Response to Anonymous Referee 1 on "Measurement of ammonia, amines and iodine species using protonated water cluster chemical ionization mass spectrometry"

We thank the referee for the constructive comments that help improving our manuscript. In the following, the comments of the referee are shown in black, shaded font. Our replies are shown in blue font. Text that has been added or revised in the manuscript is shown in red font.

There could be better clarification throughout the manuscript to indicate that the amine and iodine species are detected and that their mixing ratios are estimated semiquantitatively, as formal calibrations have not been performed with a primary standard.

We agree with the referee that the manuscript should clearly indicate that the mixing ratios for amines and iodic acid are estimated and prone to higher uncertainty compared to the ammonia measurement. We have updated the manuscript according to the specific comments from the referee. Our revised text is listed after our replies.

The title should be revised to reflect quantitation of ammonia and detection of DMA and iodine oxide species specifically instead of 'amines and iodine species' which is misleading. The discussion clearly states that the DMA and HIO3 quantities are estimates based off of scaled numbers from H3O+ or NO3- CI-APi-TOF responses to other species (e.g. NH3 or H2SO4). Converting the units from ncps to mixing ratios for those scaled responses leads to values that may be highly inaccurate. The potential for quantification and sensitive detection of these species by H3O+ CI-APi-TOF can be discussed, but the scaled response estimates should not be used to report mixing ratios, such as in Figures 5 and 8. These should be replaced with signal reported as normalized counts per second (ncps). The authors state in several locations in the discussion potential sources of bias from the assumptions made in converting signal to mixing ratios, which are not fully characterized for the CLOUD chamber and could easily represent a factor of 2 or more error. Based on the presented data, mixing ratios for these compounds should be replaced with ncps units throughout the manuscript. The authors make arguments for the validity of some assumptions throughout the manuscript as well, which seem to be undermined by other parts of the discussion. See the technical comments below for instances where this is the case and the discussion should be revisited.

In principle we agree with the referee that it should clearly be stated that the reported mixing ratios for dimethylamine and iodic acid are not based on a direct calibration with these substances. However, in the following we argue that it is nevertheless justified to report mixing ratios in Figures 5 and 8.

A recent publication by Sipilä et al. (2016) reports on measurements of iodic acid with a nitrate CI-APi-TOF (same as the one used in our study for the HIO3 measurements shown in Fig. 5 on the x-axis). No direct calibration for iodic acid was available at that time and it is still not available at present. However, there is good reason to assume that HIO3 is ionized with the same (or at least similar) efficiency as sulfuric acid (for which the nitrate CI-APi-TOFs are directly calibrated). Sulfuric acid is ionized by NO3- at the collision limit because it is a much stronger acid than HNO3. Compared with HNO3 iodic acid has a much stronger acidity. Furthermore, HIO3 is detected at m/z 175, whereas the strongest signal for sulfuric acid is found at m/z 160 (HNO3.HSO4- cluster), therefore both compounds are found at very similar masses in the mass spectrum and mass discrimination effects of the CI-APi-TOF should be very small. Both arguments indicate that HIO3 can be quantified with the nitrate CI-APi-TOF technique. Therefore, we think it is well-justified to use the concentrations from the nitrate CI-APi-TOF as the reference in Figure 5. However, we have added remarks to the abstract, Table 1 and to the caption of the Figures 3 and 5 that indicate that the reported values are not based on measurements with an instrument that was directly calibrated with HIO3. Furthermore, a comment was added to the Figure 3 caption that the estimated systematic uncertainty for the HIO3 values is +100%/-50% (same as reported by Sipilä et al., 2016).

Regarding the measurement of amines, we have also added remarks to the abstract, the main text, Table 1 and Figure 8, which indicate that no direct calibration was performed for DMA. Furthermore, we replaced "amines" with "dimethylamine" throughout the text and only mention in the outlook that other amines (and diamines) can be measured with the protonated water cluster CI-APi-TOF technique. Nevertheless, we think that the reported mixing ratios for DMA should be kept. DMA has a very high proton affinity (929.5 kJ mol-1), i.e., significantly higher than ammonia (853.6 kJ mol-1). Therefore, DMA should efficiently be ionized by protonated water clusters. Hanson et al. (2011) report that for their water cluster mass spectrometer both ammonia and dimethylamine are ionized with a similar efficiency. This was also reported much earlier by Sunner et al. (1988) although they did not report on the sensitivity of DMA but on other amines with a similar proton affinity. The second argument that supports our assumption that DMA can be quantified is based on the data shown in Figure 8 (Figure 9 in our revisited manuscript). The CLOUD chamber offers in principle the possibility to serve as a calibration system itself. With the known flow rates of DMA into the chamber, the chamber volume and the DMA lifetime (known from wall loss decay experiments) the DMA mixing ratio inside the chamber can be calculated (see, e.g., Simon et al., 2016). Figure 8b) (Figure 9a in our revisited manuscipt) indicates good agreement between estimated DMA (using the sensitivity from the ammonia calibration) and the calculated DMA inside the CLOUD chamber. Taking this together, plus the added caveats about the missing direct calibration (that has now been added to the manuscript) we think that the reported DMA mixing ratios should be kept.

Applying these arguments, also the title can be left unchanged. Especially when the lacking direct calibrations for DMA and HIO3 are immediately mentioned in the abstract below the title.

As said above, we have updated our text and Table 1 to clarify our arguments and to make clear that the only direct calibration was performed with ammonia. Specific changes made in the text and in the Table / Figures are listed after the corresponding comments below.

Intercomparison with the Picarro NH3 cavity ring down instrument does not evaluate the measurements correctly and ignores discussion regarding the limitations of the CI-APi-TOF approach (e.g. response times on the order of hours) or the experimental setup of the intercomparison (e.g. the Picarro connected to the exhaust of the CI-APi-TOF).

Our initial text may have been misleading here. The CI-APi-TOF doesn't have a response time in the order of hours. We just took averages over a time of hours to calculate e.g. the detection limits. The detection limits shown here wouldn't change dramatically if we splitted this 150minute period into e.g. 7 periods of 20 minutes:

Period	Calculated detection limit (pptv)	
Period 1	0.42	
Period 2	0.81	
Period 3	0.39	
Period 4	0.51	
Period 5	0.74	
Period 6	0.39	
Period 7	0.42	

The reason for taking a 150 minute instead of a 20 minute period was to get more data points and thus a better statistic to calculate the standard deviation. The initial text at table 1 ("The calculated detection limits are based on a 2.5 hour measurement at 278 K and 80% RH (averaging time of single data points: 1 minute).") may be misleading. Thus, we removed the extra information about the time scale of the measurement. Next to this, we updated our paper by a Figure showing the response time of the CI-APi-TOF between two steady states, which is shown on the following page (Section 3.3 "Response times").

Figure 7 (Figure 8 in our revised manuscript) shows an ammonia decay over several days at the CLOUD chamber. This may be misleading and interpreted as a response time of the insrument. The CLOUD chamber is a 26.1m³ vessel of stainless steel. Once, the chamber walls are saturated with ammonia, it takes hours to remove it (as also shown in the PICARRO trace). This time is not due to instrumental response times. We would like to refer to previous publications, eg Kupc et al. (2011) or Duplissy et al. (2016) that describe the CLOUD chamber in a more detailed way. We updated our text accordingly and we also added limitations of the CI-APi-TOF approach (depletion of primary ions at higher concentrations).

We agree with the referee that an intercomparison as shown in Figure 7 (Figure 8 in our revised manuscript) of our paper would be problematic provided the PICARRO would have been connected to the exhaust of the CI-Api-TOF. However, this was not the case during measurements carried out at the CLOUD chamber. Our previous text may have been misleading in this regard and has been updated accordingly (changes are shown at the specific technical comments). The PICARRO was only connected to the exhaust once (24 hour period) for an intercomparison between both instruments. The setup at the CLOUD chamber is shown in the Figure below.



