

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

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Received and published: 4 October 2014

We thank reviewers for useful comments and we revised manuscript based on these comments.

Comment: You et al. present CIMS measurements of gas phase ammonia and amines from the SOAS field campaign in Alabama as well as ground base studies in Kent, OH. The measurements represent some of the few higher time resolution measurements of amines available in the literature. While manuscript presents a unique dataset, there are many technical details surrounding this very challenging measurement that need to be resolved. There is no questions that this CIMS detection axis is very sensitive and capable of high time resolution detection of amines and ammonia, however the

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entire challenging these measurements is in sampling and inlet characterization. If this paper were to be published in ACP, the authors 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 modeling (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.

RE: Most of the technical issues raised here were described in detail in our previous papers [Yu and Lee, 2012; Benson et al., 2010]. The current paper intends to show only major improvements made since then and scientific discussions of the ambient data at the two sites. While in the Alabama forest, we saw only C3-amines mainly for most of time. The C5 amines were not present in the Alabama forest except biomass burning periods, so it is not possible to make ratios of C3/C5 there. We plan to build a box model by considering source, deposition, transport, nucleation, coagulation, heterogeneous uptake, salt formation, and photochemical and oxidation processes together, using the SOAS data. Since these two sites have significantly different background aerosol concentrations, different nucleation frequencies, different OH and ozone concentrations, different relative humidities and temperatures, and different acidities in the aerosol phase, their loss rates are different at the two sites. This is beyond the scope of the current paper and we will publish these results in another paper.

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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.

RE: We restate now: "The ethanol ion chemistry for the detection of NH₃ was worked out previously by Nowak and colleagues [Nowak et al., 2002 JGR] and Yu and Lee [2012] linearly applied the same technique to the detection of amines."

Comment: 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, 30 min? 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.

RE: Agreed. We will add the importance of fast time measurements. To identify the source and deposition processes and simulate them in box models, we need fast time response. Figure 7, for example, shows a rapid increase of amines during the burning event, and this short episode was captured because of the CIMS fast time response, and other traditional chromatography methods which takes days or weeks would not be able to catch. Also, Figure 8 shows the abrupt spikes of C4- to C6-amines in Kent, which are different than the C1- to C3-amines and ammonia profiles, and these spikes indicate some local emission sources. These are another example that fast time response instrument is needed even at the ground level to capture those unique profiles of ambient amines. We will add these two sentences:

"These methods are not suitable for capturing temporal variations of amines that rapidly change due to emission and deposition processes, as well as reactions with oxidants and aerosols."

"Detection of such rapid evolution of ambient concentrations of amines was enabled

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with fast time response CIMS technique."

Comment: 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 a ligand switch followed by collisional dissociation.

RE: We have used standard amine vapor (individually for one compound at a time or mixed together; in the flow tube in the lab and in the field with ambient air) as discussed also in [Yu and Lee, 2012; Yu et al., 2012; Erupe et al., 2011], and the results obtained from these different conditions consistently show that ion chemistry R2 occurs.

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.

RE: Most of these questions came from errors in Figure S1, which did not illustrate correctly what has been actually used. We have revised Figure s1 now and we apologize for these errors. The standard gases were diluted with dry nitrogen gases, but they were eventually merged to the background gases prior to CIMS. We did not see back-

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ground signals changing with RH, when we tested without the drier using the ambient air. We also did not see any differences in background signals between flowing the indoor air and the ambient air through the scrubber, so for the practical convenience in the trailer, we used room air to generate zero gases for calibration tests. We have tested transmission at different inlet points (thus different times) using the standard amine gases and we did not see that different transit time also causes different background signals. This is because the transit time is really short. Whether the wall loss will become serious is dependent on time scale of adsorption and desorption and the mass (deposited on the surface of the inlet tubing's inside wall). The three-way valve was made PFA Teflon. The IMR was at 25 C for most of time. The inlet was drilled through the trailer wall and remained at the ambient temperature without active control. We will add these in the revision:

“Our test experiments using the ambient air, without applying the drier, have shown that the drier did not affect the background ion signals. We also confirmed experimentally that the application of the drier did not change the background signals.”

“The inlet was drilled through the wall of the trailer at horizontally, in the direction precisely aligned the CIMS inlet. The inlet thus was not shared with other instruments.”

Comment: 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?

