Online Supporting Information.

1   Differences with Ball et al.

There are significant differences with the procedure of Ball et al. and it is assumed that these differences have little effect on the results. They are listed here for completeness. As noted in the text, Q_A, the N_2 flow rate over the sulfuric acid reservoir was varied to attain variations in H_2SO_4 content: also, the small tube carrying this flow was ~ 29 °C whereas in Ball et al. it was maintained at 60 °C.

There was also (i) a higher pressure, 1 atm vs. 0.8 atm, and (ii) a larger mass flow rate, 6 sLpm vs. 5 sLpm. The overall effects of (i) and (ii) result in an average flow velocity that is similar to that of Ball et al. Buoyancy driven convection is expected to be similar.

There was no (iii) periodic rinsing of the flow reactor with de-ionized water as was done by Ball et al. Rinsing the flow reactor was not done because it would be exposed to room air which is not desirable. The reproducibility of the results supports this decision. However, at one point the dry N_2 flow line (Teflon) was T-ed into to introduce an amine to this flow (and thus the mixing region); upon withdrawing the amine, particle count rates subsided quickly but plateaued after a few days at ~300 s^{-1} for NBC, indicating the line became contaminated with the amine (normal NBC conditions yield particle count rates of ~ 20 s^{-1}.) This line was removed from the system, rinsed with a 10^{-3} M HCl solution and then deionized water, dried and replaced whereupon NBC conditions yielded a typical particle count rate of 15 s^{-1}.

1   The chemical ionization mass spectrometer (iv) had an ion drift region (aka Hanson, 2005, ion

2   molecule reaction times of ~ 1 ms set by electric fields) rather than a flow arrangement (aka

3   Eisele and Tanner, 1993, ion molecule reaction times of ~1 s set by gas flows) and (v) ammonia

4   was introduced below the mixing region rather than in it. The drift arrangement (iv) is less

5   sensitive than the flow arrangement but [H_2SO_4] is more readily calculated in the absence of

6   calibrations. Nonetheless, both systems are passive monitors of sulfuric acid and should yield

7   equivalent results. The differences in ammonia introduction methods means that a direct

8   comparison between the ammonia addition experiments should be made with caution.

9   The nucleation time (vi) here of 8 s is different than that used by Ball et al. of 4 s which was

10   based on a 4 cm/s flow velocity over the ~ 15 cm nucleation zone length. A more refined

11   estimate here was obtained by using their Figure 3(a) data and noting that a 4 cm/s speed applies

12   to 1/3 of this length, 2.5 cm/s applies to the middle third, and 1 cm/s applies to the top portion.

13   The sum of times in these portions of the nucleation zone is about 8 s, which is assigned a large

14   uncertainty of +100%, -50%. Further exploration of the time for nucleation in a flow reactor will

15   be done with fluid dynamics simulations.

16   Finally, the particle inlet here did not extend into cooled section of the flow reactor which is

17   believed to lead to a high variability in the present measurements.

18   **2   Variation of mixing region temperature.**

19   Temperature of the mixing region was varied over the range of 30 to 45 C and particle numbers

20   decreased considerably as temperature increased. This is due to suppression of nucleation in the

21   mixing region, and to a lesser extent, changes in flow patterns in the transition and nucleation

22   regions.   This is shown in Fig A1(a) for NBC and a set of data taken ~13 months earlier (b), a

23   few weeks after the system was initially assembled and at a total flow rate of 4 sLpm. A much

24   stronger dependence on mixing region temperature is exhibited in Fig. A1b. The stronger effect

25   may be due to the lower flow rate and also to contaminants that may be present initially in the

26   system. Further experimentation on this effect with N bases present in the mixing region are

27   planned.

