

Interactive comment on “Aerosol dynamics simulations on the connection of sulphuric acid and new particle formation” by S.-L. Sihto et al.

S.-L. Sihto et al.

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Response to referee comments

We would like to thank the referees for the constructive comments to improve our manuscript. Below are our answers to the comments, separately for the two referees. We have made corrections according to the comments and submitted a revised version of the manuscript.

Yours sincerely,

Sanna-Liisa Sihto (on behalf of all co-authors)

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Answers to Referee #1's comments

General comments

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The authors investigate the correlation of the nucleation rate and of the formation rate and concentration of 3-6 nm particles with gas phase sulfuric acid, using a detailed aerosol model. The correlation of the concentration of 3-6 nm particles with gas phase sulfuric acid during nucleation events is available from field studies. Correlations produced by different nucleation mechanisms and their response to condensation of a non-nucleating compound are analyzed. This study is important as it shows how in situ measurements can be used to determine the mechanism responsible for a nucleation event.

In their simulations, the authors show that activation type nucleation is a good candidate to explain the correlation often observed in the boundary layer, while ternary nucleation, implemented using a parameterization, is not. The authors therefore challenge the role of ternary nucleation in new particle formation from the gas phase in the boundary layer. With this conclusion the authors join the controversy on the role of ternary nucleation (of ammonia, sulfuric acid, and water) in atmospheric new particle formation. This controversy draws on numerous conflicting results, e.g. by Ball et al. (1999); Janson et al. (2001); Kulmala et al. (2002); Napari et al. (2002a); Anttila et al. (2005); Yu (2006); Kurtén et al. (2007).

In this context it should be noted that the majority of boundary layer nucleation observations has been conducted over continents, and many of these over forested areas, where organics seem important for nucleation. Over oceans and in polluted areas, however, organic molecules may play a secondary role; in a very recent analysis of nucleation events in the Pittsburgh area, e.g., Jung et al. (2008) find, using the same parameterization of ternary nucleation (Napari et al., 2002b) as in the present work, that ternary nucleation works quite fine.

The manuscript is well written and the analysis of the results results thorough, providing new, relevant insights. Given the conflicting findings mentioned above and the uncertainties regarding the validity of the ternary nucleation parameterization

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used, the authors' quite general dismissal of the role of ternary nucleation in the boundary layer is courageous.

We agree that our conclusion about ternary nucleation was strong and possibly too courageous. In the revised version, we have extended the discussion about ternary nucleation and softened slightly the conclusions. It is true that most field measurements, which are referred to in the article, are from continental and especially forested areas, and this may bias the analysis to some extent. Therefore we don't generalize our results to e.g marine environment.

However, we still argue that most probably ternary nucleation cannot reproduce the observed slopes (between 1–2) with respect to sulphuric acid concentrations, even in polluted areas where sulphuric acid level is high and can make the main part of particle growth rate. Jung et al. (2008) showed that in Pittsburgh ternary nucleation can reproduce the event occurrence correctly, but they did not consider the predicted number concentrations or dependencies on sulphuric acid concentration. According to our simulations, ternary nucleation cannot reproduce the observed slopes with respect to sulphuric acid concentration. In predicting the event occurrence, besides the exact nucleation rates also particle growth rate and coagulation sink by background aerosol contribute to whether or not a new particle formation event will occur. Therefore the ability to predict the event occurrence does not alone proof a nucleation mechanism. Predicting the event occurrence correctly is important, but we should also get the number concentrations correct, in order to model new particle formation reliably.

Specific comments

Page 11367, line 29:

"The saturation vapour concentration of sulphuric acid is assumed to be negligible, i.e. it condenses with the maximum flux without Kelvin effect ($c_{sat}=0$)."

This is not a very good approximation for very small sulfuric acid/water aerosol particles, unless they contain sufficient amounts of ammonia. The growth rates of the particles will be overestimated, and consequently, Figures 5 and 6 show upper limits for the sulfuric acid vapor growth rate. More slowly growing particles are more affected by loss onto pre-existing aerosol and by self-coagulation. Hence there is a chance that if the actual condensation/evaporation rates of sulfuric acid were used, somewhat different correlations may have been obtained.

