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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evaluation of the accuracy of analysis tools for atmospheric new particle formation" *by* H. Korhonen et al.

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We thank the reviewer for his/her comments and suggestions. Our point-by-point reply to these comments can be found below. The page numbers refer to the version published in ACPD.

"For a broader audience, I suggest to include more descriptive information what are the parameters discussed in the paper, either in a form of text or in a form of schematic figure."

We have added a new figure showing a DMPS-type plot of one simulated new particle formation event together with the corresponding nucleation and new particle formation rates and an illustration of the fitting procedure for Δt_{N3-6}.

In addition, we have added the following text to the end of the model description (section 2.1):

"Figure 1a shows an example of a DMPS-gridded distribution from one model run. It is worth noting that while the simulated event resembles measured atmospheric events closely in most respects, the modelled data is much smoother and lacks noise that is present in typical atmospheric data due to instrumentation and inhomogeneities in the measured air mass. The smoothness of the modelled data is evident also in Figure 1b which presents the simulated nucleation and particle formation rates together with the scaled concentration of 3-6 nm particles (N_{3-6}). Note that while the modelled N_{3-6} is used as an input in the analysis described below, the simulated $J_{1.5}$ and J_3 are used only for comparison with the respective predicted values."

And to step 1 of the description of the analysis tools (section 2.2):

"The fitting procedure is illustrated in Figure 1c, which depicts the simulated H_2SO_4 (blue line) and N_{3-6} (red line) concentrations. In this specific case, when the H_2SO_4 curve is delayed by 60 minutes and raised to the power 2.31 (black dashed line), it is evident that it correlates very closely with the simulated N_{3-6}."

"Besides detail recommendation what error nucleation event analysis tools have?"

We are not quite sure what the reviewer is after here. The errors resulting from the analysis tools themselves are presented in the figures and tables of the manuscript. In case (s)he refers to the specific sources of error, then the main sources of error in the case of predicting the actual nucleation rate $J_{1.5}$ are the built-in simplifying assumptions (no intramodal coagulation, constant growth rate from 1.5 to 3 nm), as discussed on pages 26293-26294. Since the nucleation exponents and prefactors are calculated from the estimated $J_{1.5}$, the same erroneous assumptions deteriorate also their prediction.

"What is the main message of the paper?"

To articulate the main message more clearly we have added to the end of the abstract:

"Overall, while the analysis tools for new particle formation are useful for getting order-of-magnitude estimates of parameters related to atmospheric nucleation, one should be very cautious in interpreting the results. It is, for example, possible that the tools may have misdirected our theoretical understanding of the nucleation mechanism."

And before the last paragraph in the conclusions:

"Overall, we conclude that the analysis tools have built-in assumptions which can cause uncertainties in the event analysis. While this uncertainty is in most cases within an acceptable order-of-magnitude limit, it is important to be careful when interpreting the data and drawing conclusions about e.g., nucleation mechanisms or temperature dependence of nucleation prefactors, etc. Unfortunately, quantifying the error that the analysis tools have caused in previous analyses of atmospheric data is not straightforward since we do not know which of the simulated events resemble closest the atmospheric ones. Since the tools perform very well for some individual simulated events and quire poorly for others, it is equally possible that the tools have introduced only minor error in atmospheric analyses or alternatively that they have misdirected our theoretical understanding regarding e.g. the nucleation mechanism. Currently, we cannot know if either is the case; however, our study raises the point that large errors are possible and thus caution should be practiced when interpreting the atmospheric data. "

"As far as I can see all the tools used do not introduce error significantly larger then is our understanding of the new particle formation process. They actually do pretty good job with respect to our level of understanding the nucleation. To what degree this can be accounted to fact that UHMA model used in this study has built in processes and equations developed from tools the model is used to investigate?"

We agree with the reviewer that the uncertainties associated with our general understanding of the atmospheric new particle formation are large, mainly because the current instrumentation cannot measure the processes taking place at the very initial size of cluster formation at the diameter of 1.5 nm. The very reason that the analysis tools evaluated in this study have been developed in the first place is to obtain information about the "unmeasurable" size range, i.e about the initial steps of nucleation and growth and even about the nucleation mechanism.

The potential problem with these analysis tools is that if they do not give accurate information about the properties they were aimed at, they can misdirect our theoretical understanding of the nucleation phenomenon. For example, the idea of activation or kinetic type nucleation (i.e. one or two sulphuric acid molecules in a critical cluster) currently favoured by many scientists is based the use of these analysis tools on atmospheric data. However, our study suggests that the tools do in most cases a very bad job in predicting the number of sulphuric acid molecules in a cluster, and we should therefore be very cautious in our interpretation of the analysis results in this respect.

We do not expect the design of the model to affect our results to any notable effect. The simulated coagulation and condensation processes follow general widely-accepted theoretical formulations that have no direct connection to the analysis tools discussed in this study. The assumption of a sulphuric acid power law type nucleation (i.e. J = A[H2SO4]^k) is obviously derived from previous analyses of atmospheric data. However, since the tools themselves do not make any assumptions about the nucleation mechanism but should perform as well for any real or made-up mechanism, there is no reason why the nucleation mechanisms chosen for the simulation runs should bias the analysis.

"In our current understanding of nucleation and new particle formation, molecules responsible for growth from cluster size (likely organics, amines?) are probably largest unknown. To what degree your prescribed model organic vapor influences the results? What if there is more than one compound partici-

pating and/or growth from cluster size is not "linear" controlled by condensation of one vapor and coagulation?"

The assumptions made about the condensing vapour properties have a major effect in the results since the analysis tools make a built-in assumption of a constant growth rate below 3 nm. As discussed in the manuscript, deviations from the linear (i.e. size independent) growth rate can significantly deteriorate the predictions of $J_{1.5}$ and therefore of nucleation exponents and prefactors.

Should there be several organic or other low volatile compounds with different saturation vapour pressure contributing to early growth, the deviation from linearity could be even larger than discussed in this study. However, we would not expect this to change the general conclusions of the study since we already include a fairly significant size effect by varying the organic saturation pressure. Furthermore, the study already includes another deviation from the constant growth rate assumption by assuming diurnal profiles for the condensing vapours.

We have added to the end of the first paragraph on page 26294:

"Note also that while we simulate only sulphuric acid and one condensing organic compound, 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). Their combined effect could cause even a stronger deviation from the constant growth rate assumption than simulated in this study."

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 26279, 2010.