Nov2011. NBC

Oct2010. 4 sLpm total.
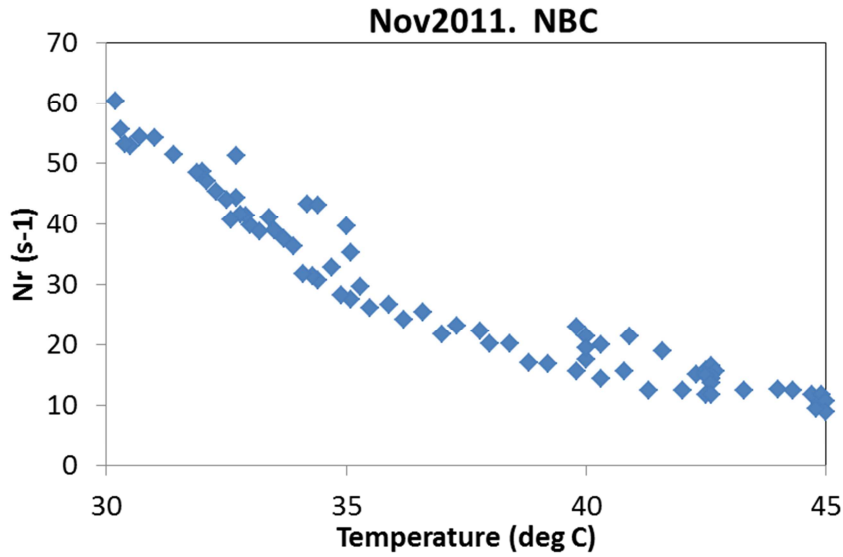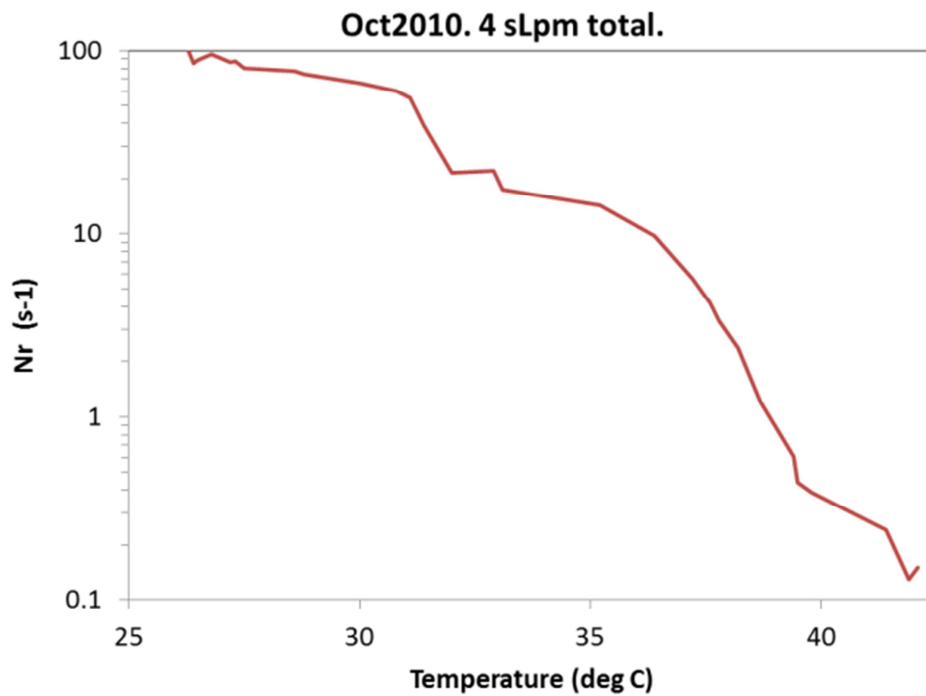
Fig. A1. Variation of particle counts as a function of mixing region temperature. Results of the particle number versus mixing region temperature performed in (a) Nov 2011 and (b) Oct 2010.
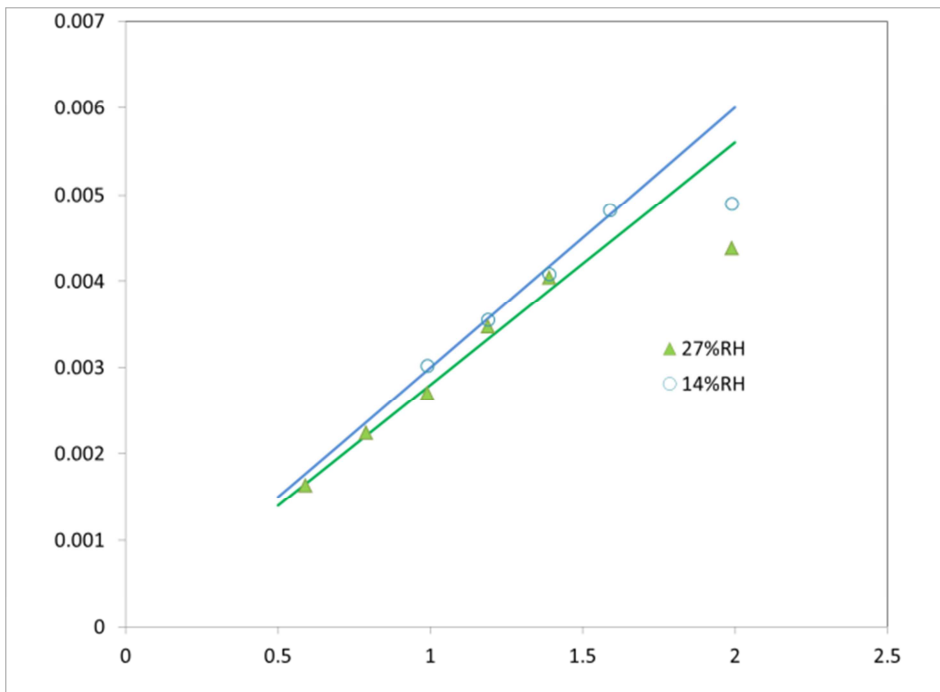
3 Mass spectrometer detection vs QA, flow rate through sulfuric acid reservoir.

Shown in Fig. A2 (a) and (b) are the ion signals for sulfuric acid versus flow rate. A linear relationship is shown. Evident in fig. A2b, deviations from this relationship occurs for flows higher than about 1.6 sLpm.
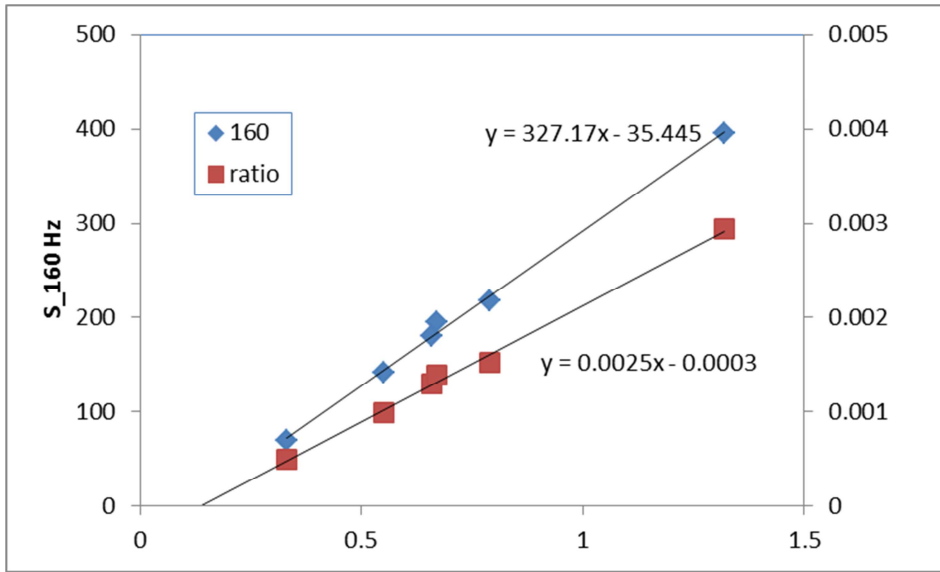
Figure A2. Variation with Q_A of the raw signal at 160 u ($HSO_4^-\cdot HNO_3$) and the ratio of signals for the HSO_4^- core ions and the NO_3^- core reactant ions.

