Ambient Pressure Proton Transfer Mass Spectrometry: Detection of Amines and Ammonia

D. R. Hanson,*,[†] P. H. McMurry,[‡] J. Jiang,[‡,§] D. Tanner,[||] and L. G. Huey[||]

[†]Chemistry Department, Augsburg College, 2211 Riverside Avenue, Minneapolis, Minnesota 55454, United States
[‡]Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota, United States
[§]School of Environment, Tsinghua University, Beijing, China
[||]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, United States

Ⓢ Supporting Information

ABSTRACT: An instrument to detect gaseous amines and ammonia is described, and representative data from an urban site and a laboratory setting are presented. The instrument, an Ambient pressure Proton transfer Mass Spectrometer (AmPMS), consists of a chemical ionization and drift region at atmospheric pressure coupled to a standard quadrupole mass spectrometer. Calibrations show that AmPMS sensitivity is good for amines, and AmPMS backgrounds were suitably determined by diverting sampled air through a catalytic converter. In urban air at a site in Atlanta, amines were detected at subpptv levels for methyl and dimethyl amine which were generally at a low abundance of <1 and ∼3 pptv, respectively. Trimethyl amine (or isomers) was on average about 4 pptv in the morning and increased to 15 pptv in the afternoon, while triethyl amine (or isomers or amides) increased to 25 pptv on average in the late afternoon. The background levels for the 4 and 5 carbon amines and ammonia were high, and data are very limited for these species. Improvements in detecting amines and ammonia from a smog chamber were evident due to improvements in AmPMS background determination; notably dimethyl amine and its OH oxidation products were followed along with impurity ammonia and other species. Future work will focus on accurate calibration standards and on improving the sample gas inlet.
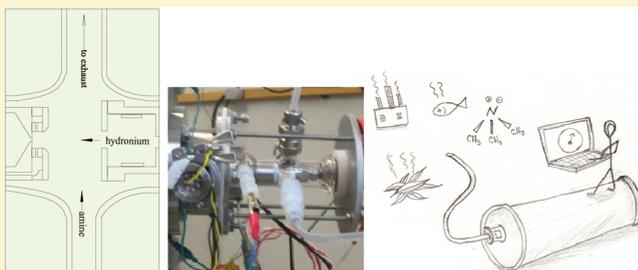
1. INTRODUCTION

Ammonia (NH_3) and amines (e.g., a primary amine, RNH_2, R = CH_3, etc.) are the most common basic compounds found in the atmosphere in both the gas[1−4] and particulate phase.[5−11] Laboratory[12] and theoretical work[13] indicates that these compounds have a potentially large affinity for the particulate phase if strong acids are present. The coaccumulation of amines and or ammonia with acids on atmospheric particles can be important for growth of atmospheric particles.[7−10] Also, nitrogen bases are believed to enhance particle nucleation rates.[14−17]

Currently, there are a variety of methods, e.g. derivatization and chromatography,[18,19] infrared absorption, etc.,[20−22] chemical ionization mass spectrometry (CIMS)[23,24] to measure gas phase ammonia. There is also a relatively large set of observations of atmospheric ammonia.[3,21] In contrast, the observations of atmospheric amines are rare because of their generally low abundance and the constraints of the measurement techniques. Consequently, the distribution, sinks, and sources of atmospheric amines are not well-established.[4]

Amines have been detected in the atmosphere using primarily chromatographic methods that are specific for individual compounds. However, these methods often lack high time resolution due to preconcentration, derivatization, and elution steps that may require hours. In recent years mass spectrometry has been used to measure atmospheric amines. Selegri et al.[25] used a modified proton transfer-reaction-mass spectrometer (PTR-MS) to detect amines (e.g., trimethyl amine) and other compounds in rural air in Finland. Eisele[26] deployed an atmospheric pressure ionization CIMS and reported detection of amines species such as trimethyl amine and picoline/aniline in addition to ammonia. Amines have been detected in atmospheric particulate matter[7−11] which indicates that these compounds can be important for particle growth and perhaps their formation.

In this work a new method for the measurement of atmospheric amines is characterized, Ambient pressure Proton transfer Mass Spectrometry (AmPMS). The AmPMS combines the specificity of chemical ionization with the high sensitivity of atmospheric pressure ionization techniques. Species with very high proton affinities (e.g., amines) are selectively ionized by reaction with large water clusters of the hydronium ion, $H_3O^+(H_2O)_n$. The design, calibration, and basic operating procedure of the AmPMS are presented here. In addition, initial observations of amines by the AmPMS in an urban environment and in a Teflon smog chamber are presented.

