**Atmospheric
Chemistry
and Physics**
Discussions

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

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

Comment: This manuscript reports measurements of gas phase amines and ammonia in Alabama and Ohio during the summer of 2013. There are relatively few high time resolution datasets that provide measurements of gas phase reduced nitrogen (ammonia, and especially speciated amines) from continental North America, so from that perspective the data are potentially quite interesting. However, the presentation of results in the manuscript is disorganized, and the most relevant complementary data is not presented until the discussion section. In this section, the authors use FTIR and TD-

CIMS data to show that amines are present in much higher abundance in sub-micron aerosol, compared to the gas phase. This suggests that gas-particle partitioning may play a key role in regulating the abundance of gas phase amines, and this discussion should be prioritized over the correlations with wind direction, CO, isoprene, etc.

RE: Agreed. Gas to particle conversion is the most important finding. We will move particle data to the earlier Section 5, prior to wind direction analysis etc.

Comment: The authors should revise the manuscript to address the following points:

General Comments

Comment: The relatively high levels of particle phase reduced nitrogen calls into question the ability of the gas phase CIMS to discriminate against particle phase ammonium and amines. Based on the inlet schematic presented in the supplementary information, there is no strategy employed to prevent particles from entering the CIMS and potentially volatilizing to generate positive artefacts. What evidence do the authors have that this is not a concern, especially given that the FTIR data suggest that conversion of only 1% of the particle amines could generate a signal equivalent to the measured gas phase amines?

RE: We have tested with different transit times with standard amine vapor produced from permeation tubes, and this did not change the background levels and the concentrations of ambient amines measured with CIMS. So we think even though only 1% of total amines correspond to gas phase amines, this did not affect the sampling issues, substantially. This is perhaps because the time needed for gas to particle conversion or adsorption/desorption may be much longer than the transit time used in this study (less than 0.2 s) and the surface area of the inlet inside wall is really small (so little mass of deposited amines).

Comment: Assuming that the concerns about particle phase artefacts can be addressed, I recommend moving the information about the FTIR, TDCIMS and ion chro-

matography measurements from pages 16426 -16427 and Figures 11-13 to Section 5, where the other measurements from SOAS are reported. More information about the particulate data would be valuable. Can the TDCIMS data be converted from mass to mass loading (presumably using the volumetric sampling rate?) to better compare the relative amounts of amines in the gas phase and in particles between 40-120 nm? If the FTIR technique only measures primary amines, then it is likely underestimating total particle amines. Do the authors (or the literature) have any insights into what fraction of ambient C1-C6 amines are primary amines?

RE: The TDCIMS data are presented as ions detected per particle mass collected. The purpose for this is to demonstrate that amines compose a smaller fraction of the small particle mass during the late morning and afternoon than in the night. The instrument was not calibrated with amine standards, so it is not possible to report actual mass loading of amines in the size ranges measured. Even if it were, the nanoparticles measured by the TDCIMS likely represent only a small fraction of the total particle amines and therefore are not suitable for comparing in an absolute way to gas phase concentrations. So the original sentence will change to:

"During SOAS, the TDCIMS measured various amines in particles in the size range from ∼ 40–120 nm. The particle amine fractions showed diurnal variations (Fig. 13) opposite to the gas-phase amines 15 (Fig. 3). There were higher fractional levels of aerosol-phase amines (C1–C3) during the night and in the early morning and lower levels from the late morning until the end of the day."

With regard to FTIR data: We were not able to find a good estimate of the primary amine contribution to total amine based on the data we have. The gas or aerosol-phase primary amine fraction of total amine in the atmosphere is currently unknown, but this may be the subject of future study.

Comment: Section 6 presents data collected in Kent, OH, later in the same summer after SOAS, but this section does not really contribute to the analysis of data from the

SOAS campaign and seems a bit orphaned in this manuscript. Given that the authors have published other papers that report amine mixing ratios from this site (e.g. Benson et al., 2010; Erupe et al., 2010), I think it would make the paper more cohesive to remove this section and just make the comparison to past datasets reported in the literature. I also recommend removing Figure 9 and related discussions because, given the short lifetime of ammonia against particle uptake and deposition, state-wide aggregate inventory data is unlikely to be representative of the individual source regions for each site.

RE: The purpose of including Kent amine data is to show that (1) the rural sites have lower amines than polluted sites, and (2) this indicates constraint of amines sources from anthropogenic emissions is important and is needed. The previous Yu and Lee, EC 2012 paper shows the winter time amines, and interestingly, we can see from the comparison of this winter and the current summer data that there is a clear seasonal difference due to temperatures, which is also consistent with the general conclusion of the this work. With regard to Figure 9: ammonia lifetimes in the atmosphere are several days, and so the regional scale transport and emissions can be also important. During the same summer in the same year, we saw quite different concentrations of ammonia at these two sites, and that is consistent with higher emissions in Ohio than in Alabama, in general. This was discussed in the text.