3.3 Response times

The response time of the water cluster CI-APi-TOF is defined as the characteristic time needed for the instrument to react on changes in the ammonia mixing ratio. The response time takes into account two processes. These are the time needed until the instrument reacts on changes in the mixing ratio and the time needed until a steady state is established in the lines. In the following, we define the response time as the time required for the instrument to reach 95% of the new mixing ratio being injected. Figure 4 indicates the typical response times of the water cluster CI-APi-TOF during calibrations (here at 60% relative humidity). It shows a decay between two calibration steps when the injected ammonia is reduced from 9509 pptv to 6911 pptv and a rise in the signal when the ammonia mixing ratio is increased from 500 pptv to 9509 pptv. Panel a) indicates a clear difference between the time needed until the instrument reacts on the changes in the mixing ratio (red line) and the time needed until the lines reach 95% of the new steady state (black line). We expect the same behavior for a decay from 9509 to 500 pptv, however, the mixing ratios were gradually reduced during calibrations. Thus, for the gradual decays, the time needed for the lines to reach a new equilibrium is rather short. While the variation of instrumental response time is small (6 to 10 seconds for decays from 9509 to 6911 pptv and 18 to 25 seconds for a rise from 500 pptv to 9509 pptv, respectively), the time until a steady state is established in the lines varies depending on precursor conditions and relative humidity (see Section 3.8). Thus, an estimation of a response time can vary significantly. In our experiments, the response times (including both processes described above) during a rise in ammonia mixing ratio varied between 535 seconds (20% relative humidity) and 890 seconds (60% relative humidity, shown in Figure 4). For a decay of ammonia mixing ratio from 9509 to 6911 pptv the response times vary between 37 seconds and 54 seconds.



Figure 4: Response time of the water cluster CI-APi-TOF during calibrations at 60% RH. The injected ammonia level is shown by the blue line. The signal of the water cluster CI-APi-TOF is shown by the grey line (here the data are shown with a 1 second time resolution (no averaging applied)). The black line shows the response time until a steady state (panel a)) or 95% of the final measured concentration is reached (panel b)). This response time is defined as the sum of the response time of the water-cluster CI-APi-TOF (red line) and the time required until the lines reach a new steady state. See text for details.

Added in Section 3.7:

The time from 25.10 to 26.10 shows a steep increase in the PICARRO trace, while the ammonia trace derived from the water cluster CI-APi-TOF flattens out at 20 ppbv of ammonia. This indicates that the primary ions of the water cluster CI-APi-TOF are depleted at high vapor concentrations. It is important to mention that not only ammonia concentrations were elevated at this time, but also other vapor concentrations were rather high. During the CLOUD13 campaign, where a revised version of the ion source was used (see Section 3.2), the significant depletion of primary ions has been observed only at ammonia mixing ratios of 40 ppbv.

For example, there is a clear background offset in the Picarro measurements from the chamber that is not accounted for, but for which the CI-APi-TOF dataset is corrected accordingly through its independent calibration. There are other important measurement concepts that are missed in the data analysis here such as the aforementioned background offset correction, inlet and instrument surface sorption/ desorption effects impact on response times, and detection limits. See the technical comments corresponding to these sections of the manuscript below for several specific comments. It is possible that the intercomparison is technically invalid based on the experimental setup and should be removed from the manuscript, but this cannot be assessed without further data provided by the authors regarding the setup of flows to direct the chamber air to the instruments.

We agree with the referee that a correction for background is important when showing analyzed data. However, the data shown for the CI-APi-TOF are not corrected for a background either (this was done by purpose to show the low instrumental background of the CI-Api-TOF). We corrected the background of the PICARRO in a revised Figure shown below (background of water cluster CI-APi-TOF still not corrected). The PICARRO data shown in Figure 7a (Figure 8a in our revised manuscript) were smoothed using a moving average of 5 minutes in our initial Figure. We updated the Figure using the same 1-minute average as for the CI-APi-TOF here to show that the PICARRO trace is below its detection limit. We used the moving average as the PICARRO trace covers half of the Figure when the 1-minute-average is applied. We updated our Figure, where we now use the Figure shown above that includes the background substraction of the PICARRO.



Figure 8: Inter-comparison between calculated (shaded blue area) and measured ammonia mixing ratios (PICARRO: solid green line; water cluster CI-APi-TOF: solid red line) at CLOUD. The PICARRO background (~200 pptv) has been subtracted, while no background was subtracted from the water cluster CI-APi-TOF. The temperature inside the chamber is indicated by the dashed black line. The speed (% of maximum, 397 revolutions per minute) of the two fans that mix the air inside the chamber is shown by the dashed blue line. The calculated ammonia mixing ratios (based on the calculated injection of ammonia into the chamber from the MFC settings) have a wide range due to uncertainties of the ammonia loss rate in the chamber. We display the maximum calculated range assuming, for the lower limit, that the chamber walls act as a perfect sink (wall loss dominated, 25s and 100 s lifetime for fan speeds 100% and 12%, respectively) and, for the upper limit, no net uptake of NH₃ on the walls and a loss rate determined by dilution (6000 s lifetime). For higher fan speeds, the lifetime decreases due to increased turbulence and, in turn, increased wall loss rate. Relative humidity is indicated by the orange line. The water cluster CI-APi-TOF reacts rapidly to changing conditions, such as the ammonia flow into the chamber, relative humidity, temperature or fan speed. At low concentrations, the ammonia lifetime is determined by the wall loss rate (panel b and initial stages of panel a). However, at high ammonia concentrations, the walls of the CLOUD chamber progressively become conditioned and a source of ammonia, with corresponding increases in the ammonia lifetime and the time to reach new equilibria at lower ammonia flow rates (later stages of panel a).

Page 1, Line 17: Diamines are not presented in the manuscript and are mentioned here. Remove. There seem to be several issues of material that was planned for inclusion in this manuscript that have been removed, but not in all locations. The authors should revisit the manuscript with this in mind to improve clarity throughout.

We updated the text according to the comment of the referee:

The instrument selectively measures trace gases with high proton affinity such as ammonia and dimethylamine, which are important for atmospheric new particle formation and growth.

Page 1, Lines 20-21: The detection limit difference for the amines should be stated as 'at least XX times lower' here to be more specific.

We updated the text according to the comment of the referee. :

The limit of detection of the water cluster CI-APi-TOF is estimated to be ~0.5 pptv for ammonia. Although no direct calibration was performed for dimethylamine (DMA), we estimate its detection limit is at least 3 times lower.

Page 2, Line 33: 2.5 is usually a subscript

We updated the text according to the comment of the referee:

Strong reductions in PM_{2.5} mass and the associated adverse health effects could potentially be achieved by decreasing ammonia emissions (Pozzer et al., 2017).

Page 2, Line 36: Use one or the other of 'new particle formation' or 'nucleation' and add 'e.g.' before each example of the ternary and multi-component systems.

We updated the text according to the comment of the referee:

However, ammonia is not only partitioning to existing particles, but is also a key vapour driving new particle formation due to its stabilization of newly-formed clusters in ternary (sulfuric acid-water-ammonia) and multi-component (sulfuric acid-water-ammonia-highly oxygenated organic molecules) systems (Kirkby et al., 2011; Kürten et al., 2016a; Lehtipalo et al., 2018).

Page 2, Lines 40-46: This clarity of this section is not very good because these sentences are discussing too many topics, which should be separate sentences. Delete 'their' and end the sentence after the Dunne et al. reference. In line 42, replace 'show' with 'support this by observing'. On line 44 end the sentence after 'water' and start the next sentence with 'For example' instead of using 'e.g.' in-line.

We updated the text according to the comment of the referee:

In the upper troposphere, model calculations suggest that ammonia can also be important for new particle formation and early growth (Dunne et al., 2016). Recent satellite measurements support this by observing that ammonia can be present at several tens of pptv (parts per trillion by volume) level over Asia (Höpfner et al., 2016).

Page 2, Line 46: It is accurate to state 'enhance nucleation rates'. The 'even stronger' is not necessary and confuses the sentence's evaluation of relative enhancements of amines over ammonia in forming new particles.

We updated the text according to the comment of the referee:

Stronger basic compounds like amines or diamines, have been shown to enhance nucleation rates, despite their much lower atmospheric concentrations (Almeida et al., 2013; Kürten et al., 2014; Jen et al., 2016; Yao et al., 2016).

Page 2, Line 48: Why have the authors stated 'in principle confirmed' here? Perhaps the specific property assessed (e.g. thermodynamically favored formation) would be a more accurate term to place here.

The quantum chemical calculations shown in the studies cited in our article (eg Kurten et al., 2008 in ACP) confirm studies from eg Almeida et al., 2013 in nature (dimethylamine). Thus, stating that the experimental observations are confirmed by quantum chemical calculations is accurate. We deleted the "in principle" in our sentence for clarification:

The experimental measurements are confirmed by quantum chemical calculations that compare the stabilizing effects of ammonia, amines, and diamines (Kurtén et al., 2008; Elm et al., 2017; Yu et al., 2018).

Page 2, Lines 52-53: The list of references for amine mixing ratios is more comprehensively summarized in a review by Ge et al. in Atmos. Environ. (2010) which can replace this list of references[1].

We added Ge et al. to the list of references shown here. However, we disagree that the studies from Ge et al. are able to replace the references listed previously. While Ge et al. is an overall summary of mesurements of amines, studies like, e.g. from You et al (2014) or from Kürten et al (2016b) show more recent measurements using CIMS techniques at low detection limits.

