

Author's response to anonymous referee #2

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.

Major Comments:

(1) Page 13265 line 27: the nitrate trimer was chosen as the normalizing ion signal. This is a strange choice and it is not very clear why this ion was chosen. The authors write, "it seems likely that this produces more stable cluster ions compared to $\text{NO}_3^-(\text{HNO}_3)$ due to efficient acid-base stabilization." The normalization ion is chosen based upon which ion is chemically ionizing the neutral molecules/clusters. The rate equations from these chemical ionization reactions (such as those given in reactions R1 and R2) are what produce equations like Equation (4) from this paper. The math can be found in many previous studies ([Berresheim et al., 2000; Eisele and Hanson, 2000] to name two). It would make more sense to add the signals of the nitrate trimer and nitrate dimer to be the normalizing ion signal since both ions could be chemically ionizing neutral entities. The authors are also assuming that clusters do not change upon ionization/entering the mass spectrometer. Each of these assumptions would alter the signal to concentration inversion math (and the predicted transmission efficiency of the clusters ion the mass spec).

It would be useful to know which reagent ion has the highest signal: is it 188 m/z or 125 m/z? From the paper it seems like the nitrate trimer (188 m/z) is the highest, but this is just a guess. This observation would be strange if this is the case. The nitrate trimer is much less stable (lifetime of 4 ms at $T=298\text{K}$) than the nitrate dimer [Hanson and Eisele, 2002; Lovejoy and Bianco, 2000]). As a result, the nitrate dimer ion should have a longer lifetime (not observed to decompose) and should be in higher abundance than the trimer. I wonder if the trimer signal is the highest is because a DMA molecule is actually attached to the cluster and evaporates upon measurement. Obviously, this is difficult to prove but it would be nice for the authors to explore/explain their reagent ion signals better.

We will start to answer this comment by providing the numbers for the primary ion count rates ($\text{NO}_3^-(\text{HNO}_3)_{0.2}$) for the present study. The nitrate monomer (NO_3^-) shows the highest signal, while the nitrate dimer ($\text{NO}_3^-(\text{HNO}_3)$) is about 20% of the monomer. The nitrate trimer ($\text{NO}_3^-(\text{HNO}_3)_2$) is even lower, i.e. 1 to 4% of the monomer (and 5 to 20% of the dimer). These ratios are independent of the added amount of DMA as the dimethylamine mixing ratios were rather low and did not deplete the primary ions. Furthermore, the ratios are constant over the whole calibration and therefore will not change the outcome considering whether the primary nitrate trimer ion alone or the dimer and trimer ion are used for the normalization. However, note that these numbers are valid for the signal measured by the mass spectrometer and are not directly transferable to the conditions in the ion molecular reaction zone as fragmentation and the ion transmission efficiency in the mass spectrometer can affect the measured primary ion distribution. In other words, the fraction of trimers could be larger in the ion molecular reaction zone.

Regarding the choice for selecting the nitrate trimer ($\text{NO}_3^-(\text{HNO}_3)_2$) as the relevant reagent ion we are essentially referring to three previous publications (Almeida et al., 2013; Kürten et al., 2014; Ortega et al., 2014). Although these publications discuss acid-base chemistry for ion clusters consisting of $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_x \cdot (\text{DMA})_y$ we think that their results are also valid if the acid is HNO_3 instead of H_2SO_4 . Almeida et al. (2013) and Kürten et al. (2014) showed that DMA can only be detected in charged clusters if at least two acids are contained in a cluster besides the bisulfate ion ($\text{HSO}_4^-(\text{H}_2\text{SO}_4)_{x \geq 2} \cdot (\text{DMA})_{1,2}$). This

indicates that clusters containing only one uncharged acid ($\text{HSO}_4^-(\text{H}_2\text{SO}_4)_1 \cdot (\text{DMA})_1$) are not stable and have a high evaporation rate regarding the base molecule (as $\text{HSO}_4^-(\text{H}_2\text{SO}_4)$ can be observed and is very stable against evaporation). This is supported by quantum chemical calculations presented by Ortega et al. (2014) suggesting that the evaporation rate of DMA from $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_1 \cdot (\text{DMA})_1$ is $\sim 5 \times 10^2 \text{ s}^{-1}$. The evaporation rate regarding DMA for the next larger cluster ($\text{HSO}_4^-(\text{H}_2\text{SO}_4)_2 \cdot (\text{DMA})_1$) is 4 orders of magnitude lower. If we transfer these results to a system of NO_3^- , HNO_3 and DMA it seems justified to assume that the $\text{NO}_3^-(\text{HNO}_3)_2 \cdot (\text{DMA})$ cluster is more stable than $\text{NO}_3^-(\text{HNO}_3)_1 \cdot (\text{DMA})$. The fact that both cluster ions $\text{NO}_3^-(\text{HNO}_3)_1 \cdot (\text{DMA})$ and $\text{NO}_3^-(\text{HNO}_3)_2 \cdot (\text{DMA})$ appear in the mass spectra can be interpreted as an indication that the larger cluster ($\text{NO}_3^-(\text{HNO}_3)_2 \cdot (\text{DMA})$) can partially fragment and lose one HNO_3 (some clusters could also lose DMA but this would remain undetected). As the referee points out it is essentially impossible to disentangle the reactions occurring in the ion molecular reaction zone from possible fragmentation in the vacuum chamber of the mass spectrometer. However, if a calibration like the one shown in the present manuscript is used it will yield in accurate results as long as the primary ion cluster distribution does not change significantly even if DMA and nitrate dimer ion clusters would yield rather stable products.