2. EXPERIMENTAL SECTION

Measurement Sites. Amine measurements are reported from two sites: ambient air in Atlanta from late July to mid-August 2009 and from a smog chamber at the University of Minnesota in 2010. The urban site in Atlanta has hosted a number of field campaigns in the past dozen years and has been described previously in a number of publications.[23,27−29] The 2009 campaign (NCCN: Nucleation and Cloud Condensation Nuclei) was focused on particle formation, and a suite of particle instruments along with sulfuric acid and particle mass spectrometers were deployed along with AmPMS. AmPMS was also deployed at a smog chamber consisting of a ~1 m³ Teflon bag in a temperature regulated steel container housed at the University of Minnesota (UM). Small amounts of amines could be introduced into the chamber with a microsyringe as either vapor or aqueous mixtures. The chamber was flushed repeatedly with air from a Pure Air Generator 737 (Advanced Analytical Device Company, Cleves, Ohio, USA.) The chamber was used for particle formation experiments using photolytic generation of sulfuric acid. The chamber and experiments will be described in detail in a future publication (Titcombe, McMurry et al. manuscript in preparation.) Also, results of periodic testing of AmPMS sampling capabilities and calibrations at Augsburg College (AC) are presented.

Apparatus Description. AmPMS was developed from a previous instrument focused on laboratory studies of ammonia[30] and consists of a chemical ionization and drift region at atmospheric pressure coupled to a standard quadrupole mass spectrometer. Reagent ions, $H_3O^+ \cdot (H_2O)_n$, are produced in a radioactive source and then drawn across a flow of sampled air with an electric field where they can react with trace gases. Reagent and product ions enter a vacuum system where they are mass selected with a quadrupole mass spectrometer and detected with a channel electron multiplier. Shown in Figure 1 are the main parts of AmPMS: ion source, drift region, curtain region, ion sampling inlet, and collisional dissociation chamber (CDC). The sample gas inlet with three way solenoid valve and catalytic converter are also shown. Details of these parts are discussed in sequence below.

Ion production was initiated with radioactive sources, either ^{241}Am (2 μCi) or ^{210}Po (~40 μCi), and the presence of water vapor[31] leads rapidly to the formation of protonated water clusters, $H_3O^+ \cdot (H_2O)_n$. A flow of ~0.020−0.050 sLpm (std. conditions L min^{-1}, 1 atm and 273 K) of UHP nitrogen (99.999%) or clean air, catalytically purified,[32] was maintained through the source for cleanliness. This flow was humidified by exposure to a liquid water reservoir containing a few cm³ of deionized water acidified with a few drops of sulfuric acid. Sulfuric acid was added to the reservoir to suppress the vapor pressure of any basic impurities such as ammonia. Ions exit the source through a hole (diameter ~0.7 cm) in a 0.07 cm thick, 2 cm diameter plate and enter the drift region. They are drawn from the source due to fringing fields near the exit aperture of the ion source.

The drift region is enclosed in a small glass manifold and consists of a gap of 1-to-1.5 cm between the exit plate of the ion source and the entrance plate to the curtain region. A voltage of typically 1.4 kV is applied across it resulting in an ion−molecule reaction time of ~0.7 ms. Sample flow of ~1 sLpm enters the drift region via a port in the manifold and exits via an opposing port. A third port on the manifold connects to a pressure sensor. The E/N, E is electric field and N is number density, is ~4 Td (1 Td = 10^{17} V cm^2) in the ambient pressure drift region and ions are essentially at the ambient temperature, and the distribution of protonated water clusters is dominated by clusters n = 5 to 8: $H_3O^+(H_2O)_{5-8}$.[33] After the
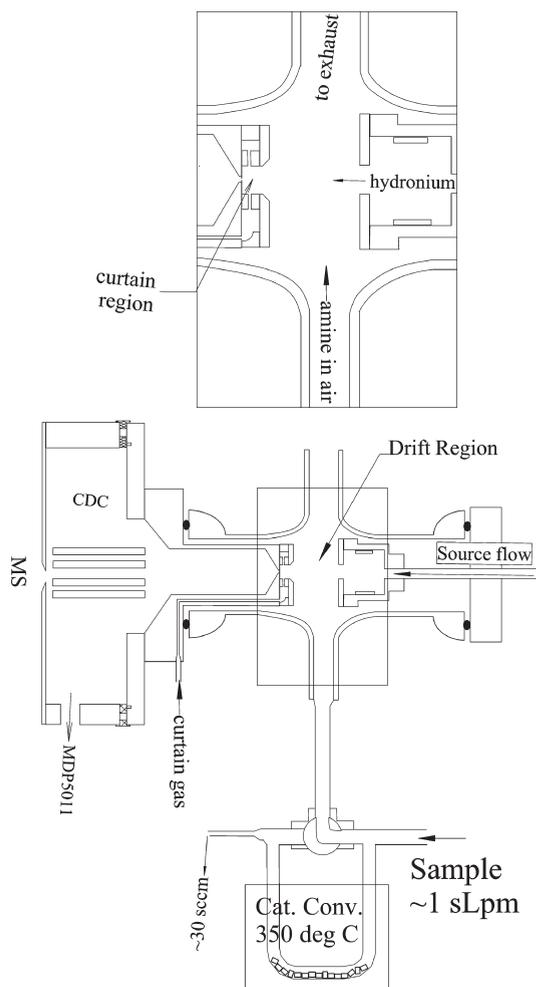
Figure 1. AmPMS ion source, gas entrance and gas exit ports, mass spectrometer inlet, and CDC with octopole ion guide. Schematic depiction of the instrument as deployed for NCCN showing the sampling arrangement, the three way valve, a small flow to the pump, and the catalytic converter. Inset is blowup showing source, drift region, and curtain region.

reagent ions react with amines and ammonia, they and the product ions are drawn into the curtain region.

