

## ***Interactive comment on “Total sulphate vs. sulphuric acid monomer in nucleation studies” by K. Neitola et al.***

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Answer to referee #1. We thank the referee for very important comments and suggestions. The author would like to apologize for inconvenience in reading the manuscript, due to numerous grammatical mistakes. The manuscript has been proof-read by a native speaker. The focus of the manuscript changed during the writing process, causing the message of the manuscript not to be very clear. Now the manuscript focuses mainly to the observed discrepancy between measured sulphuric acid and total sulphate, comparison to our previous study and thus excluding the possibility that the discrepancy is connected to production method of SA vapour. The most important changes (additions) are written in answers to referee below. The whole manuscript is

C11573

also included as a supplement with the changes tracked, (red = removed, blue = added) to help the referee to spot the changes.

Referee's main comment #1: The observed discrepancy in measured concentrations between the instruments could be of importance for the scientific community. However, the way it is communicated in this manuscript I cannot recommend it for publication. There is not any explanation for the observed discrepancy until the conclusions section (which looks more like a discussion section in the current state). In that section, the authors mention the possibility of sulphuric acid forming clusters with contaminants like e.g. ammonia. That is a possible explanation but to prove that it would have to be measured and quantified. And even then, the authors would have to motivate why they think that would be an important observation (like e.g. a higher fraction of sulphuric acid-base clusters than expected). In the abstract, there is nothing written about possible explanations for the discrepancy.

Answer #1: An explanation is now added to the abstract, together with a motivation why it is important:

“Possible reasons for the discrepancy are discussed and some suggestions include that the missing sulphuric acid is in clusters, formed with contaminants found in most laboratory experiments. One-to-two orders-of-magnitude higher sulphuric-acid concentrations (measured as total sulphate in this study) would contribute to a higher fraction of particle growth rate than assumed from the measurements by mass spectrometers (i.e. sulphuric-acid monomer). However, the observed growth rates by sulphate-containing vapour in this study does not directly imply similar situation on field, where the sources of sulphate are much more diverse.”

To prove that the missing sulphuric acid is in the clusters, one should be able to identify the peaks containing sulphuric acid from the CI-API-TOF mass spectra, determine their charging probability (calibration factor) in the CI-inlet, then sum the concentrations of those peaks and compare it to the theoretical predictions of the concentration. How-

C11574

ever, even the identification is a huge task and will take a long time to do, not to mention determination of the charging probability. This task was out of the scope of this paper. These reasons were stated in the supplementary material and in the conclusions section, but probably not well enough. A paragraph was added to the section 3.1, where a summary of the supplementary material is presented, including above mentioned reasoning:

“Extra saturator tests with mass spectrometers were done using three different carrier gas purities (N2 6.0, N2 5.0 and pressurized air) to check if the carrier gas used in our experiments (pressurized air) was more dirty than the most pure commercial ones. Two different purity sulphuric acids (~97 % and 100 %) were tested also to check if the purity of the acid itself has an influence. Changing the carrier gas or the sulphuric acid purity did not affect the observed sulphuric-acid concentration (see supplementary material, Fig. S3 and S4). The measured sulphuric-acid monomer concentration was one-to-two orders-of-magnitude lower than the prediction by Eq. 1. Tests with different saturator flowrates (0.05-2 lpm) showed that with flowrates below 0.1 lpm, diffusion losses dominated: causing the measured concentration to decrease as a function of the saturator flowrate. Above 0.15 lpm, the observed results behaved as expected. The measured cluster distributions (monomer, dimer and trimer) with different carrier gas purity were constant through the measured saturator flowrate range (Fig. S5). The ratios between monomer-to-dimer and dimer-to-trimer were between 1:10 and 1:100 with all carrier gases. From these results it is evident that the carrier gas used in our studies does not contain more contaminants than the most pure ones commercially available. CI-API-TOF mass spectra observed with different carrier gases were investigated further to find the missing sulphuric acid. A large number of peaks were found to correlate with mass 97 (HSO<sub>4</sub><sup>-</sup>), which is the ionized sulphuric-acid monomer, with all carrier gases. The number of these peaks increased as a function of the saturator temperature, suggestive that the sulphuric acid forms clusters with contaminant substances (Supplementary, section 6, Fig. S6-S8). The correlating peaks in Fig. S6-S8 are stick masses (i.e. rounded to nearest integer), which means that many of those