In order to support our choice for the nitrate trimer we have added the following sentence on page 13266 (line 6):

“Furthermore, Ortega et al. (2014) reported that a cluster of two acid molecules and one base molecule (e.g. $(\text{H}_2\text{SO}_4)_2 \cdot \text{DMA}$) will only be stable in the neutral case. As soon as this cluster will be negatively charged it becomes unstable and the base molecule will evaporate rapidly. In contrast, a cluster containing two acids besides the ion and a base molecule ($\text{HSO}_4^-(\text{H}_2\text{SO}_4)_2 \cdot \text{DMA}$) will be much more stable. Although, the acid is in our case HNO_3 and not H_2SO_4 we believe that qualitatively the ion cluster chemistry for the two acids is similar. Future studies will show to what extent this assumption holds true.”

(2) Page 13264 line 13 The authors report peaks at 170, 233, and 296 m/z in the pure water/DMA environment at $T=273 \text{ K}$. This seems to be in contrast to the peaks reported in [Jen et al., 2015]. From their graph Figure S2, do not see peaks at those masses. They are operating at higher temperatures and with sulfuric acid at about the same concentration as [DMA] in the flow reactor. Can the authors comment on this and add a comparison of their mass spectra to those of [Jen et al., 2015]? I am concerned that if the purpose of this method is to measure [DMA] at the same time as sulfuric acid and ELVOCs, then the evidence from [Jen et al., 2015] seems to indicate that nitrate+DMA clusters will not be detected in more complex experiments.

We agree with the referee that there is an apparent discrepancy between the results by Jen et al. (2015) and from this study because Jen et al. did not observe any signals at m/z 170 and m/z 233. However, what has not been mentioned so far in our manuscript is the fact that the sulfuric acid concentration was not zero all the time during the two CLOUD calibration measurements. The sulfuric acid concentration inside the chamber reaches up to $\sim 2 \times 10^6 \text{ molecule cm}^{-3}$ (ca. 0.08 pptv) during CLOUD7 and $\sim 2 \times 10^7 \text{ molecule cm}^{-3}$ (ca. 0.8 pptv) during CLOUD10T calibrations. The study by Jen et al. (2015) used $4 \times 10^9 \text{ molecule cm}^{-3}$ of sulfuric acid (ca. 160 pptv) and 110 pptv of DMA. This means, (i) that the acid concentration in the present study was by 2 to 3 orders of magnitude lower and in a range, which is atmospherically relevant and (ii) that the ratio between the lowest measured DMA and the sulfuric acid concentration was different (30 during CLOUD7, 7.5 during CLOUD10T and 0.7 in the study by Jen et al. (2015)). We can only speculate at the moment that the ratio between the DMA and the sulfuric acid concentration could be important for the detection of DMA with nitrate ion clusters.

From the paper by Jen et al. (2015) it is also 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 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 sulfuric acid could be significantly lower because sulfuric acid monomers and clusters of sulfuric acid would efficiently deplete DMA (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 $\text{NO}_3^-(\text{HNO}_3)_{1,2}\cdot(\text{DMA})$ 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) are detected by Jen et al. (2015).

Motivated by the referee’s comment we decided to add a new section to the manuscript (Section 3.5) where the discrepancy to Jen et al. (2015) is discussed as well as the applicability of our method to atmospheric measurements. In this light, we also discuss the effect that the sulfuric acid that was present during the CLOUD calibrations might have had.

“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 $\text{NO}_3^-(\text{HNO}_3)_{1,2}\cdot(\text{DMA})$ 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.”

