Response to Anonymous Referee 2 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.

Though powerful, CIMS is not an absolute measurement technique. A good, defensible calibration is necessary. The manuscript should do a better and clearer job indicating that only the ammonia detection is calibrated with a primary standard and that the mixing ratios for the other species are estimated qualitatively. It is too easy for the reader to lose sight of this fact, since no differentiation between calibrated and estimated mixing ratio results is made in the table or the figures.

We agree with the referee that the manuscript should clearly indicate that the mixing ratios for amines and iodine species are not determined by a direct calibration. We updated the relevant text passages accordingly throughout the manuscript. Major changes are listed below:

- Estimated mixing ratios shown in this manuscript are now marked in tables and figures with an asterisk and a comment that indicates that these mixing ratios are estimated.

- We added a discussion related to our approach of deriving mixing ratios for dimethylamine from the ammonia calibration factor in Section 3.9. We refer to this discussion when mixing ratios of dimethylamine are mentioned.

- We added a comment to Figure 3 stating that the estimated uncertainty for the HIO3 values is +100%/-50% (same as reported by Sipilä et al., 2016).

Updated changes in the manuscript are detailed in the replies to the technical comments below.

The main product of this work is the development of the ion source. However, details of the ion source are lacking in the text and figures. Figure 1 is more of a cartoon than a schematic. The details that are given in the text (page 5, lines 143 – page 6, 162) are difficult to translate to Figure 1. For example, a counter electrode and capillary are described in the text but not identified in the figure. Dimensions are given in the text that are not shown in the figure. This makes it unnecessarily difficult for the reader to follow how the ion source truly works and evaluate its performance. Also, details such as tubing length and flow rates for the calibration dilution components should also be given.

We thank the referee for this helpful comment. We added a panel b) to our Figure 1 showing a more detailed drawing of the ion source. This drawing is now also described in our text. The added text is shown in red font below.

