

Interactive comment on “Growth of sulphuric acid nanoparticles under wet and dry conditions” by L. Škrabalová et al.

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We thank the reviewer for the helpful comments. Please find our point-by-point responses below.

Referee 2:

General comments:

1. Please describe the experimental setup in more detail, otherwise it is very hard to understand the results of the experiments based on this paper alone.

R: Due to referee's suggestion we will describe the experimental setup more comprehensively and extra figure depicting the setup will be added.

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2. This study is based on sulphuric acid concentrations that are calculated using a formula for the temperature dependent saturation vapor pressure. How accurate are the concentrations calculated using this formula? The authors should discuss about comparison of the calculated concentrations to available measured sulphuric acid concentrations. If the measurement setup is the same as the one used by Neitola et al. (2013), authors could refer to this study for comparisons.

R: Sulfuric acid concentration in this study was determined using equation given in Kulmala and Laaksonen (1990), which is commonly used in studies of binary or ternary nucleation parametrization (Vehkamäki et al., 2002; Merikanto et al., 2007). The accuracy of this expression is demonstrated in work of Neitola et al., (2013) which shows the comparison of experimental values measured using online ion chromatograph MARGA and predicted theoretically using this equation (see Fig. 3). As can be seen, the concentrations measured with MARGA agree well with theoretical predictions.

3. Are the particle growth rates calculated assuming that nucleation occurs at the very beginning of the flow tube? If this is the case, has it been studied whether particle nucleation occurs also some distance along the flow tube, and what effect this would have on the calculated particle growth rates? What about the condensational loss of sulphuric acid to the particle phase, can this process be neglected when considering the sulphuric acid concentration inside the flow tube?

R: In this study the particles are assumed to nucleate at the beginning of the flow tube. In the work of Neitola et al, (2013), who used the same setup and comparable experimental conditions, the maximum condensational losses of sulfuric acid to the particle phase were estimated to be 1,4%. Therefore we decided to neglect the condensational losses of sulfuric acid in further analysis.

4. Are the particles assumed to grow with constant concentrations of sulphuric acid, water and ammonia in the flow tube? Is there any measurements or modelling studies about the vapor concentration profiles along the tube? How would the modelled growth

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rates change if the possible profiles of the condensing vapors were taken into account? Now the authors explain that the best agreement between the observed and modelled growth rates is achieved by using the calculated sulphuric acid concentration at the beginning of the flow tube. If the sulphuric acid concentration is decreasing along the flow tube, this would make the modelled growth rates an overestimate. Also, the authors choose not to take into account loss of sulphuric acid vapor to the tube walls, as this provides best agreement between modelled and observed growth rates. However, there are other possibilities to make the modelled results match the observations, and I would recommend the authors to include discussion on those.

R: The relative humidity was measured at the beginning and at the end of the flow tube during measurements and was found to be stable. The unknown concentration of the ammonia in the system is accounted for in the model calculations by using three different ammonia to sulfate ratios in the growing particles. Regarding the concentration profiles of sulfuric acid, we have conducted additional growth rate calculations using a modified model that accounts for the acid wall loss rate coefficients determined for the same flow tube in a previous study (Brus et al., 2010). As can be seen from Fig. 1, using the system specific wall loss rate coefficients provides better agreement with experimental values than using wall loss correction given in Hanson and Eisele (2000). Despite of this, at higher acid concentrations neglecting the wall losses provides the best agreement. We are aware that the agreement between modelled results and experimental observations presented in the manuscript should be interpreted with caution and this point will be discussed more in detail in the revised manuscript.

5. Have the authors considered taking into account the modifications proposed by Lehtinen and Kulmala (2003) and Nieminen et al. (2010) to the mass transfer equation (Equation 4 of the current paper)? For particles smaller than about 10 nm it was shown by Nieminen et al. (2010) to enhance the growth rates by upto a factor of two for vapors with molecule masses in the range 100 – 150 amu (for example ammonium sulphate which is considered in this study).

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R: We have included the modifications (equations 1-3 in Lehtinen and Kulmala, 2003) into the model and performed additional calculations in order to determine the growth enhancement. The enhancement of the calculated growth rates was ~ 5 %, which improves agreement between modelled and measured values for residence times 45 and 60 s, but contributes to growth overestimation at residence time 90 s. This will be mentioned in the revised manuscript.

Specific comments:

Chapter 2.1, Equation 3: Please give also the range of the sulphuric acid diffusion coefficient variation between dry and wet conditions.