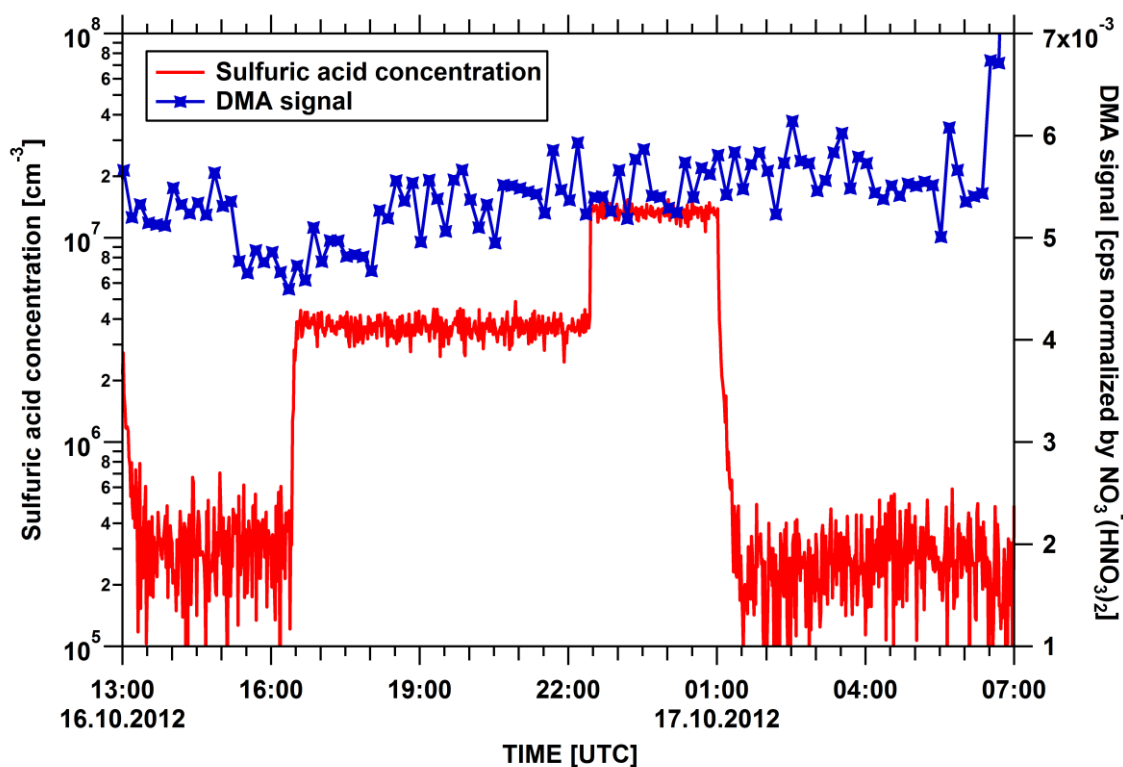


Figure 7. The time series of the normalized DMA signal and the $[H_2SO_4]$ is shown for a typical CLOUD7 run. The figure demonstrate that the DMA signal does not change significantly when $[H_2SO_4]$ is added even when the $[H_2SO_4]$ reaches $\sim 2 \times 10^7$ molecule cm^{-3} .

Also the sentence on p. 13263, l. 15-17 has been adjusted accordingly to rule out possible misunderstanding:

„For the data shown in this study, either no sulfuric acid was generated when the DMA calibration measurements (see Sect. 3.2) were performed, or the sulfuric acid and the associated condensation sink was so low that it had no effect on the DMA mixing ratio.“

(3) Section 3.4 (Page 13271): The Ci-APi-ToF measured DMA mixing ratio is compared to IC measured concentrations. This seems like a rather difficult comparison to make, given differences in sampling and instrument sensitivities. It would be beneficial to compare the nitrate measured [DMA] to [DMA] measured in positive ions using charged water clusters (or something of that sort) with the CI-API-TOF. I am not intimately familiar with the instrument but positive ions have been reported with the APi-TOF before so I believe this is possible. I bring up this comparison because positive ion quantification of amines (using water clusters or acetone, as the authors wrote in Line 59 and 60) seems to be a more “well established” method.

We agree that it would have been ideal to have a third method for a comparison. But unfortunately we were not operating a mass spectrometer in positive ion mode during the CLOUD7 and CLOUD10T campaigns. For this reason the IC is the only instrument available for a direct comparison. The difference in the two techniques (MS vs. IC) should however not be problematic in this case. If anything then we should see it from the positive side because two entirely different and independent techniques agree quite well for a rather low DMA mixing ratio (~ 20 pptv). The measurement of such low mixing ratios is not straight-forward and the reasonable agreement gives confidence that both techniques are sufficiently reliable. In this context it should also be mentioned that the IC was calibrated independently.

