

We have begun modifying the paper and have also nearly finished revising the Supplemental information and so our responses to the referee comments take past, present and future tense.

The primary objection of the referees is the stickiness issue: referee 1 essentially states that the quantitative AmpMS ambient amines data cannot be trusted. This belief appears to be based on the lack of stickiness information at low pptv levels of amines. We appreciate this point of view. In fact, in its first deployment to measure NH₃ in Atlanta, AmpMS was not expected to get meaningful amines data yet AmpMS' signals indicated single digit pptv levels of amines. False negatives in the amines were very few. Instead, ammonia developed overwhelming stickiness issues: after about ten days of sampling ambient air, the Atlanta 2009 NH₃ measurements became erratic with many false negatives.

We believe the ambient AmpMS data has quantitative value and we will include it in the revised version of the paper. We address each of the objections to the ambient data by referee 1. Furthermore, we have changed the title and added language that specifically states our assumption that the stickiness of the amines (in terms of time delays) does not depend on the level of the amine. With these statements, the data can be considered to be an example of applying AmpMS sensitivities. Readers can take (or leave) the quantitative values with this assumption in mind.

Anonymous Referee #1

Received and published: 12 June 2014

Review: "Quantifying amine permeation sources with acid neutralization: calibrations and amines measured in coastal and continental atmospheres" by Freshour et al.

This manuscript presents manufacturing homemade permeation tubes (PT's) and testing the permeation rates using acid-base titration. The second part of the manuscript is concentrating in field measurements measured in two different locations in the US using the AmpMS instrument. My first comment is that there is something missing between manufacturing PT's -> field data and therefore the title of this paper is misleading/ makes no sense to me. Making the permeation tubes and figuring out the permeation rate is one subject, calibrating/optimizing/etc. the AmpMS for field measurements the C1325

second one and going to the field would be the third subject that is addressed in this manuscript. I would consider changing the title to describe the manuscript better.

We will change the title to "Amine Permeation Sources Characterized with Acid Neutralization and Sensitivities of an Amine Mass Spectrometer".

When reporting amine levels measured by the AmpMS the authors need to show three crucial things in the manuscript before reporting ppt levels of amines/DMSO/etc; 1) Calibration 2) Zero 3) LOD (detection limit)

1) calibration

This manuscript describes calibration using the homemade permeation tubes that emit pretty high level of amines (like presented in Figures 2 & 3 and Table 2 also). You have one point calibration for six different compounds but I wonder why the authors did not measure multiple points since they had the chance to dilute?

We were able to find a set of data at sub ppbv levels for DMA, this plot is shown in the Supplemental information in a new figure (S8c). It shows nearly identical time delays as the 2000 pptv spike.

This would also give you insight to the sticking of amines in the sample line etc. (was the calibration curve linear or not)? I do not believe that calibrating the instrument in ppb-levels of amines is not (sic) enough when this manuscript is reporting 1 or 2 ppt amine levels with no uncertainty information. The fact that you are using a 3-6 meters (!!) of extra tubing to sample

ambient air makes it impossible to quantify any ambient amine concentrations. Amines and ammonia stick to that wall and evaporate back in the sample air with completely C1326 random rates depending on the conditions (like temperature).

Interestingly, most of the measured ambient amines had no temperature dependencies, which implies that the temperature of the inlet did not affect measured amines.

If during calibration (ppb levels) you already lost 10-20% of amines to the wall with 30-100 cm tubing, which is actually very reasonable result, but I doubt that 1 ppt of DMA and 6 m of tubing and with slow flow rate will ever reach the detector and the delay in the line is more or less impossible to determine.

We now discuss more fully in the Supplemental the effects of the 4-6 m inlet versus those due to surfaces internal to the instrument. The delays in detecting the larger amines are primarily due to the instrument while for ammonia and methyl amine the inlet had large effects. We also added a paragraph in the paper that puts a disclaimer on the ambient data: we report this data with certain assumptions. A small misconception here: a 10-20 % 'loss' should not be inferred from the calibrations given the +/- 25 % uncertainty in perm rates as well as uncertainties in mass spectrometer throughput etc.

I also miss some basic information like what is your charger ion/ions since the experimental section is missing a detailed description of the AmPMS technique? Hanson et al. (2011) clearly states that it is water clusters ($(\text{H}_2\text{O})_5\text{-}8\text{H}_3\text{O}^+$) that are the most abundant charger ions. In the Supplementary it is said that you feed HNO_3 + water for the ion source, why is that? Also do you actually see water clusters (if they are your reagent peaks) in the spectra? Do you detect water-analyte clusters or just pure amines (like DMA at 46 amu). I would like to see a mass spectrum of those since it has not been published in this or the previous paper describing this technique.

A mass spectrum is now included in the Supplemental. It shows the dominant reagent/charger ions. We also discuss why HNO_3 was added to the water reservoir for the source. We also state that ligands on the $\text{M}\cdot\text{H}^+$ ions for the amines are minor.