4   Nr for NBC conditions for 10 months.

A plot of measured count rates with time for NBC is shown in Figure A3. A general downwards trend is exhibited: an exponential decay with a constant is plotted as a suggested time dependency. A contamination episode is indicated during the months of May and June

1   2011 which is explained below.   Note that the large spikes in early June are due to heating of

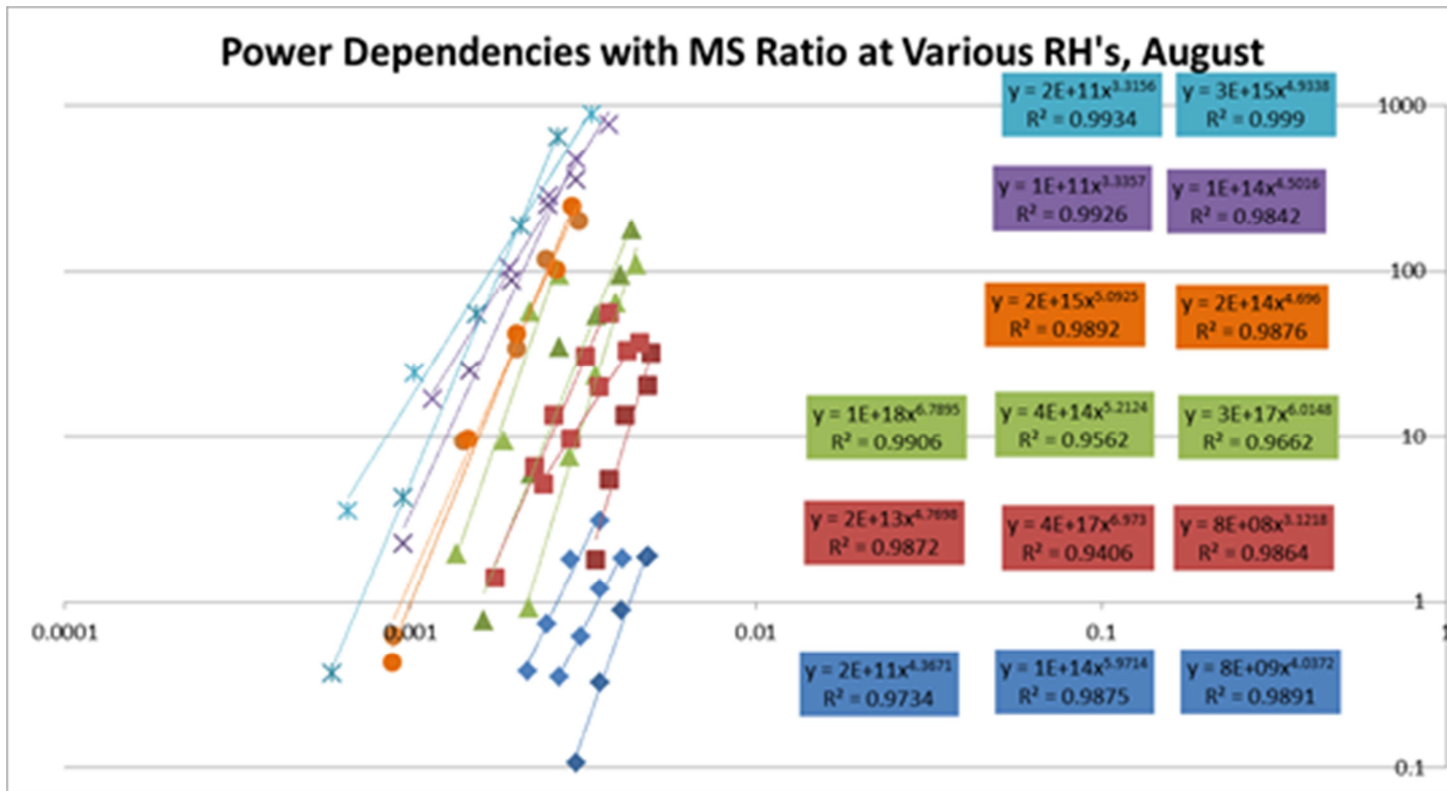2   contaminated lines that were then cleaned or replaced.
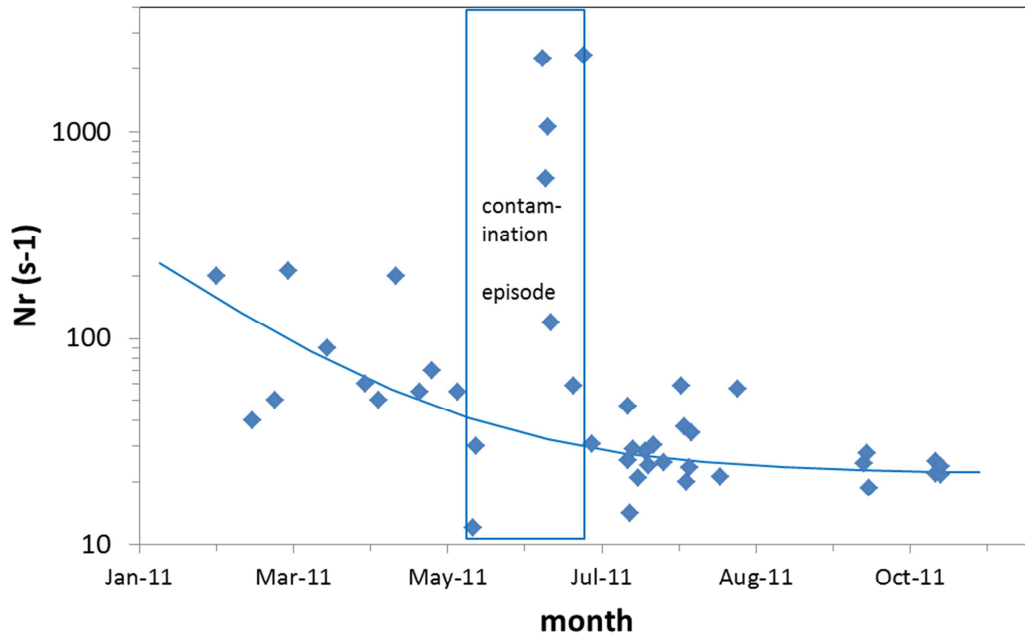
3

4   Figure A3. Nr versus date, for 10 mos. Beginning in late Jan-11, NBC conditions were chosen

5   with total flow rate of 6 sLpm and T_{H2SO4} reservoir = 30 C.

