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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Connections between atmospheric sulphuric acid and new particle formation during QUEST III–IV campaigns in Heidelberg and Hyytiälä" *by* I. Riipinen et al.

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1) Page 10844, equation (5) (6): The authors assume that the particle size distribution function at the upper size boundary, n6, is represented by N3-6/3nm. If we also assume that n3 is also represented by N3-6/3nm, we can solve for GR3. I wonder whether GR3 solved by this approach at the peak of J3 reasonably agree with GR1-3 obtained by the time-shift analysis.

By the way, we tried to apply this approach to predict the J3-6 and GR3-6 from our recent data from Mexico City. Our CoagS at 4nm in Mexico City is around 1.0e-3 sĹ-1. It turned out that GR(3-6) predicted from J(3-6) was very noisy and GR(3-6) also often unreasonably large (>100 nm/hr!!). GR in Mexico City is too large (∼ 20 nm/hr);

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therefore, it is hard to observe any time shift between H2SO4 and N(3-6). I thought that the authors may find our observations interesting.

According to our preliminary analysis the GR_3 values obtained from the data using the approximate formula

$$GR_3 \approx \frac{3\mathrm{nm}J_3}{N_{3-6}} \quad (1)$$

range at approximately 1 - 10 nm/h during new particle formation, which is somewhat higher than the GR_{1-3} values obtained with the time-shift analysis (0.4 - 2.4 nm/h in Hyytiälä, and 0.9 - 2.7 nm/h in Heidelberg). To our understanding, the higher values of GR_3 are reasonable, since e.g. Hirsikko et al. (*Bor. Env. Res.*, 2005, see the manuscript for the exact reference) report higher growth rates in the size range 3-7 nm (monthly medians 2 - 7 nm/h) than in the range 1.3 - 3 nm (0.3 - 3 nm/h), based on their analysis of the ion spectrometer and DMPS data. The reason for the difference might be that the initial steps of the growth are dominated by sulphuric acid condensation, whereas at larger sizes also other vapours start to contribute to the growth. The calculated GR_3 values seem to correlate with the GR_{1-3} values obtained from the time lags, so that on the days when GR_{1-3} is relatively high, the same seems to be true for the calculated GR_3.

The observations from Mexico City described by the referee are indeed very interesting. For Heidelberg, where the effect of traffic is clearly seen, our results are somewhat similar: the coagulation term dominates in the J_3 expression (Eq. 6 in the manuscript) causing it to fluctuate more as compared with Hyytiälä. The calculated GR3 values were also slightly higher (5 - 10 nm/h) and more fluctuating during the new particle formation event compared to Hyytiälä, where the values ranged from 2 to 7 nm/h and stayed surprisingly constant during new particle formation.

2) Page 10845, equation (7). It seems better to choose a representative CS between

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time t and t' if CS changes during this time period.

We have used the median CS from the time period [t, t'], as also stated in the text in p. 10845 line 23. We think that the accuracy of this approach is representative enough for our purpose, taking into account that the investigated time periods are 0.8 - 4.5 h, being typically about 2 h.

3) Page 10846, line 12. I have read your description of author's approach several times. However, I am not convinced about how the author's method gives more statistical weight to the temporal evolution of data. It would be helpful for readers if the authors can elaborate this statement.

We agree that the text might be a little confusing in this context. What we mean with the statement is that in least squares fittings the absolute differences in the magnitudes of the compared curves are minimized, whereas the correlation analysis gives the maximum correlation in the case where the shapes of the curves (i.e. the temporal evolution of the studied variables) are the most similar. The latter approach is more suitable for our purpose, as we want to find the exponents that best reproduce the shapes of the curves. We will add a more comprehensive explanation on the fitting method to the manuscript, as suggested by the reviewer.

4) Page 10855 line 6: It would be nice if the authors can provide potential reasons for the coefficients A and K are near order of magnitude higher in Heidelberg. If the activation mechanism is the dominant process, is it possible that the concentration of thermodynamic stable clusters may be near one order of magnitude higher in Heidelberg? If the kinetic mechanism is the dominant process, is there any third body that can lead to the apparent increase the binary collision coefficient between two monomers?

This is a good point and still requires more careful analysis in the future. One reason for the differences between the sites could be the different concentrations of the activated clusters. Other reasons might be, for instance, different variety or amount of condensing vapours, the composition of the activated clusters, or different ambi-

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ent conditions such as temperature or relative humidity. We tried to find correlations between the coefficients and several ambient variables and their combinations (e.g. temperature, relative humidity, condensation sinks as well as sulphuric acid and ammonia concentrations), but with such limited data sets it was difficult to say anything sure about them.

One aspect that definitely might have some effect on the results is that with the present method we can estimate the values of A and K only on the new particle formation event days, combined with the fact that we cannot see what happens below 3 nm. Because of the higher sink in Heidelberg, there are more days when new particle formation might start but the particles do not grow to 3 nm before scavenging to pre-existing particles. This means that compared to Hyytiälä, the particles have to grow faster and/or the values of A and K need to be higher in Heidelberg to really see a typical new particle formation event with continuous growth.

It is also possible that a 'third body' is present also in the kinetic nucleation process. Possible candidates for the third body are e.g. ammonia or some organic molecules. However, this study does not give any direct information on what other compounds, in addition to sulphuric acid, are participating the observed nucleation processes. For example, no clear correlation between ammonia concentrations and new particle formation was observed in Hyytiälä. This, on the other hand, does not necessarily mean that ammonia is not participating the particle formation; rather ammonia concentration seems not to be the limiting factor for the particle formation during the investigated period. It should also be noted that the results do not give us direct information whether sulphuric acid is participating the new particle formation as a constituent of the activated stable clusters, or merely by activating and growing them to larger sizes.

The points raised by the reviewer are definitely interesting, and we will elaborate these thoughts further in the manuscript to be submitted to ACP: According to this discussion, we will add more speculations on the differences between the two sites (Hyytiälä and Heidelberg). We will also briefly describe what kind of correlations with A and K we

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have looked at, and add some discussion on the role of organics as well, inspired by this discussion.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 10837, 2006.