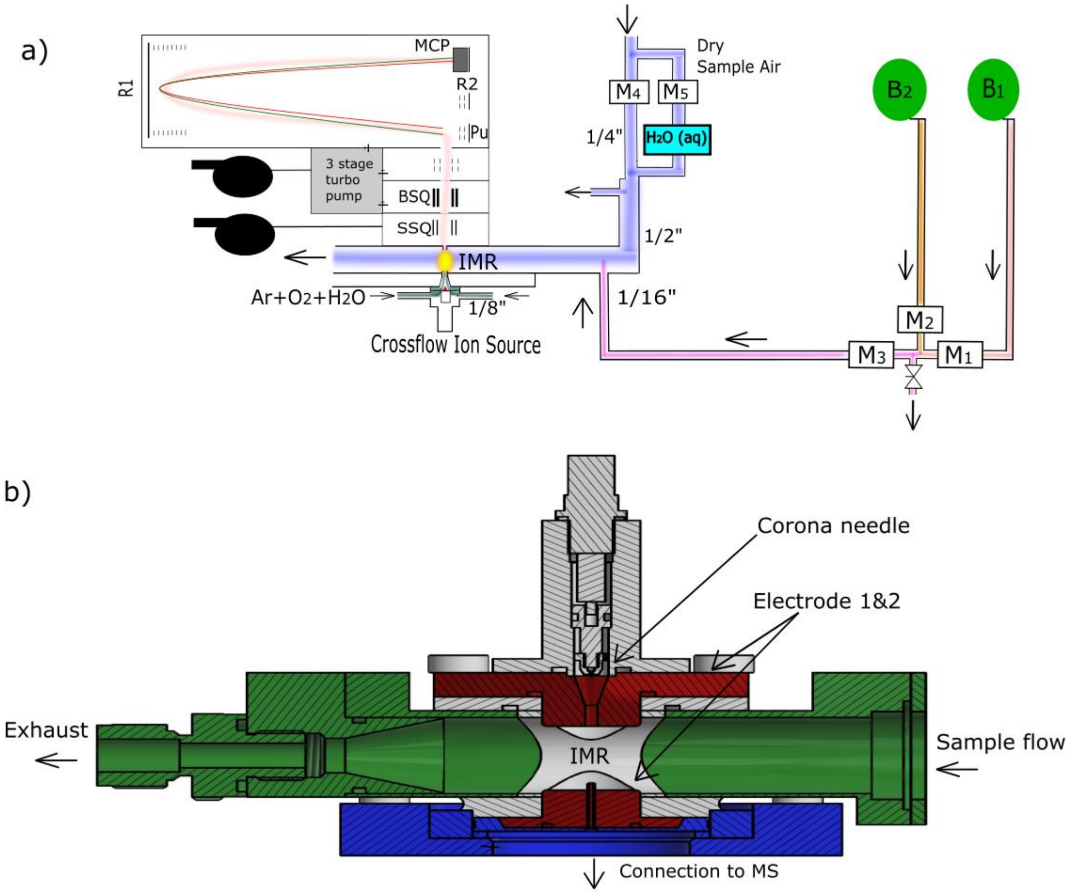


Figure 1: The experimental setup of the water cluster CI-APi-TOF during ammonia calibration is shown in panel a) The blue color indicates the sample flow. It consists of a mixture of 80% nitrogen and 20% oxygen. A portion of the sample flow can be humidified with a water bubbler (H_2O aq) to achieve 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.

Modified in Section 2.2 (Line 144):

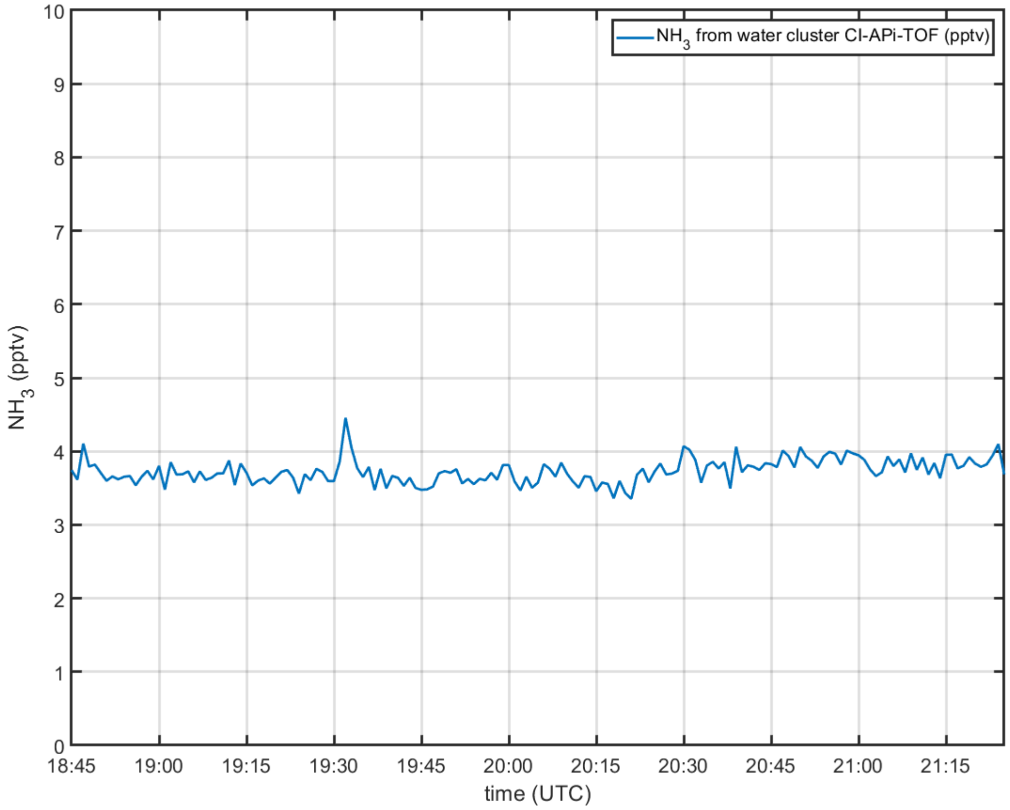
A schematic drawing of the calibration setup and the ion source is shown in Figure 1. The gas mixture for the ion source is composed of argon, oxygen and water vapor. It is introduced from two lines placed in the opposite direction to each other at an overall flow rate of ~2.6 slm (Figure 1a). The Electrodes of the ion source are displayed in red colors in Figure 1b. The connection to the mass spectrometer is shown using blue color. The 1” sampling line and the inlet (22 mm inner diameter) consist of stainless steel and are shown in green color. Components used for insulation are shown in white colors. A total sample flow rate of ~ 19.5 slm is maintained by a vacuum pump and a mass flow controller. The overall length of the sampling line connecting the CLOUD chamber and the ion molecule reaction zone is 1.3 m. A voltage of 3600 V is applied to the corona needle while 500 V are applied to the conically-shaped counter electrode (Electrode 1 in Figure 1b) made of stainless steel. The housing of the ion source is made of polyether ether ketone (PEEK). The ion source gas and the generated reagent ions flow through a funnel (smallest inner diameter 2.5 mm) before they mix with the sample flow. A small capillary (inner diameter of 0.8 mm) is located opposite of the funnel (Electrode 2 in Figure 1b). The electric field between the counter electrode and the capillary (at ground potential) accelerates the ions towards the entrance of the mass spectrometer. The pinhole plate (pinhole inner diameter of 350 µm) and the capillary are in electric contact and ~0.8 slm flow through the capillary and the pinhole into the mass spectrometer. The measured product ions are generated in the ion-molecule reaction zone (IMR, yellow area in Figure 1a) at atmospheric pressure. The dimension of the IMR is defined by the distance between the counter Electrode and the capillary (~ 16.4 mm). After passing the pinhole, the ions are transported through two quadrupoles (Small Segmented Quadrupole, SSQ and Big Segmented Quadrupole, BSQ) towards the detection region of the mass spectrometer (Micro-Channel Plate, MCP; pressure is approx. 1×10^{-6} hPa). The estimated reaction time is <1 ms. This short reaction time allows the measurement ofhigh ammonia mixing ratios (up to ~10 ppbv) without significant depletion of the reagent ions, which would be the case when using an ion source design for the measurement of sulfuric acid (Eisele and Tanner, 1993; Kürten et al., 2011), which is typically present at much lower concentrations than ammonia. The principle of a cross-flow ion source was introduced by Eisele and Hanson (2000) who used this technique to detect molecular sulfuric acid clusters. In more recent studies, this technique was used for the measurement of ammonia (Nowak et al., 2002; Nowak et al., 2006; Hanson et al., 2011).