It is important to note that ammonia can easily exceed several ppbv in the boundary layer, whereas amine mixing ratios are typically present at a few pptv only (Ge et al., 2011; Hanson et al., 2011; You et al., 2014; Kürten et al., 2016b; Yao et al., 2016).

Page 2, Lines 54-57: There is an attempted motivation here that CI-APi-TOF is more versatile than other analytical techniques for atmospheric samples of reduced nitrogen species. However, separation techniques are more selective than CI-APi-TOF, particularly when it comes to the detection of structural isomers. Optical absorption techniques by systems such as cavity ringdown and quantum cascade laser systems are easily as sensitive and with as high time resolution as CI-APi-TOF. The limitation of the prior methods that CI-APi-TOF overcomes should be made with greater clarity here in order to motivate the CI-APi-TOF analytical approach. It would be easiest to remove the first sentence of this paragraph and start the second sentence at 'Chemical ionisation atmospheric pressure interface mass spectrometry...'

We agree with the referee that optical absorption techniques and separation techniques like GC-MS can have a clear advantage regarding their selectivity. What we wanted to express, however, that CIMS can often measure many compounds simultaneously with high time resolution and very good sensitivity. To clarify this the sentence was modified as follows:

These measurement techniques are often specialized for the detection of only a few selected compounds, whereas chemical ionization mass spectrometry (CIMS) can often measure a suite of atmospheric trace gases simultaneously at low concentrations and high time resolution.

Page 6, Lines 167-171: This is a big stretch in justification for quantifying amines.

Strong acids detected by CIMS do not have the same response factors per mixing ratio detected and this is well reported in the literature even though their reaction rates would be predicted to be the same for a given ionisation technique (e.g. 2-16 counts per pptv for strong acids by proton exchange in Roberts et al. in Atmos. Meas. Tech. (2010)) [2]. This detail should be clarified here along with the potential outcome of the assumption for amines likely being up to a factor of 10 error in quantitation

as a worstcase outcome. It is likely better to report in this work the measurement of amines only in 'ncps' and to do a ballpark estimation of the mixing ratios in the discussion.

In principle we agree that thermodynamic data alone should not be used to justify the assumption of using the same calibration factor for ammonia and DMA. However, the cited study by Hanson et al. (2011) reports on the calibration with both substances and supports our assumption. Also, the study by Sunner et al. (1988) reports similar data. They studied the sensitivity of ammonia and different amines towards reactions with protonated water and found found collision limited ionization for both substances. To further support our assumption the study by Sunner et al. (1988) was added to the references and cited in Section 2.2:

When mixing ratios for dimethylamine are presented, the same calibration factor is used. This approach can introduce uncertainty as the proton affinity, as well as transmission efficiency differ for dimethylamine compared to ammonia. However, previous studies showed that the ionization efficiency from protonated water clusters is collision-limited for both compounds, ammonia and dimethylamine (Sunner et al., 1988; Hanson et al., 2011). The applicability of this approach is discussed in Section 3.9; it is estimated that the mixing ratios for dimethylamine are correct within a factor of \sim 3.5.

Page 6, Line 186: A sentence should not begin with an acronym. Rephrase.

We updated the text according to the comment of the referee:

The ammonia was taken from a gas bottle containing an NH_3 mixing ratio, *B*, of 100 ppmv diluted in pure nitrogen (Air Liquide, ±5% uncertainty for the certified NH_3 mixing ratio) that is diluted in two steps, where MFCs (shown as M_n in Figure 1a) are used to obtain different set points for the volume mixing ratio (Figure 1a). During the second dilution step the mixture from the first dilution is injected into the center of the main sample flow (flow rate, Q_{sample}).

Page 7, Lines 207-209: This is quite the string of assumptions and underscores the major issue with claimed quantitation in this work. The detection of HIO3 is, at absolute best, qualitative and units should not be assigned to the measurement in pptv, but 'ncps'.

We agree with the referee that this assumption causes uncertainty. However, we would like to refer to our previous argumentation shown on page 1 (reply to major comment 1). We changed our text in this section accordingly and added the following sentences for clarification (added to line 216-220):

This assumption introduces uncertainty when estimating the detection limit of HIO₃. However, as the reaction of sulfuric acid with nitrate ions is at the kinetic limit, the detection limits shown here based on this assumption can be seen as lower limits. Unfortunately, there is currently no direct calibration technique established for iodic acid in the gas phase. Thus, the applied assumption in the present study was also used in a previous study for deriving gas phase concentrations of iodic acid (Sipilä et al., 2016).

Page 7, Lines 209-212: This intercomparison is shown in Figure 5, but the axis labels do not communicate this. They should both be reported as normalized counts since the NO3- CI-APi-TOF signal is scaled on the H2SO4 response, which does not yield a quantitative calibration factor for HIO3, but only a relative signal.

We thank the referee for this comment. We want to refer to our response to the comments related to the Figures below.

Page 8, Lines 223-226: The authors state that the instrument was independently calibrated. This means that they have data to calculate the detection limit of the Picarro NH3 cavity ringdown system and it should be done here instead of stating the value given from the datasheet.

We thank the referee for this suggestion. However, as the PICARRO is calibrated for higher ammonia mixing ratios by using the permeation tube, a direct comparison of the calibration curves wouldn't make sense. Here we show the calibration curve of the PICARRO from CLOUD 13:



The calculated instrumental background is at 88.9 pptv (during the same 150 minute time as shown for the water cluster CI-APi-TOF). The calculated detection limit during this time is at 366.2 pptv. We added the detection limit to section 2.3 (PICARRO).

The time interval for one measurement of the PICARRO is 5 seconds for which a lower detection limit of 200 pptv is reported (PICARRO Inc., USA; Martin et al., 2016). By using the same method (at the same time period) as shown for the Water Cluster CI-Api-TOF (see section 3.5), we derive a detection limit of 366.2 pptv for the PICARRO unit used in this study.

Page 8, Line 237: The first name of the author should not be given here.

We thank the referee for recognizing this mistake. We corrected this in our new version.

For the analysis of the spectra, the software TOFWARE is used that allows analyzing high resolution spectra (Stark et al., 2015; Cubison and Jimenez, 2015; Timonen et al., 2016).

Page 8, Lines 248-251: This comparison of the stability of reagent ion should be made by calculating the change in the calibration slope (ncps vs NH3 mixing ratio) between high (1-10 ppbv) and low (<1 ppbv) ranges to reach the conclusion that the sensitivity is consistent across the full range of experimental mixing ratios used in CLOUD. The authors also state 'sufficient precision' here without defining what the value they use is. The numeric value should be given. It would also be useful here for the authors to comment on the likelihood that this calibration response will hold up under ambient observations where other atmospheric components will compete for H+ transfer.

As the calibration setup with the MFCs shown in our Figure 1 limits the range of mixing ratios, we can compare the slopes from 500pptv to 2500pptv (low) with the slope from 4200pptv to 9509pptv (high). As shown in our Figure below, the deviation between high and low range is at 4.35%, where the high slope is m[~] 6.9e-6 and the low slope is m[~]6.6e-6.

The second part of the comment ("The authors also state 'sufficient precision' here without defining what the value they use is. The numeric value should be given") refers to potential depletion of the reagent ions at high ambient concentrations of compounds with high proton affinity other than ammonia. Of course this can potentially lead to a change in the sensitivity, which could be accounted for by the addition of an internal calibration standard. A remark regarding this effect is included in Section 3.7 (lines 439 to 444):

The time from 25.10 to 26.10 shows a steep increase in the PICARRO trace, while the ammonia trace derived from the water cluster CI-APi-TOF flattens out at ~20 ppbv of ammonia. This indicates that the primary ions of the water cluster CI-APi-TOF are depleted at high vapor concentrations. It is important to mention that not only ammonia concentrations were elevated at this time, but also other vapor concentrations were rather high. During the CLOUD13 campaign, where a revised version of the ion source was used (see Section 3.2), the significant depletion of primary ions has been observed only at ammonia mixing ratios of ~40 ppbv.



Page 9, Lines 259-261: Here is the HIO3 intercomparison again. The error in the VMR is estimated based on an applied scalar, which is effectively a guess. It is more transparent, and valuable, to report

that the two independent ionisation schemes yields a strong linear response, supporting the sensitive detection of HIO3 using H3O+ chemistry. Extending this further into estimated mixing ratios is not justified.

We agree with the referee that this assumption causes uncertainty. We would like to refer to our previous argumentation shown on page 1 (reply to major comment 1), as well as to the changes made throughout the manuscript (previous reply to major comment 1). In this section, we also state that the assumption can introduce uncertainties up to a factor of 2. As there is no established technique to calibrate iodic acid in the gas phase, this assumption has also been made in a previous publication, e.g., Sipilä et al. (2016).