Regarding further instrument inter-comparison we think it would be a good idea to bring together different instruments for amine measurements. This would provide an opportunity to compare the

different absolute measurements, the levels of detection and to rule out potential systematic errors or cross-sensitivities.

(4) The comparison with IC (page 13271 Line 10) is off by 5 pptv. Do the authors know if this agreement worsens with decreasing [DMA]? The authors report [DMA] as low as 5.8 pptv from the nitrate measurement. What is the uncertainty associated with this mixing ratio?

We do not assume that there exists a constant offset of 5 pptv between the IC and the CI-APi-TOF. Instead, we interpret this difference in terms of a relative deviation meaning that the IC shows ~77% of the CI-APi-TOF measured value for the time period displayed in Fig. 6. In this case the absolute difference would become smaller when going to lower mixing ratios. The IC has been calibrated independently by direct injection of aqueous solutions but has its own uncertainty which can be estimated to be 25%. In contrast, the uncertainty of the CI-APi-TOF measurements are determined to be 14%. From this point of view the agreement between the two instruments is quite good. Unfortunately, no further data are available for a comparison over a wider range of mixing ratios which does not allow to draw any conclusions regarding a possible bias depending on the DMA concentration level.

Minor Comments:

(5) Page 13259, line 9: “This observation...” is an awkward sentence.

The sentence has been modified as follows:

“Calibration measurements were made at the CLOUD chamber during two different measurement campaigns.”

(6) Page 13259, line 14-16: Awkward sentence.

The sentence has been modified as follows:

“Amines are potentially an important agent contributing to atmospheric aerosol nucleation events in those regions where amines are emitted. Their measurement in the gas-phase has therefore recently received considerable attention.”

(7) Page 13260, Line 7: Comparison with Kürten et al is great, though for readers who do not know what the kinetic limit is, a reference to [Rao and McMurry, 1989]. The authors should note the specific sulfuric acid and DMA concentrations of the experiment in Kürten et al. where the kinetic limit was observed. As written now, the reader thinks sulfuric acid and DMA always proceeds at the kinetic limit which is untrue. This is shown in [Jen et al., 2014] where there are regimes of [DMA] and [sulfuric acid] that lead to the kinetic limit. Also, the kinetic limit refers to the sulfuric acid kinetic limit. DMA likely evaporates from the cluster.

We agree with the referee and modified the sentence. In addition the new reference has been added:

“Kürten et al. (2014) and Jen et al. (2014) studied the formation of neutral (i.e. uncharged) H₂SO₄-DMA clusters and showed that the cluster formation process proceeds at or near the kinetic limit (Rao and McMurry, 1989) when the DMA to sulfuric acid ratio is high (~ 10 to 100).”

(8) Page 13260, Line 14: “near ground” what does near ground mean?

“near ground” has been replaced with “boundary layer”:

“Evidence for the participation of amines in aerosol nucleation in the boundary layer has been found (e.g. Mäkelä et al., 2001; Smith et al., 2010; Zhao et al., 2011; Creamean et al., 2011; Yu et al., 2012; Chen et al., 2012).”

(9) Page 13260, Line 16: “...in how far amines are indeed” the are indeed part makes the sentence sound awkward

The word “indeed” has been removed:

“However, the extent to which amines are participating in atmospheric nucleation is still not established.”

(10) Page 13260, Line 17: “This lack of knowledge” is a strange phrase

The phrase has been removed, therefore the sentence has been modified as follows:

“This is to a large degree due to the difficulty of measuring amines in real-time at low pptv to sub-pptv mixing ratios.”

(11) Page 13260, Line 21: “low enough limit” maybe change to high sensitivity and maybe put a number on it

The sentence has been modified as follows:

“These methods have sufficient time resolution and high sensitivity to measure atmospherically relevant mixing ratios in a range between ~0.1 and 40 pptv.”

(12) Page 13261, Line 4-7: “The simultaneous. . .” awkward sentence

The sentence has been modified as follows:

“The fact that DMA can be measured in the presence of H₂SO₄ and ELVOCs is very useful as all three compounds are relevant for aerosol nucleation and growth.”

(13) Page 13261, Line 14-15: “. . . vessel to study. . .” the to study phrase read awkwardly as the chamber does not study. It is used to study

The word “used” has been added to this sentence:

“The Cosmics Leaving OUtdoor Droplets Chamber (CLOUD) at CERN a 26m³ cylindrical vessel is used to study aerosol processes such as new particle formation.”

(14) Page 13261, line 16: “Care is taken. . .” awkward sentence

The sentence has been modified as follows:

“Great effort is made to minimize contamination by any condensable substances that may influence new particle formation.”