RE: We have background mode for 5 min at every 20 min cycle (remaining 15 min is for ambient measurement mode). Our sample time is slightly longer than 1 s (actually ~1.2 s). So we have 250 data points in each background mode. We remove 40 data points in the beginning and 10 data points at the end, to get rid of those unstable signals that occur while switching between different modes (from “background” to “ambient” or vice versa). So, 200 points are used to calculate the background level. Therefore we do not detection limits with 5 min or 20 min integration. Table 1 shows detection limits for 1

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s integration time. The data shown in time series of all figures in the paper are those further averaged values over 20 min. With the integration time of 1 s, 5 s, 30 s and 60 s, detection limits are calculated and they will be shown in additional tables which will go to Supporting material (shown below also). The background signals were stable during the entire campaign and in Kent, and they similar to those shown in Figure 1. The mean background signals will be shown in another tables (in Hz and ppt, both) in the Supporting material.

Comment: 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?

RE: At this moment, we can only provide calibration curves using amines at ppb level, mainly because we don't have low concentrations of standard gases with accurately known concentrations. So we extrapolate the calibration curve down to ppt, but we have no evidence that the CIMS has linear response to over ppt through ppv level. This is one of the issues we will need to explore in the future.

Comment: 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.

RE: The conclusion that background signals are not dependent did not come from tests using the drier and came from tests without drier. The drier was applied, in order to prolong the lifetime of the scrubber, after we confirmed that RH does not change the background signals. Without the drier, we tested background signals at different ambient RH conditions at both measurement sites, and we did not see any changes in the background signals with RH. Therefore, using drier does not affect the background signals, which we also confirmed experimentally. We will clarify this in the revision. We will add:

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“Our test experiments using the ambient air, without applying the drier, have shown that the drier did not affect the background ion signals. We also confirmed experimentally that the application of the drier did not change the background signals.”

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 most all of the Alabama experiment. What is the detection limit for a 20 min 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.

RE: Please see our earlier response. As will be seen from additional tables in the supporting material for detection limits as different integration times for all amines and ammonia, we can see detection limits start to level off from 5-10 s.

Comment: 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.

RE: The CIMS was located in the trailer at the ground. The air was sampled directly through an inlet drilled through the wall of the trailer, in the exact direction aligned with the center of mass spectrometer detectors and octopoles and the CIMS inlet. We did not sample from the tower. The inlet was used only for amine-CIMS, not shared with other instruments. This will be added in the sampling section. We will add:

“The inlet was drilled through the wall of the trailer at horizontally, in the direction precisely aligned the CIMS inlet. The inlet thus was not shared with other instruments.”

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 measurement

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shown 1s?

RE: We will change to “below the detection limit’. The detection limit indicated in Table 1 was calculated from 1 s integration time. The time series in all figures are averaged from 20 min. We will clarify this in the text and figure captions.

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

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Table 1. Detection limits (3 sigma of background signals) derived from SOAS.

SOAS	1 s	5 s	30 s	60 s
NH ₃ (pptv)	53.6	43.3	40.1	35.1
C1 (pptv)	1.18	0.37	0.21	0.13
C2 (pptv)	4.75	1.51	0.86	0.52
C3 (pptv)	5.55	1.89	1.19	0.77
C4 (pptv)	23.1	8.09	5.15	3.24
C5 (pptv)	17.3	5.44	3.05	1.88
C6 (pptv)	13.0	4.05	2.27	1.40

Fig. 1.

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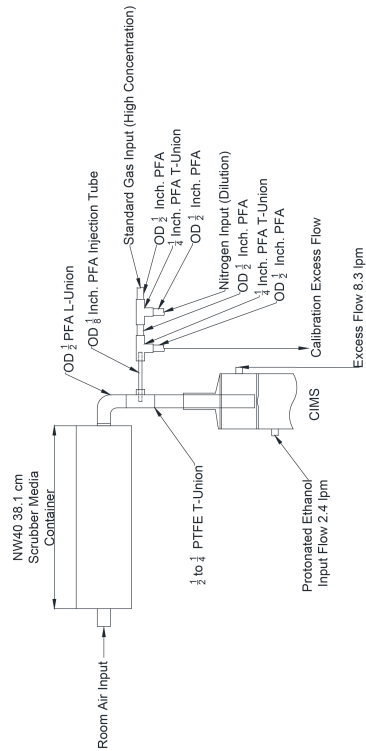


Fig. 2.

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