. 11. The text now states: “The results are presented in Table 1, with each entry representing an independent simulation, together capturing the general trends in all basic scenarios.”

(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?

Table 1 represents 11 individual simulations, whereas Table 2 was constructed from analyses of the first nucleation event in Table 1. The carefully selected variations represent a wide range of imaginable (realistic) scenarios. For changes in MS, please see previous question; additionally: “We performed more detailed calculations on the 1st simulation in Table 1, and the results are presented in Table 2.”

(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

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more favourable.

The referee is correct – we cover only one plausible nucleation mechanism in our simulations. This, however, has no effect on our analysis since we try to estimate the apparent formation rate at 3 nm, from observed size distribution evolution. What happens below 3 nm will not affect our analysis.

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

Thank you. Corrected.

(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?

So, in both studies the J3 from Eq. 6 (previously Eq. 8) is more accurate than J3 from Eq. 5. We do not understand the question here.

References Korhonen et al (2011), Atmos. Chem. Phys., 11, 3051–3066. Kuang, C., et al (2008), J. Geophys. Res., 113, D10209, doi:10.1029/2007JD009253,2008. Riipinen, I., et al, (2007), Atmos. Chem. Phys., 7, 1899–1914. Sihto, S.-L., et al (2006), Atmos. Chem. Phys., 6, 4079–4091. Smith, J. N et al (2010), P. Natl. Acad. Sci., 107, 6634–6639, 2010.

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