Specific Comments Comment: P 16413, L 6 – 'on a daily basis' makes it sound like the sampling interval was once per day

RE: Change to "every day".

Comment: P 16417, L 10 – What do the values (â′Lij17–40%) refer to?

RE: This is the frequency of new particle formation events. We will change this to "with the frequency of new particle formation from 17-40%".

Comment: P 16417, L 23-25 – Are ethanol clusters used to detect the ammonia and

amines, or are they only quantified using BH+? This is mentioned in passing later, but could be clarified here.

RE: In CIMS spectra, we see ethanol monomer, dimers and trimmers for ethanol reagent ions. And for the product ions, we see only BH+ ions. We will add this:

"As shown in CIMS spectra (Figure 1), there were ethanol monomer, dimer and trimmer reagent ions, whereas for the product ions, there were only BH+ ions."

Comment: P 16419, L 3-4– 'National Institute and Technology' - is this the correct name?

RE: Should be "National Institute of Standard Technology (NIST)".

Comment: Table 1 – NH3 concentrations are given in ppbv, but the unit for the detection limit is probably pptv.

RE: that is right – corrected.

Comment: Table 1 – The detection limits are given for 1 Hz data, but the ambient data appear to be averaged to 20 min. Do the detection limits change for 20 min averages? If they don't improve with signal averaging, then why not?

RE: We have the background mode for 5 min at every 20 min cycle. Because of our sample time is slightly longer than 1 s (actually ∼1.2 s), we have 250 data points in each background. We remove 40 data point in the front and 10 data points in the back to remove unstable signals that appear when changing between different modes (from "background" to "ambient" or vice versa). So, 200 points (corresponding to approximately 4 min) are used to calculate the average background. Therefore we do not calculate detection limits for 5 min and 20 min integration. The data shown in time series of all figures in the paper are those further averaged values over 20 min for "ambient" measurement data (in mixing ratio). 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 this will go to Supporting material.

Comment: P16420 – To what factors do the authors attribute the improvement in sensitivity and detection limits compared to past campaigns? The explanation for lower sensitivities of the amines compared to ammonia implies that the amines are more prone to surface adsorption than ammonia, but is that known to be true? Have the authors examined the ion chemistry of the amines carefully to ensure that there is no fragmentation?

RE: The lower detection limits and sensitivities were achieved mainly because of lower background signals and much more stable background signals, independent on ambient RH. Yes, amines are stickier than ammonia, as we can see from their thermodynamics data. This was clear during the calibration. For amines, we had to have really long time (> 20 hr) to "condition" the permeation tube to have reproducible calibration curves. With regard to fragmentation: we have only BH+ ions as the product for all amine isomers we tried. We added this:

"These improvements in the detection limits and sensitivities were mainly because background signals were lower, less variable and independent of ambient RH conditions."

Comment: Figure 2 – It would be useful to indicate the timing and duration of rain events on this Figure since they are referred to in the text.

RE: Done.

Comment: Figures - What is the averaging time for the CIMS data displayed in all of the time series?

RE: 20 min. We will also include this clearly in the text and figure captions.

Comment: Figure 4 – What is the physical basis for the exponential fits provided in the figure panels and why is isoprene included in the figure?

RE: This is based on BVOCs emission rates derived by Gunther et al., 1995, where the authors showed that BVOCs, such as isoprene, have the exponential temperature

dependence. We were trying to see if this is the case for amines, similarly to isoprene. In response to this comment and another below, we revised the relevant sentence to:

"Concentrations of C3-amines and NH3 detected in the Alabama forest showed some exponential dependences on the ambient temperature, like isoprene (Figure 4). Such exponential temperature dependences, as typically found for BOVCs emitted from trees [Guenther et al., 1995], may suggest as some biogenic sources of C3-amines; but there is also caveat in this interpretation, because the temperature dependence was also simply due to the dominant gas-to-particle conversion process, as discussed above."

Comment: Figure 6 – I find the explanation of the data in the related text confusing. It seems that around 14:00 the wind shifted from southerly to northerly and the T, CO and amines all dropped at the same time. This doesn't seem to provide a clear example of amines NOT correlating with SO2 and CO, as indicated in the text.

RE: We have done comprehensive data analysis to see whether amines are correlated to CO and SO2 pollutants in very detail for each day for the entire SOAS campaign. And from this systematic analysis, we found that regardless of wind direction or time of the day (rush hours) or day in the week, there was no any correlation of amines and these pollutants. We will make this more clearly stated in the revision. For the case of the day shown in Figure 6: around 14:00 wind direction changed and CO was dropping, but SO2 were low in the afternoon prior to that time and this did not cause low C3-amines or ammonia. We removed the entire paragraph related to Figure 6 in Sections 5 and 7, but instead, we state now briefly in Section 5:

"We made systematic data analysis for each day of the campaign, and we found that amines and NH3 concentrations measured in the Alabama forest were not associated with traffic or with transported anthropogenic SO2 and CO plumes, regardless of wind direction, time of the day (rush hours) or day in the week (e.g., Figure 6)."