6

7   **5   Representative data sets for Nr vs.both MS ion ratio and QA,**
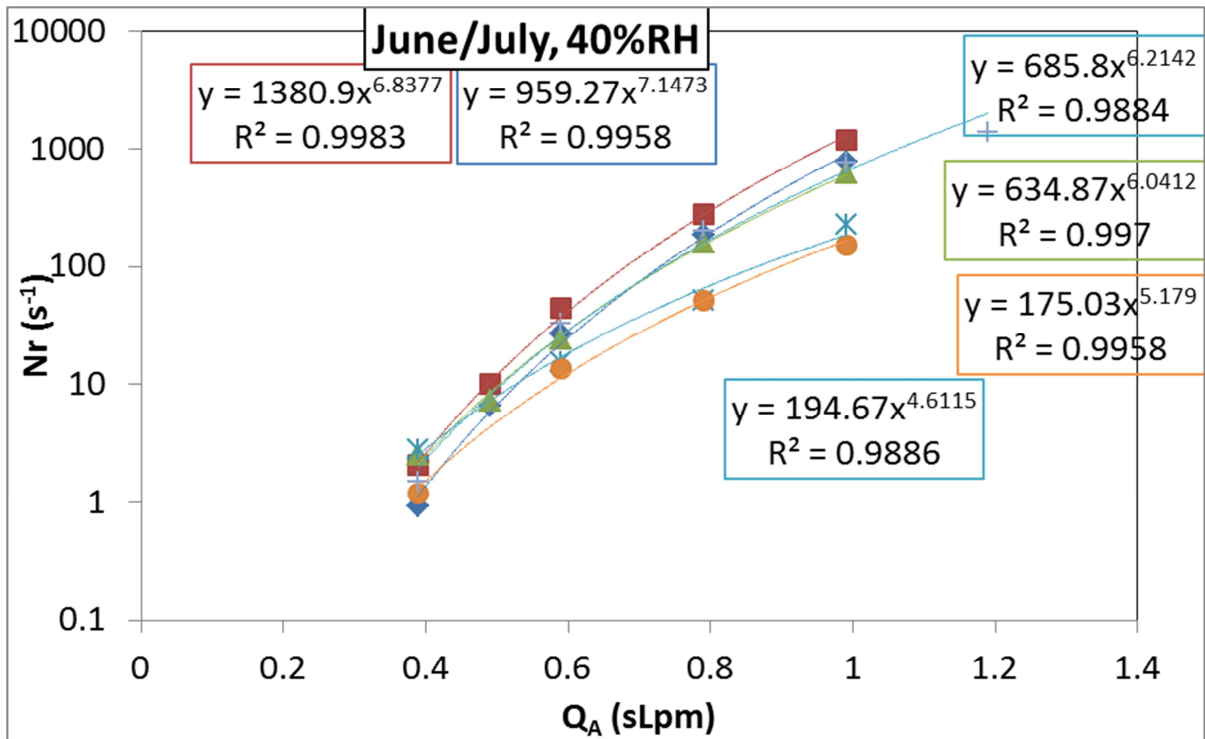
8   A plot representative of the scatter of particle count rate vs. ion ratio from negative ion AmPMS

9   is shown in Figure A4. This is all the data for the month of August, 2011.   For June and July

10   2011, AmPMS was generally not operational and this data it plotted with Nr vs. Q_A (for QA 1.5

11   sLpm and less) in FigA5: (a) 14 % RH and (b) 40% RH.

Power Dependencies with MS Ratio at Various RH's, August

$y = 2E+11x^{3.3156}$
$R^2 = 0.9934$

$y = 3E+15x^{4.9338}$
$R^2 = 0.999$

$y = 1E+11x^{3.3357}$
$R^2 = 0.9926$

$y = 1E+14x^{4.5026}$
$R^2 = 0.9842$

$y = 2E+15x^{5.0925}$
$R^2 = 0.9892$

$y = 2E+14x^{4.696}$
$R^2 = 0.9876$

$y = 1E+18x^{6.7895}$
$R^2 = 0.9906$

$y = 4E+14x^{5.2124}$
$R^2 = 0.9562$

$y = 3E+17x^{6.0148}$
$R^2 = 0.9662$

$y = 2E+13x^{4.7098}$
$R^2 = 0.9872$

$y = 4E+17x^{6.973}$
$R^2 = 0.9406$

$y = 8E+08x^{3.1218}$
$R^2 = 0.9864$

$y = 2E+11x^{4.3671}$
$R^2 = 0.9734$

$y = 1E+14x^{5.9714}$
$R^2 = 0.9875$

$y = 8E+09x^{4.0372}$
$R^2 = 0.9891$

Figure A4. Nr plotted versus MS ion ratio for a range of relative humidities: dark blue, 14%; red, 20 %; green, 27%; orange, 40%; purple, 54%; turquoise, 68 %.

