Answers to referee comments.

We thank referees for useful comments. Below are the answers. Besides small changes related to referee comments one major change was made to the present manuscript. It turned out, namely, that one of the mass flow controllers of the system used to produce the DMA containing vapour to the CLOUD chamber was operated below its specified linear range. That resulted in a small offset i.e. the true value was larger than the assumed. The reanalysis of the [DMA] concentration resulted in approximately by factor of 8 higher [DMA] in the calibration experiment. Thus all the reported DMA concentrations are now updated in the manuscript and figures. This change was also accounted for in the conclusions of the paper. Now it is stated that in field measurements the concentration never exceeded 150 ppq instead of 20 ppq, and the wording related to role of DMA in nucleation was made softer. Now we state that "DMA concentration never exceeded the detection threshold of ambient measurements (150 ppqV), thereby questioning, though not excluding, the role of DMA in nucleation at this location. " **We also removed the word "ultra" from the title of the manuscript. Even though our LOD of 70ppq is still very good, we thought that calling the method "high sensitivity" would be more appropriate than "ultra-high sensitivity". Also the ion cromatograph data was re-evaluated and as a result the ammonia concentration was changed by a factor of 1.8. This change was also accounted for in the text and figures.**

Answers to referee comments and related changes to the manuscript are discussed below.

Anonymous Referee #2

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This paper presents the adaptation of an existing APi-TOF-MS utilizing a modified inlet for the detection of amines. Detection limits down to 8 ppq are reported for a 15-minute integration time under chamber conditions. The authors conclude based on the first field deployment following calibration and characterization experiments at CLOUD that atmospheric amines, specifically DMA was never present above the detection limit of 20 ppq at the SMEAR II research station in rural Finland. This work merits publication in AMT as part of a growing number of time of flight mass spectrometers utilized for ultra low concentration detection of atmospheric gases after a few comments are addressed.

General Comments: The instrument appears to operate as intended during the chamber work where an independent calibrated instrument is available for confirmation/ calibration. How might the instrument sensitivity change during deployment at other locations? Is no calibration standard available for in field calibrations to ensure the instrument is operating in a stable state? The instrument appears to function well at the chamber, however the atmospheric measurements do little to prove the instrument is applicable to the atmosphere for detection of DMA.

Sensitivity may change if for example temperature of the CI system becomes too high. As stated in the text chapter 2 the DMA.(SA)3.SA- cluster formed in reaction R6 may become unstable therefore affecting the detection. With ammonia the problems would be larger as ammonia containing clusters are less stable and thus more temperature dependent signals are expected (See chapter 3.2). To improve the situation a precise temperature control should be implemented (Chapter 2 and 3.2). Producing low, ppt range concentrations of DMA vapours is in practice very difficult and requires high quality facility which was not available on field. Therefore we performed our test calibrations at CERN, in the ppt range. Efforts will be made to design and develop a field deployable source in the future. Until that our results from field should be taken as preliminary and proof-of-concept.

"However, since no calibration standard was available during field measurements, our results should be taken with grain and considered as a proof-of-concept." **was added in Chapter 4 and in Chapter 5 (Conclusions)**

Specific Comments: pg. 3671 26-30: It might help readers follow this section by separating out more clearly the issues common to all techniques for amine measurements (backgrounds etc), and then mass-spectrometer related issues (eg. resolution, mass accuracy, etc).

pg. 3673 20-23: How does the effective declustering strength change the cluster stability? Presumably the fields in the APi region of the mass spectrometer could de-cluster ions significantly – how are these set, controlled, optimized?

The fields are set and controlled by APi-TOF's hardware and in our case, optimized by manually tuning them. We added two paragraphs regarding declustering – and cluster heating and enhanced evaporation as suggested by other referee – in chapter 2. "Besides evaporation in the CI-system clusters can decompose in energetic collisions in the electric fields of APi quadrupoles. Also the cluster temperature will increase as a result of the collisions with the residual gas molecules thereby increasing the cluster evaporation rates. Detailed understanding of these effects is a hot topic in mass spectrometry in general, but will require significant experimental and modeling efforts. Collision energies inside APi are not very temperature dependent and thus once the fields are stable any de-clustering processes should be independent on environmental conditions. However, since the tuning significantly affects the ion transmission, fragmentation and evaporation it is highly important, that instrument is calibrated using the same settings as used in the field measurements.