The comparison of the LOD and low background for this water cluster CI-APi-TOF instrument to others is not as straight forward as presented here. Here the calculated detection limits are based on a 2.5 hour measurement of synthetic air generated from liquid nitrogen and oxygen with a 1 minute average for a single data point (See 2.1 and Table 1). This leads to the question are the values given in Table 1 those after sampling the synthetic air for 2.5 hrs or the values for the full 2.5 hr time period? If is the latter, what was the time required, if any, for the signal to drop to the 3 pptv level after removal of a 5-10 ppbv ammonia calibration addition?

The values shown in Table 1 are values shown for the entire 2.5 hour time period (i.e. we didn't wait for 2.5 hours before measuring these values). If we splitted this period into 20-minute-periods, our LOD wouldn't change significantly:

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 mean value of these periods would yield a mean LOD of 0.525 pptv. A time series of this period is shown below:



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 (these changes on table 1 are shown in another reply below). The calibrations shown in our study are carried out by stepping the mixing ratios from high to low values using the technique shown in our new section 3.3 (which is described at another comment below). Thus, we can show response times for small steps (e.g. from 10ppbv to 7ppbv), where we don’t have data for a decay from e.g. 10 ppbv to 3 pptv.

Unfortunately, no data is presented to support the low background and LOD claim. The time series in Figure 7 is not applicable because the effects of the CLOUD chamber cannot be separated from those of the instrument. Here a time series showing the addition of ammonia and the instrument response to its removal in the set-up shown in Figure 1 would be extremely useful. This would also better mimic field measurements, for example, measurements at a ground site when wind shifts from a region with ammonia sources to one without. Then a better comparison could be made to other instruments and their field measurements. Other factors, affecting signal stability, i.e., LOD, include vibrations, for instruments on mobile platforms such as vehicles or aircraft, and heat, for instruments in trailers, on towers, in vehicles, and in aircraft. In many ways the controlled laboratory conditions associated with the CLOUD chamber provide an ideal environment. While the work presented here is impressive, care should be taking comparing the performance there to that reported in a field campaign. This also highlights the necessity of evaluating instrument performance in-situ for every campaign and not relying on spec sheets or one laboratory test.