The curtain region is ~0.45 cm long and is purged with dry nitrogen (~0.1-to-0.2 sLpm) via a small Teflon manifold (i.d. 0.5 cm) to minimize the amount of water vapor entering the system. An electric field draws ions across the curtain region (E/N = 2-to-4 Td) to the ion sampling orifice, where a portion enters the CDC and vacuum system via a 125 μm hole in a ~130 μm thick stainless steel disk.

Ions pass through the CDC, a region about 6 cm long at a pressure of ~0.5 hPa maintained with a drag pump (MDP5011, Alcatel), where they are stripped of water ligands. The CDC has an octopole ion guide to center ions onto a 3-to-4 mm orifice, the entrance to the first chamber of the MS system. The average E/N in the CDC is ~40 Td, and the ionized (protonated) trace species that were monitored had very few water ligands with the exception of the reagent ions: the water-proton clusters did not fully detach water ligands with the most abundant water proton cluster at $H_3O^+ \cdot H_2O$. Note that the octopole ion guide likely causes the ions to experience a range of E/N, both higher and lower than the average value.

Next the ions enter a differentially pumped quadrupole mass spectrometer vacuum system. For deployment in the 2009 Atlanta campaign this system was a Georgia Tech mass spectrometer (300 L/s turbos, 16 mm OD rods) which was equipped with an octopole ion guide in the first chamber at ∼3 × 10^{-3} hPa.[34] For AC testing and calibrations and the UM Teflon chamber measurements the vacuum system was equipped with larger pumps, two 1000 L/s turbo pumps (Varian Inc.), and the first chamber was at ∼0.5-to-1 × 10^{-3} hPa and had a series of ion lenses rather than an octopole ion guide. The second vacuum chambers held the quadrupole mass analyzers at low pressures (∼5 × 10^{-5} and ∼10^{-5} hPa, for Atlanta and AC and UM, respectively.) Note that the ion throughputs of the two systems were not evaluated, and mass dependent effects were assumed to be negligible. See the SI (Supporting Information) for more discussion of mass dependent effects.

Gas Sampling. The gas sample flow rate was ∼0.8 (UM chamber) and 1.5 (ambient air, Atlanta 2009) sLpm drawn through a port in the glass manifold. Flow exiting the manifold was metered downstream with a mass flow meter positioned before a pumping line. For the Atlanta work, the sample gas lines were 1/4" OD Teflon tubing in two sections: a ∼40 cm length between a Teflon three-way valve on the catalytic converter (see below) and a ∼2 m length that ran up and out the trailer and was about 2 m above the ground. A small polyethylene cone to divert rain from the tip of the inlet was attached over the end of this tube for the field instrument. For the UM chamber and AC experiments, the three-way valve was mounted directly on the glass manifold, and the sample line was ∼1 m of 6.2 mm Teflon tubing. For some AC tests of ambient air, this was extended to 8 m.

Catalytic Converter. The instrument background was measured by passing the sample gas through a catalytic converter, a ∼30 cm length of 1/4" OD stainless steel tube containing Pt on alumina beads held at 350 °C. The sampling lines and converter are schematically depicted in the lower part of Figure 1. For the field experiments, a flow of ∼0.030 sLpm continually flushed the catalytic converter. For the UM and AC work, the catalytic converter was rebuilt with inlet and outlet tubes crossed so that the hot gas exiting the converter could transfer heat to the gas entering it.

Calibrations. The sensitivity of the instrument was evaluated (post-Atlanta mission) for a few amines and some VOCs by evaporation of aqueous solutions of known composition. Small aliquots (1–10 μL) of dilute aqueous solutions containing one to three compounds were injected through a port in a glass vessel or a large Teflon tee in series with the sample flow. With known amounts of compounds entrained in a flow of clean gas, sensitivities can be obtained from integrated count rates.[32] The gas sample flow of 0.3–1.0 sLpm of catalytically cleaned room air was at ambient relative humidity. Solutions were prepared gravimetrically, and by serial dilution their concentrations were known to an accuracy of 10%. One solution containing methanol, acetone, and 3-pentanone (at concentrations of ∼0.1 to 0.01 M, reagent grade, VWR) and a few solutions with amines (∼ 10^{-4} M, methyl and dimethyl amine from ∼40 wt % solutions, Sigma Aldrich; 4-picoline, VWR, 97%) were used. The concentrations of the reagent MA and DMA solutions were verified by titration with known HCl solutions.