C11575

peaks have actually several peaks within them. This is shown in Fig. S9-S11 where the mass spectrum from CI-API-TOF is zoomed in. Unfortunately, summing up all of these correlating peaks to calculate the total sulphuric acid concentration is not feasible, since these clusters are not identified (i.e. it is not known what molecules those clusters are composed of) and the sheer number of these peaks is overwhelming. For more details and discussion of the extra saturator tests, see supplementary material.”

The conclusion section has been improved and it is named discussion and conclusions.

Referee's main comment #2: The authors seem to have done a good job in performing their measurements and in evaluating the importance of potentially important factors like e.g. relative humidity, wall losses, and flow rates on measured concentrations. However, since the reason for the discrepancy in the measured concentrations is not known there is no clear message in this manuscript. The manuscript is generally unfocused, and it is unclear what the actual goal is of the study. When introducing the study in the introduction the authors write: “Here we present a way to produce sulphuric-acid vapour from thermally controlled saturator in a wide range of sulphuric-acid concentrations”. Reviewer 2 from the review of this manuscript in ACPD in 2013 pointed out that the use of an H<sub>2</sub>SO<sub>4</sub> saturator is not new” and the authors seemed to agree on this in their response. Still one gets the feeling when reading both the introduction and conclusions sections that this method of producing H<sub>2</sub>SO<sub>4</sub> is one of the main points of the paper. In addition, the language would have to be checked by a native English speaker.

Answer #2: The manuscript was not clearly focused, with the weight on the saturator as it should have been on the discrepancy between the measured sulphuric-acid and total-sulphate concentrations. The explanation why the nucleation measurements were done and motivation for the measurement conducted with different production method (mentioned in the answer #1) were added in to the Abstract section:

“The saturator provided an independent vapour-production method, compared to our

C11576

previous method of the furnace (Brus et al., 2010 and 2011), to find out if the discrepancy is caused by the production method itself. The saturator was used in a sulphuric acid-water nucleation experiment, using a laminar flow tube to check reproducibility of the nucleation results with the saturator method, compared to the furnace.”

The importance of the discrepancy is motivated also at the end of the introduction and conclusions section and the motivation of the whole manuscript is shifted towards the saturator-test results, instead of the saturator usage. The reason for the discrepancy is not known and proven in the manuscript, as the referee mentioned. However, there are quite reasonable suggestions towards the sulphuric acid to be “hidden” in the clusters. Even though it is not quantified, the results presented in Fig. S7-S11 in the supplementary material are pointing quite clearly towards the clusters. In the Fig. S7-S11 it is shown that there are numerous clusters containing sulphuric acid, which are not taken into account when determining the sulphuric-acid concentration from CIMS or CI-API-TOF measurements. These results are more exposed with the added paragraph (mentioned in answer #1) in the section 3.1.

Detailed comment #1: The motivation of sections 3.3-3.4 is vague. The authors should spend more effort in motivating why they compare their formation rates with Brus et al. rather than presenting a lot of figures and describing what they show. There seems to be no important lesson to be learnt here, or at least it is not communicated well enough. Answer to detailed comment #1: The motivation for the flow tube nucleation measurements and comparison to our previous results is: a) to remove the sulphuric acid vapour-production as possible reason for the discrepancy and b) to be able to compare the measured sulphuric-acid monomer and total-sulphate concentrations with similar particle formation rates. With the flow tube we can ensure that conditions are similar (temperature, relative humidity and particle formation rates), in which the sulphuric-acid concentrations are measured. The motivation for sections 3.3-3.4 has been improved for the whole manuscript. Here are listed the larger changes including the additions to the Abstract:

C11577

“The saturator provided an independent vapour-production method, compared to our previous method of the furnace (Brus et al., 2010 and 2011), to find out if the discrepancy is caused by the production method itself. The saturator was used in a sulphuric acid-water nucleation experiment, using a laminar flow tube to check reproducibility of the nucleation results with the saturator method, compared to the furnace.”