We agree with the referee that vibrations, e.g. when measuring on an aircraft or mobile vehicles can affect the LOD. However, despite its ultra clean air, the CLOUD chamber in particular is not an ideal place. Although it is possible to purge the lines at CLOUD for long time periods, the surface of the

CLOUD chamber is huge (26.1 m^3). Thus, precursors from previous experiments can desorb for a long time. Next to this, the instruments are limited by the length of the sampling lines (1.3m) and by the flow rate (in order to maintain the overpressure of the chamber, there is an upper limit at ~20 slm). Furthermore, the CLOUD chamber is not an ideal place compared to e.g. field stations in regard to boundary conditions like vibrations. The CLOUD chamber is located in the east hall at CERN, with the instrument presented here installed alongside <20 other instruments (including their pumps and other installations) on a steel platform. There are sufficient sources for possible vibrations along the CLOUD chamber. Figure 7 (Figure 8 in our revised manuscript) shows a measurement of the water cluster CI-APi-TOF on the chamber with no instrumental background deducted. Thus, the low background shown in Figure 7 (close to 1pptv) should give sufficient evidence on the detection limits shown in this paper.

No data is shown to support that this is a fast time resolution measurement either. Similar to my previous comment, a time series showing the signal decay after removal of ammonia would be helpful in evaluating the time response of the instrument. Also, if this is a fast time resolution measurement why does it take at least 20 minutes (Page9, line 254) for the signal to reach the mean value of a steady state measurement used in the calibration curve shown in Figure 3a?

We thank the referee for this comment. We added a section (3.3, response times) to describe the time resolution of the water cluster CI-APi-TOF. Changes made to the manuscript are shown 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.

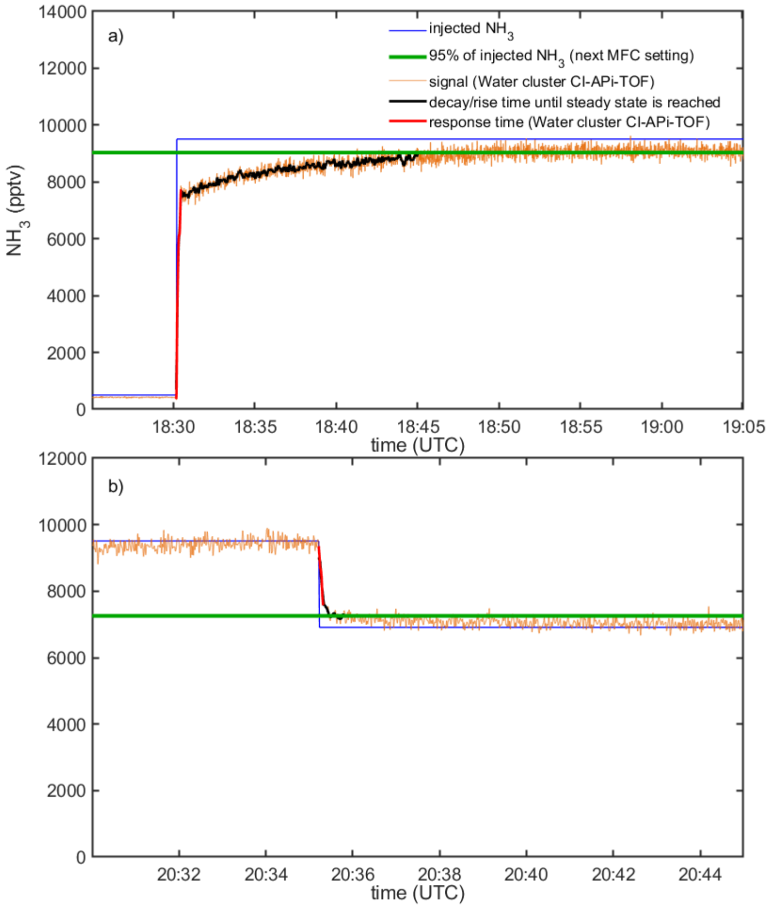


Figure 4: Response time of the water cluster CI-APi-TOF during calibrations at 60% RH. The injected ammonia level is shown by the blue line. The signal of the water cluster CI-APi-TOF is shown by the grey line (here the data are shown with a 1 second time resolution (no averaging applied)). The black 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.