The amine calibrations were quite variable, presumably due to interactions with the room temperature glass and Teflon surfaces; several trials (3 to 5) were needed before results were reproducible. Even then, they exhibited variabilities at ∼30%, much greater than the typical ∼10% variabilities for methanol

Table 1. Calibrations of the Laboratory Instrument Using the Evaporation Method[b]

compound	P.A. (kcal mol^{-1})	S_x/S_{max}
methanol	180	4 × 10^{-4}
acetone	194	3 × 10^{-3}
3-pentanone	200	2 × 10^{-2}
methyl amine	215	∼0.2^a
dimethyl amine	222	∼0.15^a
4-picoline	226	∼0.2^a

[a] As discussed in the text and SI, the calibrations for these compounds were biased low; the S_x/S_{max} for the laboratory and ambient data for all the amines including methyl amine were assumed to be unity, consistent with the Sunner et al.[37] data. [b] t_{ion} was 0.66 to 1.2 ms. S_{max} according to eq 1 with $k = 2 \times 10^{-9}$ cm^3 s^{-1}.

and acetone.[32] Furthermore, the signals ∼30 min after the injection were observed to increase slightly with each trial, indicating significant sticking. Significant signal for the amines existed when clean air was flowing through the calibration cell several days after their calibrations. The methanol-acetone-pentanone calibrations did not require several trials for reproducible behavior, and the system was flushed in ∼3 min.

3. RESULTS AND DISCUSSION

Calibrations. Shown in Table 1 are the compounds, their proton affinities,[35,36] (also see the SI), and their sensitivities expressed as a fraction of the maximum sensitivity, in Hz pptv^{-1}

$$S_{max} = S_0 kt \times (2.4 \times 10^7 \text{ cm}^{-3} \text{ pptv}^{-1}) \tag{1}$$

where S_0 is the reagent ion signal, k is the ion molecule rate coefficient = 2×10^{-9} cm^3 s^{-1}, and t is the ion drift time (∼1 ms, see the SI.) The factor in parentheses is the number density for a mixing ratio of 1 pptv for 1 atm and 300 K, typical operating conditions for AmPMS. Equation 1 is an approximation of one presented below and is accurate for reactant concentrations up to about 2000 pptv.

The observations presented in the preceding section indicate that the calibration procedure did not capture the full allotment of amine and thus results were biased low; the S_x/S_{max} for the atmospheric data for all the amines including methyl amine were assumed to be unity, consistent with the Sunner et al.[37] data. Note that a rough calibration for DMA with the UM chamber discussed below and a calibration for ammonia during NCCN (SI) bolster the assumption that $S_x = S_{max}$ for the amines.

The dependence of sensitivity on PA shown in Table 1 is consistent with previous work. Sunner et al.[37] showed that the reactivity of large $H_3O^+(H_2O)_n$ clusters with VOCs has a relatively sharp dropoff for compounds with PA below about 204 kcal/mol, the PA for ammonia. This steep dependence simplifies mass spectra of ambient air because highly abundant species such as methanol, acetaldehyde, and acetone are not readily ionized because of their low PA.

Calibrations lead to sensitivities that incorporate both ionization efficiency and relative ion transmission with respect to 37 u, the main mass where the reagent ion was observed. The relative ion transmissions of the field MS and the MS instrument in the laboratory are not known, and for simplicity they are assumed to be unity. Future calibration work with an instrument of known

relative ion transmission should allow for a better determination of the dependence of sensitivity on PA.

Specificity and Detectable Compounds. Because compounds with low proton affinities (<200 kcal/mol) do not react fast with the reagent ions, there is a limited class of compounds that are detected efficiently with AmPMS: amines, amides, imides, etc. The alkyl amines: methyl-, C2-, C3-, C4-, C5-, and C6- amines were detected at m/z = 32 u, 46 u, 60 u, 74 u, 88 u, and 102 u. Note that structure information is not meant to be conveyed by these assignments as many isomers are possible. For example, 46 u could be either protonated ethyl or dimethyl amine but is not likely to be influenced by formamide which has a proton affinity of 196 kcal/mol.[35,36] Previous work[4] shows that dimethyl amine, DMA, dominates. Also, amides with more than 1 carbon may have high enough proton affinities[35,36] that they could be detected at the amine masses for 60 u and greater: for example, 74 u could be a C-3 amide or a C-2 secondary amide. Imines (C=N bond) and imides (cyclic) would not interfere with amine detection, as they generally differ from amines by 2 u.

For standard conditions of the AmPMS, these compounds give ions that the CDC dehydrates to primarily the protonated parent compound. For example, ammonia gave 90–95% NH_4^+, the remainder at $NH_4^+ \cdot H_2O$. The amines were likewise dehydrated. The reagent ion, heavily hydrated H_3O^+, was dehydrated to mostly $H_3O^+ \cdot H_2O$ at 37 u (~10% each at 19 and 55 u) for the Atlanta campaign, while dehydration was more pronounced at times for UM and AC experiments; H_3O^+ at 19 u could be up to 50%. The amount of hydration of H_3O^+ can be greatly affected by small changes in the E/N within the CDC.

