

## ***Interactive comment on “Total sulphate vs. sulphuric acid monomer in nucleation studies: which represents the “true” concentration?” by K. Neitola et al.***

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We thank the referee for their helpful comments and observations.

R3C: Nothing is said regarding the CI-API-TOF results other than H<sub>2</sub>SO<sub>4</sub> monomer concentrations! Are there any other clusters visible? What's the matter with H<sub>2</sub>SO<sub>4</sub>-base or H<sub>2</sub>SO<sub>4</sub>-organic compounds? How the authors checked the carrier gas impurities? How can carrier gas impurities influence or explain the observed disagreement of total sulphate and H<sub>2</sub>SO<sub>4</sub> monomer concentration?

Au A: We present only the monomer values of sulphuric acid concentration due to the

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fact that CIMS can measure the monomer concentration reliably. As it is stated in the manuscript (page 2320, lines 25-28), the dimer concentration of sulphuric acid is only ~1% of monomer concentration. Identifying peaks from CI-API-TOF mass spectra comes more and more difficult with increasing mass. Jokinen et al., (2012) states in their manuscript that identifying peaks with four sulphuric acid molecules would need integration times over two hours due to the overlapping of the peaks arising from other compounds. CI-API-TOF was measuring up to 2000 Da and peaks were observed up to 500 Da at 273K and 1000 Da at 303K, thus correlating with sulfuric acid concentration dependency on temperature. However there were no peaks with high intensity at higher mass range containing sulphuric acid. The sulphuric acid of course, has not vanished anywhere. It is probably bound to some organics and base molecules, and clustering up to higher masses with wide distribution to different mass peaks in the CI-API-TOF mass spectra. Identifying these peaks is impossible at this moment.

We measured background concentration of contaminants in the carrier gas with MARGA. Only concentrations of ammonia in levels of 60 pptv (< detection limit of 67 pptv) and 126 pptv as stated in manuscript page 2330, lines 21-22 were observed, which most probably arises from the water used for the humidity of the carrier gas, since the concentration is only RH depended. Other contaminants like amines were below detection limits. There are most probably other contaminants involved in the system, but even if some of them could be identified from the mass spectra of CI-API-TOF, quantification is still currently impossible. This is due to unknown charging efficiency (rate constant) of these molecules by the NO<sub>3</sub>- ions in the CI-inlet. These contaminants can cause the discrepancy between the monomer and total sulphate concentration, as it is stated in the conclusions section (page 2332, line23 to page 2333 line 2).

R3C: In a single paragraph the MARGA technique should be compared with CIMS and CI-API-TOF stating the detection limits, upper detectible concentrations, calibration results and the expected measurement errors.

Au A: Detection limits are briefly mentioned in the manuscript (page 2321). Authors

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apologize for missing details of the instruments and a paragraph will be added, where the differences between the measurement techniques, detection limits and errors will be compared.

R3C: The authors should explain more in detail equation (1) regarding the “simple” equation of H<sub>2</sub>SO<sub>4</sub> vapour pressure as derived from experimental data by Ayers et al.! I guess it is not enough to reference only to the work by Kulmala and Laaksonen. Au A: Authors agree with the referee and a more detailed description of the equation (1) will be added to the manuscript (page 2318, line 12): “Ayers et al., (1980) use in principle similar technique to produce the sulphuric acid vapour. Ayers et al. trapped the vapour in a cold trap with alkaline solution and determined the concentration by change in pH. Their temperature range of the vapour production was 338-445 K. They come up with a semi-empirical equation for the saturation vapour pressure of sulphuric acid. Kulmala and Laaksonen, (1990) theoretically expanded this equation to be applicable also in lower temperatures (down to 150 K) by considering the temperature dependence of the enthalpy of vaporization, which was assumed to be constant by Ayers et al.:

We used K&L equation since it is often used in nucleation binary and ternary parameterizations containing sulphuric acid (e.g. Vehkamäki et al., 2002; Merikanto et al., 2007).”

R3C: The authors observed nucleation for H<sub>2</sub>SO<sub>4</sub> concentrations of about 10<sup>(7)</sup> cm<sup>(-3)</sup> in line with former results from the same experiment but using another H<sub>2</sub>SO<sub>4</sub> source. Do they believe that there was no third body involved in the nucleation process? They should explain their findings in light of the current knowledge of atmospheric nucleation.

Au A: Authors do not use word ‘binary nucleation’ anywhere within the manuscript as we know that there are at least “a third body”, but most probably many other species also involved in the nucleation process. Authors explicitly report concentrations of ammonia in the manuscript page 2330, lines 21-22. As it is currently impossible to identify and quantify all the other contaminants present in the system, authors do mention only

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that other species are under detection limits of analytical method used. In our system and also in our previous studies (Brus et al. 2010 and 2011), we consider that the only driving force is concentration of sulphuric acid, since all other variables are kept constant. Moreover we believe that concentrations of impurities are at saturated level and further addition of ammonia or amines will not significantly change the observed nucleation rate (Neitola et al., conference abstract, EAC2011). However, we are aware that presence of impurities in our system is triggering nucleation easier than compared to “pure” binary case.

R3C: The work by Ball et al.(1999) and Zollner et al.(2012) has been mentioned in the manuscript. Both studies used also a liquid H<sub>2</sub>SO<sub>4</sub> source and H<sub>2</sub>SO<sub>4</sub> monomer measurements by CIMS. A discussion of the findings of this manuscript regarding the former papers would be fine.

