**Atmospheric
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Discussions

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thank the referee for the comments but at the same time we are sorry that the referee thinks that the manuscript should not be published. We think that here has happened a misunderstanding between what we want to show and what is understood from the manuscript.

R1C: These flow tube results are used to assess the differences in sulfuric acid monomers and sulfate concentrations. I reject this paper for publication because the method used in the study cannot be validated and the conclusions drawn from these

measurements and analysis are skewed.

Au A: The manuscript is written in a style that anyone can repeat the experiments done here. Our results are compared to data published earlier in Brus et al., (2010, 2011). Our results compare well also to Sipilä et al., (2010), where three different methods of producing sulphuric acid vapour (SO2 oxidation with use of UV-light, ifT-LFT), saturator method from neat sulphuric acid (ifT-LFT) and evaporation of weak solution sulphuric acid in furnace (FMI) and two different flow tubes (ifT-LFT and same flow tube as in this study) are used. These three different sulphuric acid vapour production methods compared well to each other, as well as to results in this study via comparison to Brus et al., (2011) also used in Sipilä et al., (2010). Moreover in Brus et al., (2010) we provide parameterization and validation of proper operation of the flow tube used in this work.

R1C: One usually assesses a theory or parameterization using observation data. In this manuscript the authors evaluate CIMS measurements, by assuming that the sulfate concentrations predicted from Kulmala and Laaksonen, (1990) equation, together with mass flow measurements and wall losses, are the "correct" values of sulfate (although, they indicated that the equation predicts sulfuric acid vapor, but the language changes to sulfate in the manuscript later on)

Au A: The assumption in this study is that only source of sulphuric acid vapour is originating from the temperature controlled saturator. In this case, Kulmala and Laaksonen, (1990) expression predicts the sulphuric acid vapour concentration and the MARGA measured total sulphate concentration is expected to originate only from this sulphuric acid vapour. We have made one small mistake (page 2331, line 7) by saying "...theoretical prediction for the total sulphate case...". This will be corrected to "...theoretical prediction for sulphuric acid when comparing the total sulphate case...". This is done not to mix up the fact, that Kulmala and Laaksonen, (1990) can be used to predict sulphuric acid concentration as function of temperature, and not the total sulphate. Actually the original vapor pressure measurements of sulfuric acid made by

Ayers et al., (1980) are conducted in very similar fashion.

We do also assume that CIMS measurements are correct. CIMS is selective method which measures concentration of gas phase free sulphuric acid monomer compared to MARGA which measures total sulphate. The concentration of total sulphate measured by MARGA is determined as measured total sulfate with subtracted background. Here, we have a mistake in figure 3 in the manuscript, where the background is still in the MARGA data. The updated figure 3 is at the bottom of this file, and it will be added in to the manuscript. A text will be added to the manuscript to emphasize that the background values have been subtracted from the MARGA measured points and to clarify how the background was measured (page2323, line 5): "The background of total sulphate was measured by averaging 20 hours of MARGA data with closed saturator using the same setup as with the saturator tests. The background is subtracted from the MARGA values to be sure that the sulphate originates from the sulphuric acid vapour coming from saturator." This does not affect the overall situation.

In the strongly clustering systems like sulfuric acid, the presence of higher clusters (containing not only sulphuric acid) is expected, and that these clusters cannot be registered with CIMS as pure sulphuric monomer or dimer. Also charging efficiency for these higher clusters (containing not only sulphuric acid) is not known yet.

R1C: Wall loss is empirically estimated, although this does not follow the ïňA̧rst order of loss process.

Au A: : The wall losses estimated do follow first order loss, but in manuscript we refer to (page 2324, line 12) "Total losses of sulphuric acid, Total Loss Factor (TLF)". Total Loss Factor is a sum from wall losses and losses to particle phase. Total loss factor do not follow the first order loss process due to sulphuric acid lost into the particles.

R1C: The tube also has a considerable amount of impurities of base compounds, which are not determined at all, even though several unanswered questions are thrown at the end of the manuscript as the conclusion, which implies that base compounds are

responsible for differences in sulfuric acid monomers and sulfate concentrations. With the high uncertainties in several key variables, I am skeptical that the predicted values of sulfuric acid (or sulfate) from these experiments are meaningful to properly assess CIMS measurements.

Au A: Only concentration of ammonia in the flow tube was measured with MARGA. The concentrations of amines were not measured but we expect them to be present in the system. The lower detection limit for ammonia is given by the MARGA manufacturer as 0.05 μg/m3 which is approximately 67 pptv. The level of ammonia contaminant can be estimated to be on the same level as for example in CLOUD experiments (Kirkby et al., 2011). In work of Benson et al., (2011), the concentration of ammonia was measured with CIMS in positive mode, at dry (with nitrogen as carrier gas) and wet conditions (RH~40%) and the linear dependency of ammonia on RH was found. With dry conditions and carrier gas as nitrogen, ammonia concentration was found to be NH3 <~ 20 pptv and RH between 6-40% ammonia was NH3 < 100 pptv. This is very close to our observations mentioned on Page 2330, line 20-22: "The concentration of background ammonia was measured with the MARGA system in this study. An average concentration of ammonia was 60 ppt (which is below the detection limit) at dry conditions and 126 pptv for RH 30 % supporting our previous results."

R1C: The title is also misleading. "Which represents the "true" concentration?" True concentration of what? Why would one expect concentrations of monomer should be the same as those of sulfate? They are different chemical substances.

Au A: The referee states that the title is misleading. After a consideration we agree and the title will be corrected not to mislead any of the readers. New title will be "Total sulphate vs. sulphuric acid monomer in nucleation studies." We do not expect that the monomer concentration should be the same as total sulphate. The assumption which was also proven by our tests is that the only source of sulphate measured by MARGA is the saturator containing sulphuric acid.

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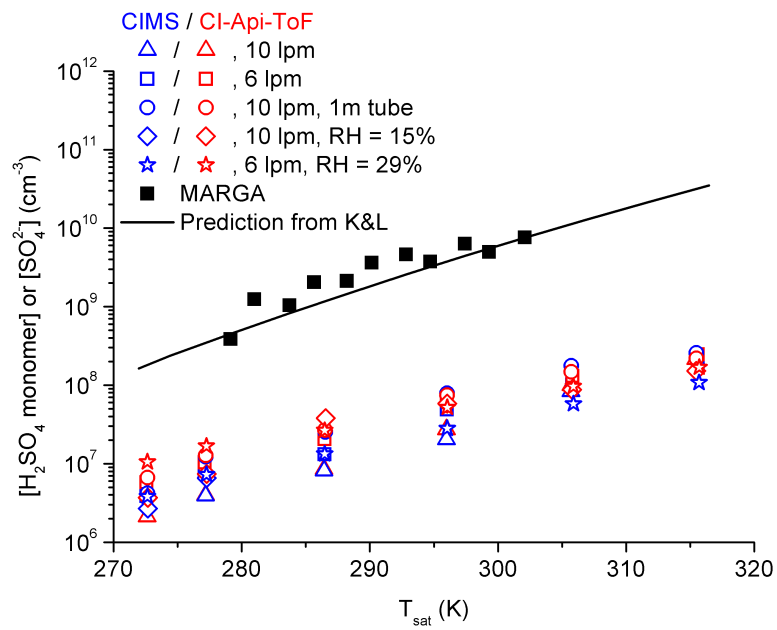Interactive comment on Atmos. Chem. Phys. Discuss., 13, 2313, 2013.

Fig. 1. Updated figure 3 for manuscript. In the original figure, from MARGA measured points the background was not subtracted.

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