Author's response to anonymous referee #1

M. Simon on behalf of all authors

We thank the reviewer for carefully reading our manuscript and for providing constructive comments, which have improved the quality and clarity of our manuscript. The reviewer's comments are repeated in full below (in black font), with our replies indicated immediately after each comment in blue font. Text which has been added to the manuscript is shown in red font.

(1) Recommend removing 'Technical note:' from the title, unless the authors are truly attached to this.

We agree with the referee and have removed "Technical note:" from the title in the revised version.

(2) P13259, L2: may be useful suppose here that atmospheric concentrations of amines are low, and thus motivating the statement that 'highly sensitive' measurements are needed.

The sentence will be changed accordingly:

"Amines are potentially important for atmospheric new particle formation, but their concentrations are usually low with typical mixing ratios in the pptv-range or even samller. Therefore, the demand for highly sensitive gas phase amine measurements has emerged in the last several years."

(3) P13260, L5,L9; P13261, L1: These sentences may read better with the removal of the word 'already'.

The word "already" has been removed from these sentences.

(4) P13267, L18-20: Please clarify that the sum of these two DMA cluster ions are used in figs 3-6.

The sentence has been changed to clarify that the sum of the two product ion clusters ($NO_3^-(HNO_3)_1 \cdot (DMA)$ and $NO_3^-(HNO_3)_2 \cdot (DMA)$) is used:

"The red line shows the sum of the signals for $NO_3^-(HNO_3)_1 \cdot (DMA)$ and $NO_3^-(HNO_3)_2 \cdot (DMA)$ normalized by the primary count rate from the $NO_3^-(HNO_3)_2$ ion."

(5) P13268 L24-25: a 10% uncertainty in the accuracy of the MFC seems a bit high if the range of the MFCs is matched to their use. Generally, when calibrated by the manufacturer these have accuracy of at least 1% or better of the full scale value.

We agree that the accuracy of MFCs has generally an uncertainty, which is lower than 10%. However, the MFCs were operated at the lower end of their recommended range and therefore we think at least a 5% uncertainty is justified. In addition, the overall error of the calculated DMA mixing ratio (equation (3)) is dominated by the uncertainty of the wall loss rate. Therefore, even if the error for the MFCs would be lowered, the error bars would not be affected much. Nevertheless, we will change this information accordingly in the text and figures.

(6) P13269: Fig. 5 appears to be discussed before Fig. 4. Suggest swapping the numbering of these figures.

It is true that Fig. 5 is discussed before Fig. 4 although Fig. 4 is mentioned earlier (p. 13268, l. 11). However, we agree with the referee that the order of Fig. 4 and Fig. 5 should be swapped. Therefore the sentence on page 13268 (lines 10 to 12) now reads as follows:

"Furthermore, this assumption should be justified by the fact that the calibration lines (discussed in Section 3.2) show no steepening when going from low mixing ratios to higher values which is evidence that no wall saturation occurs."

(7) P13269: A change of ~2.3 in the sensitivity factor seems large if the ionization configuration (flows, pressures, interaction time, etc) has not changed. Can the authors discuss in more detail what may be the cause of this? Generally, we do not observe significant shifts in CIMS sensitivity so long as the configuration remains the same. I do note that it is interesting that the inferred ratio of transmission factors between these experiments (0.6) is in the opposite direction, and if assumed equal would cancel out a large fraction of the sensitivity difference. Have the authors done the simple inlet length test to verify the inferred transmission factors (e.g. inlet lengths of 1, 2, 4m)?

We agree with the referee that the difference in the calibration factor is rather large (factor of 2.33). Regarding the sampling line losses we are quite sure that the derived factors (factor 4 for CLOUD7 and factor 2.5 for CLOUD10-T) are accurate. Unfortunately, we have not done tests where the sampling lines were removed and used with a different calibration set-up. This would be required as the CLOUD chamber would not allow bypassing the sampling lines because these penetrate into the chamber by ~0.5 m and also bridge the distance between the CLOUD chamber and its thermal housing. Therefore, a minimum sampling line length of 0.7 m is required. An alternative would be to duplicate the sampling lines from CLOUD and set-up a calibration system for DMA in the lab. However, this has not been done yet.

Regarding the difference in the sensitivity we have, however, an alternative explanation, which will be discussed in a newly added section (Section 3.5, see below).

(8) P13270, L24-25: perhaps better as '...can be drawn, reduced line losses may be realized.'