Page 1 line 17, If the authors did not explicitly demonstrate the quantitative measurement of diamines (see page 16 line 504) then they should not be mentioned in the abstract. Similarly, amines should be changed to dimethylamine since that is the only amine for which data is shown. Speculative future application should be saved for the discussion in the manuscript not the abstract.

We agree with the referee and updated the text accordingly:

Here we describe the design and performance of a new water cluster Chemical Ionization-Atmospheric Pressure interface-Time Of Flight mass spectrometer (CI-APi-TOF). 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 line 22, Classifying 10 ppbv ammonia as high is very subjective. What is high for the CLOUD experiment may be typical or even low for many areas as seen in many of the publications cited in this manuscript.

While You et al (2014) reported ammonia mixing ratios of ~200 to 2000 pptv in remote areas (forests), ~ 50 to 100 ppbv of ammonia have been measured next to sources (after fertilization in an agricultural area; v. Bobrutzki et al., 2010). Thus, we consider 10 ppbv as a rather high mixing ratio. Nevertheless, we replaced the word "high" with the word "elevated" in the abstract.

Page 5 line 151, Please show how the reaction time is estimated here.

The reaction time can be determined by using the calibration (VMR_{NH3} = (1/6.9*10-6 pptv) * ncps) and the equation [NH3] = 1/(t*k)*ncps. Making use of the fact that 1 pptv corresponds to 2.5e+07 molecule cm-3, the relationship

$$\frac{1}{t*k} = (1/(6.9 \times 10^{-6} pptv)) \cdot 2.5 \times 10^{7} molecule\ cm^{-3}\ pptv^{-1}$$

yields a reaction time of 0.14 s for a collision-limited reaction rate of 2e-09 cm^3 $molecule^{-1}$ s^{-1} (Sunner et al., 1988). This reaction time is consistent with an estimate that takes into account the geometry and the applied electric field across the ion-molecule reaction region. However, due to electric field and flow inhomogeneities no exact reaction time can be derived using only the geometry and the flows.

Page 5, line 158, Are all tubing diameters given in the manuscript representing the outer diameter? The inner diameter should also be given as that affects the flow characteristics.

We agree and added information about the inner diameter of the stainless steel sampling line. For the remaining tubing we do not consider the inner diameter important and report only the outer diameters.

The Electrodes of the ion source are displayed in red colors in Figure 1b. The connection to the mass spectrometer is shown using blue color. The 1" sampling line and the inlet (22 mm inner diameter) consist of stainless steel and are shown in green color. Components used for insulation are shown in white colors.

Page 6, line 180, What is the uncertainty in the mixing ratio of the ammonia bottle and who is the manufacturer? It should be given here with the calibration set-up details not later in the manuscript discussing the calibration results.

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).

Page 7 line 199, What is meant by 'a fairly short equilibration time'? Minutes, hours, seconds? Please show the time series of the ammonia signal as a function of the step changes in ammonia added in addition to the calibration curve shown in Figure 3.

We added a new section (3.3) indicating the response time of the water cluster CI-APi-TOF. In the discussion of this section estimated equilibration times are reported.

Page 7, line 209-210, How is the assumption given here that both sulfuric and iodic acid are detected with the same efficiency by the nitrate CI-APi-TOF justified? Wouldn't this make the estimated iodic mixing ratio a limit in some regard?

We agree with the referee that the estimation of the iodic acid mixing ratios rely on the assumption that sulfuric acid and iodic acid are detected with the same efficiency by nitrate ionization.

Unfortunately, there is no established method for a direct calibration with iodic acid (neither for the nitrate nor the water cluster CI-APi-TOF). Thus, for the nitrate CI-APi-TOF the same calibration factor as for sulfuric acid has been used. This method can at the moment be regarded as the best that can be done and has been adopted elsewhere (see Sipilä et al., 2016). However, we agree with the referee that this results in a lower limit for the iodic acid concentration since sulfuric acid reacts at the kinetic limit with the reagent ions. We added marks on mixing ratios shown throughout this manuscript related to iodic acid to show more clearly that the mixing ratios are estimated.