(15) Page 13261, Line 19: “Results are reported. . .” consider adding “for this study” so the reader knows you are not referring to the previous studies

The sentence has been modified as follows:

“For this study results are reported from the CLOUD7 and CLOUD10-T experiments (October–December 2012 and April–May 2015) in which the aerosol nucleation for the sulfuric acid-water-dimethylamine system was investigated (Almeida et al., 2013; Kürten et al., 2014).”

(16) Page 13262, Line 3: “In order to have...” awkward sentence

The sentence has been reworded as follows:

“A specially designed gas system has been implemented at CLOUD for precisely controlling the amount of dimethylamine which is fed into the chamber.”

(17) Page 13262, Line 9: What is B?

The parameter B denotes the fraction of DMA inside the gas bottle (this fraction is 0.01). This information has been added to the revised manuscript:

“The amount of DMA introduced into the chamber can be calculated from the fraction B of DMA inside the gas bottle ($B = 0.01$) and the MFC flow rates (see Fig. 1).”

(18) Page 13262, Line 9-10: why mention the by-pass valve if it is never used?

We agree that it is not absolutely necessary to mention the bypass valve in the context of this study. However, the bypass valve is installed and can be used to achieve high mixing ratios. The bypass-valve is a standard feature for all the trace gas inlets and it is frequently used for some of the other trace gases (e.g. NH_3). The drawing shown in Fig. 1 could therefore also be used as a reference for future papers where the CLOUD gas system is relevant. For this reason we would like to keep the figure and the text unchanged.

(19) Page 13262, Line 15: Since I do not know what B is (or its units), what are the units of A? volumetric flow rate? Molar flow rate?

The parameter B denotes the fraction of DMA inside the gas bottle (value of 0.01 without any units). Therefore, the unit of A_{DMA} is flow rate for pure DMA. This information is already provided (p. 13262, l. 13-15).

(20) Page 13262, Line 13-14: standard temperature and pressure can be abbreviated as STP. I believe this is a common abbreviation.

We follow the referee’s suggestion, the sentence now reads:

“The flow rates (denoted with MFC1, MFC2, and MFC3) have units of $\text{cm}^3 \text{ s}^{-1}$ (at STP, in this case 293.15K and 1013 hPa), and the quantity A_{DMA} is the flow rate of DMA.”

(21) Page 13262, Line 24: a priori should be italicized

Not necessary anymore because “a priori” was removed, see next comment.

(22) Page 13262, Line 24-page 13263 Line 5: these two sentences confused me. Consider shortening the sentences and combining them? Or changing their order.

The sentences have been modified to improve readability:

“Assuming that the walls act as a perfect sink the wall loss rate can be assumed to be proportional to the square root of the gas-phase diffusion coefficient for an aerosol chamber (Crump and Seinfeld, 1981). For sulfuric acid the wall loss rate constant was experimentally determined as $2.2 \times 10^{-3} \text{ s}^{-1}$. For DMA it should be higher because it is a lighter molecule compared to sulfuric acid and has a higher diffusivity. The value for sulfuric acid therefore provides a lower limit for the wall loss rate of DMA.”

(23) Page 13263, Line 11: “...which is indicating” awkward phrase

The sentence has been modified as follows:

“Alternatively, the wall loss rate can be determined from the decay rate of the signal, which is used to calculate the DMA mixing ratio in this study (see Sect. 3.1).”

(24) Page 13263, Line 17: how low is the condensation sink? What qualifies it as so low? Perhaps put a number on this

The sentence has been modified as follows:

“For the data shown in this study, either no sulfuric acid was generated when the DMA calibration measurements (see Sect. 3.2) were performed, or the condensation sink was more than an order of magnitude lower than the wall loss rate and had no significant effect on the DMA mixing ratio.”

(25) Page 13264, Line 3: change recently to previously

Done

(26) Page 13264, Line 10: ELVOCs has already been defined

“extremely low volatile organic compounds” was replaced by ELVOCs in this sentence

(27) Page 13264, Line 12: comma after “in the next section”

Done

(28) Page 13264, Line 12: DMA has already been defined

The definition was removed from the sentence.

(29) Page 13264, Line 13: The convention is to put a • between the ligands of the cluster. So for 170 m/z, the formula would be $\text{NO}_3^- \text{HNO}_3 \cdot \text{DMA}$

Done

(30) Page 13264, Line 15: It is not necessary to write the exact mass down for these clusters. It does not provide any additional information than just saying high resolving power of the ToF. I would consider moving the description of resolving power and accuracy of the MS to the first paragraph in this section and masses of the detected ions to section 2.4

We have modified the part of the relevant sentence (p. 13264, l. 14/15) as follows:

“... however, the exact masses of these ion clusters are used to evaluate the signals.”

