

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

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Received and published: 26 January 2015

Answer to referee #2. 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

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

Referee's comment #1: In my view, the most interesting results are those from the saturator itself (Figure3). It is more difficult for me to understand the purpose of the nucleation experiments. No reason for performing these experiments is mentioned in the introduction, and it is not until Section 3, Results and Discussion, that we see an overview of the study and an explanation for why these nucleation experiments are presented. According to the authors, the purpose is to compare their results with previous studies. My recommendation is to put a paragraph similar to this (p2596, ln16) in the introduction (p25790).

Answer #1: The motivation for the flow tube nucleation measurements and comparison to our previous results was added to manuscript: Abstract:

“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) reported 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 too. 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

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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 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.”

Referee's comment #2: If the purpose of the nucleation experiments is to compare the results with previous studies, this could be extremely difficult due to the fact that nucleation rates are not actually being measured in this study. As stated on p25800, In 7, the residence times in this flow tube were so long that by particles had grown to 8 nm when detected at the outlet. As Sipila et al showed, this will greatly affect both the power dependence on sulfuric acid as well as nucleation thresholds.

Answer #2: Referee is right on the fact, that actual nucleation rates are not directly

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measured in our study. Relatively long residence time will affect the observed formation rates. The point was here to compare to our previous results measured with the same experimental setup, except for the different sulphuric-acid-vapour production method. As the conditions and the setup are the same in our previous measurements (Brus et al. 2010 and 2011) and in this study, comparison of the apparent formation rates are justified. As mentioned above, this was done to rule out the vapour production method as a reason for the discrepancy. The reported slopes in Fig. 8 are presented to show the similarity of the apparent formation rates, not to argue anything about the overall power dependency of nucleation rates on the sulphuric-acid concentration. The text within the manuscript is corrected to emphasize that the observed formation rates are rather apparent formation rates and not actual nucleation rates.

Referee's comment #3: Also, except for the comparison to the Brus et al study (Figure 10), no other comparisons are made. Likely, it was because it would be difficult due to the above-mentioned problem with nucleation rates (Item 3). This study would be a lot more useful to readers if you can place it in context by comparing results to prior studies.

Answer #3: It is true that comparison to other studies might help to put the nucleation experiment results more into context. The comparison to other results found in literature was left out from this study as it is not in the main scope of this manuscript. A paragraph was added to the end of section 3.4: “The comparison to literature data was omitted in this manuscript as the formation rates in the present study are very similar to our previous results (Brus et al., 2010 and 2011). However, for comparison and review of experimental data on sulphuric-acid nucleation, we refer to Zollner et al., (2012) and Zhang et al., (2012).”

Referee's comment #4: If Items 3 and 4 are not consistent with the authors' intentions, it would be good to have a clear explanation as to the value of the results in Figures 6 and 7.

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Answer #4: The purpose of Fig. 6 and 7 is to show reproducibility of the results between the experiments with mass spectrometers and with MARGA, as well as to show the response of different variables to the increasing saturator temperature to justify the use of the saturator in the experiments. The most interesting of these variables is the mean diameter of the particles, as it points out fast growth rate in the flow tube. To emphasize the effect of the sulphate to the growth, we used the model described in Škrabalová et al. (2014) to calculate the resulting particle diameter ( $D_p$ ) and growth rate (GR) of the particles using the initial sulphuric-acid monomer and total-sulphate concentrations as an input. 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).”

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Referee's comment #5: Since contaminants are a likely source of the discrepancy between sulfuric monomer and sulfate, it's important to state exactly how the purified air is generated for the saturator and flow tube experiments. What, exactly, is the “carbon capsule” shown in Figures 1 and 2? How do you know that any residual amines or ammonia have been removed from this air? Hanson et al. used a weak phosphoric acid denuder to scrub bases from their air supply. Was something similar done?

Answer #5: The carbon capsule is commercially available from Pall, Corp., USA, it is a plastic capsule filled with activated carbon, which removes all organic vapour via diffusion to the surfaces from the carrier gas flow. A sentence was added to first paragraph of section 2.1:

“Carrier gas flows were purified in all experiments first with activated carbon capsules (Pall Corp., USA) to remove all organic vapours via diffusion to the surfaces and after with a HEPA (Pall Corp. USA) filters to remove any particles left in the flow.”