Introduction:

“Brus et al. (2011) found a discrepancy in sulphuric-acid mass-balance between a known concentration of weak sulphuric-acid solution introduced to the experimental setup and a measured sulphuric-acid concentration, even though correction for wall losses and losses to particle-phase was applied, one-and-half orders-of-magnitude difference in sulphuric acid concentration was found (see Fig. 5 in Brus et al., 2011). A large discrepancy between measured sulphuric-acid monomer and total-sulphate concentration was observed in the present study. To investigate the reason for this discrepancy, we applied a thermally controlled saturator (e.g. Wyslouzil et al., 1991; Ball et al., 1999) to produce sulphuric-acid vapour. The output of the saturator was tested with two independent detection methods (mass spectrometry and ion chromatography) before using the saturator in a sulphuric acid-water nucleation study in a laminar flow tube. Applying the saturator as the source of the sulphuric-acid vapour made it possible to compare the saturator to the furnace, which was used as the source of the sulphuric acid previously (Brus et al., 2010 and 2011) and eliminate the production method as a reason for the discrepancy. The flow-tube measurements with the saturator and the two sulphuric-acid or total-sulphate detection methods were conducted to check reproducibility of particle formation rates between the saturator and the furnace, with similar observed sulphuric-acid or total-sulphate concentrations.”

as well as in the section 3.3:

“The purpose of these nucleation measurements is to be able to compare the formation rates and the sulphuric-acid or total-sulphate concentrations, between the two

C11578

sulphuric-acid vapour-production methods.”

and 3.4:

“Figures 8 and 9 show that apparent formation rates are reproducible with both sulphuric-acid production methods, with similar observed sulphuric-acid or total-sulphate concentrations. This eliminates the sulphuric-acid production method as a reason for the discrepancy between the measured monomer and total sulphate concentrations.”

Detailed comment #2: Figure 5 shows how the particle number concentration and diameter change as the sulphuric-acid monomer concentration increases. The sulphuric-acid concentration is within the range of typical atmospheric concentrations, so what is the reason for the rapid growth when the vapour concentration increases? In the atmosphere, growth rates are normally a few nm per hour and organics do most of the job. Here the residence time is only 30 s.

Answer to detailed comment #2: The referee has pointed out one of the possible consequences arising from the discrepancy. If sulphuric-acid concentration in the flow tube is between  $10^6$  and  $10^7$  cm<sup>-3</sup>, the growth rate should not be as high as observed in the flow-tube experiment. However, if the concentration is one-to-two orders-of-magnitude higher, measured growth rates are consistent with the amount of sulphate containing vapour available. We used the model described in Škrabalová et al. (2014) to calculate the particle diameter ( $D_p$ ) and growth rate (GR) of the particles accounting for the initial sulphuric-acid monomer and total-sulphate concentrations as an input. Measured sulphuric-acid monomer and total-sulphate concentrations (presented in Fig. 6 and 7, panel d)) were converted to initial concentration (i.e. at the beginning of the flow tube) with the determined TLFs (factor of 10 sulphate and 14.2 for SA monomer concentrations). Diameter of 1.5 nm was used as an initial cluster size (Kulmala et al., 2007). Three different scenarios of particle neutralisation by ammonia were used in the model: (0) no neutralisation, sulphuric acid-water particles, (1) neutralisation to