We agree that in principle sulphuric acid should have a finite vapour pressure. In the simulations the ambient ammonia concentration was set to be 5 ppt, which we think is big enough to justify our assumption to neglect the saturation vapour pressure of sulphuric acid. With this ammonia concentration, the smallest particles (at nm size range) take up ammonia so that particles contain approximately as many NH_3 molecules as H_2SO_4 molecules (i.e. the composition of ammonium bisulphate). Using a finite vapour pressure for sulphuric acid would result in smaller growth rates for the smallest particles, but because sulphuric acid made only 20–25 % of the total growth rate, it is unlikely that the change would be so big that it would affect our results significantly.

A statement that resulting growth rates by sulphuric acid will be upper estimates of the real growth rates has been added to the manuscript.

Page 11381, line 17:

"Simulations with ternary H_2O - H_2SO_4 - NH_3 nucleation yielded too steep dependence on sulphuric acid, with regard to observed exponents of 1-2 in field measurements. The correlation exponents were always greater than 4 for both J3 and N38722;6, suggesting that ternary nucleation is not the valid nucleation mechanism for particle formation in atmospheric boundary layer."

This is the passage I am referring to in the "General comments" section.

We have extended the discussion about ternary nucleation and softened slightly the
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conclusions.

Answers to Referee #2's comments

General comments

Sihto et al report on aerosol dynamics simulations in order to investigate how the relation between H₂SO₄ and particle formation rate and concentration changes as they grow from nucleated size to 3 nm. They used the activation mechanism and ternary nucleation as the two candidates for nucleation, and then compared the simulation exponents ($J_{\sim[H_2SO_4]exp}$) to those found in selected atmospheric measurements.

Not surprisingly, the activation mechanism produces smaller exponents for J₃ and N₃ than ternary nucleation. Therefore, and in light of the known exponents (for J₁ at least) for the different nucleation mechanisms (1 for activation, 2 for kinetic, and substantially larger for ternary nucleation), I don't understand why the authors didn't include kinetic nucleation in their simulations, perhaps even instead of ternary nucleation. The conclusion that the ternary nucleation mechanism doesn't provide a similar exponent as the measurements is hardly surprising. Generalizing that conclusion, while other studies found that the ternary nucleation parameterization produces good results in a different location, is not warranted. I suggest running simulations using kinetic nucleation, since that is a candidate with some promise to provide similar exponents as the measurements under consideration, and it would be interesting to compare those results with activation nucleation.

We performed simulations with kinetic nucleation and included the results in the revised version (Figure 1 and a new table, Table 3). The general behaviour of the correlations with respect to saturation concentration of organic vapour was similar as with activation nucleation. Kinetic nucleation resulted bigger correlation exponents (n_{N_3-6} and

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n_{J_3}) than activation nucleation, as would be expected. However, the difference between exponents for kinetic and activation nucleation depends on the particle growth rate (thus saturation concentration of organic vapour), see Table 3 in the manuscript. The difference between exponents was less than 1 (0.5–0.8), meaning that aerosol dynamical processes affect the correlations, and therefore the difference in nucleation exponents ($2 - 1 = 1$) is not transferred directly to the correlation exponents at 3 nm size.

As said above (see answers to Referee #1), we softened the conclusions about ternary nucleation and expanded the discussion about it. Still we keep our conclusion that most probably ternary nucleation cannot reproduce the observed slopes ($n=1-2$) with respect to sulphuric acid concentrations, even in polluted areas where sulphuric acid level is high. This result may not be surprising, but it is an important thing to note, because it demonstrates that ternary nucleation is unlikely to be the correct mechanism for new particle formation, even if it reproduces the event occurrence correctly in some places (Jung et al., 2008). Ternary nucleation may involve some essential characteristics of nucleation, such as the role of ammonia, and therefore it is able to predict event occurrence correct, even though the actual nucleation rates would have too steep dependence on sulphuric acid.