As for the following sentences we would like to keep them where they currently are.

(31) Page 13265, Line 17: The ions detected and their masses are written here. I would then remove the entire paragraph starting Page 13264 Line 12.

The sentence will be deleted on page 13264 line 12 and the following sentences will be moved to the first paragraph accordingly.

(32) Page 13264, Line 22: needs paragraph transition, and “on the contrary to” is an awkward phrase and the sentence is rather unclear

This section has been modified as follows:

“One important aspect to consider is sampling line losses when evaluating the DMA signals. During CLOUD10-T the CI-API-TOF was connected to the chamber by its own sampling line, while in CLOUD7 the instrument was sharing the sampling line with another instrument. Therefore, a y-splitter was used. For this kind of inlet the sampling line losses cannot be easily calculated in the same way as for a straight tube and laminar flow.”

(33) Page 13264, Line 22: I could not understand from this paragraph how the CIMS compares to CI-API-TOF from the experimental setup

The CIMS was only used for the measurement of sulfuric acid during CLOUD 7 and had its own sampling line. The CIMS was operated in peak hopping mode and was not measuring the ions at m/z 170 and m/z 233. Therefore, the DMA signals could only be evaluated from the CI-API-TOF which measures the full ion spectrum over a wide range. The CI-API-TOF was connected to the CLOUD chamber with a y-splitter. Since both the CIMS and the CI-API-TOF measured sulfuric acid and were calibrated with the same method the sampling line losses could be evaluated from a comparison with the CIMS.

(34) Page 13265, Line 9: The newer Cluster CIMS detects sulfuric acid via ligand switching with NO_3^- HNO_3 [Zhao et al., 2010].

It is true that ligand switching is a possible reaction but we consider this, in the context of the present study, a detail, which does not necessarily need to be mentioned.

(35) Page 13265, Line 15: How long is the ion-molecule reaction time in the CI reaction zone? This number is useful in determining if ion products have time to decompose at atmospheric pressure or if they fragment in MS.

The ion-molecule reaction time is about 50 ms. We have added this information to the sentence in line 15/16 (p. 13265):

“The association reactions (R1) and (R2) could both occur in the ion-molecule reaction zone (~50 ms reaction time) of the CI-APi-TOF ...”

(36) Page 13265, Line 20: “more important reaction” What do you mean by more important? The dominant reaction? Compared to what? R1? This is a confusing sentence.

The sentence has been modified as follows:

“Since fragmentation could occur in the APi section it is possible that this fragmentation is responsible for a high signal at m/z 170 although reaction (R2) could be dominant.”

(37) Page 13266, Equation 4: using T to mean a correction factor is confusing because T is normally used for temperature.

We agree and replaced “T” with “SL”.

(38) Page 13266, Line 13: If T is losses in the sample line, shouldn't it have units? A better description of T would be useful.

T (now SL) is dimensionless as it is the inverse of the penetration ($P = c_{\text{exit}}/c_{\text{center}}$ describing the ratio of the concentrations exiting and entering the inlet line), which is frequently used to characterize sampling line losses of aerosol particles or molecules.

By adding the following (p. 13266, l. 12-14) this should now be clearer:

“An additional factor SL (inverse of the penetration usually used to characterize sampling line losses of aerosol particles and molecules in tubes) is required to take into account losses of DMA molecules in the sampling line during the transport from the chamber to the instrument; ...”

(39) Page 13267, Line 4: Any hypotheses on why no clusters containing 2 DMA were observed? Also, it would be useful to note the [DEA] of Luts et al. The concentration of base will determine what types of clusters are observed.

We agree that the concentration of the amine generally determines which types of clusters are observed. For high DMA concentration a clusters containing two DMA molecules could still be observable if this cluster is stable with respect to evaporation of the second DMA molecule. Unfortunately, Luts et al. (2011) did not report what amine concentration was used but we speculate that it was significantly higher than the [DMA] in our study.

(40) Page 13267, Line 8: “Figure 2” The authors switch between writing Fig. and Figure. From the captions of the figures, the appropriate one should be Fig. But, staying consistent is the only important point.

We agree on this point. In this case we follow the AMT standards, which advises that the abbreviation "Fig." should be used unless it is used out the beginning of a sentence (in this case “Figure” should be used).

(41) Page 13267, Line 17: Move experimentally to before determine in line 16

Done

(42) Page 13267, Line 21: comma after shut-off

Done

(43) Page 13268, Line 4: “Using the diffusion...” awkward sentence from the “one can” part

We agree that this sentence is somewhat confusing and decided to remove it (p. 13268, l. 3-6).