R: The diffusion coefficient D for dry condition is $D=0,376 \text{ cm}^2/\text{s}$ and for wet conditions $D=0,319 \text{ cm}^2/\text{s}$.

Chapter 2.2, line 28: Is the initial particle diameter the size of the nucleated critical cluster? How well is it known at which point of the diffusion tube the particles are nucleated? This affects the residence time in the tube and therefore the growth rates calculated by Equation 7.

R: The particles are assumed to nucleate at the beginning of the flow tube. As stated in the manuscript, the initial particle diameter is not the size of the nucleated critical cluster, but the mean diameter of the nucleation mode, which was obtained by fitting the log-normal distribution to the number size distributions from DMPS. The particle growth rates were then obtained from the change of the modal geometric mean diameter as a function of time.

End of Chapter 2.1: In the last paragraph of Chapter 2.1, Equation 7 is used to calculate the particle growth rate. It should be given more clearly what is the initial particle diameter d_{init} used in the calculations. The growth time for the particles is taken as the residence time of the sample air travelling through the flow tube. Does this mean that the particle formation is assumed to occur right at the beginning of the flow tube? Is

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there any evidence that this really is the case, or whether the formation occurs at some length into the tube? This would directly affect the calculated growth rates. Is there any information about the sulphuric acid concentration profile along the flow tube, if it is constant or decreasing along the tube? This would also affect the particle growth as they are moving along the flow tube. Could the uncertainties on the calculated growth rates caused by these effects be estimated?

R: The initial particle diameter, used in Equation 7, is mean diameter of the nucleation mode, which was obtained by fitting the log-normal distribution to the number size distributions from DMPS. The particles are assumed to nucleate at the beginning of the flow tube, but no simulations were performed to verify this assumption. Additional calculations will be performed to estimate the total uncertainty of the calculated growth rates resulting from uncertainties regarding the particle formation place and acid concentration profile and will be mentioned in the revised text.

Page 24101, end of Chapter 3.3: Could the changing behaviour of growth factors in higher sulphuric acid concentrations be explained by a larger fraction of acidic (and therefore more hygroscopic) particles at higher H₂SO₄?

R: Thanks for pointing out possible explanation for the changing behaviour of growth factors. This will be mentioned in the revised manuscript.

Chapter 3.4: In Neitola et al. (2013) describing experiments using the same setup, wall losses were estimated to be similar as in this study. However, in this study the authors conclude that the wall losses are estimated to be too high, or do not correctly take into account the sulphuric acid concentrations the particles are exposed to during their growth in the flow tube. Therefore, the authors have chosen to neglect the wall losses entirely in this study. Since this is very crucial assumption regarding the conclusions of the paper (namely agreement between the modelled and observed growth rates), the validity of neglecting the wall losses should be discussed in more detail. Also, what would be the implications of neglecting the wall losses for the Neitola et al. (2013)

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study? Is there any information about the sulphuric acid concentration profile along the flow tube, or could this be estimated? The particles are growing the whole time they are travelling through the tube, and if there are differences in the concentrations of the condensing vapors along the tube, this affects the particle growth rates. Assuming that the particles grow the whole time with the rate determined by the vapor concentration at the start of the tube is probably an overestimation.

R: Please see our response to comment 4. Additional calculations concerning sulfuric acid profiles and wall losses were performed and respective discussion will be added to the revised manuscript.

Technical comments:

Page 24105, line 3: Consider revising "A trend line which presents the theoretical predictions of the growth of ..." into for example "The theoretical predictions of the growth of ...".

R: The required change will be done.

Page 24105, line 15: In reference to the iodine species, the reference for O'Dowd et al., (2002) listed in the reference list is probably incorrect, should be O'Dowd et al. (2002): Marine aerosol formation from biogenic iodine emissions, *Nature*, 417, 632–636. Also, the reference to Kulmala et al. (2013) is probably misplaced here, it does not discuss condensation of iodine species.

R: The references will be corrected.

References

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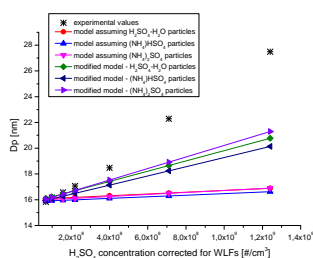


Figure 1: The comparison of the experimental median particle diameters from a measurement conducted at $T=283$ K, with a RH of $\sim 30\%$ and a residence time of 60 s and values predicted theoretically from a model using the H_2SO_4 concentration corrected for wall losses, determined according to Hanson and Eisele (2000) and modified model, accounting for a system-specific wall loss rate coefficients (Brus et al., 2010).

Fig. 1.

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