Specific comments

P 11375, on estimating the time delay: In the text (lines 7-10) it is mentioned that the time delay is estimated visually rather than by investigating what resulted in the maximum correlation, but caption of Fig 3 mentions that the time delay of 1.5 hours corresponds [to] the best correlation. Looking at Fig 3 a and b, I fail to see that the correlation would be independent of the time delay, as is implied by the text. If I misunderstand something here, then please clarify. The labels seem to be mixed up for N_{3-6} and H_2SO_4 in either fig 3a or 3b.

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We determined the time delay by looking visually which time delay gave the best correlation in the scatter plots. The determination was not based on calculated correlation coefficients, but visually looking which time delay made the points to fall on one line in the scatter plot.

In the revised manuscript we have reformulated the explanation of the estimation of the time delay to make this clearer:

"In this study, we determined the time delay visually by searching for the value that gives the best looking correlation between N_{3-6} and $[\text{H}_2\text{SO}_4]$, i.e. the time delay which made the points to lie on a same line in the scatter plot see Fig. 3). Previously Sihto et al. (2006) and Riipinen et al. (2007) determined correlation exponents and time delays by finding a combination that gave the maximum correlation coefficient between J_3 or N_{3-6} and $[\text{H}_2\text{SO}_4]^n$. This method worked well with measured data, but not with the simulated data used here: the simulated J_3 , N_{3-6} and $[\text{H}_2\text{SO}_4]$ were so smooth, that correlation coefficient was close to unity with any choice of exponent and time delay, and therefore the method could not distinguish the best correlation exponent and time delay. Nevertheless, with scatter plots the correlation between J_3 or N_{3-6} and $[\text{H}_2\text{SO}_4]$ could be investigated easily, and time delays and correlation exponents were straightforward to determine by visual perception. The accuracy of the time delays determined by this method is about ± 0.1 h."

The labels in Fig. 3 have been corrected.

P 11376. Size dependence of the growth rate: Based on the text, I assume that fig 5 is for $csat = 10e6$ (please mention this clearly). Fig 6 however makes me think differently, or are the labels mixed up? (The text mentions that the minimum in the growth rate disappears when $csat$ goes to zero.) All in all, this is very confusing. The size dependence of the growth rate seems to have a significant effect on the resulting exponents for $N3$ and $J3$. It is therefore important to provide the reader with some sense of the uncertainties involved: How dependent is the size

dependence on other factors besides c_{sat} ? How dependent are the exponents on different factors than c_{sat} ? The authors mention oligomer[iz]ation as a candidate to explain the low apparent value of c_{sat} . Are there other possibilities that could also explain the results? Different concentrations of H_2SO_4 and/or organics for example? Or different values describing the molecular behavior in equations 1 and 2? I would like to see the discussion expanded here.

The value of $c_{\text{sat,org}}$ has been added to the caption of Figure 5. I checked the labels of Figures 5 and 6 and they were correct. The difference between the figures is that Fig. 5 presents the fractions of organic and sulphuric acid in the total growth rate, but Fig. 6 presents the total growth rate curves, i.e. contributions of organic and sulphuric acid summed together. The black solid curve of Fig. 5 is the same as the black curve with solid circles (curve with $c_{\text{sat,org}}=10^6 \text{ cm}^{-3}$) of Fig. 6.

Besides the saturation vapour pressure, other factors that may affect the correlations are the concentrations of condensable vapours (both sulphuric acid and organic) and the coagulation sink. If these quantities change during the simulation, they can shape the J_3 and N_{3-6} profiles: varying vapour concentration causes varying particle growth rate, and varying coagulation sink causes varying removal rate for small particles. For example, if the organic vapour would have a sinusoidal profile, this would yield a bigger correlation exponent for J_3 and N_{3-6} than in the case where organic vapour concentration is constant.