June/July, 14%

$y = 0.683x^{4.8974}$
$R^2 = 0.9968$

$y = 0.3546x^{5.9911}$
$R^2 = 0.9865$

$y = 0.2815x^{7.0878}$
$R^2 = 0.9972$

$y = 0.5753x^{4.8308}$
$R^2 = 0.9968$

$y = 0.9694x^{3.6498}$
$R^2 = 0.9954$

$y = 0.6059x^{4.8612}$
$R^2 = 0.9821$

Nr s-1

Sulfuric Flow
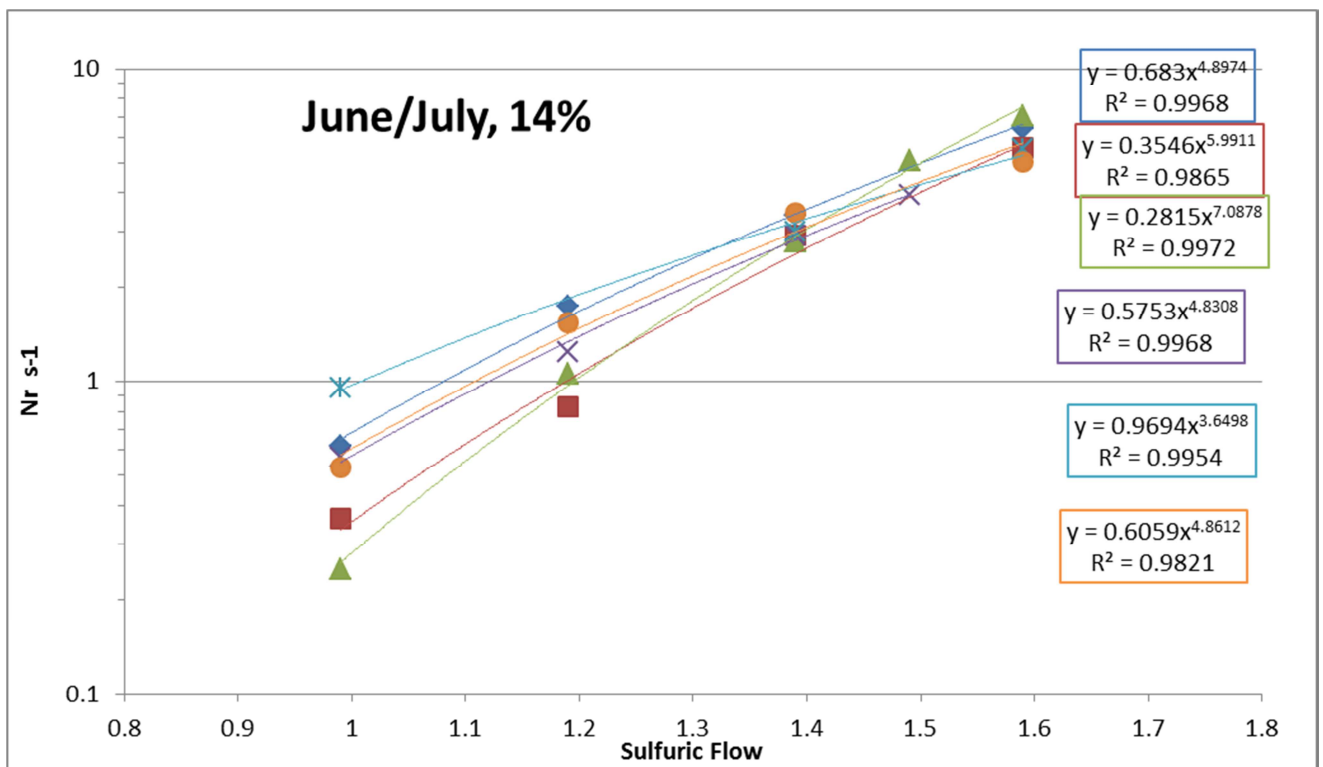
Figure A5. Nr plotted versus Q_A at (a) 14 % rh and (b) 40% RH.

6 Particle Sizes.

The particle size distributions for Q_A= 1 and 0.4 sLpm are shown in Figure A6. These two sets of conditions represent typical and low sulfuric acid concentrations respectively.   Particle charging efficiency of Fuchs [1964] and long DMA loss equation of Birmili et al. [1997] were applied. The log normal particle distributions are shown and have peak diameters of 6 and 7.7 nm and lnσ was 0.25-to-0.3. Even though the charging of nanoparticles by the custom-built charger has not been evaluated and the particle sampling lines may cause additional particle losses, this measurement shows that the particle sizes are well above the detection threshold of the instrument, about 2 nm in diameter.
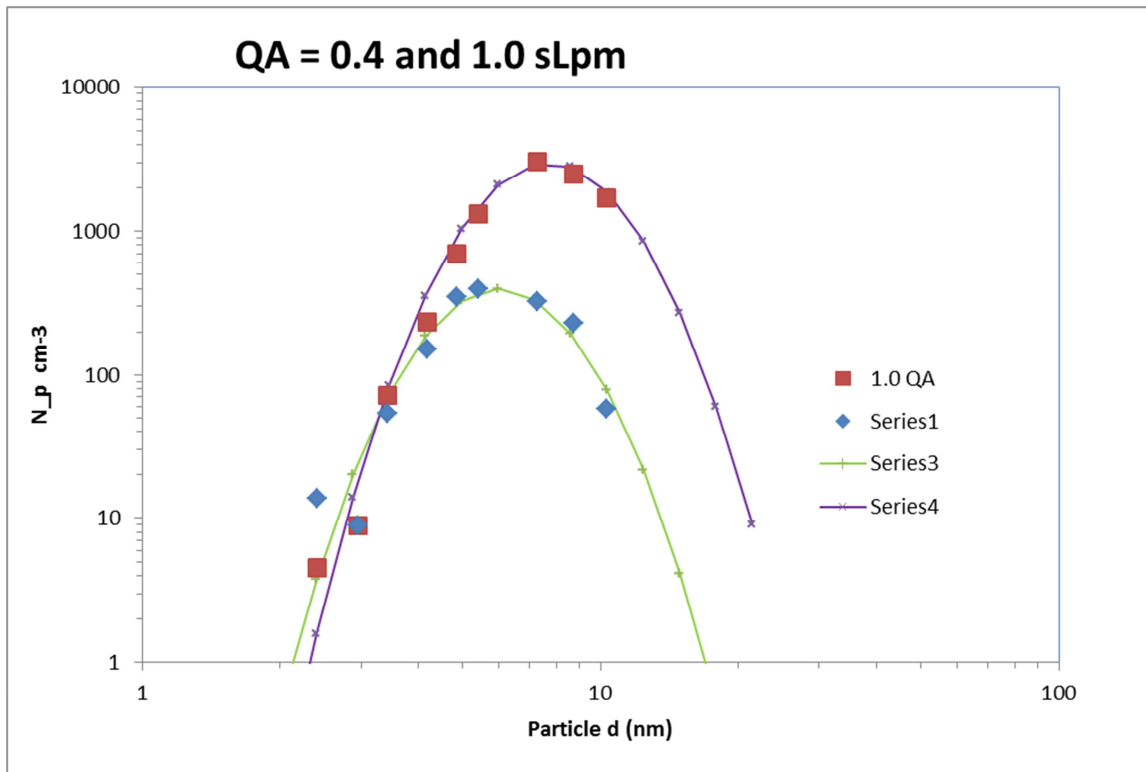
1

2 Figure A6. Particle size distributions for two different sulfuric acid levels. A rough conversion

3 of the vertical axis, Nr, to dN/dlnD can be done by multiplying by the ratio of sheath to aerosol

4 flows [Stolzenburg and McMurry, 2008] (sheath flow was 7.2 sLpm and the aerosol flow was

5 1.3 sLpm.)

