

Interactive comment on “Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms” by S.-L. Sihto et al.

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Response to Referee #2's comments

We would like to thank the referee for the constructive comments to our manuscript. Below are our answers to the comments.

General comment: We want to point out that in this paper we don't specify exactly whether the particle formation occurs according to the activation or kinetic mechanism on a particular day. For N_{3-6} we give exact exponents, but for J_1 (which is the nucleation rate, and directly related to the proposed activation or kinetic mechanism) we don't yet specify exact exponents due to big scatter in J_1 data. That is the reason why we also determined both activation and kinetic coefficients for every day. N_{3-6}

exponent gives hint about the nucleation mechanism, especially exponent 1 points to activation nucleation, but the exponent can also change when going from J_1 to N_{3-6} due to e.g. growth by sulphuric acid. Therefore exponents of N_{3-6} should not be interpreted directly as exponents of nucleation mechanism.

Specific points:

1. The event period of the day was taken in this study to be the period when number concentration in size range 3-6 nm (N_{3-6}) was significantly above background value, say, one order of magnitude above the level before or after the event. For example in Fig. 1a the event period is about 84.35-84.78 and in Fig. 2a about 85.38-85.70 (looked from N_{3-6} curve). During QUEST 2 campaign most of the events were strong, so for every event day "the time period of the event" was clear to determine.

In determining the time delay between N_{3-6} and sulphuric acid, we searched for the time delay that gave the best agreement between the curves. It is not possible to give an exact criteria on how the time delay was determined and in what weights the rising part and other part of the curves were treated. Generally the time delay is most evident in the rising part of the curve, and therefore in most cases that part was given the greatest weight. Also similar peaks in N_{3-6} and $[H_2SO_4]$ during later stages of the event were used in some cases. On some days, the form of the whole curve was used to determine the time delay, because that gave overall better agreement between the curves. Example of that is in Fig. 2a (day 85), when a long time delay between the rising parts of the curves is probably partly due to big condensation sink that prevents nucleated particles from growing to 3 nm size and not only due to a slow growth rate.

In general, the time delay was determined by looking the N_{3-6} and $[H_2SO_4]$ curves as a whole and not restricting to the rising part only. We recognise that this method certainly contains some subjectivity. It is expected that the time delay varies during the day because of varying growth rate. With this method we get a rough estimate for an average time delay during the particle formation event.

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A short explanation of the determination of the time delay will be added to the final version of the paper.

2. The number concentration in size range 3–6 nm and sulphuric acid concentration were clearly correlated after the time delay was taken into account, i.e. when the sulphuric acid curve was delayed by the time shift. Without the time shift the correlation of number concentration and sulphuric acid was poor, the correlation coefficients being significantly lower than with time delay taken into account.

3. We are aware of difficulties in using the log scale. To be sure that log scale doesn't affect the results, we looked the plots also at linear scale. It is true that curves $y = x$ and $y = x^2$ will look very close to each other if y-axis range is chosen properly. However, in our analysis this is not a major problem, because here we have two curves to compare, of which N_{3-6} is fixed and $[H_2SO_4]$ is raised to exponent 1 or 2, delayed by the time shift and scaled to the same peak height as N_{3-6} . Because one of the curves is fixed, we can't play with the y-axis scale to get better fitting between N_{3-6} and $[H_2SO_4]$ or $[H_2SO_4]^2$. If the form of N_{3-6} curve resembles $[H_2SO_4]^2$, we see a clear difference also with log scale between $[H_2SO_4]$ and $[H_2SO_4]^2$ because we look the curves at the same y-axis range.

We agree with the referee that in some cases it might be difficult to fit the complete curve with any of the two functions $N_{3-6} \sim [H_2SO_4]$ or $N_{3-6} \sim [H_2SO_4]^2$. There may be some interfering peaks in the data or rapid changes in meteorological conditions (e.g. change of air mass) that can disturb the analysis. It is also possible that on some days there may be multiple processes going on (both exponent 1 and 2 behaviour), and therefore neither of the exponents gives good fit for the complete curve. However, on most days the type of correlation was fairly clear to determine and choosing one exponent and time delay for one day gave a reasonably good fit for the whole event period.

Our aim was to fit the curves during the event period (see discussion of defining the

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event period in point 1.), and therefore we ignored the data prior to and after events in examining the correlation of N_{3-6} and $[H_2SO_4]$. The observation that on some days there was a fairly good correspondence between N_{3-6} and $[H_2SO_4]$ also outside of the event period (e.g. day 84 in Fig. 1a), was more like a surprise that suggests that the correlation of small particles and sulphuric acid may apply more generally than only for the daytime event period.

The referee discussed the choice of exponent 2 correlation for day 85 (Fig. 2a). We have undergone similar considerations, and ended with the decision of the exponent 2 based on several arguments: (i) the correspondence of the overall form of the curves is much better with exponent 2, (ii) a long time delay between the rising parts of the curves (about 2.0 h) is probably partly due to big condensation sink that prevents nucleated particles from growing to 3 nm size and not only due to a slow growth rate, and (iii) the short time delay (1.2 h) related to exponent 2 dependency is supported by the J_1 - and J_3 -curves (see Fig. 5), which have better correspondence with the J_1 and J_3 calculated from $[H_2SO_4]$ concentration using time delay 1.2 h and corresponding growth rate. As noted above, the delay time would be significantly different assuming the exponent 1 relationship, namely 2.0 h, compared to the delay of 1.2 with exponent 2 relationship.

4. It is true that difference in correlation coefficient R is in many cases so small that only based on it, it would be impossible to say which correlation is the better. However, by looking the data visually, in most cases it was quite clear which correlation was better. By visually looking the curves we can exclude from the analysis e.g. some pollution peaks that are clearly not related to new particle formation, but which would contribute to correlation coefficient significantly. The chosen dependency between N_{3-6} and $[H_2SO_4]$ - with exponent 1 or 2 - was always decided based on both correlation coefficients and visual perception. For days 78 and 92 we didn't give any exponent, because for those days it was not possible to say even looking by eye which exponent was better.

When calculating the correlation coefficients for the two dependencies (exponent 1 and

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2) we used time delays that were determined independently for the two dependencies. In most cases we got somewhat different time delays for exponent 1 and 2 relationship, and in some cases even significantly different values. The correlation coefficients are affected by the used time delay. We have taken this into account and the values presented in Table 1 are the biggest correlation coefficients for the two exponents (i.e. values with the appropriate time delay).

5. The correlation coefficients for GR_{1-3} , A and K with other quantities (e.g. $[OH] \times [terp]/CS$ and $[O_3] \times [terp]/CS$) were calculated with daytime averages (from 9 a.m. to 15 p.m.). The time delay was not taken into account when calculating the averages. Taking the time delay into account would have a minor effect on the average values using this large averaging window. Moreover, with A and K it is more correct to use data with no delay, because nucleation coefficients are expected to correlate with values at the time of nucleation. Also, because at this stage of research we are assuming a constant value of GR_{1-3} , A and K for the whole day, it is unnecessary to consider the time delay in calculating the correlation coefficients.

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