Also, for these calibrations, the experiments shown in the remainder of the manuscript are not collecting 20 minute time-resolution data. Averaging at timescales more relevant to the measurement timescale would give a more accurate estimate of calibration response and quantitation accuracy, so long as 20-30 data points are pooled for each calibration mixing ratio.

We agree with the referee that longer timescales would be advantageous. However, when creating these data points, we must adapt to the steady-state periods at the CLOUD experiment, which cannot be longer depending on the experiment (especially during the studies of iodic acid chemistry).

Page 9, Lines 263-264: The resulting difference in the forced and unforced slopes should be reported with the numeric value of the percent difference.

We updated the text according to the comment of the referee:

The fit is forced through the origin; however, even when the fit is not constrained, the resulting slope is essentially the same (the results for the slopes/sensitivities differ by 1.35%).

Page 9, Lines 265-267: 'concentration steps' should be 'calibration mixing ratios' and 'confidence bounds (95 % confidence intervals)' should be '95 % confidence intervals'.

We updated the text according to the comment of the referee. As the calculation of the mixing ratios is shown in this chapter, we use "mixing ratios" instead of "calibration mixing ratios" to stay consistent:

Figure 3 shows that all measured mixing ratios lie in the area of the confidence intervals (95% confidence intervals) and thus the linear model describes the dependency very well.

Page 9, Lines 272-274: The response time of the CI-APi-TOF to a stable signal following the steppeddown changes in NH3 VMR should be provided here explicitly. The discussion following this section states that the instrument and line surfaces contribute to background signals observed. Here, the 'diffusion of ammonia from the capillary into the sampling line' should be clarified to indicate that the background observed also has contributions from all surfaces in the calibration system, the instrument inlet, and the instrument walls.

We added a section 3.3 that discusses response times as already mentioned in a comment previously. Possible wall effects are discussed in this section and in Section 3.8 and are also shown in our new Figure 4 (as shown previously). Regarding the background due the diffusion from the capillary it can be said that this exactly describes the difficulty in determining representative background values. Only after sufficiently long flushing times with clean air, with the calibration capillary removed, representative instrumental background values can be determined. This is discussed in Section 3.5.

Pages 9-10, Lines 282-286: The changes in calibration factor should be explicitly given. Are they a factor of 2 different or a factor of 5? This is a measurement technique manuscript and it is VERY important to highlight how small changes in instrument operation and setup can affect the quality of the measurements. Was the CI-APi-TOF re-calibrated with these slight changes? How was the calibration factor derived for these CLOUD experiments? Did the response time of the inlet change? All of this information has high value here.

As there are too many factors that have been changed in parallel between these two campaigns, a direct comparison is not very meaning in our opinion. The changes between CLOUD12 and CLOUD13 included:

- The sampling flow rate was 5.6 slm during CLOUD12, while it was 19.5 slm during CLOUD13.
- The voltages inside the mass spectrometer were different between the campaigns as shown below. Thus, the transmission efficiency inside the mass spectrometer changed between the campaigns, as well as the response time.
- The distance between injection of primary ions and pinhole of mass spectrometer was different, which affects the ion-molecule reaction time.

This is due to a different ion source (designed for a 0.5" sampling line in CLOUD12 compared with a 1" line in CLOUD13), a different sample flow rate and different tuning of the CI-APi-TOF.

Page 10, Line 294: What does 'including all components' mean?

Including all components means in this case the voltages on the ion source, the voltages in the APi section and in the time of flight region. We updated our text for clarification:

In addition, the detection efficiency as function of the ion mass can vary depending on the voltages applied to the ion source and the APi-section, as well as the time of flight region of the mass spectrometer. Thus, the mass spectrometer does not have a constant detection efficiency over the full mass range (Heinritzi et al., 2016).

Page 10, Lines 301-306: This section of discussion is unclear and difficult to follow.

Rewrite for clarity since looking at Figure 7, there seems to be disagreement with what is stated here regarding 15 % and 3 % change in signal. Perhaps there is a way to depict this more clearly in a new figure?

The drop in ammonia shown in Figure 7 (between 30.10. and 31.10.) coinciding with the temperature decrease from 298 to 278 K can be attributed to a change in the ammonia wall desorption rate when no ammonia is actively injected into the chamber. During the previous experiments (until 25.20.) very large amounts of ammonia were injected, thus the walls became saturated with ammonia. The temperature decrease led to a sudden decrease of the wall desorption rate and therefore the measured NH₃ dropped significantly. However, this drop is not related to a change in the sensitivity of the water cluster CI-APi-TOF. Due to the change in the ammonia wall loss and desorption rate with the chamber temperature, a potential effect of temperature on the sensitivity cannot easily be tested. We tried this by measuring constant ammonia from the calibration system, while the instrument is connected to the chamber during a temperature transition. No clear trend was observable during this test. We agree with the referee that this section is not very clearly written. Although our test was disturbed by an initial instrumental drift, we concluded that the temperature dependency is much smaller compared with the effect of relative humidity. Therefore we replaced the section mentioned by the referee with the following text:

The effect of temperature on the sensitivity could not be tested during a dedicated calibration experiment as our calibration setup is not temperature-controlled. However, during a transition from high to low temperature in the CLOUD chamber and constant ammonia injection, no significant change in the measured ammonia was observed, which indicates a weak influence of temperature.

Page 10, Lines 308-310: Rewrite this sentence, removing all information in brackets and either placing it explicitly in the sentence or removing it. Also, should the reference to Figure 4 here actually be to Figure 5?

We rewrote the sentence from "While NH_4^+ (without a water molecule) is the dominant signal for ammonia, $H_4IO_4^+$ (H₂O·HIO₃H⁺ or HIO₃·H₃O⁺) yields the highest signal for iodic acid (higher than HIO_3H^+)" to:

While NH_4^+ , without a water molecule, is the dominant signal for ammonia, $H_4IO_4^+$, which is $H_2O \cdot HIO_3H^+$ or $HIO_3 \cdot H_3O^+$, yields the highest signal for iodic acid.

The reference towards Figure 4 (now Figure 5) is correct.

Page 11, Section 3.4: Detection limit calculations require a stable background signal when the instrument is known to be sampling a negative control. Quite a bit of this section discusses contamination issues, which should be made into its own section and kept separate from detection limits.

As a drifting background, e.g. due to contamination issues, can have an influence on the standard deviation of the measurement, this discussion can be important when evaluating detection limits. We changed the title of this Section to "Detection limits and instrumental backgrounds".

Page 11, Lines 326-327: These facts should be moved to the calibration section as an addition to the statement about the capillary NH3 contamination since all of these components can be causing the described time lag in the calibrations and the observations.

As the calibration setup is independent from the CLOUD chamber measurements, the capillary from the NH3 calibration setup was not connected to the instrument during this time, which decreases the instrumental background compared to the situation with the calibration setup connected. For this reason, these arguments are well placed in the discussion of Section 3.4 (Section 3.5 in our revised manuscript).

Page 11, Lines 334-335: This is a sentence fragment and does not belong in the part of the discussion. It should be moved to the discussion of the RH-dependent sensitivity along with context driven by the data presented in Figure 4.

We agree that this sentence belongs to the CLOUD chamber discussion as this effect is especially observed on the chamber walls due to the huge volume of the chamber. We moved this sentence to Section 3.7 (CLOUD chamber characterization) and discuss it for clarification:

The influence of relative humidity on the gas phase concentration of ammonia is shown (time from 29.10. to 30.10.). In addition to the change in sensitivity with relative humidity shown for the water cluster CI-APi-TOF (Section 3.4), a change in humidity can lead to an increased ammonia mixing ratio in the gas phase. This is due to the fact that water molecules can displace adsorbed ammonia on surfaces (Vaittinen et al., 2014). This effect can be pronounced when the chamber walls have been conditioned with high ammonia concentrations. It is important to note that the instrument was

characterized for humidity dependency during the following CLOUD13 campaign. While changes in sensitivity with relative humidity were taken into account during CLOUD13, this was not the case during CLOUD12. The observed increase in mixing ratios at this time is a combination of a change in sensitivity of the instrument and an increase in the gas phase concentration of ammonia due to re-evaporation from the wall of the CLOUD chamber. Here, the PICARRO trace can provide insight into the magnitude of both effects indicating that the re-evaporation from the chamber walls dominates over the change in sensitivity.

