

Interactive  
Comment

# ***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.**

**N. A. Freshour et al.**

hansondr@augsborg.edu

Received and published: 18 July 2014

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please see attached (it is stuck on some comments by Gruber et al...) See the 'Figure' instead.

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PDF attachment not working properly so here it is in black and white:

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Anonymous Referee #3 Received and published: 11 July 2014 This manuscript describes amine measurements, including the calibration procedure using home-made permeation tubes and field measurements at two different sites in the U.S. Amines play important roles in new particle formation and secondary organic aerosol formation, but measurements of amines are extremely challenging. Dr. Hanson and his colleagues developed an atmospheric pressure proton transfer mass spectrometer (AmPMS) to measure ppt level of amines and did measurements in an urban Atlanta site previously. The current work extends to some unresolved technical issues from the early work, especially related to calibration, background, and time responses and added also new atmospheric observations. The paper contains various techni- C1663 cal information, in an extraordinary detail and objective manner, that is very useful to the amine community. This work is within the scope of the journal and I recommend publication after the authors address the following comments. The calibration of amines with home-made permeation tubes can be tricky – since the emission rates are temperature dependent, as discussed fully in this work as well, so it would be genuinely concerned how accurate these calibrations can be. Also, using the acid-base wet chemistry to calibrate the permeations tubes imposes additional technical challenges for in-situ calibrations in field studies. Background signals of amines and ammonia are sensitively dependent on RH in this AmPMS method. In the previous work, for this reason, ammonia concentrations were not reported. I wonder why RH has such a profound effect on backgrounds and how this could be resolved so that more consistent treatment on background signals can be made in the future. This is a different feature than the CIMS by Yu and Lee (2012) and Yi et al. ACPD (2014), where background signals are not affected by RH and temperature, as long as the scrubbers are dry, and for ammonia especially the background signals never had such problems.

Response: It is interesting that the instrument by Lee and coworkers has little or no RH dependence for the BG signals: perhaps it is related to different ion source' chemistry and flow rates? We think that speculations on this are beyond the scope of this work.

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The time response seems not as fast as I would have expected and I wonder how the authors would improve this in the future also.

Response: Time response is rapid, 20 s, for the first ~70% of a change in amines. The long time constants for the next 30% change in AmPMS response may be related to the preceding issue: stickiness on surfaces and re-entrainment into the sample air due to variations in water content. Water is interacting with the adsorbed amines and driving them off or perhaps hydrolysis of proteins is occurring. The source of the RH dependency remains speculative. We think that gentle heating of the glass enclosure and parts in the ion drift region might help. This was done for the Lewes campaign and it may be the reason for less 'sluggishness' in the Lewes amines data.

Regardless these above issues, I am impressed by the sensitivities, especially for large molecular weight amines, assuming reliable calibrations from the home-made permeation tubes. Measurements made in a marine and continental sites are very interesting. Ammonia and amines were reported from these two sites show drastically different characteristics, especially for C4- to C7-amines. These features show different sources, emissions, chemistry and sink processes at different atmospheric environments. Minor comments: C1664 Page 3836. Line 20: please cite Yu et al. GRL 2012 and Erupe et al. ACP 2011. We will cite at least one of these two at this point. Apologies for the oversight. Page 3837. Line 2. Please cite Yi et al. ACPD 2014. Will do (the referee means You et al. ?) Page 3840. Line 26. What is the relative signals between the reagent ions and ammonium ions? A mass spectrum is shown in the Supplemental now. The NH<sub>4</sub><sup>+</sup> signal can be as low as 10 % or as high as about 100 % of the H<sub>3</sub>O<sup>+</sup> based signals. Page 3842. Line 7. Why not subtract background signals in Figure 2? This way the figure contains background levels and also shows the stability of them over this time period. Figures should be improved for quality in the main text and the supporting material. Some of them are missing axes labels and units and annotations for tracers. And annotations of each peak would be better indicated by compound names rather than amu values for clarity. The Figure captions

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identify them by compound names. We will work on the figures to make the data more presentable. Supporting material. It is not clear how SI6 stands in this paper particularly, while the information is still very useful to the amine nucleation studies. Fig. S15(?) speaks to the use of the permeation tubes in the flow reactor studies. Two references listed in the SI refer to these uses.

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/7/C1777/2014/amtd-7-C1777-2014-supplement.pdf>

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

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Minor comments:

C1664

Fig. 1. Hopefully this works

C1781

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**Fig. 2.** minor comments