C11579

ammonium bisulphate-water particles and (2) neutralisation to ammonium sulphate-water particles. Using the sulphuric-acid monomer concentration as an input resulted in growth rates ranging from 1 to 15 nm h<sup>-1</sup>, as the referee is stating. With these growth rates the particles grew up to 2 nm only, which is well below the observed diameters (Fig. 6, panel b)). Using total-sulphate as an input, the growth rates ranged from 1250 to 2300 nm h<sup>-1</sup> resulting in diameters fitting well with the observed diameters. The results of the model are presented in supplementary material section 7 and Fig. S12. A paragraph was added in the end of section 3.3:

“The measured sulphuric-acid monomer concentration is at typical atmospheric levels, but the growth rates are much higher: indicating much larger concentration of condensing vapour than the detected sulphuric-acid-monomer concentration by CIMS. The growth is rather driven by the total sulphate, originating exclusively from the sulphuric acid inside the saturator, than the sulphuric-acid-monomer concentration. To show the contribution of the sulphate to the growth rate, the model from Škrabalová et al. (2014) was used to calculate the diameter ( $D_p$ ) and growth rate (GR) of the particles. Measured sulphuric-acid monomer and total-sulphate concentrations (Fig. 6 and 7, panel d), RH 30 %) were multiplied by the TLFs to obtain the initial concentrations at the beginning of the flow tube. Diameter of 1.5 nm was chosen as the initial cluster size according to Kulmala et al. (2007). The model was used with three scenarios of particle neutralization by ammonia: (0) no neutralization, particles composed of sulphuric acid and water, (1) neutralization to ammonium bisulphate-water particles and (2) neutralization to ammonium sulphate-water particles. When accounting for the initial sulphuric-acid monomer concentration as an input, the resulting diameter ( $D_p$ ) was always below 2 nm with growth rates (GR) ranging approximately from 1 to 15 nm h<sup>-1</sup> as a function of the sulphuric-acid concentration (i.e. saturator temperature  $T_{sat}$ ) with all scenarios. When total-sulphate concentration was used as an input, the resulting particle diameters and growth rates fit well with the measured particle diameters presented in Fig. 7 for all scenarios (see suppl. Material, section 7 and Fig. S12).”

C11580

Detailed comment #3: Is there a reason for the total sulphate concentration measured by the MARGA (saturator only) being higher in Fig. 4 (2\*109 at 280K) than in Fig. 3 (1\*109 at 280K)?

Answer to detailed comment #3: The values presented in Fig. 3 are the actual measured values. In Fig. 4 the different mixing ratios of saturator flow and the mixing flow between saturator tests and nucleation measurements has been taken into account to be able to determine the Total Loss Factors (TLF) in the section 3.2. In the nucleation measurements, the mixing flow was kept at appr. 11 lpm to have similar conditions as in our previous experiments where the furnace was used, but the saturator flow rate was varying. To account for the different mixing ratios, total-sulphate concentration (saturator only) was divided by a factor of 1.9. The usage of the mixing ratios is mentioned in the section 3.2 (page 25798, line 17):

“By accounting for the different mixing ratios of saturator flowrate and mixing flowrate, these measurements become comparable and the total losses in the flow tube can be determined. The Total Loss Factor (TLF) includes wall losses and losses to the particle phase (nucleation and condensational losses).”

Detailed comment #4: Some of the typing errors.

Answer to detailed comment #4: All mentioned and lot more typing errors have been corrected by help from a native English speaker. Thank you for listing some of these out.

References: Kulmala, M., Riipinen, I., Sipilä, M., Manninen, H. E., Petäjä, T., Junninen, H., Dal Maso, M., Mordas, G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R. M., Hanson, I., Leung, C., Lehtinen, K. E. J., Kerminen, V.-M.: Towards direct measurement of atmospheric nucleation, *Science*, 318, 89, DOI: 10.1126/science.1144124, 2007.

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C11581

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C11573/2015/acpd-14-C11573-2015-supplement.pdf>

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 14, 25787, 2014.

C11582