

Interactive comment on “Atmospheric amines and ammonia measured with a Chemical Ionization Mass Spectrometer (CIMS)” by Y. You et al.

Anonymous Referee #2

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Overview and General Comments: You et al present CIMS measurements of gas-phase ammonia and amines from the SOAS field campaign in Alabama as well as from ground based studies in Kent, OH. The measurements represent some of the few higher time resolution measurements of amines available in the literature. While the manuscript presents a unique data set, there are many technical details surrounding this very challenging measurement that need to be addressed. There is no question that the CIMS detection axis is highly sensitive and capable of high time resolution detection of ammonia and amines, however the entire challenge with making these measurements is in sampling and inlet characterization. The current manuscript does not adequately address these points and as such leaves the reader to question the validity of the measurements. If the paper were to be published in ACPD, the authors

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need to make major modifications to the paper and likely conduct a series of laboratory experiments to demonstrate analyte transmission through the entire sampling manifold used during SOAS (and in Kent) at conditions (RH, temp) relevant to these sampling sites.

Beyond the technical shortcomings, there are serious issues in the organization of the discussion section. At present, the specific conclusions of the study are not clear. I would suggest either refocusing the paper on the technical aspects of the measurements and a discussion of the relative ratios of the aliphatic amines measured here. For example, C3/C5 in Alabama is orders of magnitude larger than in Kent. If they have similar loss rates, what does this imply for the primary emission rates for these compounds in the two environments? Simply 0-D box modelling (of both kinetics and gas-particle partitioning) could prove remarkably useful in the interpretation of these preliminary measurements. This is the unique strength of the SOAS data set, as a box model would be very well constrained.

Specific Comments: Page 16415, line 18: This is slightly misleading as the ethanol ion chemistry for detection of NH₃ was worked out nearly a decade prior to this (Nowak et al., 2002 JGR). To the best of my knowledge, Yu and Lee linearly applied the technique to the detection of amines.

Page 16416, line 2: There are multiple times where the authors state “fast-time response”. It would be nice to see some discussion in the introduction of why we need fast-time response measurements for these compounds from ground sites such as this. What is needed? 1Hz, 30min? The justification for fast-time response from aircraft and ship platforms (or for measurements via eddy covariance) are clear, but it is not clear what is needed here to answer the science questions posed.

Page 16417, R2: With what certainty can the authors say that this is the ion molecule reaction? It is clear in the mass spectra that they detect amines as BH⁺, but that does not mean the ion-molecule reaction proceeds through a proton transfer as opposed to

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a ligand switch followed by collisional dissociation.

Page 16418, Line 1: Were any attempts made to assess the transmission efficiency for amines in this system? While a transit time of 0.17s is short, this does not ensure there is no wall loss? This needs to be accounted for in the discussion. I would assume that mass accommodation of ammonia/amines could be close to one at the wall, especially under the high RH conditions sampled here. What is the number of collisions with the wall in transit? Many other questions also need to be addressed: 1)What is the composition of the three way valve? 2)How does switching from high to low RH for the zero impact any amine that is on the inlet or IMR walls? 3)What is the temperature of the inlet, was it actively controlled? 4)What is the temperature of the IMR? 5)It appears from Fig S1 that the gases for the calibration were added to dry air directly at the inlet to the CIMS, but not to the instrument inlet. Why was this done and what artifacts does this introduce. I find it impossible to believe that adding NH₃ or amine to the inlet of the CIMS under dry conditions equates to a standard addition of NH₃ or amine to the actual inlet tip under high RH sampling conditions.

Page 16419, line 25: How many data points were used to calculate the three signal of the background? All of the background determinations for the campaign? Daily values?

Page 16419, line 27: The calibration curves are for concentrations that are 2-3 orders of magnitude larger than ambient. What evidence do the authors have that the instrument has a linear response from 1 ppt to 1ppb?

Page 16420, line 19: This is confusing, why would you expect the background signals to be sensitive to ambient RH if you are drying the air before detection? I presume that the backgrounds are sensitive to RH, but your method of determining this is not adequate.

Section 3: What was the averaging time that was used to make the measurements? It appears from table #1 that the 1s measurements would be below the detection limit for

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most all of the Alabama experiment. What is the detection limit for a 20min sampling period? At what point does signal averaging not improve your detection limit (in many CIMS instruments this can be as short as 30-60 seconds as the sources of error are no longer random), thus requiring frequent background determinations.

Section 3/4: Was the CIMS instrument located on the tower? With an inlet collocated with the other instruments? Or was the instrument on the ground? If so, the inlet must only be through the wall of a trailer? This needs to be expanded on.

Page 16422, line 6: What does "within" the CIMS detection limit mean? This is a threshold, the measurement is either below or above. If the measurement is below the detection limit, why are the figures shown? Is the measurement below the 1s detection limit but not the detection limit for a longer integration time? Are the measurements shown 1s?

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 16411, 2014.

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