In our experiment, electric fields inside the APi were optimized by manually tuning to provide maximum transmission and minimum fragmentation for the preferred mass range through the APi. In the present experiment we did not tune the instrument specifically for the purpose but we used the settings optimized for dimethyl amine – sulphuric acid nucleation experiments presented in Kürten et al. (2014). Therefore, the sensitivity of the instrument could still be improved by improving the APi transmission especially in the mass range of 300 – 500 Da."

pg. 3674 13-20 and Generally: If the cluster distribution and ionized products are sensitive to operation temperature – how does atmospheric temperature changes effect the stability (and therefore sensitivity, detection limits) of this technique?

This issue has been widely discussed in the text. In case of ammonia temperature variations can significantly affect the measurement while in case of DMA the problems should be minor in sub 25C operation temperatures.

Given that there is a high laminar sample flow rate does the incoming air equilibrate with the trailer temperature?

No.

Or instead is the effective ionization temperature a function of ambient temperature?

Sheath flow was at trailer temperature, and sample flow followed the ambient temperature. Once the flows meet the temperature start to equilibrate but the exact ionization temperature is not known. It is between the two temperatures. Again, the lack of precise temperature control (all flows and the whole CI) will affect the applicability of the technique especially for ammonia, but less for DMA (as long as the temperatures are below some 25 C)

How would these types of temperature changes influence measurements under atmospheric conditions?

See above

pg. 3676 15-16: Does this introduction of an orthogonal saturator flow influence the inlet transmission of amines as it seems likely it disrupts the laminar flow developed during transit down the inlet tube? How would this effect the transmission of amines down the inlet through the saturator to the chemical ionization region?

It certainly can affect flow dynamics and therefore e.g. increase the amine wall contact. Calibration is therefore needed.

pg. 3677: 1-2: What is the material of the 40 cm long inlet tube? If metal (for example stainless steel) could that not introduce significant memory or equilibration effects? Would amines be better transmitted via Teflon tube?

It is stainless steel. Which can have some memory effects. Our experience with CI-MS has shown that generally SS is better material than Teflon, which can be a source of numerous contaminants. All the lines of the system including the zero gas line were stainless steel. Flow through the 40 cm inlet is high and surface to volume ratio of the tube is reasonably small, so memory effects should not be significant. But they cannot be completely excluded.

pg. 3677 3-6: Is the charging efficiency always the collision limit? Other chemical ionization techniques are sensitive to (for example) water vapor, which is often present in high concentrations as well as functional groups present. Have there been any experiments that show this ionization method to be sensitive or insensitive to the water vapor concentration (under atmospherically relevant concentrations)?

No, we only made experiments at one RH. The referee #1 raised a similar question. See, the answer to that one below.

pg 3678 10-15: Is this type of unambiguity true for the other masses as well – it would seem likely that at lower masses the probability of chemical and ion source related backgrounds would be higher?

Sulfuric acid has such a strong negative mass defect that any clusters of sulfuric acid (with or without base) have a total defect far larger than e.g. any highly oxidized organics (clustered with nitrate or bisulfate ion) and potentially present to some extend in the spectrum. On the otherhand, our system originating (source unknown) chlorine containing hydrocarbons have defects that have still larger negative defect and thus they do not interfere the peak separation. But still, there certainly can be compounds with close similar defect as the compounds we are interested in and those could then create uncertainty.

It would be nice to show the actual high-resolution fit, with all the isotopes constrained (Figure 5) as discussed in the text.

Ok. Fit was added.

pg. 3681 7: mass slow ! mass flow

Corrected

pg. 3681 10-18: Was the zero gas ever humidified to match ambient air? Could the increases during the zero for DMA be re-equilibration of the walls of the inlet tube when a clean zero air flow is introduced? Where is the zero gas delivered? Similarly does the presence of O2 (from air instead of cryogenic N2) effect the zero determination or the ion chemistry at all?

Zero air was not humidified. It could be speculated that the change in humidity could result in outgassing of molecules from the inlet wall. Gas was delivered at the sample inlet outside the measurement container. O2 could play some role in early ionization process as normally O2- is the first negative ion before the charge is rapidly transferred forward. Our sheath gas was pure N2 and thus lack of O2 could change the exact steps of ionization somewhat. However, the primary ion

spectrum do not significantly change upon switching from air to N2 and thus we see no reason to think that it would be an issue.