The simulations indicated that with regard to particle growth rate (GR), there are two qualitative features influencing the correlations: i) the size dependence of GR (through $c_{\text{sat,org}}$) and ii) the time dependence of GR (through the profile of condensable vapours). Both a strong size dependence in GR with a minimum around $d_p=2 \text{ nm}$ (see Fig. 5) and a sinusoidal time dependence for GR increased the correlation exponents for J_3 and N_{3-6} . However, the saturation vapour concentration of organic vapour (or some other property of the vapour that lowers the equilibrium pressure, see Eqs. 1 and 2) was a

key parameter: without decreasing $c_{\text{sat,org}}$ we were not able to reproduce exponents close to $n_{N_{3-6}} \approx 1$.

We have added more discussion about the effect of size dependent growth rate and about sensitivity studies related to it. In the revised manuscript there is a separate subsection for sensitivity studies (Sect. 3.2.2.).

P 11379 regarding size and composition of the critical cluster: The critical cluster in ternary nucleation is expected to consist of 5–6 H₂SO₄ molecules (corresponding to the exponent value) and to be around 1 nm diameter. This raises the question what the critical cluster exists of in activation nucleation, when according to the exponent it would only consist of 1 H₂SO₄ molecules, but is likely 1.5 to 2 nm in diameter?

In ternary nucleation the critical cluster consists of 5–6 H₂SO₄ molecules plus associated water and ammonia molecules. The size and composition of the critical cluster are predicted according to the thermodynamical theory of ternary nucleation (Napari et al., 2002).

In activation nucleation the nucleation rate is assumed to depend linearly on sulphuric acid. Even if the exponent $n=1$ would suggest that number of sulphuric acid molecules would be 1, this need not to be the case: exponent 1 could refer to the limiting reaction or step in the nucleation process, which would cause the linear dependence on sulphuric acid. This process could be e.g. heterogenous nucleation of sulphuric acid on molecular clusters of unspecified composition.

In the simulations we must assume some size and composition for the critical cluster in activation nucleation. The critical cluster size is taken to be 1–2 nm, based on measurements which have shown a persistent cluster pool existing at 1–2 nm (Kulmala et al., 2007). Particles are assumed to consist of sulphuric acid only. For a diameter of 1 nm this means that nucleated cluster consists of 6 H₂SO₄ molecules. In the simula-

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tion these clusters are equilibrated with ammonia concentration and relative humidity (parameterization by Napari et al., 2006), which results in an average composition for the nucleated clusters: 6 H₂SO₄ molecules, 7 NH₃ molecules and <1 H₂O molecule. This composition corresponds approximately to ammonium bisulphate. With the added ammonia, the size of the nucleated cluster increases from 1.0 nm to ≈1.12 nm.

In the kinetic nucleation, we assumed similarly the nucleated cluster to consist of only sulphuric acid, which is immediately equilibrated with ambient ammonia and water concentration; thus composition corresponding approximately to ammonium bisulphate.

A more detailed explanation of the assumptions for the composition of critical cluster has been added in the revised manuscript.

P 11380, line 13-15: This conclusion is too strong and generalized, see also the comment of referee 1.

We have reformulated the conclusions and softened the statement about ternary nucleation.

Abstract line 13-16: mention to which nucleation mechanism these results apply.

Please reword P 11367 Lines 22-25

Define peq, org (eqs 1 and 2, p 11368)

P 11370 line 21: "These studies have considered" to make it clear that you refer to the just referenced studies.

P 11371 line 1-2. I appreciate the attempt to put these equations in words, but it would be more helpful if the symbols are then described in words as well, otherwise it fails the purpose.

P 11372 line 7. Using equation 7 (instead of 6). One equation (before eq 7) is unnumbered.

P 11376, line 3: In field measurement data [from the Boreal forest], etc

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We have corrected the points listed above in the revised version.

Figures 2-4 and 7 are too small, especially the axes labels and legends.

Figures 1–4 and 7 are intended to be 2-column wide. This should make the font sizes more readable.

Here and there the language needs to be corrected.

We have tried to address this request while proofreading the manuscript.

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