There was no evidence for fragmentation of low molecular weight amines. Yet, ionization of high molecular weight amine/amide compounds could yield fragments that would interfere with detection of low molecular weight amines, as suggested by a reviewer. Whether high molecular weight base compounds are abundant enough to interfere in this way is not known; however, a recent review suggests that the low molecular weight alkyl amines are the dominant amine species.[4]

Concentrations from Ion Signals. The most abundant species that reacts readily with the hydrated clusters is ammonia which can be present at several ppbv and thus NH_4^+ can become a prominent ion. Viggiano et al.[38] showed that amines react readily with NH_4^+-$(H_2O)_n$ clusters so that the sensitivity of AmPMS for amines is not significantly impacted when the reactant ion becomes ammonium. However, S_0 must include the NH_4^+ ion count rate in addition to that for the water clusters $H_3O^+(H_2O)_{0-2}$, abbreviated as $S_{H_3O^+}$. With $S_{Y+} \ll S_0$ and $S_0 = S_{H_3O^+} + S_{NH_4^+}$, amine concentrations [Y] were extracted from the net signals for the amine, S_{Y+}, using eq 2 and assuming a maximum sensitivity, i.e., $k = 2 \times 10^{-9}$ cm^3 s^{-1}

$$[Y] = (S_{Y+}/S_0)/kt \text{ in molecule cm}^{-3} \qquad (2)$$

$$[Y] = S_{Y+}/S_{max} \text{ in pptv, using (1)} \qquad$$

Ammonia concentrations were extracted from the signals using the following equation

$$[NH_3] = \ln[(S_{H_3O^+} + S_{NH_4^+})/S_{H_3O^+}]/kt \qquad (3)$$

Note that $[NH_3]$ from eq 2 agrees well with (3) when ammonia is less than ~2000 pptv. For a large portion of the NCCN campaign, the $S_{NH_4^+}$ count rate including background was 15% or less of S_0. However, background count rates for ammonia for NCCN were difficult to separate from the ambient signal because
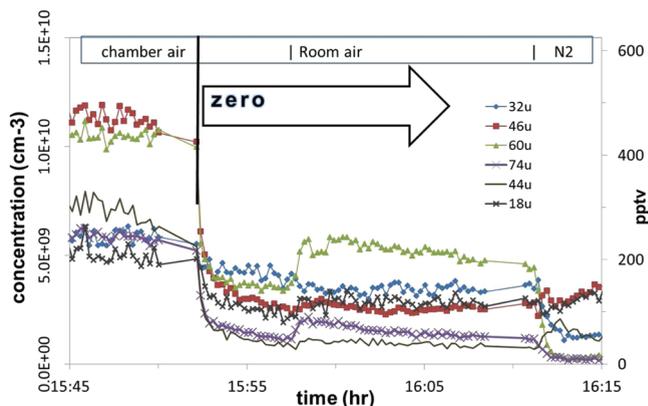

Figure 2. AmPMS sampling chamber air without added amines. Levels of amines at 100 s of pptv seemed unavoidable even with repeated flush-fill heat cycles of the chamber and Teflon bag. Instrument background determination was initiated at 15:52 and during this zero AmPMS sampling was changed to room air and then to dry N$_2$.

of the sampling line arrangement. See the SI for more discussion of the detection of ammonia in Atlanta for a seven day period, the ion chemistry, and instrument sensitivity. The SI also presents the results of the application of (2) and (3) for ammonia and amine concentrations when ammonia was relatively high in AC measurements of urban air in winter.

Background. The measurement of the amine background signals of the AmPMS had a relatively fast response time of one minute or less: a set of data is shown in Figure 2. During this zero, the system was taken off the UM chamber and sampled room air whereupon changes in the backgrounds for some signals are apparent. Room air contained much higher levels of amines and other compounds and more water vapor than the chamber air. Whether the converter fully eliminates amines is a concern, but it is clear that composition of the sample air most likely water vapor influences the backgrounds. This is illustrated when (@ 16:12 in the figure) dry UHP nitrogen was sent through the catalytic converter, and a marked change in the background levels for several compounds is apparent. The instrument background for many compounds depended on the relative humidity of purified air (catalytically cleaned) sent in as the sample gas. This effect was not explored further, but frequent zeroing is recommended especially when the RH of sampled gas undergoes a large change.

Instrument background signals for NCCN were determined by diverting the flow through the catalytic converter for ten minutes every two hours. It was observed that the background levels for the amines were highly temperature dependent. Increases were on the order of a factor of 5 as outside temperature rose from 20 to 37 °C. The periodic ten minute zeroes were used and were linearly interpolated during the two hour intervening times. For the C-2, C-3, and C-6 amines, uncertainties in background levels were low enough such that single digit pptv ambient levels were readily detected on the minute time scale. The background levels for many compounds were well determined in the ten minute zero: signals reach a plateau in ~1 min after the zero was initiated. Methyl amine was apparently very low for the entire campaign, perhaps 1 pptv on a background that had only a modest temperature dependent variation, from 2-to-5 pptv. For the C-4 and C-5 amines, the background levels were quite high, 50–100 pptv at 4 a.m. when temperature was generally <22 °C increasing to as much as ten times this at high temperatures. The ambient
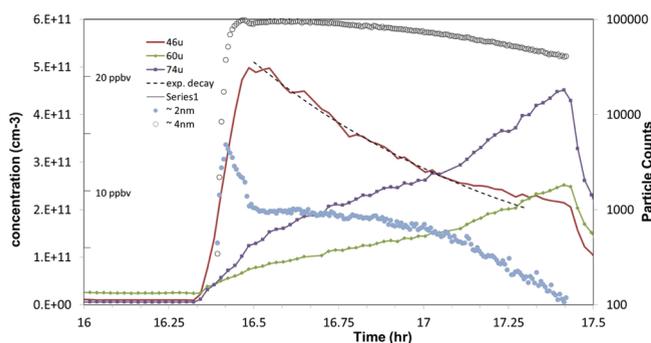
Figure 3. Chamber air sampled during UV photolysis of ozone (10 ppbv) with ~20 ppbv DMA, 10 ppbv SO$_2$, 20% RH with the balance N$_2$. DMA vapor was injected concomitant with initiation of photolysis and DMA levels are seen to rise quickly and then decay away with the apparent DMA oxidation products growing. Particle count rates from a PHA CPC[43] are shown on the right axis; they were binned into two size ranges, roughly 2–3 nm and ~4 nm.