The sentence has been changed according to the referee's suggestion:

"In the field there is no restriction on the available amount of air that can be drawn, therefore reduced line losses may be realized."

(9) P13271, L22: perhaps better as 'Applying the correction factor increases these values correspondingly'

The sentence has been changed according to the referee's suggestion:

"Applying the correction factor increases these values correspondingly."

(10) Figures 2-6: The readability of these figures is not too good in the AMTD version, and I fear it will be even worse as the AMT if they are displayed as single column figures. Suggest increasing the font-size of all text and tick-lengths by at least a factor of 2.

(11) The paper ends by with a few statements about the agreement of the CIMS DMA measurements with the IC observations, and concludes that the agreement is good. I would suggest that the authors should delve into this a bit more. What is the detection limit and accuracy for the IC? Does the 1-1 regression of the observations yield parameters that are consistent with the detection limits and accuracy uncertainties for the instruments?

Based on the calibration of the IC the accuracy uncertainties of the instrument are 25%, while the uncertainties of the CI-APi-TOF are 14%. Regarding Praplan et al (2012) the detection limit for the IC instrument ranges from 0.2 to 1 pptv for DMA depending on instrumental conditions and sampling time. Unfortunately, the only available data for this instrument comparison cover mostly the range of 10 to 25 pptv. For that reason the comparison do not allow to draw any conclusion regarding a possible bias depending on the DMA concentration level.

To add this information about the uncertainties of the instruments we modified Fig. 6 and the figure caption as follows:
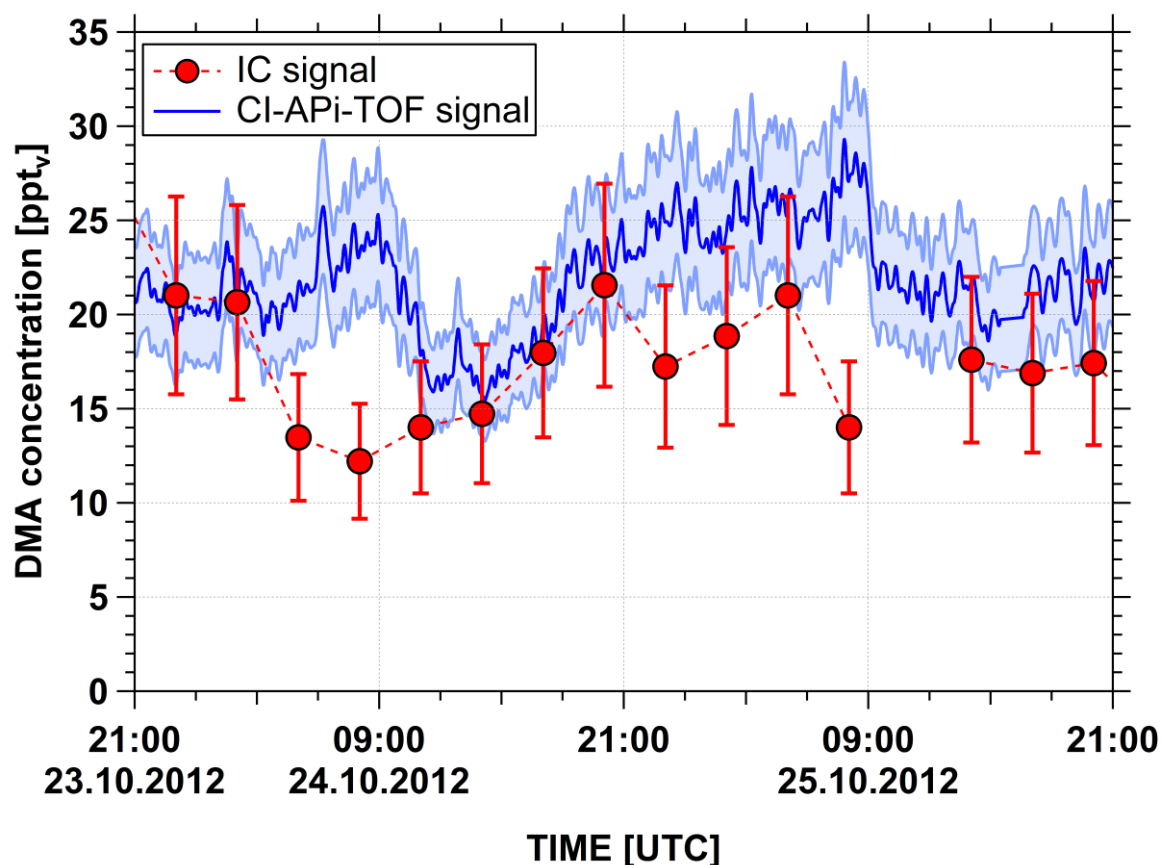