Comment: Figure 10 and associated discussion – Given the many reasons that ambient trace gases can have similar diel profiles, the suggestion that the similarity between

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C3- amines and isoprene can be attributed to biogenic emissions of tri-methyl amine seems quite speculative. Given the strong indication later in the manuscript that ambient volatilization of particle amines can act as a significant source of gas phase amines, I would remove this section.

RE: Agreed - we will remove Figure 10 and will restate: "The exponential temperature dependence of C3-amines, as typically found for BOVCs such as isoprene [Guenther et al., 1995], may suggest as some biogenic sources of C3-amines; but there is caveat in this interpretation, because the temperature dependence was also simply due to the dominant gas-to-particle conversion process at this site, as discussed above."

Comment: P 16424, L7 – Should ppbv actually be pptv for the amine concentrations given here?

RE: Corrected.

P16425 – I suggest changing 'photo-degradation' to 'oxidation' so that it is clear that direct photolysis is not considered an important sink of amines in the atmosphere.

RE: Done.

P16427, L8-12 – I don't understand the discussion about the temperature dependences and thermodynamics here. Presumably it's not just the vapor pressure, but the enthalpy of vaporization that influences the temperature dependence. Furthermore, on P16426, the authors argue that the amines could be taken up into acidic aerosol water, in which case it's the enthalpies of the Henry's Law and acid dissociation constants that should be considered.

RE: These are very interesting comments. In response to these, we actually performed simple enclosure calculations of amines and ammonia in gas and aerosol phases to see their relative differences in gas to particle conversion processes of an amine versus ammonia as the following, and we will include them in the revision.

Consider an ammonia or amine compound A(gas), Henry's law equilibrium:

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reaction: A_gas == A_aq

[A_aq] = H_a [A_gas] (Eq.1)

where H_a is Henry's coefficient. Now consider dissociation followed by reaction:

A_aq + H+ == AH with K_a = [A_aq][H+]/[AH] so [A_aq] = K_a [AH] /[H+]

Put into Eq.1:

[A_gas] / [AH] = K_a / (H_a[H+]) (Eq. 2)

this is the gas to particle ratio for chemical A (neglecting A_aq which is probably very small at acidic pH).

Similarly for another gas, B:

[B_gas]/[BH] = K_b / (H_b [H+])

Take ratio:

[B_gas]/[BH] / [A_gas]/[AH] = (K_b/K_a) (H_a/H_b) (Eq. 3)

Equation 3 gives the RELATIVE particle/gas partitioning of the two compounds A and B. Now consider A = ammonia, B = some amine:

Henry's law coefficients are similar in general, so assume that H_b/H_a $\sim$ 1, for simplicity.

But pKa is very different: -9.2 for ammonia, -10.6 to -11 for typical alkyl amines. Taking a difference of 1.6, K_a/K_b $\sim$ 10^(-1.6) $\sim$ 2.5%.

So the amine is 40 times (1/2.5%) more likely to be on particles than ammonia. If the ammonia gas/particle ratio is between 1 and 2 (Figure 10), then for the amines the gas/particle ratio should be 2.5% of that, or between 2.5% and 5%. Figure 12 shows this ratio to be between 0.8% and 1.2%, so in pretty good agreement within a factor of 2 which could be easily explained by the ratio of Henry's law coefficients, H_b/H_a,

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which above we took to be near unity.

So, the much higher particle/gas partitioning for amines, relative to ammonia, is consistent (within a factor of 2) with the amines being stronger bases, and pK $\sim$1.6 lower than for ammonia.

Of course this neglects the effects of salt formation, which is probably likely at pH of 3 at this forest site. So it is not an exactly most accurate calculation, but this still shows the qualitative consistency. We will include the following in the revision:

"We have performed a simple calculation to determine the relative likelihood of gas to particle conversion of an amine versus ammonia. In our calculation, we considered only Henry's Law equilibrium and acid dissociation, and neglected salt formation and other processes. Henry's Law constants are quite similar for an alkali amine and ammonia [Sander, 1999]. But their acid dissociation rates (pKa) are different. So if we take pKa for a typical alkali amine as -10.8, and pKa for ammonia as -9.2 [NIST, 2005], then we can derive the relative gas to particle conversion of an amine compound is nearly 40 times stronger than for ammonia. The ammonia gas to particle ratio is between and 1 and 2 (Figure 10), so according to our calculation, then the gas to particle ratio should be between 2.5% and 5%. Figure 12 shows this ratio to be between 0.8% and 1.2%, so this is consistent within a factor of 2 with the prediction from our simple calculation. These results show that it is reasonable to expect much stronger gas to particle conversion than for ammonia, based on their Henry's Law constants and acid dissociation rates."

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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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