(44) Page 13268, Line 6: “The fact that” this is a confusing sentence as it makes it sound like DMA and sulfuric acid have the same diffusion coefficients. The last phrase of the sentence is always awkward phrasing as sink and sticks efficiently are the same thing.

The sentence has been modified as follows:

“The fact that the wall loss rate for DMA is slightly faster than the one found for sulfuric acid implies that the walls act as a perfect sink for DMA at these low mixing ratios and rather short exposure time at a temperature of 278 K and a relative humidity of 38 %.”

(45) Page 13268, Line 18: This one sentence paragraph can be moved into the previous paragraph

Done

(46) Page 13268, Line 23: what is tau? Also the numbers in the parentheses have more significant figures than what the error allows.

The parameter τ_1 is a result from the double-exponential fit and is the inverse of the wall loss rate:

“The error in the targeted mixing ratio during CLOUD7 is calculated based on the 1σ -standard deviation for the parameter τ_1 (τ_1 is the average decay time, i.e. the inverse of the wall loss rate, $\tau_1 = 433\pm 48$ s) from a double-exponential fit which was performed with the software IGOR.”

(47) Page 13269, Line 8: Even though the CI-APi-ToF uses the same clean air for the sheath as the CLOUD chamber, is it not also possible for DMA molecules to desorb from the walls (i.e. holdover effects)? This would be a bigger problem at higher [DMA].

The lines for the clean air and for DMA are totally separated, so there will be no interference or holdover effects in the instrument.

(48) Page 13269, Line 10: s after shows, also Figure should be Fig.

Done

(49) Page 13270, Line 1: what is evaporating from this cluster? DMA? Or nitric?

In this context the evaporation of DMA matters. For the larger clusters it could also happen that first HNO₃ evaporates followed by loss of DMA. However, in the end it would only matter that the DMA molecule would not be detected in the mass spectrum because of evaporation:

“One explanation for this behavior could be that the evaporation rate of the NO₃⁻(HNO₃)₁₋₃•(DMA) clusters regarding DMA is non-negligible.”

(50) Page 13270, Line 4: Is the APi section the first portion that is below atmospheric pressure?

Yes, the APi section is the first portion which is below atmospheric pressure:

“It is still an open question, whether this evaporation occurs inside the ion source, where the temperature is close to the chamber-temperature or within the APi section (first stage which is below ambient pressure), where a higher effective temperature is expected due to energetic collisions of the ions (that are accelerated by electric field) and neutral gas molecules.”

(51) Page 13270, Line 9: hyphen between ion and molecule

Done

(52) Page 13270, Line 18: the first two sentences of this paragraph read a bit awkwardly

The sentences have been modified as follows:

“Since the CI-APi-TOF sampling line in CLOUD7 leads to a factor of 4 reduction in the DMA concentration reaching the instrument, a considerably lower detection limit (~0.7 pptv) would result for a situation where sampling line losses are negligible. While zero wall loss cannot be realized in reality, a considerable reduction in the sampling line losses can be achieved in field studies.”

(53) Page 13271, Line 19: “anyhow” read awkwardly

The word “anyhow” has been deleted from the sentence.

(54) Page 13271, Line 20: no need to write statements after conclusions

“or statements” has been deleted from the sentence

(55) Page 13271, Line 22-24: “Applying the correction factor...” I do not understand these two sentences. Applying the correction factor would significantly increase the [DMA] reported by Kürten et al. How does this not imply a significant change? (I think I understand the sentences now, but they are confusing.)

We reformulated the second sentence to clarify what is meant:

“Applying the correction factor these values increase correspondingly. Since the exact DMA mixing ratios were not used in the data analysis by Kürten et al. (2014) the adjustment of the reported DMA values does not imply a significant change of the conclusions of Kürten et al. (2014).”

(56) Page 13272, Line 2: “at low mixing ratios” what qualifies as low? Maybe put a number on this. Also, this study only shows the DMA can be detected with nitrate CI when no sulfuric acid is present. This detail should be included.

The sentence has been changed as follows:

“It is demonstrated that dimethylamine (DMA) can be detected at mixing ratios in the pptv-range using nitrate chemical ionization mass spectrometry.”

(57) Page 13272, Line 10: “the method introduced...” this phrase is a bit misleading. The other chemical ionization methods do not just detect amines. They detect many other compounds too (water clusters can even detect certain types of sulfuric acid clusters).

The sentence has been changed as follows (also considering the next comment):

“While there are other techniques yielding similar or even better detection limits for DMA (or amine measurements in general) the method introduced in this study should allow for simultaneous measurements of sulfuric acid and extremely low volatile organic compounds (ELVOCs).”

