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

Anonymous Referee #1

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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 TDCIMS 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.

C5535

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

General Comments

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?

Assuming that the concerns about particle phase artefacts can be addressed, I recommend moving the information about the FTIR, TDCIMS and ion chromatography 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?

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

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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.

Specific Comments

P 16413, L 6 – ‘on a daily basis’ makes it sound like the sampling interval was once per day

P 16417, L 10 – What do the values (17–40%) refer to?

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.

P 16419, L 3-4– ‘National Institute and Technology’ - is this the correct name?

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

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

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?

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.

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

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

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.

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

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

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

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.

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

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