signals at 74 and 88 u were dominated by background levels, and only several hour averages are presented for NCCN.

For most nights a long time zero was established from 9 p.m. to 4 a.m. local standard time. This was done because the background level for ammonia was not being obtained in the ten minute zeroes. This procedure resulted in the ammonia background level for 4 a.m.; however, its dependency on temperature was not known. Therefore, ambient ammonia levels are not reported for the NCCN campaign, except for a short period discussed in the SI.

Chamber Data. Air was sampled at ~0.8 sLpm from a ~1 m^3 capacity Teflon bag filled with purified air, humidified to ~20% relative humidity, with trace amounts of SO$_2$ (10 ppbv), O$_3$ (10 ppbv), and an amine (up to 30 ppbv.) This mixture was then irradiated with 254 nm light. Figure 2, discussed above, shows a typical 'zeroing' of the AmPMS when sampling chamber air containing several hundred pptv of dimethyl amine (46 u) and an amine/amide that gives 60 u along with other compounds: ~100 pptv ammonia and methylamine; ~200 pptv on 74 u; and a few hundred pptv equivalence that gives 44 u, possibly an amide breakup ion at 44 u, CONH$_2^+$ or cyanuric acid.[39] The zeroing apparatus worked well for all these compounds monitored in the chamber experiments, and its superior performance over the Atlanta deployment could be due to a number of things: more uniform catalysis conditions; the N$_2$ for the source flow and curtain gas was taken from a liquid nitrogen gas pack; a lower and a more uniform in time instrument temperature for the UM work; elimination of tubing between three-way valve and ion drift region; and low exposure to ambient air and particulate matter.

Figure 3 shows concentration data as a function of time during an experiment where dimethyl amine vapor was injected into the chamber and signal at 46 u rose rapidly; it was estimated that 20 ppbv was present in the chamber, in good agreement with eq 2 and the assumed maximum efficiency. The amount of amine added was estimated from the partial pressure of DMA over a 40 wt % (14 m) DMA solution at 0 °C using a Henry's law coefficient of 150 m/atm.[41,40] The signals for 60 and 74 u rise as DMA decreases upon OH-initiated oxidation. These signals are likely oxidation products of DMA, possibly N-methylformamide and diformyl amide, respectively.[42] A flush and fill cycle began at about 17:25, and large variations in signals are evident. Ammonia levels were low (~100 pptv) and were detected along with the amines. Particle data using an ultrafine condensation nucleus
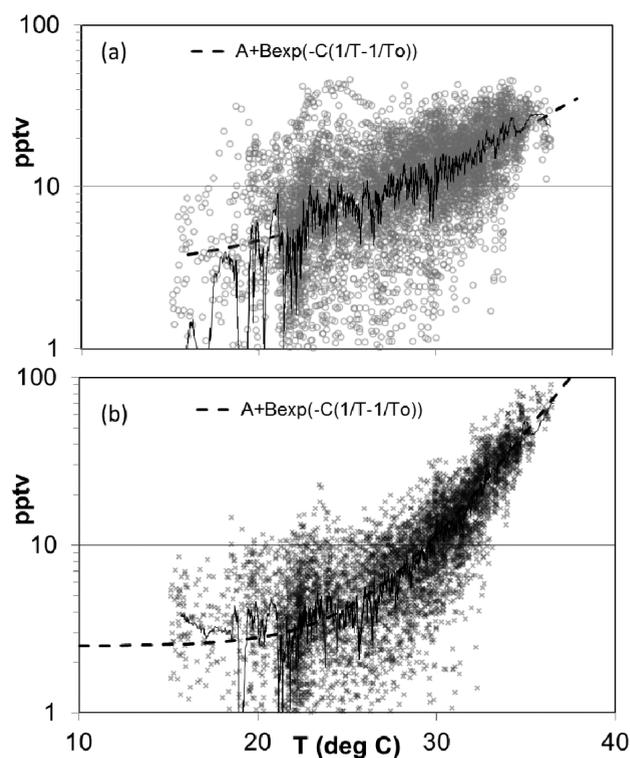

Figure 4. The mixing ratios of two alkyl amines (a) 60 u, trimethyl amine and (b) 102 u, triethyl amine (or isomers or isobaric amides, etc.) plotted versus temperature (5 min averages from NCCN.) The three parameter curves shown are for illustration purposes where a constant mixing ratio has been added to an exponential: A+Bexp(-C(1/T-1/To)). With To = 308.15 K, the values are as follows: (a) A = 3 pptv, B = 20 pptv, C = 15,000 K and (b) A = 2.5 pptv, B = 45 pptv, C = 30,000 K.

counter[43] is shown on the left axis, and a large number of particles were formed upon UV irradiation.