6 As discussed in the text, Kuang et al. [2012] presented modified conditions for UCPCs where the

7 saturator temperature of the UCPC can be increased, increasing the detection efficiency of

8 nanoparticles of 2 nm diameter and smaller. To test if the particles detected here are of this size,

9 different saturator temperatures were used at NBC. It was found that when the saturator

10 temperature was increased (and condenser flow was increased), the particle number density did

11 not change, however the pulse heights (i.e., channel number from Maestro) decreased. The pulse

12 heights correspond to the size of the particles after growth with butanol, which did not affect the

13 detected number of particles. This observation that the temperature of the saturator has no direct

14 effect on the number density of particles that are detectable indicates that they are likely to be of

15 a significantly greater size than the ~ 2 nm diameter cut point that Kuang et al. presented.

16

1   **7   Ammonia and amine additions.**

2   **7.1   Effect of 10 ppqv of base.**

3   A decrease in the vapor pressure of H_2SO_4 due to base would increase the stability of H_2SO_4 in

4   the critical cluster. This can be estimated using the E-AIM website (Clegg et al., 1998.) At 30 %

5   RH and a 0.3-to-1 NH_4^+ to sulfate ratio (suppressing formation of ammonium bisulfate) the

6   equivalent NH_3 and H_2SO_4 mixing ratios at 1 atm total pressure are about 10 and 7 ppqv,

7   respectively. Because this is close to that for H_2SO_4 vapor over neat H_2SO_4-H_2O solution at 30

8   % RH (9.7 ppqv), this level of ammonia would probably not significantly affect nucleation.

9   With methyl amine (Ge et al. 2011b) in the H_2SO_4-H_2O calculations, a one to one mole ratio of

10   methyl amine to sulfuric acid at 30 % RH gives equivalent mixing ratios (1 atm total pressure) of

11   2.4 ppqv for H_2SO_4 and ~10 ppqv for methyl amine. Note: in the current implementation there

12   are important assumptions regarding the amine's activity coefficients in sulfuric acid solutions

13   (S. Clegg, 2011, private communication.) Nonetheless, the suppression of pH_2SO_4 due to base is

14   likely to be less in small clusters than for bulk solutions, and therefore only a modest effect on

15   particle formation is expected due to the presence of 10 ppqv levels of NH_3 while a significant

16   effect for methyl amine at 10 ppqv levels cannot be ruled out.

17   **7.2   Other experimental considerations.**

18   The ~30 pptv level of amine added at the top port gave extremely high N_r for $Q_A= 1$ such that

19   live time was reduced to essentially 0 and thus N_p could not be reliably monitored. For the base

20   addition experiments therefore, the N_2 flow over the bulk sulfuric acid was set to 0.4 sLpm for

21   these 27 % RH measurements: this being the lowest sulfuric acid level used in any neat

22   experiment (i.e., at 40 % to 68 % RH.)

23   Different addition methods (for example, 1.7 mm ID vs. 4 mm ID inlet tubes) resulted in

24   significantly different N_r for nominally the same amine mixing ratios. The variability here was

25   most likely due to how well the base was mixed into the main flow: a smaller ID tube has a

26   stronger jet, which can go across the flow reactor and interact rapidly with the wall. This was

27   verified in an experiment where a constant amount of methyl amine was introduced at the bottom

28   of the flow reactor with varying amounts of N_2 flow through the inlet. The measured amine

29   concentration of 3 to 17 pptv with AmPMS depended on inlet tube flow rate as it varied from 10

30   to 150 STP cm^3/min; above ~ 40 STP cm^3/min it decreased strongly. The maximum observed

1 level of ~17 pptv is consistent with the calculated amount added, 25 pptv. Amine and ammonia

2 addition and calibrations will be discussed in forthcoming papers (Panta et al., Carlson et al.,

3 *manuscripts in preparation.*)

4

8 Previous work on amines/ammonia.

6 Enhancement factors (EF) for ammonia and amines are convenient for quantifying and reporting

7 their effects on nucleation. It is defined as the ratio of particles formed in the presence of added

8 base to that in the absence of added base.

9 For NH_3 for example, Kirkby et al. [2011] report EF of ~100 for 70 pptv NH_3 (6 pptv H_2SO_4 and

10 38 % RH); Ball et al. [1999] show an EF of ~20 for an estimated NH_3 of ~3 pptv (+200/-67 %) at

11 15 % RH and ~1000 pptv H_2SO_4; Berndt et al. [2010] report EFs up to 100 for 50000 pptv at low

12 RH but less than 10 at 47 % RH. Benson [2010, 2011] report EF of 10 or less for 20000 pptv for

13 RH values of 15 % and higher. These values are much lower than the ~ 10^3 to 10^5 values

14 reported here for 3 to 45 pptv, respectively, for ~ 200 pptv $[H_2SO_4]_{NZ}$. The differences of the

15 present results with Ball et al. can be explained because of differing H_2SO_4 levels; at lower

16 H_2SO_4 EF due to NH_3 will increase according to theory (Coffman and Hegg). The studies that

17 used very large ammonia levels that saw very low EFs could be due to the presence of

18 contaminants in their system: as discussed in the text and by Kirkby et al. [2011] and Benson et

19 al. [2011].