Page 11, Lines 336-340: Giving approximated detection limits, along with the assumptions being made for HIO3 and the amines in the discussion is alright, so long as it is very clear that these are initial guesses. Where these numbers absolutely do not belong is in Table 1, which should be removed from the manuscript. It is highly likely that these numbers will be used out of context and with disregard for the assumptions made here for the estimation (e.g. not everyone will have a NO3- CI-APi-TOF calibrated for H2SO4 to scale their measurement against for HIO3, along with the assumption that the sensitivity is equal on top of that). The authors need to be clear throughout this work that the estimated mixing ratios are consistent with expectations, BUT that a calibration with known quantities of the target analytes should be performed by anyone wanting to make quantitative measurements of these compounds. Again, any figures showing mixing ratios or amines or HIO3 should be converted back to units of ncps since these estimates are based on tenuous assumptions. Keeping some mention of the potential detection limits in the discussion is alright as it motivates further work in using this instrumental platform for guantitative analysis. For this reason, the title of the manuscript needs to be revised to reflect what species can be quantified and which can only be detected. Without calibration from a primary standard, HIO3 and amines are only detected in this work, while NH3 is quantified and this should be kept clear.

We agree that it should be made very clear that the numbers provided in the table and in the figures are subject to some uncertainty because no direct calibration was applied. However, as outlined in our reply the first major comment, we still would like to keep the numbers as there are good arguments, in our opinion, to keep them. In the revised manuscript we have, however, made very clear that uncertainties exist and that the direct calibrations are lacking. One specific change, relevant for this comment, is the addition of remarks to the numbers provided for DMA and iodic acid in Table 1. An updated version of Table 1, including its caption, is provided in the following:

Table 1. Estimated limits of detection (LOD) for some compounds with high proton affinity, and for iodic acid, measured with the water cluster CI-APi-TOF. The LOD is derived by background measurements at the CLOUD chamber, where LOD = $3 \cdot \sigma$ (You et al., 2014). σ is defined as the standard deviation of the background signal. The detection limits are based on a measurement at 278 K and 80% RH (1 minute averaging time). The measured instrumental background mixing ratios (mean values) during this time period are also indicated.

Detected compound	LOD (pptv)	Instrumental	Measured	m/z
		background (pptv)	values (Th)	
NH_3 (ammonia)	0.5 ± 0.05	3.73 ± 0.35	18.0338 36.0444 ((H ₂	(NH4 ⁺); O)NH4 ⁺)
(CH ₃)₂NH (dimethylamine)*	0.047*	0.058*	46.0651 ((CH	3) 2NH2 ⁺)

0.007**

< LOD**

176.9043 ((HIO₃)H⁺); 194.9149 ((HIO₃)H₃O⁺)

- *Amine mixing ratios are estimated using the same calibration factor derived for ammonia. This can cause uncertainties. The applicability of this assumption is discussed in Section 3.9.
- **Iodic acid mixing ratios are derived from an inter-comparison with a nitrate CI-APi-TOF, which evaluates HIO₃ based on a calibration factor derived for sulfuric acid. This assumption can lead to uncertainties but is necessary because no direct calibration method exists for such low gas phase HIO₃ concentrations.

Page 11, Lines 341-347: This part of the discussion is quite unclear. 'E.g.' should be 'For example,'. What is the peak with the highest count rate for the amines and why does this avoid interference for the mentioned fragments? This is not adequately explained.

As shown in Table 1, the peak with the highest count rate is $(CH_3)_2NH_2^+$ for dimethylamine. Interference with other masses strongly depends on the resolution of the mass spectrometer. As the water cluster CI-APi-TOF was mainly used during experiments on the CLOUD chamber, where either biogenic or urban regions were simulated, there were more compounds injected than just ammonia and/or DMA. Thus, compounds interfering can also be reaction products, e.g., from reaction of alpha pinene or o-cresol with ozone. On the integer mass of $(CH_3)_2NH_3O^+$ (m/z 63) we observe, e.g., interference with at least 5 other species (e.g., a compound tentatively assigned to C₅H₄⁺).

In the final two sentences, the authors undermine their assumptions regarding the detection of amines identically as they detect ammonia, stating that they omit the use of larger product ions, which will skew the sensitivity of detection. Then, this bias is dismissed as negligible because the water cluster signals are smaller for the bases than ammonia. Clearly, this indicates different reagent ion chemistry and product distribution for the amines relative to ammonia, which is inconsistent with assumption that they are the same and that the NH3 calibration factor can be applied to the calculation of amine mixing ratios and detection limits. This is strong evidence against reporting mixing ratios and detection limits for C2-amines in this work. The strength of this paper lies in the quantitative detection of NH3 and show focus on that data, with discussion of these additional species kept to a minimum.

We want to refer to our manuscript, where we state that $(CH_3)_2NH_2^+ > (CH_3)_2NH_3O^+$ which is also the case for the NH3 chemistry. The studies from Sunner (1988) and Hanson et al. (2011) indicate that the ionisation mechanism is comparable to the NH₃ case. However, we agree that there is an uncertainty in our assumption of scaling the calibration factor from ammonia to dimethylamine. We discussed the applicability of our assumption in a more detailed way in Section 3.9 and refer here to this discussion. Additionally, the following was added to Line 367:

The applicability of the assumption (using the calibration constant derived for ammonia for dimethylamine) is discussed in Section 3.9.

Page 12, Line 361: 'Thus, the sensitivity...' this sentence is redundant with the preceding discussion and can be removed. This paragraph and the one preceding are nice guides to some of the technical considerations for measuring these target analytes and the controls on signal/noise for each of the

ions. The discussion of LOD in these two paragraphs for amines and iodic acid should be changed to discuss signal-to-noise of the instrument.

According to our replies shown above, we changed the discussion in chapter 3.5 by adding "calculated detection limits" in front of the values discussed for ammonia, while adding "estimated" in front of the values discussed for amines and iodic acid. Together with the note placed below the table (shown above), the reader should be aware that the use of the estimated detection limits creates a degree of uncertainty. As suggested by the referee, we removed the sentence in Line 361.

We updated a sentence in line 362:

Besides the **calculated** values for ammonia, Table 1 lists the **estimated** backgrounds and LODs for dimethylamine and iodic acid.

We added "estimated" to a sentence in Line 371:

The instrumental background for $\rm NH_3$ is higher than the estimated backgrounds for the other compounds shown in Table 1.

Page 12, Line 372: 'up to the tetramer (...' could easily be replaced with 'molecules containing 1-4 iodine atoms' and be much more accurate. This should be changed throughout the manuscript, including Figure 6. Calling these species monomers, dimers, etc suggests that the rest of the atoms are part of a fundamental subunit one would typically find in describing a polymer, which does not seem to be the case here?

If there are fundamental subunits for these I-containing species and the terminology of monomers, dimers, etc holds, then this should be more clearly written to specify the atoms found in remainder of the subunit.

We agree with the referee that 'molecules containing 1-4 iodine atoms' is more accurate than 'monomers, ...tetramers'. We adapted our manuscript accordingly, as well as Figure 6 (as shown below in the discussion related to the figures).

During this time period, we observed compounds containing up to 4 iodine atoms.

Page 13, Line 395: The accuracy of the chamber concentrations being much less certain than those from the measurements of NH3 by the CI-APi-TOF should be used earlier on to motivate the need for this instrument being characterized fully.

The instrument shows the correct mixing ratios based on an independent calibration. The chamber concentrations can spread over a huge range and are shown here to give an overview on the response time of the instrument. In addition, it can be estimated how quickly the instrument reacts, e. g., on injections of ammonia or on changes in fan speed. The chamber is suitable for the determination of instrumental backgrounds and detection limits due to the ultra-clean conditions, provided no ammonia was added to the chamber. Measurements in ambient air can also result in large potential mixing ratios, depending on source and transport terms.

Page 13, Lines 400-401: Could this difference in response time during NH3 mixing ratio increases be due to inlet location differences between the instruments inside the chamber? Are the different responses due to concentration gradients as NH3 mixes throughout the chamber? Or are there very different inlet line lengths? The intercomparison description on Page 7, Lines 219-223 are insufficient to determine if these strumental measurements are even capable of being properly compared. The authors suggest that in 'some intercomparison measurements' that the Picarro was hooked up to the

exhaust of the CI-APi-TOF instead of sharing the same sampling line. Surely there are huge losses of NH3 inside the CI-APi-TOF such that it is unreasonable to expect quantitative transfer of NH3 out of the instrument exhaust? This type of setup would dramatically bias an intercomparison and may invalidate its applicability altogether in this work. The authors should re-evaluate whether the experimental setup was sufficiently robust to expect NH3 to be transmitted to both instruments in a manner that does not compromise the sample composition. If the conclusion is that this is not possible, then this section of the manuscript needs to be removed as it is likely invalid.