Referee #1

1 General Comments

In the manuscript the authors present a technique to measure amines using stable ion-molecule clusters, the employed technique seems to have potential to reach high sensitivity. Although the results of the lab measurements are promising, dealing with the ionmolecule clusters seems to increase the complexity of measurements compared to sulfuric acid measurements.

A chapter that deals with the thermodynamics of the ion-molecule clusters seems to be missing in the manuscript.

We think that the chapter 2 provides enough information for the purposes of this technical proof-of-concept paper. We discuss on cluster stabilities in light of the state-of-art theoretical results and we do not see the point of adding a chapter dealing with cluster thermodynamics?

Although the technique seems to work under lab conditions, it might fail if more stable ion-molecule clusters are formed. So a discussion of amine concentrations below the detection limit is a bit early before the characterization of the measurement technique is not finalized. I would suggest to aim this manuscript to instrument characterization because the field measurements presented include only poor results.

Well, we think that field results regarding [DMA] are not "only poor" but they are just below the detection limit. If one can give an upper limit that may be sufficient. As in our case, we give an upper limit (150ppq), which can be compared to results from amine driven nucleation. Naturally they are "proof-of-concept" type, but still we believe, they exclude some of the earlier suggestions of amine concentrations exceeding several ppt or even 100 ppt and provide support to those observations (Schobesberger, 2015) that suggest [DMA] upper limit to be below 1 ppt. Discussion on the role of amines in atmospheric nucleation is hot, and it would be very bad not to publish our (even bit uncertain) observations as long as the uncertain or preliminary nature is properly stated, which now after some improvements is the case (We e.g. added ". However, since no calibration standard was available during field measurements, our results should be taken with grain and considered as a proof-of-concept.**" in Conclusions). Two last papers reporting amines in Hyytiälä suggest completely different order of magnitude for [DMA]. One states values exceeding 100 ppt and the second one states that DMA concentrations are at least below 1 ppt. Because there is and most likely will not in near future be any other viable option to measure and quantify amines in sub 1 ppt or sub 0.1 ppt range than the one presented in our paper we consider that reporting our values from field is completely justified.**

2 Detailed Major Comments

general point: Collision induced dissociation provides energy to take apart ion molecule clusters, additionally the acidified walls are absorbing amines. It seems difficult to judge the nucleation by measurements with results below the detection limit because other effects may play a role and change the sensitivity of the instrument. general point: You have calibrated the instrument by the measurements at the cloud chamber? How do you avoid effects that change the instrument performances during the field campaigns, e.g. MCP aging, temperature fluctuations or other chemical species present?

MCP aging unlikely affected our measurement because the instrument left almost directly from CLOUD calibration experiment to the field campaign. Temperature fluctuations and the problems they would create are discussed in the paper. And in the response to referee #2 above. We cannot

avoid other chemical species present because air is full of them. Fortunately almost none of them attach with sulfuric acid – bisulfate clusters. Ultimately it will be the mass resolution and mass accuracy that would determine whether or not those potential other chemical species would interfere the amine detection.

Wouldn't an online calibration be more reliable? Permeation tubes for DMA are available by companies which are well known to sell permeation tubes (cf. Bertram et al. (2011)).

Yes, we have used but the thing is that when we are talking about concentrations around 1 ppt the challenges increase drastically. With the permeation tubes it may be straightforward to produce concentrations in the range of few 100 ppt or ppb but not in the range of ppt. We do not have good enough technique available and therefore we calibrated at CLOUD where we were able to dilute the amine containing flow to flow of ~100 lpm of cryogenic air. In the future, it is naturally highly important to develop the field deployable calibration standard.

general point: Cross sensitivities might be caused by other species, e.g. nitric acid sulfuric acid ion clusters are be more stable, as discussed in Kurtén et al. (2011). So the sensitivity could also change with the nitric acid concentration in the reactant gas stream.

Nitric acid bisulfate clusters are stable, but collision with a sulfuric acid results in substitution of nitric acid by sulphuric acid resulting in sulfuric acid "dimer" formation and nitric acid should leave the cluster. There seem to be no nitric acid in our sulfuric acid – bisulfate clusters, thus at least relatively small changes in nitric acid concentration should not change anything. Also the nitric acid flow was kept constant and the temperature of the nitric acid saturator was not drastically fluctuating.

High water concentrations might cause an exchange of the amine in the sulfuric acid amine ion cluster, depending on the stability of clusters with many water molecules.