20 Comparisons of the present measurements to the predictions for ammonia's effect on nucleation

21 seem to indicate that the predictions either overestimate nucleation rates or EFs. The Coffman

22 and Hegg [1995] predictions show EFs of ~100 and 1000 for 1 and 5 pptv respectively (for 75 %

23 RH and 200 pptv H_2SO_4) however nucleation rates are predicted to be ~10^{10} to 10^{15} cm^{-3} s^{-1}.

24 Korhonen et al. [1999] suggest an EF of ~ 10^{14} at 2 pptv (52 % RH and 109 H_2SO_4) and J = 10^5

25 cm^{-3} s^{-1} and Napari et al. [2002] an EF of 10^8 for 2 pptv (using 0.1 pptv as the binary nucleation

26 rate) with J = 10^4 cm^{-3} s^{-1}. The enhancement factor reported here is in better agreement with the

27 theoretical treatment of Coffman and Hegg [1995] however the measured nucleation rate of 5

28 cm^{-3} s^{-1} is very much lower (a factor of 10^9 or greater) than they predict. Although the EF of

29 Korhonen et al. and Napari et al. deviate significantly from the current measurement, their

30 predicted rates are somewhat closer, factors of only 10^3-10^4 too large.

31

9   Contamination Episode.

For a period of time there was an unknown contaminant in the system, evidenced by a sharp rise in particle numbers, to almost uncountable levels for periods of tens of minutes during heating of suspected contaminated lines. To investigate further the effect this contaminant had on the experiment, several power dependencies were taken at 27% RH while particle numbers remained above normal NBC. They decreased day after day as the contaminant was slowly eliminated from the system, and normal levels for NBC were achieved in about a ten days. While particle numbers were high and as they decreased, the power dependency did not vary (Figure A7). It is concluded that the unknown contaminant "X" changed only the total number of particles, not the power dependency on H_2SO_4, and by extension the number of H_2SO_4 in the critical cluster. The mass spectrometer system was not operational for most of this episode.
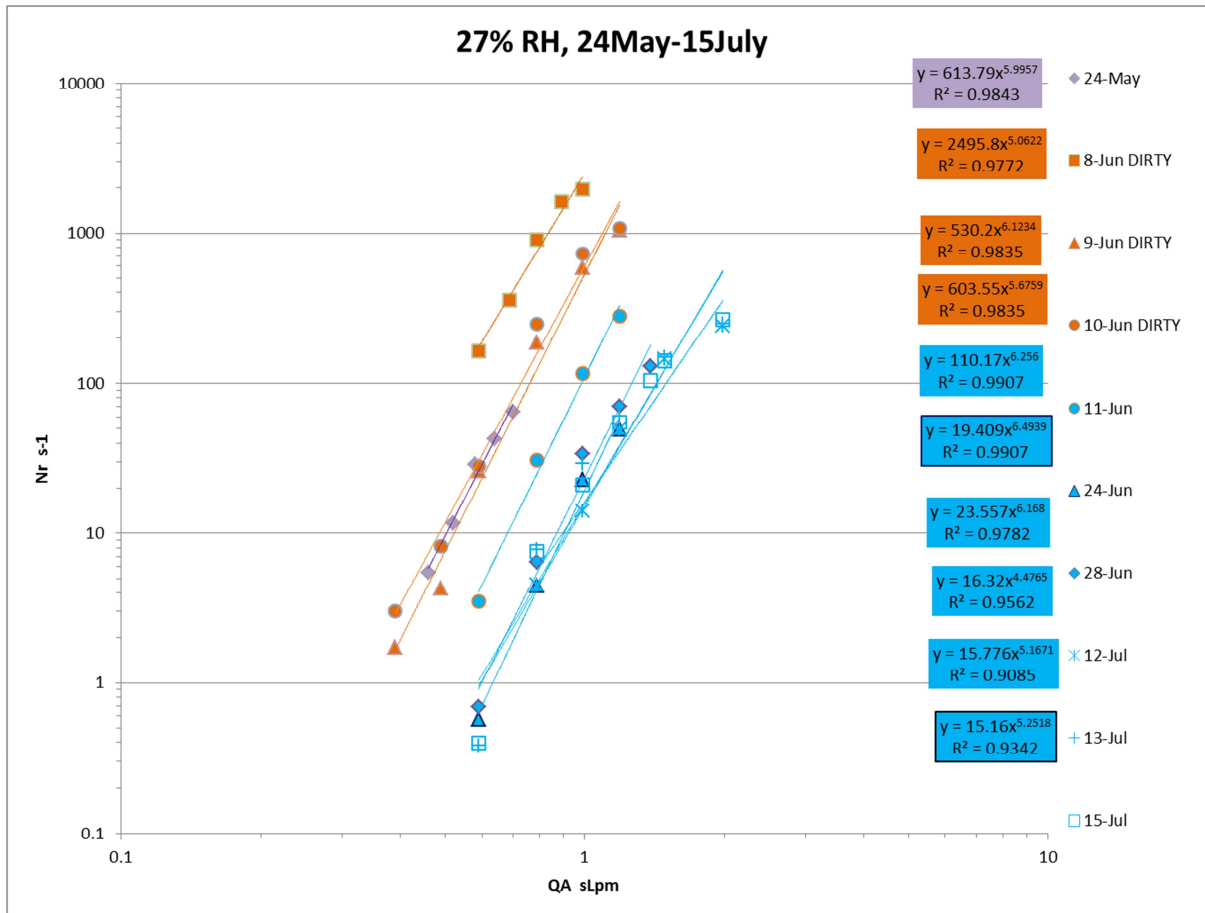

Figure A7. Nr and power dependencies at 27% RH. During contaminatioin episode. Data for May 24th, June 8th to 11th all show enhanced leels of particle number but power dependencies were not appreciably affected.