Au A: As pointed in the manuscript (page 2330, line 13): “Comparison to similar laboratory studies is done in Brus et al. (2010) and Zollner et al., (2012) and is not shown here. The results obtained in this study are very similar to the results in Brus et al., (2010) as seen in Fig. 8, so the comparison is not necessary here.” No comparison to other literature was shown in this manuscript, since we consider it redundant. As mentioned above the comparison of recent studies was done by Zollner et al (2012), we think they did very good job.

Zollner et al., (2012) provide their data of flow rate test as ion ratios and not as sulphuric acid concentration in their supplementary material. We have done many similar flow rate tests as presented in Zollner et al., (2012). Our data is presented in Figure S3 (below) together with the Zollner et al., (2012) flow rate data. Both data sets are presented as ion ratios and can be transferred to Sulphuric acid concentrations by multiplying with calibration constant K=1011 and K=5·109 from Zollner et al. and our data, respectively. Figure S3 shows that our data is parallel to Zollner et al., (2012) data but it is somewhat lower on ion rate. This can be explained as our data set is measured at saturator temperature of 273K and the mixing flow is 40 lpm. Zollner et al., (2012)

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had saturator temperature of 303K and total flow of 6 lpm. Figure S4 shows ion ratio as a function of saturator temperature for several different saturator flow rates. From figure S4 one can see that flow rate of 0.05 lpm is too low as the ion ratio decreases as a function of saturator temperature. The slopes of other flow rates are parallel. With 1 lpm saturator flow rate, the data set 'saturates' with higher saturator temperature but this is because the monomer count is already at the higher detection limit of CIMS. Here the mixing flows were between 7 and 9 lpm. These figures will be added to the supplementary material.

R3C: Finally, I guess, the authors should try to find out the reason for the missing H<sub>2</sub>SO<sub>4</sub>. They have the best technique at the moment doing that.

Au A: As stated above, the identification of the peaks containing sulphuric acid from CI-API-TOF is impossible due to enormously wide distribution of those peaks up to 1000 Da at 303 K. Quantification of the concentration is even more difficult, as the rate constants for these clusters are unknown. Authors mention in the conclusions (page 2332, lines 23- page 2333, line 2) possible reasons for discrepancy in monomer and total sulfate concentrations. There is indication that sulfuric acid is distributed along the mass spectra of CI-API-TOF but at the moment we are not able to identify and quantify the sulphuric acid containing clusters from mass peaks in CI-API-TOF spectra.

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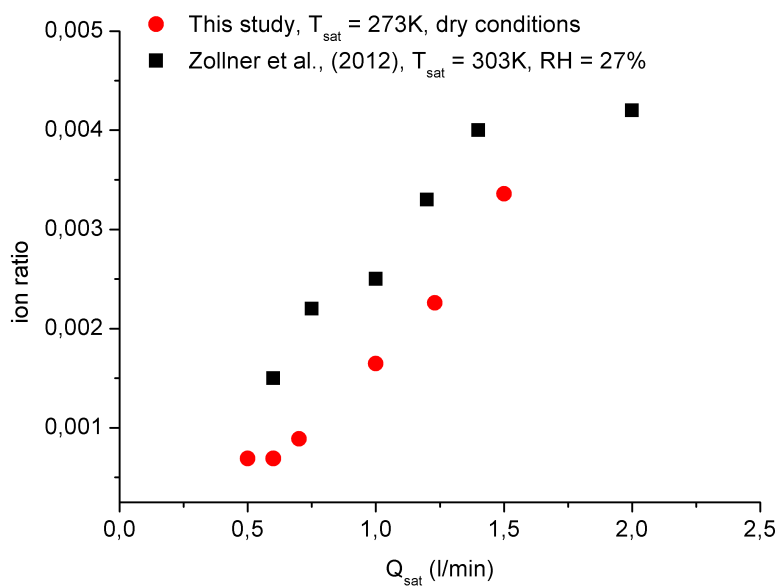
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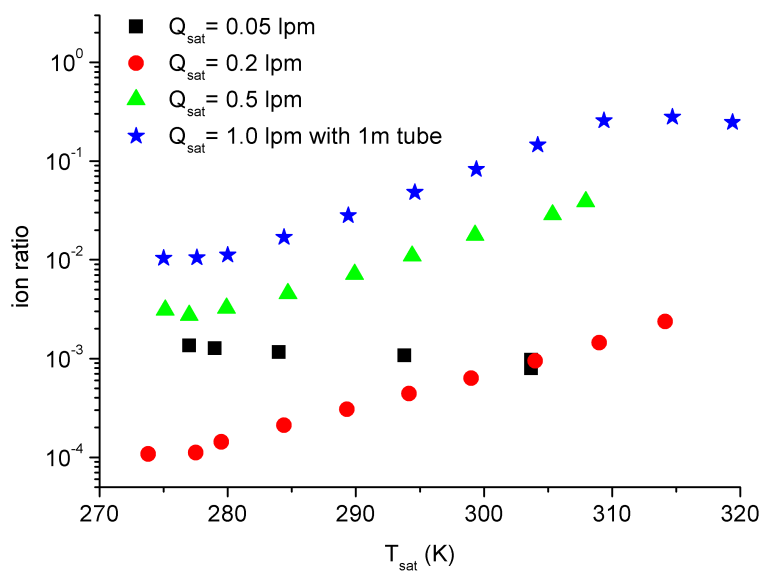
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**Fig. 1.** Figure S3. ratio of core ion and reagent core ion measured by CIMS as a function of saturator flow rate from this study and from Zollner et al., (2012), will be added to supplementary material.

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**Fig. 2.** Figure S4. ratio of core ion and reagent core ion measured by CIMS as a function of saturator temperature for several different saturator flow rates, will be added to supplementary materials.

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