It would be a little surprising that dimethyl amine, the strongest base in the cluster would evaporate and leave the water in the cluster, but we cannot exclude that. We have not seen any water in sulfuric acid clusters, though, but that can be because water evaporates in APi low pressure. To solve that, calibration experiments with different RH should be performed in CLOUD, which is not feasible in near future, unfortunately.

general point: Do you see any interaction of the ion clusters with aerosol particles or signals that are correlated to nucleation events?

Sub-second residence time in the CI-system is too short that ion clusters would have time to coagulate with aerosol particles to measurable extent even in elevated concentrations during nucleation event. Regarding signals, we have not analyzed the correlation between signals and events.

p. 3669, l.12-14: It should be specified whether "minute signals" are above the SN ratio and which species are found.

The sentence was bad, it was changed to "While minute signals above the signal to noise ratio that could be attributed to trimethyl or propyl amine were observed,…"

p. 3671, last paragraph: Collisions induced by electrostatic fields used are increasing the temperature of the ion molecule cluster to a few 100 C, which is well below 1 eV. Typically energies around 1 eV are reached in transfer stages. Thereby the evaporation rate is higher in the transfer stage.

We do not exactly know what the referee wants to point out here, but we have added two paragraphs dealing with evaporation and declustering etc. to chapter 2. See answer to referee #2.

p. 3674, l.12-14: The temperature stability of the instrument is mentioned on this page, in the field the temperature stabilization is more problematic. How is it granted for the field instrument?

It is not granted. As it says in the text for the compounds that would only cluster with SA3.SA- the precise temperature control would be required (or high frequency calibration maybe). In our experiment the precision of instrument temperature was determined by the air conditioning system of the measurement container and the ionization temperature is determined by the instrument (and sheath gas) temperature and the incoming sample air temperature, which depends on ambient temperature. Therefore the temperature control is not good enough for reliable quantification of all compounds (at least without frequent field calibration).

general point: I'm missing some remarks how the amine background had been reduced, are the acidified walls the only approach used?

Acified walls, Cryogenic nitrogen as sheath gas, and stainless steel surfaces. We added "Also the use of cryogenic nitrogen as a sheath gas and stainless steel surfaces in instrument as well as in gas lines between the nitrogen dewar and the instrument help in decreasing the background signals. **" in end of chapter 2.**

general point: How did you get rid of wall effects in the cloud chamber?

In CLOUD the experiments were conducted starting from lowest DMA concentrations in order not to allow the chamber wall to equilibrate with the gas phase. Also the experiment was performed with sulphuric acid in the chamber and (the wall) which should prevent the desorption from the wall. Naturally, desorption from the chamber wall takes place to some extent but as the experiment was conducted from low concentration to high concentration that should not significantly affect the measurement. Also the very high correlation in Fig 6 would not point toward any significant non-linear artefacts. In case of ammonia the situation can be more complicated and that may be a cause of the less high quality data. It is stated in the text that reason for the bad quality data can be in fluctuating or poorly defined NH3 in the chamber. We do not speculate with the reasons because there can be many of them, not only the wall effects. Before feeding DMA in the chamber, the chamber was baked at ~100C and flushed with cryogenic air in presence of O3 and OH (UV-light) to desorb and/or oxidize the contaminants including DMA from the chamber wall. We wrote e.g. "…cleaning the chamber by baking at ~100°C and flushing with cryogenic air in presence of O_3 and OH (UV-light) to desorb and/or oxidize any contaminants on the chamber wall." in the Sensitivity studies chapter.

3 Minor Comments/Corrections

general point: also often ppt or ppq is used as unit it is more precise to use pptV or ppqV

OK

p. 3671, l.17: "chemical ionization by either protonated water clusters...", better known as proton transfer reaction MS using water or other species.

OK, we changed the wording but wrote" proton transfer reaction using protonated water clusters**" instead of just "**water**" to make a difference to more common (low pressure)PTR-MS technique that uses H3O+, not clusters.**

p. 3675, l.11: ...in the space between...

OK

p. 3675, l.12: ...carries the ions produced downstream toward...

OK

p. 3681, l.7: ..., mass flow controller...

OK
p. 3681, l.17: ...when the instrument worked stable...

Isn't "worked stably" rather correct than "worked stable", like "reliable" vs. "reliably"?
Added "the"

p. 3683, l.4: "collision limited ionization detection" makes no sense for me

Removed word "detection**".**