"Figure 6. Comparison between the measured ion chromatograph signal (IC) and the calculated CI-APi-TOF signal in pptv. The CI-APi-TOF signal is determined by the raw ion counts multiplied by the calibration factor *C* which is defined by the slope of the linear fit for CLOUD7 (red line of Fig. 4). Both signals show in general a reasonable agreement but the IC signal is lower on average and point-to-point variability is large. The uncertainty (shown as error bars) of the IC instrument is based on the calibration and yields 25%. The 14% uncertainty of the CI-APi-TOF is shown as light blue shaded area. The mean

values over the entire time period displayed are 17±3 pptv for the IC and 22±3 pptv for the CI-APi-TOF."

Following up on comment (7) and on a similar comment made by referee #2 we have added the following section (new section 3.5) in order to discuss the uncertainty in the calibration factor, differences between this study and the study by Jen et al. (2015) as well as the possibility to measure sulfuric acid and amines simultaneously:

"**Section 3.5**

Detection of amines by means of nitrate chemical ionization has the benefit that other substances relevant for new particle formation, such as sulfuric acid and ELVOCs, can be measured simultaneously with the same instrument. This is demonstrated in Fig. 7 for sulfuric acid and DMA, which shows that both compounds can be measured at the same time (data from CLOUD7) and that the DMA signal is not affected by the presence of atmospherically relevant concentrations of H_2SO_4. Figure 7 only shows the normalized DMA signals and no DMA mixing ratios because during the early phase of CLOUD7 the CI-APi-TOF was tuned differently and therefore the calibration curves from Fig. 5 could not be applied. In conclusion, it is crucial to calibrate the instrument for each instrumental setting.

Jen et al. (2015) have also performed measurements using nitrate chemical ionization, while sulfuric acid and DMA were present in a flow tube at the same time. However, they did not report signals at m/z 170 and m/z 233 indicating that the nitrate DMA clusters were not present. We have no definitive explanation why Jen et al. (2015) could not observe these clusters but it might be related to the fact that they used rather high sulfuric acid concentrations (4×10^9 molecule cm^{-3}, i.e. ~160 pptv). DMA was also present at a relatively high mixing ratio (110 pptv), however the ratio between DMA and sulfuric acid was only about 0.7. From the paper by Jen et al. (2015) it is not evident if the DMA mixing ratio was measured during the presence of sulfuric acid, or before sulfuric acid was added. Assuming that the reported DMA mixing ratio was determined without sulfuric acid would probably mean that the actual DMA (free DMA molecules not bound to any other molecule or cluster) during the experiment with added sulfuric acid could be significantly lower because sulfuric acid monomers and clusters of sulfuric acid would efficiently deplete DMA at such a low DMA to sulfuric acid ratio (Ortega et al., 2012; Jen et al., 2014; Kürten et al., 2014). In the case that the DMA molecules are not "free" but attached to sulfuric acid (or to sulfuric acid clusters) they might not lead to a signal for $NO_3^-(HNO_3)_{1,2} \cdot (DMA)$ but rather end up in a cluster involving the bisulfate ion associated with sulfuric acid and DMA. Such mixed clusters (bisulfate, sulfuric acid and DMA) were detected by Jen et al. (2015). In summary, the depletion of DMA by sulfuric acid and clusters could be responsible for the missing signals at m/z 170 and m/z 233. If this was the case nitrate chemical ionization would yield accurate results for DMA measurements as it would only measure the free (unbound) portion of the amines."
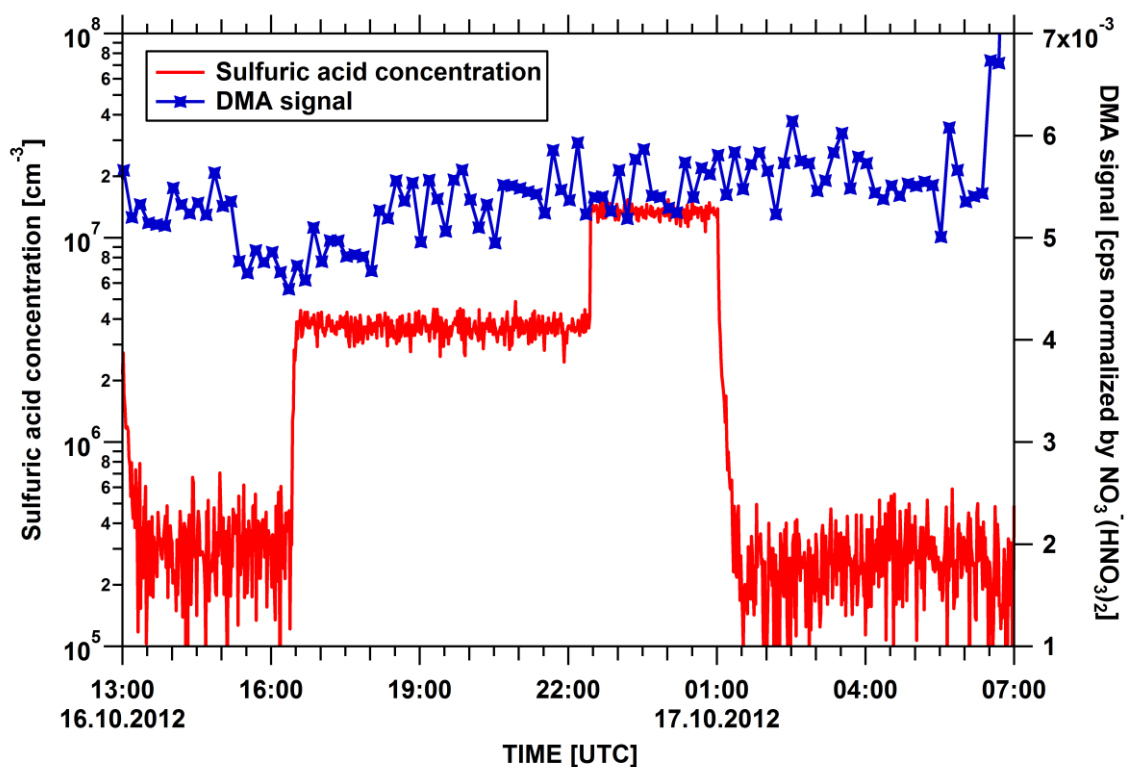
"Figure 7. The time series of the normalized DMA signal and the [H₂SO₄] is shown for a typical CLOUD7 run. The figure demonstrate that the DMA signal does not change significantly when [H₂SO₄] is added even when the [H₂SO₄] reaches ~2x10⁷ molecule cm⁻³."