An exponential decay with a time constant of 3×10^{-4} s^{-1} is shown as the dotted line. With this first order loss rate, a rate coefficient for OH + dimethylamine of 6.5×10^{-11} cm^3 s^{-1},[42] an OH concentration of 5×10^6 cm^{-3} is derived. The growth of probable amide species at 60 and 74 u are prominent during the ~1 h photolysis. The signals exhibit nonexponential behavior near the end of experiment when the bag was close to empty.

NCCN Field Data. Amines (and/or the isobaric amides) and other compounds were monitored with AmPMS during NCCN in Atlanta at Jefferson street station in 2009. The amine concentrations had large variations during the campaign with many days exhibiting a pronounced diurnal cycle: peaking in the late afternoon, correlated with temperature. This is shown for 60 and 102 u in Figure 4 as a plot of five minute averages versus ambient temperature where an equation with an exponential dependence on temperature is shown. The amine species that is detected at 102 u is especially sensitive to temperature, and the exponential portion is quite pronounced for this data. The exponential dependence suggests a very high activation energy (~60 kcal/mol for 102 u) that may be consistent with aminium salt evaporation.[10] MA and DMA (32 and 46 u) had low correlations to temperature: linear R^2 values of 0.0 and 0.06, respectively.

The ambient levels of methyl and dimethyl amine were found to be less than 5 and 10 pptv, respectively, consistent with previous measurements that indicate they are generally <1% of ammonia
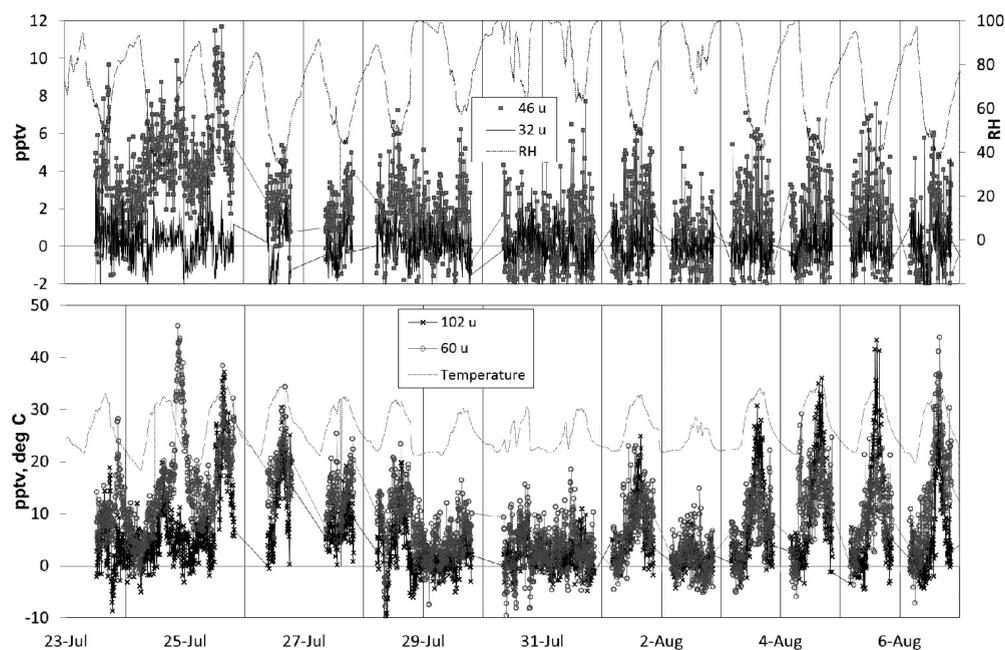
Figure 5. Five minute average amine data over a ∼15 day period in Atlanta 2009 for methyl-, dimethyl-, trimethyl-, and triethyl amine or isomers or isobars (amides, etc.) Relative humidity (right axis) is shown in the top plot, and temperature is shown in the bottom plot.

levels.[4] The dominant amines (or isobars) observed were trimethyl amine and a six carbon amine. These compounds had late afternoon averages of 15 and 25 pptv, respectively, showed a diurnal cycle, and were temperature dependent. The trimethyl amine observations are somewhat lower than the observations by Selegri et al.[25] who report median trimethyl amine levels that ranged from 50 to 80 pptv with peak values in the late afternoon.