## 10 Computational Fluid Dynamics: [H₂SO₄]NZ versus measured [H₂SO₄].

Shown in Figure A8 and A9 are contour plots of the mass fraction of H_2SO_4 in a 2D simulation of the flow reactor. The diffusion coefficient for H_2SO_4 in N_2 was taken from Hanson and Eisele [2000]. Thermal properties of the gas mixtures are very close to those used by Herrman et al. [2010]. A complete description of the model is being prepared (Panta et al., [2012], manuscript in preparation.)
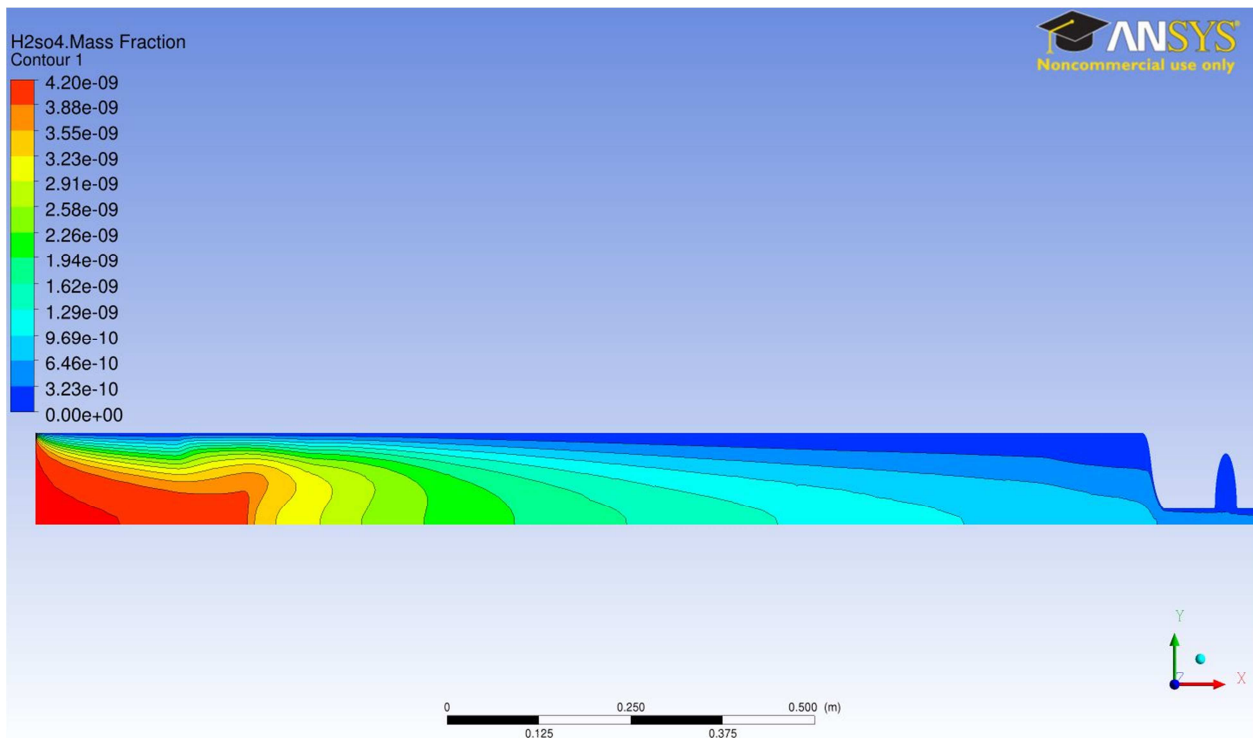
Figure A8. Mass fraction contours of H2SO4. Axis of symmetry is at the bottom, vertical coordinate is multiplied by ten. Nucleation zone is about 1/3 down the tube with an average mass fraction of $2x10^{-9}$ for H_2SO_4.
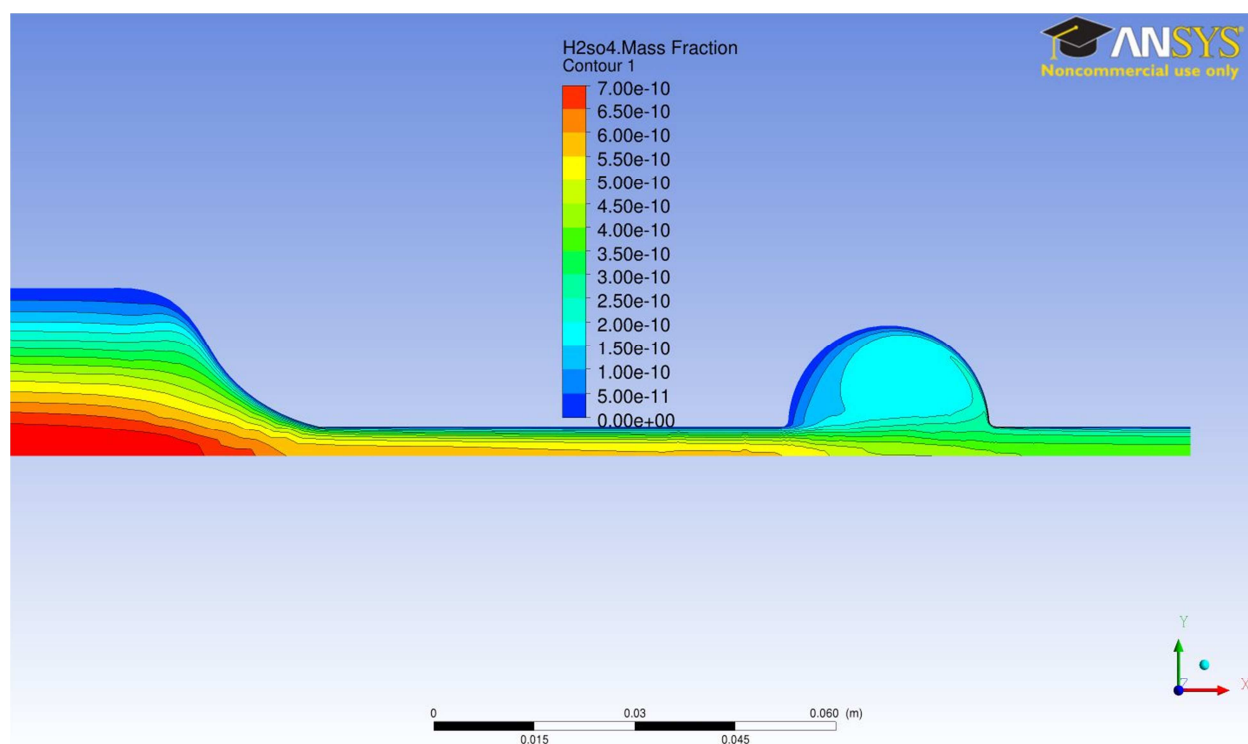
Figure A9. Blowup of mass spectrometer detection region in the middle of the small sphere of radius 1.5 cm. Average H_2SO_4 mass fraction is about 3×10^{-10} in the ion drift region.

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5   2008.

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