(58) Page 13272, Line 14-16: “Being capable of measuring...” This sentence implies that nitrate can detect DMA in the presence of sulfuric acid and ELVOCs. This study has not shown this. Also, this sentence is phrased awkwardly.

This sentence was incorporated into the previous one (see comment (57)). In addition, as outlined in the new Section 3.5 simultaneous measurement of DMA and sulfuric acid at atmospherically relevant concentrations has been demonstrated.

(59) Page 13272, Line 19-21: “For this an amine source...” Confusing sentence.

The sentence has been changed as follows:

“For such measurements an amine calibration source providing well-defined concentrations to the CI-API-TOF (e.g. Freshour et al., 2014) would be desirable.”

(60) Figure 1: MFC1 and MFC3 have DMA that passes through it. Is there any issue with DMA holdover/other contamination that is introduced by DMA in a MFC?

We are not exactly sure what the referee is pointing to. The MFCs are used only for DMA and nitrogen and were not exposed to any other gas. In addition, we do not think that accumulation of DMA in a MFC is affecting our measurements. MFC1 is always exposed to a constant DMA mixing ratio. MFC3 is exposed to varying mixing ratios but we have not observed any drifts, e.g. that a reduction in the nominal DMA (by adjusting MFC3) takes a long time to reach the new equilibrium value due to memory effects.

(61) Figure 2: The y axes show signal in cps but the highest value is 1. This seems like these signals were normalized? It would be useful to instead see raw signals and the signals of the nitrate ions. Also, since the graphs are labeled A-D, it would be helpful to just write the cluster identity for each letter on the graph.

The signals shown in this graph are not normalized. It is simply coincidence that the values reach almost 1 cps. We will add the cluster identity to each of the panels. The nitrate ion count rates were ~13500 cps (for NO_3^-), ~2600 cps (for $\text{NO}_3^-(\text{HNO}_3)$) and ~340 cps (for $\text{NO}_3^-(\text{HNO}_3)_2$). We added this information to the figure legend.

(62) Figure 3: The gray shaded region makes me think that DMA was injected in an integrated time (or something strange like that). It would make more sense to just draw vertical lines with labels that show when DMA was injected/shut off or have the gray region cover the entire vertical dimension.

The grey shaded area should illustrate the different DMA flows into the chamber. The units do not show the absolute values in pptv and should only give an idea of the relative changes and when DMA was shut off. By removing this area this information would get lost; therefore, we would like to keep it.

(63) Figure 5: it is difficult to see the gray area which is the [DMA] set point. Maybe try just a solid line (not red)? Looking at panel A, there appears to be [DMA] carryover from somewhere in the system (seen at 17:00). The set point drops but the signal of the DMA clusters remains more or less constant (about a factor of 2 off). This seems to suggest that this method (not necessarily the nitrate chemical ionization) is not sensitive to quick changes in concentration.

We will adjust the gray area to improve the readability of the figure.

We very much appreciate that the referee had such a careful look at our data. So far, we have no definitive explanation why the DMA cluster remains constant at this time while the set point drops about 3 pptv. However, these DMA-levels are very close to the detection limit of the instrument which might cause a higher uncertainty in this concentration range. We also want to point out, that at these very low levels of DMA the CLOUD chamber itself might behave differently compared to higher concentrations. Small effects, like re-evaporation of DMA from the chamber walls and conditioning of the DMA inlet lines might enhance the equilibrium time at these concentrations significantly and introduce additional uncertainty. Also it can be seen in fig. 4 that this data point is clearly off and the error bar of this point does not intersect with the fitted line. Therefore, more data points at this low mixing ratio are needed to draw any further conclusion. Despite this data point we would not generally conclude that our measurement technique is insensitive to quick changes in concentration. We can see a fast response of

the instrument for higher concentrations of DMA, for both, an increase and a decrease of DMA in the same figure.

We modified the sentence (p. 13269, l. 19) to take this more in consideration:

“This indicates that the applied methodology is capable of quantifying DMA at low mixing ratios in the pptv range. However, note that for mixing ratios below 7 pptv additional effects of the CLOUD chamber itself, like re-evaporation of DMA from the chamber walls and conditioning of the DMA inlet lines might enhance the equilibrium time significantly and therefore introduce additional uncertainty.”

References

Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurtén, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppä, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petäjä, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Tröstl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H., and Kirkby, J.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, *Nature*, 502, 359–363, 2013.

Freshour, N. A., Carlson, K. K., Melka, Y. A., Hinz, S., Panta, B., and Hanson, D. R.: Amine permeation sources characterized with acid neutralization and sensitivities of an amine mass spectrometer, *Atmos. Meas. Tech.*, 7, 3611–3621, 2014.

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.