2) Zero

This is the most important thing when measuring something this sticky. I don't see proper zero measurements in this manuscript that would point out that this instrument is capable to measure ppt-levels of amines. The only exception is figure S4.

We expanded S4 by adding a (b) figure that shows five minute data with zeroing that demonstrates single digit detection of amines. This is our bottom line: that the ambient measurements indicate that single digit pptv levels were detected. This surprising result is supported by evidence presented in the Supplemental.

The authors have clearly tried several methods, compared the methods to each other and deployed then in the field. The problem is that you feed in the catalytic zero next to the ionizer and not from the sample line inlet 3-6 m away from the instrument. Figures in the main manuscript show large background levels of ammonia (Fig 2, >2000 ppt) and DMA (Fig 3 zero measurement).

We did do inlet tests with 2000 pptv as previously shown in Fig. S8a_b, and we located some calibration data using 400 pptv for DMA. This data is now included as Fig. S8c in the Supplemental and it indicates that time lags depend only weakly on amine level.

In figure S2 there is a pretty good zero presented but mostly with masses (amines) that you did not report in the main text. Figure S3 shows zero behavior of 46 amu (DMA), during the zero the level stays in 200 ppt range like the "real" signal as well. You try to justify this sluggish behavior or delayed zero by analyzing the data using similar procedures but how do you really define sluggish delayed zero?

Is it always different C1327 period.

No it is always the same timing. We stated how we treated the data which defines what we consider sluggish: essentially it is due to about a half hour delay (from the initiating of a zero) in

the bottoming out of the detected [amines] at the ion beam. We postulate further that there seems to be also about a half hour delay in the rise after ambient air sampling is re-established. Note that these delays are not due to the 4-6 m inlet but to the surfaces within the zeroing tee, the glass manifold, and possibly the stainless steel surfaces of the source and near to the ion orifice. Whether to accept as hourly data the sluggish or the regular zero was determined by whichever resulted in the greater abundance for the amine. We will add a statement to this effect in section 3.3.2.

The supplementary concludes (p.9): "Therefore the data, represents some sort of average of the proceeding 10 to 30 minute ambient amines". I would prefer a little more accuracy in the zero- and ambient measurements or the authors need to state error estimates.

We now refer to the data in these cases as representing a 'lagging' average. We agree with the reviewer that this is not ideal. We have discussed that there is a potential bias due to this procedure because the zero-levels and the ambient levels may not have been fully realized. We postulate that this potential bias results in the measured amines being up to 30 % lower than ambient amines. Note that not all the data exhibited sluggishness for the amines. The previously published Atlanta amines data was reanalyzed and showed little evidence for sluggishness (the NH₃ data has not been reanalyzed). The Lewes results were mostly obtained with the normal zeroing procedure.

3) LOD

From zero measurements you can calculate the detection limit for the detected amines. These are not presented in this manuscript for the measured amines (or in Hanson et al. 2011).

We added a section presenting detection limits from a zero determination near the middle of the campaigns for the two measurements sites. These detection limits are for 10 s measurement intervals. We also added a discussion regarding the false negatives that are induced in the data by interpolating between the ~ 2hr zero determinations.

I cannot accept the field data being published in this journal if the authors do not carefully review and correct these three major issues related to AmPMS measurements. I am afraid this information is interesting qualitatively but not quantitatively.

We presented evidence that the stickiness of the inlet is not an issue for dimethyl amines and larger. Furthermore the ambient data had little or no dependence on temperature, which also indicates that stickiness in the inlet is not important. We also have supporting arguments that stickiness of the amines (defined as time delays) does not depend on the level of amines present and we assume that this extends to very low levels whether in the inlet or on surfaces within the drift region. The change of title and the statement of this assumption now allows for the reader to take or leave the quantitative ambient amines data. We believe the additional information now included in the Supplemental and in this rebuttal will increase the readers' interest in the quantitative nature of the ambient amines data. There still may be quantitative problems with how we treated the data as well as problems with our main assumption. The bottom line is that the data consistently indicates that AmPMS is detecting single digit pptv levels of the alkyl amines, and this is an interesting (and perhaps surprising) finding.

Other general comments: - Figures 4 and 5 are too small to read so I would consider resizing.

Will do.

- I would like to see a summary of all the compounds that you measured with AmPMS. At the moments I see masses (60a, 102a etc.) but clarification, a table maybe, that connects masses with compounds would be very helpful.

Will do.

- There might be an explanation why TMA (60 amu) does not correlate with other amines or otherwise behaves differently. As the authors report, mass 59a is identified as acetone and since acetone is more abundant in the atmosphere, I would check that mass 60 amu is not acetone's isotope.

Acetone is detected much less efficiently than are the amines (about 1/1000 as efficient) and its isotopes have no contribution to signal at 60 u. This is quite evident in the new mass spectrum in the Supplemental. - Supplementary is not finished. Figures lack captions, x- and ylabels and legends.

We have added captions and more discussion to the existing captions.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 3835, 2014.