References

Jen, C. N., Hanson, D. R., and McMurry, P. H.: Stabilization of sulfuric acid dimers by ammonia, methylamine, dimethylamine, and trimethylamine, Journal of Geophysical Research: Atmospheres, 119(12), 7502–7514, doi:10.1002/2014JD021592, 2014.

Jen, C. N., Hanson, D. R., and McMurry, P. H.: Towards Reconciling Measurements of Atmospherically Relevant Clusters by Chemical Ionization Mass Spectrometry and Mobility Classification/Vapor Condensation, Aerosol Science and Technology, ARL, 49(1), i-iii, doi:10.1080/02786826.2014.1002602, 2015.

Kürten, A., Jokinen, T., Simon, M., Sipilä, M., Sarnela, N., Junninen, H., Adamov, A., Almeida, J., Amorim, A., Bianchi, F., Breitenlechner, M., Dommen, J., Donahue, N. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hakala, J., Hansel, A., Heinritzi, M., Hutterli, M., Kangasluoma, J., Kirkby, J., Laaksonen, A., Lehtipalo, K., Leiminger, M., Makhmutov, V., Mathot, S., Onnela, A., Petäjä, T., Praplan, A. P., Riccobono, F., Rissanen, M. P., Rondo, L., Schobesberger, S., Seinfeld, J. H., Steiner, G., Tomé, A., Tröstl, J., Winkler, P. M., Williamson, C., Wimmer, D., Ye, P., Baltensperger, U., Carslaw, K. S., Kulmala, M., Worsnop, D. R., and Curtius, J.: Neutral molecular cluster formation of sulfuric acid-dimethylamine observed in real-time under atmospheric conditions, Proc. Natl. Acad. Sci. USA, 111, 15019–15024, doi/10.1073/pnas.1404853111, 2014.

Ortega, I. K., Kupiainen, O., Kurtén, T., Olenius, T., Wilkman, O., McGrath, M. J., Loukonen, V., and Vehkamäki, H.: From quantum chemical formation free energies to evaporation rates, Atmos. Chem. Phys., 12, 225-235, doi:10.5194/acp-12-225-2012, 2012.