From the comparison measurements among commercially available N<sub>2</sub> of different purity, it is clear that contaminants of similar level were still present in the carrier gas (pressurized air) used in our experiment. No extra denuders were used in this study.

Referee's comment #6: Section 3.5 provides important insights into the possible source of this discrepancy between sulfuric monomer and sulfate. It may in fact be the most important section, since possible contaminants in the flows provide an explanation for these observations. The authors just refer to the supplemental information and state that the results and a discussion are provided there, but I see very little discussion there about the effects of contaminants. Since 100ppt is about  $2.5 \times 10^9$  molecule cm<sup>-3</sup>, or about the reported concentrations of the sulfuric acid monomer, that and other contaminants are sufficient to neutralize the acid. Please provide a summary of the results of your “extensive measurements” in the main article so the reader can better interpret these results. For example, if dirty air was used then it could fully explain most of these results . . . and of course make them inconsequential since

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most nucleation experimenters go through great lengths to characterize and eliminate contaminants.

Answer #6: This summary of the obtained results was added to section 3.1:

“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 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

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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.”

Referee is completely right that 100 ppt of contaminants is in the same order as the measured sulphuric-acid monomer. The ammonia-to-total-sulphate ratio ranges from 1:1 to 1:10 as a function of increasing saturator temperature. The model and discussion of neutralization by ammonia to three different levels was added to manuscript (end of section 3.3 and suppl. Material, section 7 and Fig. S12), see answer #5.

Referee's list of technical corrections. The manuscript was proof-read by a native speaker.

abstract, ln12: the online technique did not detect sulfuric acid concentrations, but sulfate.

Answer: This is corrected throughout the manuscript.

p25789, ln22: Zollner et al., (2102) is in the list.

p25793, ln20: please explain what a 2x100 cm log chamber is. Is it two sections of 100cm long tube? Or something with a diameter of 2 cm? In general, the description of this flow tube is very confusing. For example, I have no idea of what this is (ln24): “. . . with one hole in 5 cm Teflon connector between the 100 cm pieces.” Does this refer to the fact that you have 2 pieces of 100 cm tubing? Updating Figure 2 to reflect this would be all you need to do.

Answer: The Fig. 2 is updated.

p25794, ln14: Don't the two CIMS also differ in the type of mass spectrometer used? Also please define what a “differentially pumped Api” is. Also “m/z ratio” should be replaced by mass-to-charge ratio.

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Answer: Yes, the actual mass specs are different, CIMS has a quadrupole type of MS, and CI-Api-TOF has a Time-of-Flight type of MS. This is added to the manuscript. The Atmospheric pressure interface (Api) has several stages of pumping, lowering the pressure from the atmospheric pressure towards the TOF pressure.  $m/z$  ratio is now changed to mass-to-charge.

p25796, In3: in this paragraph you should use consistent term for the UCPC (that, or UFCPC).

Answer: all is now corrected to UFCPC.

p25797, In2: please explain why the experiments were run at different RH (dry and 15% for the CIMS and dry for MARGA).

Answer: Paragraph was added to the beginning of section 3.1: "Tests with MARGA were performed with dry conditions, since it was noticed that the RH did not have any influence on the results from the tests with mass spectrometers. MARGA uses supersaturated conditions to grow the particles and collect them in the SJAC, hence initial RH is not expected to have any influence."

p25800: for all figures with multiple panels, using letter designators for each panel makes it much easier to understand (e.g., (a) – (d)).

Answer: Figures have been updated accordingly.

p25801, In12: If the CPC is saturated in number concentration, then how do you know that coagulation is not an effect?

Answer: CPC 3772 has lower limit of  $104 \text{ cm}^{-3}$  which is very low compared to other particle counters used in the experiment ( $105 \text{ cm}^{-3}$ ). As there are no larger particles present, coagulation can be considered to be marginal.

Škrabalová L., Brus, D., Anttila, T., Ždímal, V. and Lihavainen H.: Growth of sulphuric acid nanoparticles under wet and dry conditions, *Atmos. Chem. Phys.* 14, 6461-6475,

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doi: 10.5194/acp-14-6461-2014, 2014.

Zhang, R., A.F. Khalizov, L. Wang, M. Hu, W. Xu, Nucleation and growth of nanoparticles in the atmosphere, *Chem. Rev.* 112, 1957-2011, DOI: 10.1021/cr2001756 (2012).

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C11583/2015/acpd-14-C11583-2015-supplement.pdf>

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

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