As shown in our reply to major comment 2 above, both instruments were connected to the chamber directly with their individual sampling lines. The PICARRO was connected to the exhaust of the water cluster CI-APi-TOF only during a calibration measurement that was carried out during a ~24 hour period. As stated in our text, the change in response time is also due to higher sampling line losses that are, e. g., caused by different sampling flow rates: The water cluster CI-APi-TOF samples air with flow rates of ~20 slm (no core sampling applied), while the PICARRO samples with <1 slm. This is also mentioned in section 2.4 (PICARRO). During all measurements, the flow towards the PICARRO was increased using core sampling (5slm). The connection to the exhaust of the water cluster CI-APi-TOF was arranged directly behind the ion source, where the aim was to increase the flow rate towards the PICARRO to 20 slm to reduce the response time. As we didn't see a sufficient change, this setup was not used during measurements carried out on the CLOUD chamber. During the time period shown at Figure 7 (Figure 8 in our revised manuscript), both instruments were connected to the CLOUD chamber independently, where both instruments were sampling using the flow rates mentioned above. We realized that it leads to confusion when we report these tests without further discussion. As this test is not relevant for our manuscript and for the data shown in this study, we removed the sentence from our manuscript. Next to this, we replaced the sentence in line 401 (previous draft; line 419 in the updated manuscript):

This is due to the much higher LOD of the PICARRO and its much higher sampling line losses that require a considerably longer time for equilibration.

By the following sentence:

This increased response time can be explained by a combination of the longer sampling line (~1.8 m compared to 1.3 m for the water cluster CI-APi-TOF), the lower flow rate (~ 1 slm with a core sampling of 5 slm compared to ~ 20 slm for the water cluster CI-APi-TOF) and the higher detection limit of the PICARRO.

Also, why was a background correction not applied to the Picarro data based on having it sample zero air? The Picarro gas analyzers typically arrive from the factory with a calibration factor and offset applied and can be much more sensitive than the operators' specifications sheets. Given that an independent calibration was done using a permeation device and, presumably an overflow with zero air, the instrument detection limits should have been possible to independently calculate, along with any systematic offset in the instrument response, which could be corrected where this is identified as a factory offset. The calibration of this instrument with external NH3 would have allowed the LOD for the instrument to be determined the same was as it was for the CI-APi-TOF (i.e. using S/N=3 from the blank observations and comparing that to the background measurement). Making the intercomparison with more consistent treatment of the calibrations performed on both instruments would strengthen the discussion throughout this portion of the manuscript.

We evaluated the PICARRO detection limit by using the same background measurements from the CLOUD chamber used for the water cluster CI-APi-TOF, based on the PICARRO calibrations (as shown in a previous comment above). As shown on our reply to major comment 2, there was no instrumental

background subtracted for both instruments to show the low instrumental backgrounds of the water cluster CI-APi-TOF. In our revised manuscript, the background of the PICARRO has been subtracted in Figure 8.

Page 14, Line 417: The material used for the sampling line is not discussed. Part of the discussion from literature line losses (Line 426) talks about stainless steel, but this would be atypical for an NH3 sampling inlet. The authors need to clarify this material so the context can be properly evaluated. Given the incredibly long decay time constants from the chamber (on the order of days according to Figure 7?), which are also not presented for the instrument from the calibrations, it is hard to determine the relative order of the effects here. See comments on the calibration figures for some improvements to the manuscript with additional figures that could be made.

We would like to refer to Section 2.2 of our manuscript ("water cluster CI APi-TOF"): "The inlet of the water cluster CI-APi-TOF consists of a stainless steel tube with 1 inch outer diameter that is housed by a stainless steel body that also holds the ion source and the counter electrode; additional parts made of PEEK insulate the electrodes." The reason for using stainless steel instead of e.g. glass is that the CLOUD chamber is- next to low contamination studies- also designed for studying effects of ions on atmospheric physics and chemistry. Thus, stainless steel is needed when voltages are applied to the chamber (see Duplissy et al., 2016). As mentioned in our comments above, we added a new Section (3.3) discussing response times during calibrations (together with a Figure (4)). The decays shown for the chamber measurements (that are in the order of days) are discussed in Section 3.7 (CLOUD chamber characterization). These long decays are also due to the huge surface of the CLOUD chamber (26.1 m³ volume), where ammonia desorbs from the walls over a long time.We updated a sentence in Line 455 (updated manuscript):

At CLOUD, the sampling line is made of stainless steel and is kept as short as possible. The total length is still 1.3 m because the sampling line protrudes into the chamber over a distance of 0.5 m in order to sample air from the well-mixed center region of the chamber.

Page 14, Lines 426-434: The water effects on line losses seem to be ignoring an established effect from the literature. Water on inlet surfaces can allow weak acids and bases to dissociate into their conjugate compounds on the surface, increasing the partitioning to the surface. Adsorption on surface sites alone is too simple of an interpretation. Further to this, data is not presented that decouples the effect of the inlet lines from the desorption of NH3 from the CLOUD chamber walls. The value for inlet desorption is only described as 'it can take a long time'. It would be nice to see some form of time constant determined for the inlet to return to initial conditions and a reflection on whether this waiting period is reasonable compared to replacing the lines between experiments.

We thank the referee for pointing out the additional effect of wall uptake followed by dissociation. We will include a remark regarding this effect in the revised manuscript. Added to line 460:

Water on surfaces can affect the uptake or release of ammonia. Vaittinen et al. (2014) showed that increased humidity can displace ammonia from surfaces. Additionally, water on surfaces can allow weak acids and bases to dissociate into their conjugate compounds on the surface, thereby affecting the partitioning to the surface (Coluccia et al., 1987).

Furthermore, we agree that a remark should be added that it is currently not possible to distinguish sampling line effects from chamber wall effects. Added to line 470:

At CLOUD, the sampling lines are attached to the chamber and cannot easily be removed during the experiments. Thus, it is not possible to quantitatively distinguish between interactions with the surface of the sampling line and the surface of the CLOUD chamber.

This effect should clearly be further investigated in the future as it can have an important effect on the measurements. Replacing the sampling lines is, however, not an option during the CLOUD chamber runs as the sampling lines cannot easily be removed from the chamber. With the inlet line being attached to the chamber during the runs, desorption of ammonia from the inlet lines cannot easily be decoupled from desorption from the chamber walls. Thus, a time constant for inlet line desorption would be associated with huge uncertainties and variations depending on the chamber conditions.

Page 14, Line 441: All of Section 3.8 needs to be rewritten in terms of signal instead of mixing ratios, except where estimates are discussed. Figures referred to in this section should all report signal using units of ncps since a direct calibration has not been performed.

The comments on how the estimated calibration factor and the observations in the chamber are consistent within the factor of 10-100 uncertainty for DMA put in the chamber can be retained to demonstrate that the assumptions for the CI-APi-TOF calibration factor are also likely within this same factor of 10-100. In particular, the line of reasoning on Page 15 from Lines 461-464 is based on biased expectations where an arbitrary correction estimated at a value of 2 would bring the observations 'into even better agreement' with the expected mixing ratios, but this does not have much factual basis since the concentrations shown in Figure 8 span an order of magnitude depending on wall losses and chamber dilution. Perhaps stating that the observations fall within the expected range of values is sufficient for this section and the speculation on correction factors can be removed since a direct calibration of DMA was not actually performed.

In our replies to previous comments we have argued that dimethylamine mixing ratios should be reported instead of ncps.

However, we agree with the referee that the discussion regarding Figure 9 and the approach of deriving an uncertainty for the dimethylamine measurements should be revised.

We have implemented the following modifications to the data shown in Figure 9:

- (1) We know from a previous study regarding dimethylamine measurements inside the CLOUD chamber (Simon et al., 2016) that the life time of dimethylamine is dominated by wall loss for the low mixing ratios relevant for this study. The wall loss life time is 432 s for a fan speed of 12%. From previous chamber measurements, we know that the wall loss life time decreases by a factor of 4 when the fan speed is increased from 12% to 100%. Thus, we used 108 s for a fan speed of 100%. Therefore, the shaded area (which previously included the dilution life time) has been replaced with a line that takes only the wall loss life time into account (gray line).
- (2) Since we know from Simon et al. (2016) and from the CLOUD measurements of the current study that dimethylamine sticks to the chamber walls, a wall loss correction is required for the mixing ratios measured with the water cluster CI-APi-TOF, a wall loss correction factor of 1.96 was therefore applied to the data, which is based on a flow rate of 18.5 slm, a diffusivity of $0.1 \text{ cm}^2 \text{ s}^{-1}$ and a sampling line length of 1.3 m.

