

Thanks to the referee for the timely review and for their comments which have revealed deficiencies in the manuscript. The reviewer raises several major comments which we address in turn below. A severe objection was raised that substantial improvements have not been made in the experimental apparatus and that the results described in this paper might not represent a significant step forward (points 8, 9 below.) This is connected to their assertion that the paper cannot be properly reviewed (points 1,6) without access to a computational fluid dynamics simulation of the flow reactor. We show in our response that the reviewer overlooked or did not sufficiently value several aspects of the paper and thus our response to points 1, 6, 8 and 9 are given in some detail. The presentation of the results will be improved due to this reviewer's in depth comments.

Anonymous Referee #3 Received and published: 5 March 2012

The manuscript describes flow tube measurements to study the binary nucleation of sulfuric acid-water particles as a function of sulfuric acid concentration and as a function of relative humidity. Furthermore, some ternary nucleation experiments with two nitrogen containing bases are described. While the findings are interesting there are several major comments that need to be addressed in detail before the paper can be considered for publication in ACP.

Major comments:

The quantitative results of this study are all (1) critically dependent on the validity of the fluid dynamics and chemistry model calculations that complement the measurements (e.g. the sulfuric acid concentration is estimated to be a factor of 5-10 higher in the nucleation zone than at the point of measurement (2), methyl amine is estimated to be a factor 100 higher (3)!). All the features, results and assumptions of the model are left to an unpublished reference: Panta et al., manuscript in preparation. The calculations of the maximum concentration of nucleating vapors in the nucleation zone are very complex(2). All gas concentrations are strongly varying radially and longitudinally(2). The mixing process of the gases is difficult to describe(4), and how can the nucleation time be reliably estimated in the rapidly changing environment (5)? It is necessary to publish the model calculations alongside to be able to judge the presented data (has the Panta et al. manuscript been submitted by now? (7)). Otherwise the main findings of the paper (1,6) cannot be reviewed at the required level of scrutiny.

(1) We point out that only Figure 6 depends on a result from Panta et al. All the other main results of the work do not: (i) the H_2SO_4 power dependencies as a function of RH (Fig. 3, Table 2), (ii) the RH dependencies (Fig. 4, Table 3) and the treatment of their power dependencies to obtain critical cluster information (eqns. 1-3, Table 3), (iii) the consistency of the particle number density for a given set of experimental conditions over long periods of time (Fig. 2, A2 and A3) (iv) the results of the N-base addition experiments (Fig. 5, table 4; also see point 3), (v) the arguments in the Supplement that undetectable amounts of N-bases (sub pptv) can affect these types of measurements.

(2) This information and the point of maximum nucleation is discussed in the Supplement, section 10. The two referrals to Panta et al. in the main body of the manuscript unfortunately lost their accompanying 'see the Supplement' designation in the copy editing process. We also apologize for overlooking a referral to CFD studies in the abstract that no longer applied to the ACPD published version. **We will revise the abstract and also add some explanation to the Supplement, section 10.**

(3) We believe this reviewer was misled by the wording of this section and we will clarify: the factor of 100 was not the result of a computation fluids dynamics simulation, it is the ratio of the added amount to the measured amount. The factor was quoted to point out that a large loss of gas-phase base from top to bottom of the reactor was observed. We will reword **p1124 l22 and add a sentence on p 1128** accordingly.

(4) We agree: the initial mixing at the top of the mixing region is difficult to describe. However, the flow is plug by the time it exits the mixing region (see the flow visualization results and discussion in Ball et al.) and the analysis here is based on the Ball et al. analysis. This will be pointed out more clearly in the manuscript (**p 1125**, see 9 below.)

(5) The nucleation time estimation was presented in the Supplement (section 1) and it does not depend on results from Panta et al.

(6) As mentioned in point (1), one finding of the paper, i.e., ‘placing’ the current data set in Fig. 6, depends on Panta et al.: it is the factor of 7 between the measured and the nucleating sulfuric acid (this factor has been called by other researchers: ‘wall loss factor’.) The factor of 7 ($\sim \pm 40\%$) is reasonable: We can justify this number in two other ways. (A) Ball et al. estimated sulfuric acid losses and gradients in different portions of the flow reactor and their points (I) and (IV), yield a ‘wall loss factor’ of 8. (B) Another rough lower limit of > 5.4 comes from using the plug flow approximation (below the NZ, the flow is close to plug, Ball et al.: Figure 1). (i) The diffusive loss of a trace species between the NZ (using that identified in Ball et al.) and the tip of the funnel is about a factor 2.7 as follows: - The plug flow first order loss rate coefficient, $k(\text{s}^{-1}) = 5Dc/r^2 = 0.064 \text{ s}^{-1}$. - There is approximately 90 cm of travel to the funnel which is a flow time of 15.5 s. - The fraction lost is: $\exp(-15.5 \cdot 0.064) = 1/2.7$. (ii) The factor of 2 between the on-axis concentration and the average concentration (i.e., point IV of Ball et al.) This is a lower limit because it does not count loss along the 16 cm sampling line or within the 3 cm sampling sphere. **We plan to add the B estimate to the Supplement section 10. Conclusion:** The three estimates we have are in agreement and are likely as accurate as those presented by most of the previous studies in Fig. 6. Faults in the overall comparison due to uncertainties in nucleation times and wall losses are dwarfed by the 4 or 5 orders of magnitude discrepancies shown in the figure.