Page 7, line 219, The text mentions the PICARRO being connected to the exhaust line of the water cluster CI-APi-TOF for comparison. Is this comparison discussed or shown in the manuscript? If not, why? Or am I incorrect that Figure 7 is showing PICARRO measurements being made from its own sampling line on the CLOUD chamber and the comparison is shown in Figure 7? The text also mentions tests when the flow is increased to the PICARRO. When is this used? If used when the PICARRO is sampling the exhaust of the water cluster CI-APi-TOF is the flow to the water cluster CI-APi-TOF increased also? Again, another instance lacking enough detail to evaluate the experiment and experimental results.

As the PICARRO was only connected to the exhaust from the water cluster CI-APi-TOF for a ~24 hour-period (which was not during the campaign but during tests after the CLOUD campaign), this intercomparison is not shown in our manuscript. One reason why we didn't show the direct comparison was that the time until the PICARRO reached a steady state was too long and thus, no clear steady state for the PICARRO was reached during these calibrations. We updated the section comparing water cluster CI-APi-TOF and PICARRO for clarification. We realized that it leads to confusion when we report these tests without further discussion. Thus, we removed the sentence from our previous manuscript.

Added to Section 2.4, PICARRO:

The G1103-t was installed at the CLOUD chamber with its own sampling line coated with Sulfinert (Restek GmbH, Germany), where the coating reduced the losses of ammonia to the sampling line walls considerably.

Added to 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.

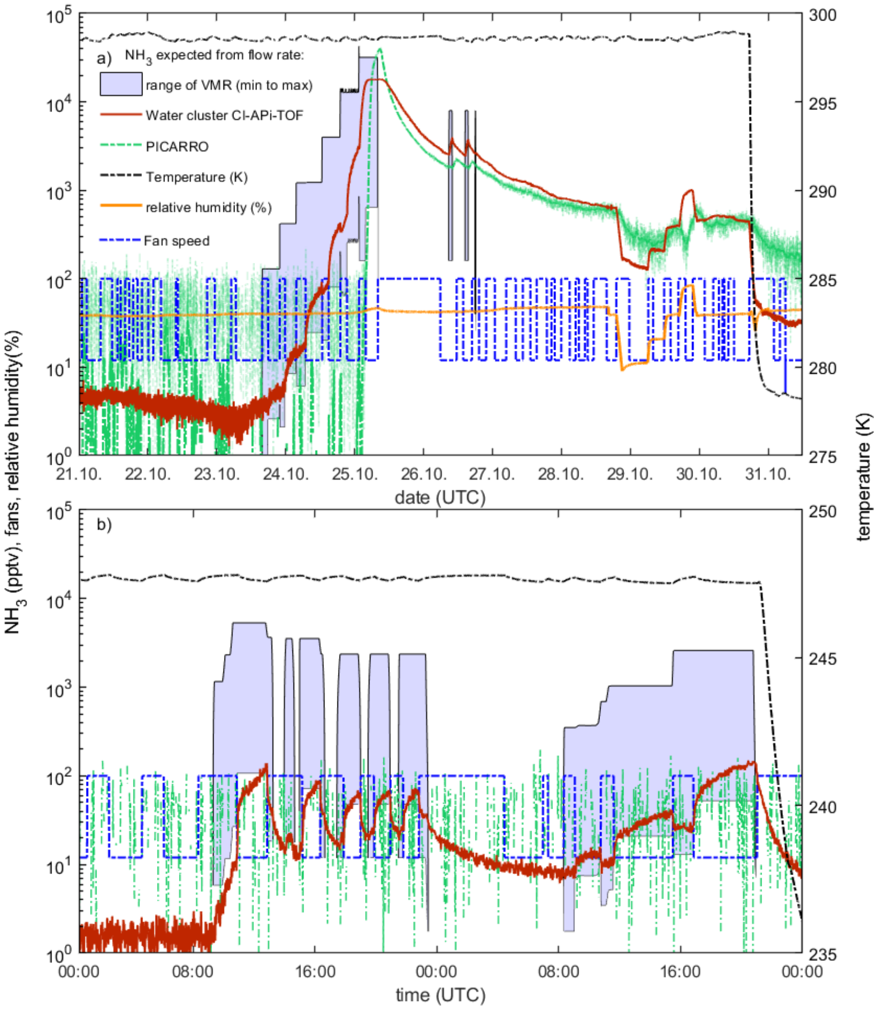


Figure 8: Inter-comparison between calculated (shaded blue area) and measured ammonia mixing ratios (PICARRO: solid green line; water cluster CI-APi-TOF: solid red line) at CLOUD. The PICARRO background (~200 pptv) has been subtracted, while no background was subtracted from the water cluster CI-APi-TOF. 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 NH_3 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 9, line 264, I am confused by the use of ppm in this context. Please clarify.