After implementing the described modifications, the mean ratio between measured and calculated/expected DMA is 3.48. We take this value as the uncertainty of the dimethylamine measurments.

We changed this Section (Section 3.9 in our revised manuscript), where the focus is now on the discussion regarding the uncertainty of our approach (scaling of the calibration factor from ammonia to dimethylamine). As the chamber background shown in this chapter is based on the estimated mixing ratios, we now show the comparison between the wall loss lifetime and the estimated mixing ratios in panel a). This Figure compares our approach directly with calculated mixing ratios, thus, it is important to keep the unit mixing ratio, where we show a range (factor +3.48/-3.48) now in our time series in panel b).

As mentioned in Section 3.5 and shown in Table 1, the same calibration factor derived for ammonia was used to estimate the mixing ratio of dimethylamine. We caution, that this assumption can lead to uncertainties as the sensitivity of the measurement is expected to depend on the proton affinity of the measured substance (Hanson et al., 2011). To estimate the validity of this assumption, we compared the mixing ratios measured with the water cluster CI-APi-TOF with the calculated mixing ratios for a period when dimethylamine was actively injected into the CLOUD chamber. A chamber characterization for dimethylamine was already conducted by Simon et al. (2016), where the wall loss lifetime was determined as 432s for condtions where the chamber walls acted as a perfect sink (12% fan speed). Additionally, as discussed in Section 3.7, we use a lifetime of 108s at 100% fan speed (change in a factor of 4 when the fan speed is changed from 12% to 100%). The dilution life time during CLOUD13 is 6000 s and represents the maximum possible life time when wall loss would be negligible. Thus, the wall loss lifetime used in this study gives a lower limit for dimethylamine mixing ratios in the CLOUD chamber. Figure 9a shows the time period when dimethylamine was added. Since it takes a certain time until the stainless steel pipes of the gas dilution system are saturated with dimethylamine there is a short time delay between the switching of a valve that allows dimethylamine to enter the chamber and the rise in the measured dimethylamine mixing ratio. Once the lines are conditioned and the dimethylamine is homogenously mixed into the chamber, the measured and estimated mixing ratios are generally in good agreement with each other when the wall loss life time is used to estimate the mixing ratios. Fluctuations in the measured mixing ratio can be explained by changes in the fan speed. To estimate the consistency of the approach of scaling the calibration factor derived for ammonia to estimate dimethylamine mixing ratios, we use the ratio between the mixing ratio calculated for the Water Cluster CI-APi-TOF and the calculated mixing ratios based on the wall loss lifetime for the CLOUD chamber. For these measurements, we estimated a wall loss rate in the sampling lines of ~1.96 for dimethylamine, where a diffusivity of 0.1 cm²s⁻¹ was used (Freshour et al., 2014; Simon et al., 2016). The mean deviation between the estimated dimethylamine mixing ratio and the calculated mixing ratio is 3.48 indicating that the approach of scaling the calibration factor derived for ammonia introduces uncertainties within a factor of ~3.5. The deviations at the end of the time series shown in Figure 9a are caused by nucleation experiments in which high concentrations of other vapors are used. During these stages a significant uptake of dimethylamine on particles can explain the discrepancy between measured and expected dimethylamine. Figure 9b shows a measurement of the chamber background for dimethylamine carried out during CLOUD13 over a time period of 5 days. The mean instrumental background for the time period shown in Figure 9b is ~0.14 pptv (for a temperature of 278 to 290 K and a relative humidity between ~50 and 60 %). The background values shown here are close to the background values obtained for 80% RH and 278 K (see Table 1). The observed variations are in a range of ~0.1 to 0.3 pptv provided that the measurement is not interrupted, e.g., due to the replenishment of the water source that humidifies the flow for generating the reagent ions (which explains the first drop of the background measurement in Figure 9b). The estimated detection limits shown here are below or at similar detection limits reported in previous publications (You et al., 2014; Simon et al., 2016).



Figure 9: Dimethylamine mixing ratios (magenta line) during the CLOUD13 experiment. The dashed black line shows the temperature inside the CLOUD chamber. The dashed blue line shows the fan speed. Panel a) shows the dimethylamine signal during active injection into the chamber. The grey line indicates the dimethylamine mixing ratio in the chamber calculated from the MFC settings and the wall loss lifetime. The upper limit for the uncertainty in the dimethylamine mixing ratio is a factor of ~3.5 (see text for details). Panel b) shows a measurement of background dimethylamine in the chamber over a period of 5 days, when there was zero dimethylamine flow. We consider this to be due to instrumental background and not to an actual dimethylamine background in the chamber. The thin red lines show the possible range of dimethylamine based on the scaled calibration factor (factor 3.48, 95% CL). The thick magenta line indicates a moving average of the dimethylamine background measurement. The water source has been replenished during the period shown (green line). The mean instrumental background of dimethylamine over this period is ~0.14 pptv.

*Note that the dimethylamine mixing ratio is determined with the calibration factor for ammonia.

Page 15, Line 473: The specific analytes discussed are ammonia, dimethylamine, and iodic acid and this should be specified here. Depending on the actual chemical species comprising the remaining iodine oxides (or up to tetramers of iodic acid if this is the case), the iodine species detected can be made more chemically specific in the conclusion. Based on Table 2, iodine oxides seems to me to be the best term, and it could be used effectively throughout the manuscript.

We adjusted this section according to the comment from the referee:

The present study demonstrates the successful application of a water cluster CI-APi-TOF during controlled chamber experiments for ammonia, dimethylamine and iodic acid measurements. During the experiments involving iodide, neutral clusters containing up to 4 iodine atoms are detected.

Page 15, Line 474: Neither fast time response or time resolution values are given in the manuscript. Indeed, they could yield wonderful proof of the developed technique and should be included. See comments on Figures with some suggestions.

We thank the referee for this suggestion. As shown in our previous comments, we added a Figure as well as a section discussing the time response of the water cluster CI-APi-TOF.

Page 16, Lines 488-491: In addition to having high proton affinity, this perfluorinated amine is also a strong surfactant which promotes its ionisation further.

We thank the referee for this interesting information but have suggested not to implement any changes to the manuscript regarding this comment.

Page 16, Conclusions: Revise in light of all other changes to the manuscript.

We added a sentence concerning the estimated iodic acid detection limits for clarification:

As there is no established calibration method for iodic acid, detection limits have been derived under the assumption that HIO_3 is measured with the same efficiency as sulfuric acid, for which the nitrate CI-APi-TOF is calibrated for. The estimated LOD for the water cluster CI-APi-TOF regarding iodic acid was as low as 0.007 pptv.

Page 27, Table 1: Remove. The only true detection limit measured is for NH3 and the rest are estimated based on assumptions that may have significant error. Further to this, the LODs were acquired over 2.5 hours of signal acquisition, while the measurements are reported at 1 minute intervals. A more accurate assessment of detection limits would have been determined at similar timescales, using about 20-30 background measurements.

We want to refer to our replies above, where we discussed the changes made to Table 1 and where we also discussed the reason for using 2.5 hour time scales.

Page 29, Figure 1: Numeric or alphabetic labeling of the instrument parts with corresponding descriptions in the caption would make this diagram easier to follow as a lot of the text is obscured by color or very small. The 'argon+oxygen+water vapour' could be replaced with 'Ar + O2 + H2O'.

We thank the referee for this suggestion. We changed the Figure accordingly. We also added a panel b) showing the technical details of the ion source in a more detailed way. This additional information was requested by the other referee.



Figure 1: The experimental setup of the water cluster CI-APi-TOF during ammonia calibration is shown in panel a) The blue color indicates the sample flow. It consists of a mixture of 80% nitrogen and 20% oxygen. A portion of the sample flow can be humidified with a water bubbler (H_2O aq) to achieve different relative humidities. B_1 represents the ammonia gas bottle, while B_2 represents a gas bottle containing pure nitrogen. There are five mass flow controllers (MFCs; labeled as M_{1-5}) allowing two dilution steps. Three MFCs (M_1 , M_2 , M_3) control the amount of ammonia that is added through a 1/16''capillary into the center of the sample flow, where the second dilution stage occurs. The reagent ions (i.e., protonated water clusters) are produced when the ion source gas (argon, oxygen, water vapor) passes a corona needle at a positive high voltage (detailed in panel b). The calibration setup is disconnected during the measurements at the CLOUD chamber to reduce backgrounds (leakage from the 1/16'' capillary). Details of the ion source used during CLOUD13 are shown in panel b. The primary ions are guided towards the sample flow using a counter electrode (Electrode 1). Additionally, a funnel is used to accelerate the primary ions towards the sample flow. A second electrode (Electrode 2) is installed directly in front of the pinhole of the mass spectrometer. The ions enter the mass spectrometer through a capillary on the top of Electrode 2.

