

Interactive comment on “Quantifying amine permeation sources with acid neutralization: calibrations and amines measured in coastal and continental atmospheres” by N. A. Freshour et al.

Anonymous Referee #1

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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.

Measuring amines from ambient air is extremely important since only very few papers have been published so far but as the authors already know, it is also extremely hard task to carry out quantitatively because amines are very sticky and they cause memory effects in the instrument, sample lines and ionizer.

What is good about this manuscript is to see handmade permeation sources and valid experiments to test the permeation rates but I have my concerns about the AmPMS results, calibration and thus about the field campaign data. 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)

The AmPMS is nicely described in Hanson et al. (2011) but even that paper does not answer all these points I made. My main concerns and general comments to these points:

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? 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 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). 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.

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 $(H_2O)_5-8H_3O^+$ 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 being published in this or the previous paper describing this technique.

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. 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).

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

time for every zero measurement? In figure S5 I can't detect one zero measurement period. 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.

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).

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. In the other hand, reporting the PT's I can accept as they are.

Other general comments: - Figures 4 and 5 are too small to read so I would consider resizing. - 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. - 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 acetones isotope. - Supplementary is not finished. Figures lack captions, x- and y-labels and legends.

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

C1328