(7) The Panta et al. manuscript has just been submitted to J. Phys. Chem. A. This is appropriate as its main point is a new description of binary nucleation, which stands as a separate and significant contribution. This journal has published previous work on this subject (Herrmann et al.) as well as some of our own CFD work involving diffusion of NH_3 and H_2SO_4 molecules (Hanson and Eisele, 2002, JGRD, 107, 2001JD001100; Hanson and Kosciuch, 2003, Hanson and Lovejoy, 2006.) We believe that the Zollner et al. and the Panta et al. work stand alone, each making their own contribution to understanding $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ binary nucleation.

While previous flow tube measurements (Ball et al., Young et al., Benson et al., Berndt et al., Sipilä et al., Brus et al., etc.) all faced similar problems (and they all disagree – varying over 4-5 orders of magnitude in $[\text{H}_2\text{SO}_4]$ for $J=1$, as demonstrated by Fig. 5), another data set should only be added if it is documented that substantial progress in the methods and in the quantitative results has been achieved! (8,9) There is a large risk that concentrations and temperatures in the mixing and nucleation zone are not estimated correctly. (9)

(8) The present measurements do represent substantial progress as documented in point (1) above, particularly the quantitative power dependencies and the derived water content of the critical cluster. We also have presented an analysis of how low levels of N-bases can affect $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ binary nucleation experiments. The wide scatter in the published results calls for more experiments. The results we present do not increase the magnitude of the disagreement: instead they suggest a coalescence of results around a subset of the published data on $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ binary nucleation rates. **In a new section 4.4, we plan to add a discussion of this coalescence and the application to the atmosphere.**

(9) Much of the experiment is based on the apparatus of Ball et al. but with better detectors for both particles and sulfuric acid. The similar flow conditions here as in Ball et al. allows for the use of their measured temperature of $\sim 2\text{K}$ higher than wall in the NZ. **A new paragraph on p1125 ~119** will be added to emphasize this. H_2SO_4 concentrations are already addressed in (6) above.

RH dependence of nucleation rate

Why do the measurements depicted in Fig. 3 not all line up? The measurements at 55-70% RH were made at a factor 2 lower flow rate but when multiplying the values by 2 (10), the results still do not line up with the lower RH measurements. Why?

(10) To properly treat this adjustment in J (or N_p), the power dependency on H_2SO_4 must be invoked: $[\text{H}_2\text{SO}_4]$ decreased by $1/2$ would make J decrease by 0.5 to the 5 th power. So a factor of 32

must be applied to the high RH data in Fig. 4. Then it is seen to be in alignment with the trend in the other data. **We plan to mention this in the Figure caption.**

Furthermore, the purity of the water vapor addition could cause problems. Using deionized water without further purification might lead to substantial contamination with organics. These impurities can change the measured RH dependence.

(11) The reviewer may not have appreciated that a small amount of 98 wt% sulfuric acid was added to each of the water reservoirs (p 1121 |21-23) to scavenge any N-base organic compounds that might be introduced with the deionized water. The de-ionized water source has been used to saturate clean air for calibrating a PT-MS for ~ 5 years. We have never detected any (upper limit, ~10 pptv) organic compound in the gas phase using PT-MS over the past 6 years (PT-MS and calibrations described in Hanson et al. IJMS, 2009, 282, 29-37.)

In addition, as both, water concentration (13) and temperature (12), are not directly measured in the nucleation zone, I have doubts about the stated relative humidity (12,13).

(12) The point about the temperature is a good one and we will emphasize the need to correct the reported RH due to the fact that the peak of nucleation occurs at a temperature of ~2 K higher than the 296 K RH values that are reported. **We will add text discussing these issues in the paragraph to be added on p1125** (see point 9): strict RH comparisons with the present work should be with RH values that are about 0.9 of the reported values, with ~ 10 % uncertainty in RH. Finally, we will include this decrease in RH when using eq (2) and (3) and also calculate an additional uncertainty in the results listed in Table 3.

(13) Note that the water content that the dew point monitor reports is not affected by any temperature uncertainties in the experiment.