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 282- page10, line 286, This supports my earlier comment that every instrument needs to be evaluated in the in-situ setup employed.

We agree with the referee that instrument calibration can differ depending on the setup. It is important to mention here that between the setups applied during CLOUD12 and CLOUD13, several parameters changed in parallel:

- The ion source was different (other dimensions of inner diameter of inlet).
- The voltages applied to the ion source were different.
- The voltages applied to SSQ and BSQ area of the mass spectrometer were different.
- The flow rate through the ion source (primary ions and sample flow) was different.

Thus, a change in the calibration factor is expectable.

Page 11, line 337-338, This is fairly deep into the manuscript before stating that the calibration factor for ammonia is used for dimethylamine and pyridine. It should be made clear to the reader earlier.

We marked tables and figures with an asterisk and a comment that indicates that these mixing ratios are estimated. We also added a subsection in Section 2.2 (water cluster CI APi-TOF, line 175-181):

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 ~3.5.

Page 27, Table 1, It should be noted here that only ammonia was directly calibrated and the other calibration factors were assumed or parameterized from other measurements.

We agree and updated Table 1 to indicate more clearly that the mixing ratios are estimated:

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•σ (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 background (pptv)**	**Measured values (Th)**	***m/z***

NH_3 (ammonia)	0.5 ± 0.05	3.73 ± 0.35	18.0338 (NH_4^+); 36.0444 ($(H_2O)NH_4^+$)
$(CH_3)_2NH$ (dimethylamine)*	0.047*	0.058*	46.0651 ($(CH_3)_2NH_2^+$)
HIO_3 (iodic acid)**	0.007**	< LOD**	176.9043 ($(HIO_3)H^+$); 194.9149 ($(HIO_3)H_3O^+$)

*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 HIO_3 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 HIO_3 concentrations.

Page 29, Figure 1, This figure needs better labeling of the parts, consistent with the description in the text. Include the lengths of tubing. Consider a blow-up insert of the ion source with more detail.

We thank the referee for this helpful comment. We have updated Figure 1 accordingly (see reply to major comment 2 above).

Page 31, Figure 3, Why no x-axis error bars in panel b? Page 9, line 259 seems to suggest that there is a factor of 2 uncertainty in the iodic acid mixing ratio determined by the nitrate CI-APi-TOF.

We added a sentence stating the overall uncertainty accorind to Sipilä et al. (2016) to the Figure. As the data will most likely shift systematically, adding error bars to panel b of Figure 3 would only show the region where the data could shift, but not the error of the measurement.

