

## ***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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We thank the referee for the encouraging and constructive comments and questions on our manuscript. We think that accounting for these suggestions will significantly improve the manuscript. Our answers to the referee's comments are as follows:

1) *The authors point at the possibility describing atmospheric new particle formation by an activation mechanism or by a kinetically controlled mechanism being second order for H<sub>2</sub>SO<sub>4</sub>. For the latter, lab studies in the pure system H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub> show new particle formation for H<sub>2</sub>SO<sub>4</sub> concentrations of 10<sup>10</sup> cm<sup>-3</sup>. What is a possible third body being responsible for the observed particle formation at both sites? Weber et al. (Weber, 1996) considered NH<sub>3</sub> as a candidate. As a result of simultaneous NH<sub>3</sub> measurements*

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*in Hyytiälä the authors stated at page 10848: " ... new particle formation would not be here limited by the ammonia concentration." What does it mean? Is the  $\text{NH}_3$  concentration in a saturation range or, generally, ternary nucleation  $\text{H}_2\text{O}/\text{H}_2\text{SO}_4/\text{NH}_3$  does not work?*

The classical ternary nucleation theories predict the exponent in the power law dependence between particle formation rates and  $\text{H}_2\text{SO}_4$  to be well over 2 (typically 4-5, see e.g. Napari et al., 2002; Anttila et al., 2005). Therefore the classical ternary  $\text{H}_2\text{O}/\text{H}_2\text{SO}_4/\text{NH}_3$  nucleation is incapable to explain the reported observations from Hyytiälä and Heidelberg. To the revised version of the manuscript, we will write a paragraph where we speculate the possible role of ammonia and the ternary nucleation scheme, related to this discussion, and cite Napari et al., 2002 and Anttila et al., 2005.

Although the classical ternary nucleation is not a likely option in our case, ammonia might have a role in new particle formation, as suggested by e.g. Weber et al. (1996). However, we did not see any significant correlation between the ammonia concentrations and new particle formation rates in Hyytiälä. This could imply either that ammonia plays no role in new particle formation, or that its effect is hidden by e.g. other nucleation processes taking place at the same time, or changing ambient conditions. This is what we mean with the statement ‘...new particle formation would not be here limited by the ammonia concentration’. We will modify this statement in the revised version of the manuscript. It could also be noted that the ammonia concentrations measured during QUEST IV were significantly higher than the concentrations usually detected in Hyytiälä (see e.g. Sihto et al., 2006).

Another possibility for a ‘third body’ enhancing new particle formation could be some organic molecule emitted by the forests.

As pointed out by the referee, some studies do suggest that the sulphuric acid concentrations should be as high as  $10^{10} \text{ cm}^{-3}$  to see new particle formation in the binary

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H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub> system. However, e.g. Berndt et al. (Science, 2005) have reported new particle formation with sulphuric acid concentrations close to ambient values, namely 106 - 108 cm<sup>-3</sup> in studies where the gaseous sulphuric acid was formed in the reaction of SO<sub>2</sub> and OH, rather than using gaseous H<sub>2</sub>SO<sub>4</sub> generated from bulk liquid. These results suggest that no such 'third body' is necessarily needed for new particle formation in ambient conditions. We will add a reference to the work by Berndt et al. (2005).

*2) For the days with NH<sub>3</sub> measurements a comparison of experimentally determined particle numbers with model predictions using the actual ternary nucleation rate should be possible, like plot 3b or 4a for the H<sub>2</sub>SO<sub>4</sub> power-law. This comparison helps to elucidate the possible role of NH<sub>3</sub>.*

Yes, the calculation of the ternary nucleation rate is possible. However, it is out of the scope of this paper: as explained in our answer to the referee's first comment, the observed clear linear or square dependence between particle formation rate and sulphuric acid rules out the classical ternary nucleation scheme in our case, since it would predict too high exponent (>3) for the power-law dependence between sulphuric acid and new particle formation. We will add a comment related to this statement and cite the papers by Napari et al. (2002) and Anttila et al. (2005) in the revised manuscript.

*3) The overall nucleation process is expected to be strongly temperature-dependent and, therefore, at least the fitting parameters  $A$  and  $K$  are a function of temperature. The measurements span a relatively long time range during winter and spring-time. Is a  $T$ -dependence visible for  $A$  and  $K$  in the whole data set?*

We did try to find a correlation between the activation and kinetic coefficients ( $A$  and  $K$ ) and the ambient temperature. With the investigated data sets we found only a weak positive correlation (correlation coefficients between  $A$  and  $K$  and temperature ranged from 0.01 to 0.35 in different data sets). However, with such small data sets it is difficult

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to say anything sure about the possible temperature-dependence.

We agree that the nucleation processes are likely to be temperature-dependent. Particularly a negative strong temperature-dependence would be expected in the case of thermodynamically limited nucleation (where the saturation vapour pressures of the vapours play a significant role). However, in the case of kinetically limited processes (i.e. where the collision rate limits the nucleation) the temperature-dependence would more likely be positive and weaker as compared with the thermodynamic case. The observed weak positive correlation with temperature could therefore suggest the same thing as the linear or square relations between sulphuric acid and new particle formation: the ternary nucleation, at least if treated with the classical nucleation theory, is not suitable for explaining these results.

We will add a paragraph to the revised manuscript where we shortly describe what kind of correlations between the nucleation coefficients and ambient data we looked for, and what were our conclusions from them. The data sets were so small that it was difficult to draw any strong conclusions about the correlations. In the future we hope to analyse longer continuous data sets with measured sulphuric acid and particle concentrations.

*4) The measurements in Hyytiälä have been done during april - may connected with starting biogenic activity in the forest. A statement is needed for the importance of organics for the growth process.*

The organics have a significant role in the growth of freshly nucleated particles, and this role is enhanced during the spring and summertime (see e.g. Kulmala et al., 2004, and Hirsikko et al., 2005). We will add a sentence describing this and citing these references in the revised version of the manuscript.

However, in April-May no clear spring recovery transition is seen in Hyytiälä, since in April the photosynthetic activity of the forest is usually already strongly going on (March-April would have been more interesting time frame in this sense). Therefore we do not expect to see e.g. any clear increase in the growth rates as the spring

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proceeds towards May, and no systematic temporal trend in the growth rates, time lags or exponents was observed from the data either.

References:

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