NH₃ and MA measurements

Here, just a few sample measurements have been made, far from a systematic analysis. All measurements are made at high sulfuric acid concentrations, much higher than any atmospheric conditions (in order to ensure the fast growth necessary to detect the particles with the CNC). For all cases it is tried to measure the NH₃ and MA concentration with the mass spectrometer but only for one case an enhancement of signal corresponding to 0.4 pptv above the 3 pptv background is detected, which is converted to a mixing ratio of 35 pptv in the nucleation zone assuming a factor 100 of losses (p 1129, 5-9).(14) Without a direct measurement and a more thorough investigation of the losses, the results of Table 4 are far from quantitative. I am sceptical that the stated mixing ratios in the nucleation zone are known, maybe within a factor of 10 (15). I also do not understand how the mixing of the main flow and the flow from the top port is done. From the graph it seems that fairly separate (and asymmetric) flows can develop and there is no turbulent mixing zone as for the H₂SO₄ and H₂O injection. How can the concentrations in the nucleation zone be derived if the gases are not rapidly well mixed? (15) Could the main nucleation take place in a zone where the amine/ammonia concentrations are still strongly enhanced over the stated mixing ratios, while sulfuric acid is not a limiting factor as it is supplied in fairly high concentration (16). The authors note that for the NH₃ case substantial amounts of amines from a previous measurement were present. Can it be excluded that the contaminant amines aided the NH₃ nucleation? Therefore also the relative comparison between the role of NH₃ and MA for nucleation might be affected.(17) The authors state that "AmPMS detection of ammonia or amine when it was added at the top port was much less than that estimated by assuming what was added had mixed well with the main flow." (1124, 20-22). What is meant by this statement? Does this just refer to the large losses (factor 100 as stated above) or does it mean that the flows are not mixed?(14) Did the H₂SO₄ signal change during these experiments?(18) Apparently, the data only comprises the five individual measurements listed in Table 4. Were the authors able to repeated and confirm their measurements? (19) It is obvious that by

addition of NH₃ or MA the nucleation rate will be increased over the neat sulfuric acid system, but, for the above arguments, I do not accept the stated mixing ratios and the quantitative statements. (20)

(14) As stated in (3) above, the factor of 100 was not used to get the NH₃ mixing ratio. The **wording of the offending statement will be simplified**: it refers to the large observed loss.

(15) With the information presented in the paper, the referee makes a reasonable assessment. However, our point is to show the relative efficacy of methyl amine vs. ammonia addition and a rough power dependency for each. We make some extrapolations using the power dependencies reflected in the numbers in Table 4. The qualitative conclusions from that analysis (contamination with un-seeable amounts of N-base is a problem) are valid even with large uncertainties in concentrations.

(16) This is possible. We suppose that this is what is meant by 'a factor of 10' higher N-base than we quote. Although the detailed knowledge of the mixing is important, it is not necessary for the analysis we present. **We will add text that outlines our assumptions regarding the N-base mixing: we will point out on p1124 I4** that a 3D Fluent study exists (Hanson and Eisele, 2002, JGRD, 107, 2001JD001100) that simulated ammonia introduction into a sulfuric laden flow. In that study, NH₃ was observed to distribute into the main flow rapidly.

(17) It would make the relative strength of amines over ammonia even larger. The amount of amine leftover was NOT substantial; it was below detection even when added straight to the mass spectrometer. Although we think that the ammonia addition is responsible for the large increase in N_p, the recent Yu, McGraw, Lee paper (see referee#1) showed an interesting measurement where a mix of ammonia and dimethyl amine had a larger effect than either one alone. **We are adding this reference and will add this to the discussion on p1128.**

(18) We are fairly certain that negative ions were not monitored during N-base addition. Decreases in H₂SO₄ are something to look into in the future: we suppose this would be due to a greatly increased loss to particles?

(19) We are working hard at performing a more systematic study of N-base addition. Repeatability for the measurements in the paper was discussed in section 3.1.

(20) **We will add a cautionary sentence about the quantitative numbers to reflect the referee's assessment.** See point 16 as well. Note that the measurements are in qualitative agreement with a number of studies.

Finally, we have recently reconfigured the mass spectrometer sampling so that the N-bases in the effluent of the reactor can be more accurately determined (i.e. sampling with a zeroing mechanism as for the atmosphere or aerosol chamber, Hanson et al., ES&T, 2011.) **We plan on showing a figure in the Supplement showing the 'measured' amines (that is, the upper limits.)**

Minor comments: All of these will be changed.

1120, 4-7: This sentence should also reference Kirkby et al., 2011.

1126, 2: "Above 1.5 sLpm, [H₂SO₄] does not increase in a linear fashion with QA." Why? Please discuss.

We will state in the Supplement that at high flow rates, the nitrogen cannot pick up as much H₂SO₄ vapor as it can at low flow rates either from finite rate of diffusion and/or because the N₂ does not attain a temperature of 30 C.

Technical corrections:

1118, 20: "Nels", change to "Nel"

1119, 3: "nucleation rates. . . have been presented."

1119, 10: "Zhang et al. report . . ."

1119,14: ". . . Young et al. (2008) report values of. . ."

1121, 10: STP is defined twice