Representative 5 min averages for ∼15 days (23Jul09 to 07Aug 09) are shown in Figure 5 with nominal concentration in pptv. The instrument background was measured for an extended period on most nights, thus, the data are primarily for 0400 to 2100 local time. A prominent diurnal cycle is displayed for many days. Days with precipitation and overcast conditions showed low levels of all amines (see the 100% humidity time periods.) A few overnight measurements are shown, and generally low levels are exhibited except for around 10 p.m. on 24Jul09 where the amines were elevated.

The diurnal hourly averages of the amine data from 23Jul09 to 25Aug09 is shown in Figure 6. The diurnal hourly averages for methyl amine were very low for this time period and essentially zero (<0.2 pptv). Averages for dimethyl amine ranged from 0.5 to 2 pptv peaking in the early afternoon, while trimethyl amine ranged from ∼4 pptv in the early morning to a peak of around 15 pptv in the afternoon. The 4 and 5 carbon amines had overall average levels of about 4 pptv (4 a.m. to 8 p.m.). The background count rates were equivalent to many 100s of pptv so these levels are highly uncertain with upper limits (set as ∼5% of the average background) of 10 pptv for 4 a.m. to noon and 30 pptv for noon to 8 p.m. The most abundant amine detected in NCCN was a 6 carbon amine possibly triethyl amine, and it also exhibited a strong diurnal cycle with average values of ∼3 pptv in the morning peaking at 25 pptv in the late afternoon. Note that signal at 102 u could also arise from a number of amides. Finally, the 10 p.m. hourly average has a small number of samples which was dominated by the ∼10 p.m. 24Jul09 event.
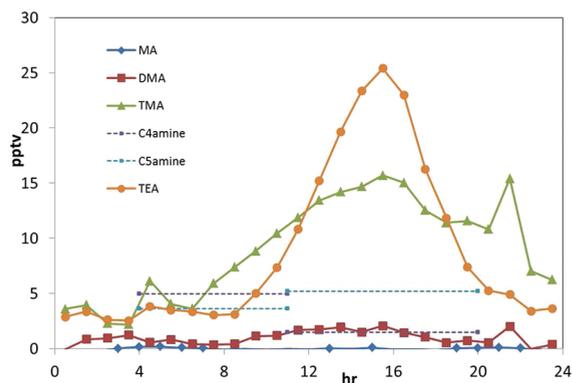
Figure 6. NCCN hourly diurnal averages (LST) for ambient air in Atlanta late July and August, 2009. The 4 and 5 carbon amines 8 h averages are shown. Uncertainty for these two species are on the order of 10 pptv and 30 pptv for the two time periods 4 a.m. to noon and noon to 8 p.m. Isomers and isobaric species are possible.

The C6 amine was one of the most abundant amines that AmPMS observed during NCCN. A previous observation of particulate C6 amine at the NCCN site has been reported[7] where mass spectra of particles with diameters >100 nm were determined to have the signature of triethyl amine. Furthermore, the frequency of the observation of the triethyl amine marker was anticorrelated with relative humidity which qualitatively agrees with the temperature dependency of gas phase C6 amine depicted in Figure 4 assuming gas-particle partitioning is temperature (and water content) dependent. It appears that the C6 amine plays a role in particle growth. The diurnal cycle/RH/temperature variation of the amine signal attributed to C6 amine at another site showed behavior that is consistent with partitioning between gas and particles.[8]

Particle nucleation at the site has been tied to SO_2 and its oxidation product H_2SO_4,[44,11] and recently a weak sensitivity to

ammonia[45] for nucleation was observed. Preliminarily for NCCN, and in general previously observed at this site, nano-particle concentrations indicative of new particle formation happen during sunlit conditions and with ppbv levels of SO_2 present. Amines were generally present at the 10 pptv level or higher during the new particle formation events, which may be a level high enough to significantly affect new particle formation, as is predicted for ammonia using ternary classical theory[14] and for DMA using *ab initio* calculations.[17] A full correlation study of the 2009 particle observations to the amine data will be presented in the future.

Detailed measurements of ambient, nonfeedlot related, gas-phase amines and other basic nitrogen species is rare so little guidance is afforded from previous work.[4] The ambient data from Atlanta suggest temperature dependent sources such as soil or vegetation; they may be strongly temperature dependent. The amines may also be semivolatile with respect to aerosol and gas-aerosol partitioning might be an explanation for the observed diurnal cycle/temperature dependence. A local NH_3 source for this site that is temperature or sunlight dependent has been proposed.[23]

Future work will focus on the following: 1) determining the source of the temperature dependent background signals in particular for ammonia so that measurements in the field will be more reliable, 2) calibration standards for amines, amides, etc., 3) exploring the use of high resolution ($\Delta m < 0.02$ u) mass spectrometry to ascertain the relative importance of amides and amines, and 4) more measurements to assess the importance of amines in other locations.

■ ASSOCIATED CONTENT

S **Supporting Information.** Additional information on the ionization process, the effects of high ammonia on the instrument's sensitivity to amines, and an ammonia intercomparison for NCCN. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*Phone: 612-330-1620. Fax: 612-330-1649. E-mail: hansondr@augsburg.edu.

■ ACKNOWLEDGMENT

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