Page 31, Figure 3: If a fit is forced through the origin, then a measure of instrument signal while ultra pure zero air should be included as a blank to determine if there is an offset in detection, particularly for NH3. For the HIO3 measurement, the x-axis is a scaled value based off of H2SO4 detection and not a true measure of HIO3 and a comparison of ncps would be more useful to describe the sensitivity of the H3O+ CIAPi- TOF versus the NO3-. For this second plot, was any background value subtracted?

As shown in our comments above, the deviation between forced and unforced slope is small (9.48e-8 or 1.35%). We changed the label of the x-axis to clarify that our mixing ratios for iodic acid are scaled from the calibration factor for sulfuric acid determined for the Nitrate CI-Api-TOF and added a

sentence under the Figure. For the comparison between the mass spectrometers, the background of the NO3- Api-TOF was subtracted.



Figure 3: Calibration curves for ammonia (a) and iodic acid (b) at 40% relative humidity. The *y*-axes show the normalized counts per second (ncps) measured with the water cluster CI-APi-TOF. The ammonia mixing ratios are determined from the calibration set-up and the iodic acid mixing ratios are taken from simultaneous measurements with a nitrate CI-APi-TOF at the CLOUD chamber. The systematic uncertainty of the iodic acid mixing ratios is estimated as +100%/-50% (Sipilä et al., 2016). The inverse slopes from the linear fits yield the calibration factors (see equation (1) and (2)). *Note that the iodic acid mixing ratio is derived by applying a calibration factor for sulfuric acid to the nitrate CI-APi-TOF data.

An important component of instrument performance that can be evaluated while doing calibrations such as these is instrument response times (both with increasing and decreasing analyte concentration) from 0-95 % of max signal and 100-5 %. The authors claim that the instrument has a rapid time response with high time resolution, yet no such data is presented in figures and no numeric values reported. This is critical to report as it also helps provide clear context in the interpretation of the chamber observations.

We thank the referee for raising this important point. As shown in our replies above (reply to major comment 2) we have added a section (3.3) indicating response times during calibrations.

Page 32, Figure 4: Was this sensitivity dependence on RH used to correct the dataset shown from the chamber? With the changes in temperature, if there is water in the chamber, then there will be a change in sensitivity that should be applied and may change the interpretation of the datasets.

During CLOUD13, the change in sensitivity due to RH was taken into account and thus, all data (including detection limits and instrumental backgrounds shown here) are corrected for these changes. However, during CLOUD12, this change in sensitivity was not taken into account when another version of the ion source was used. This is also mentioned in our manuscript in Section 3.7. We added a sentence to Table 1 for clarification (see reply to a comment on page 17-18 above).

Page 33, Figure 5: The x-axis should also be signal-based units. The caption states that there is no RH dependence, yet there is a clear difference within the regressed data that shows this and suggests that it is also statistically significant between 40 to 80 % RH (color suggests that T is constant for these), and consistent with the findings for detection of NH3 increasing in sensitivity with increasing RH.

We want to draw attention that Figure 5 is now Figure 6. We changed the x-axis label of Figure 6 to clarify that our mixing ratios are scaled values and added a sentence under the Figure. The intention here was to show that the dependency on the relative humidity is small compared with the temperature dependency. We changed our caption for clarification.





* Note that the iodic acid mixing ratio is derived by applying a calibration factor for sulfuric acid to the nitrate CI-APi-TOF data.

Page 34, Figure 6: The logarithmic scale for the marker size should be provided here. The nomenclature replacing 'monomers', etc. should be revised as necessary. We want to draw attention that Figure 6 is now Figure 7. We changed our Figure 7 according to the referees comment. We added a sentence in the caption giving the marker size of the logarithmic scale.



Figure 7: Mass defect plot for the iodine compunds, as well as the most prominent reagent ions, during a CLOUD experiment on new particle formation from iodine. The estimated iodic acid mixing ratio is ~0.98 pptv. The *y*-axis shows the mass defects of the compounds (see Table 2 and text for details), while the *x*-axis shows the absolute masses. The size of the symbols is proportional to the measured signal intensities on a logarithmic scale (from $1.24 \cdot 10^{-6}$ to 14.04 ions/s).

Page 35, Figure 7: The two data components on the y-axis should be separated with a ',' and not with a '/' which implies division. The font size of everything in this figure needs to be made larger. Depending on the outcome of the details of the intercomparison assessment, the Picarro data may need to be removed from this figure, especially if it was connected to the exhaust line of the CI-APi-TOF here. Panels a) and b) are not described in the caption and should be. An additional panel that may be of use in the intercomparison is a regression of the CI-APi-TOF measurement against that of the Picarro when both detection limits are properly accounted for (i.e. properly background corrected based on calibrations that were performed). In the case where one instrument has a higher detection limit than the other (which seem likely to be the case given the sensitivity of the CI-APi-TOF), then the higher LOD should be used as the cut-off for the intercomparison.

We want to draw attention that Figure 7 is now Figure 8. We changed our Figure according to the comments from the referee. We showed in our comments above that the PICARRO was measuring

while being connected to the chamber directly (i.e. not through the exhaust line). We also showed that the background of the water cluster CI-APi-TOF is not subtracted in this plot. In our updated version, the PICARRO background is subtracted. The PICARRO calibrations were shown in our comments above, where we think that the addition of a third panel to this plot wouldn't add more information as the range of mixing ratios is different compared to the water cluster CI-APi-TOF.



We added a relative humidity trace to Figure 8 as this Figure shows CLOUD12 data, where the change in sensitivity with RH was not taken into account for the water cluster CI-APi-TOF.

Figure 8: Inter-comparison between calculated (shaded blue area) and measured ammonia mixing ratios (PICARRO: solid green line; water cluster CI-APi-TOF: solid red line) at CLOUD. The PICARRO background (~200 pptv) has been subtracted, while no background was subtracted from the water cluster CI-APi-TOF. The temperature inside the chamber is indicated by the dashed black line. The speed (% of maximum, 397 revolutions per minute) of the two fans that mix the air inside the chamber is shown by the dashed blue line. The calculated ammonia mixing ratios (based on the calculated injection of ammonia into the chamber from the MFC settings) have a wide range due to uncertainties of the ammonia loss rate in the chamber. We display the maximum calculated range assuming, for the lower limit, that the chamber walls act as a perfect sink (wall loss dominated, 25s and 100 s lifetime for fan speeds 100% and 12%, respectively) and, for the upper limit, no net uptake of NH₃ on the walls and a loss rate determined by dilution (6000 s lifetime). For higher fan speeds, the lifetime decreases due to increased turbulence and, in turn, increased wall loss rate. Relative humidity is indicated by the orange line. The water cluster CI-APi-TOF reacts rapidly to changing conditions, such as the ammonia flow into the chamber, relative humidity, temperature or fan speed. At low concentrations, the ammonia lifetime is determined by the wall loss rate (panel b and initial stages of panel a). However, at high ammonia concentrations, the walls of the CLOUD chamber progressively become conditioned and a source of ammonia, with corresponding increases in the ammonia lifetime and the time to reach new equilibria at lower ammonia flow rates (later stages of panel a).

Page 36, Figure 8: Add a marker where the H3O+ source water was changed on panel a) and make a note of it in the caption. Convert the mixing ratio to ncps and comment on the expected range of values with an assumed calibration constant in the caption. It is surprising that a direct calibration of DMA was not performed since permeation devices for this compound are commercially available, as they are for NH3.

We want to draw attention that Figure 8 is now Figure 9. As shown in our comments above, we changed this Figure according to the changes made to chapter 3.9:



Figure 9: Dimethylamine mixing ratios (magenta line) during the CLOUD13 experiment. The dashed black line shows the temperature inside the CLOUD chamber. The dashed blue line shows the fan speed. Panel a) shows the dimethylamine signal during active injection into the chamber. The grey line indicates the dimethylamine mixing ratio in the chamber calculated from the MFC settings and the wall loss lifetime. The upper limit for the uncertainty in the dimethylamine mixing ratio is a factor of ~3.5 (see text for details). Panel b) shows a measurement of background dimethylamine in the chamber over a period of 5 days, when there was zero dimethylamine flow. We consider this to be due to instrumental background and not to an actual dimethylamine background in the chamber. The thin red lines show the possible range of dimethylamine based on the scaled calibration factor (factor 3.48, 95% CL). The thick magenta line indicates a moving average of the dimethylamine background measurement. The water source has been replenished during the period shown (green line). The mean instrumental background of dimethylamine over this period is ~0.14 pptv.

*Note that the dimethylamine mixing ratio is determined with the calibration factor for ammonia.