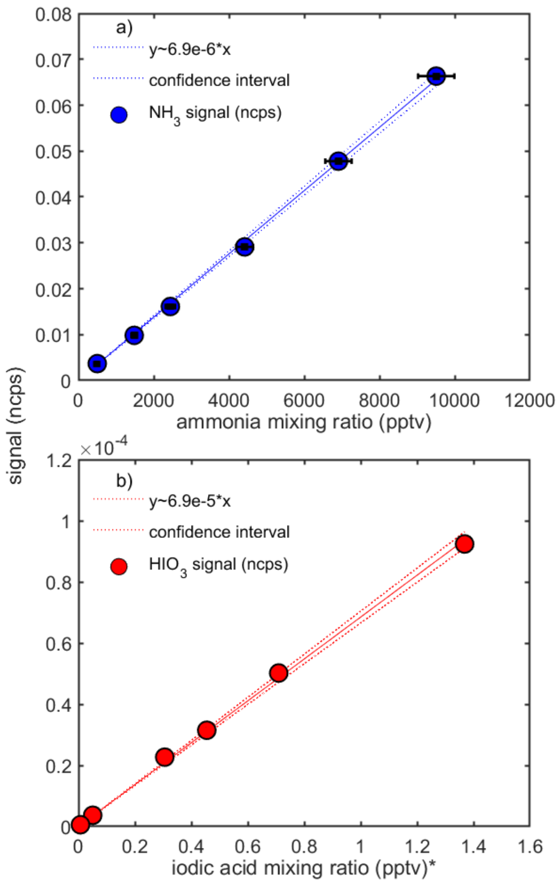


Figure 3: Calibration curves for ammonia (a) and iodic acid (b) at 40% relative humidity. The *y*-axes show the normalized counts per second (ncps) measured with the water cluster CI-APi-TOF. The ammonia mixing ratios are determined from the calibration set-up and the iodic acid mixing ratios are taken 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.

Page 35, Figure 7. Figure 7 is very busy. The agreement between the water cluster CI-APi-TOF and the PICARRO is mediocre, especially when noting that the ammonia mixing ratio access is logarithmic, though for the most part they are trending in the same direction. However, what is causing the deviation observed 29.10 – 30.10 where the water cluster CI-APi-TOF shows a significant ammonia drop and then increase that does not correlate with fan cycling or temperature changes?

We want to draw attention that Figure 7 is now Figure 8. There are several reasons for deviations between the PICARRO and the water cluster CI-APi-TOF (high detection limits (PICARRO) and depletion of primary ions (water cluster CI-APi-TOF)). Those are stated in our updated text. The mentioned deviations observed between 29.10. and 30.10. are explained in the updated text and shown in the following:

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. 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.

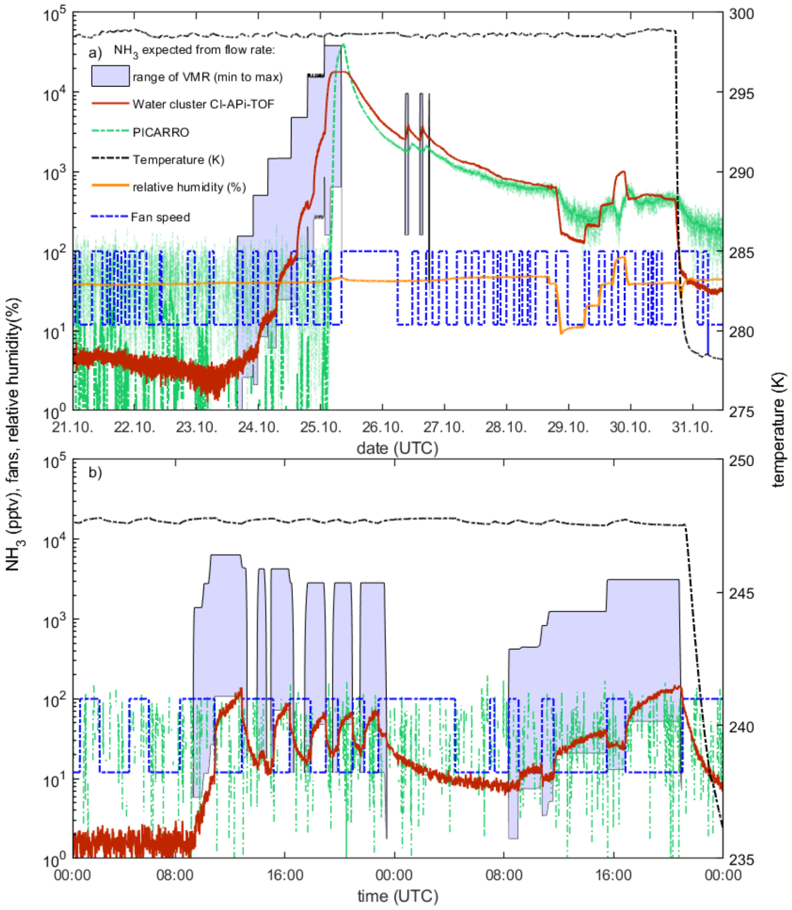


Figure 8: Inter-comparison between calculated (shaded blue area) and measured ammonia mixing ratios (PICARRO: solid green line; water cluster CI-APi-TOF: solid red line) at CLOUD. The PICARRO background (~200 pptv) has been subtracted, while no background was subtracted from the water cluster CI-APi-TOF. 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 NH_3 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).