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Quantifying amine permeation sources with acid neutralization: calibrations and amines measured in coastal and continental atmospheres

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Abstract

An acid titration method for quantifying amine permeation rates was used to calibrate an Ambient pressure Proton transfer Mass Spectrometer (AmPMS) that monitors ambient amine compounds. The method involves capturing amines entrained in a N_2 flow by bubbling it through an acidified solution ($\sim 10^{-5}$ M HCl), and the amines are quantified via changes in solution pH with time. Home-made permeation tubes had permeation rates (typically tens of pmol s^{-1}) that depended on the type of amine and tubing and on temperature. Calibrations of AmPMS yielded sensitivities for ammonia, methyl amine, dimethyl amine, and trimethyl amine that are close to the sensitivity assuming a gas-kinetic, ion-molecule rate coefficient. The permeation tubes were also designed to deliver a reproducible amount of amine to a flow reactor where nucleation with sulfuric acid was studied. The high proton affinity compound dimethyl sulfoxide (DMSO), linked to oceanic environments, was also studied and AmPMS is highly sensitive to it. AmPMS was deployed recently in two field campaigns and mixing ratios are reported for ammonia, alkyl amines, and DMSO and correlations between these species and with particle formation events are discussed.

1   Introduction

Amines play an important role in atmospheric particle nucleation (Weber et al., 1996; Zhao et al., 2011; Ge et al., 2011; Zollner et al., 2012; Chen et al., 2012; Almeida et al., 2013) and they have a strong affinity for the particulate phase when it contains strong acids (Angelino et al., 2001; Barsanti et al., 2009; Bzdek et al., 2010; Smith et al., 2010). Through their effects on the abundance and properties of aerosol, amines can influence cloud condensation nuclei which has important climate implications. Techniques for measuring amines in the air include: (i) wet chemical techniques that trap gas-phase amines followed by their derivatization and then chromatographic separation and (ii) gas-phase sampling with mass spectrometry that can yield short

time-resolved measurements. Recent efforts using mass spectrometry (Eisele, 1988; Sellegri et al., 2005; Hanson et al., 2011; Yu and Lee, 2012) show real time capabilities for measuring gas-phase atmospheric amines. The development of mass spectrometry techniques and other apparati require a continuous gas-phase source for reliable calibrations.

Permeation devices (Neuman et al., 2003; Brito and Zahn, 2011; Yu and Lee, 2012) can provide a continuous source of a desired substance, and homemade permeation tubes were constructed with various amine compounds and used to perform calibrations of AmPMS (Hanson et al., 2011). Base permeation rates were determined via trapping with an acid solution and quantification was accomplished with pH monitoring during the acid-base titration.

AmPMS was deployed at Lewes DE in the summer of 2012 and in Lamont OK in the spring of 2013. Amine and ammonia abundances from these field studies are presented. DMSO has been previously detected in a marine environment with a similar mass spectrometry system (Nowak et al., 2002) and a DMSO permeation tube was constructed to calibrate a PTrMS (Hanson et al., 2009) and AmPMS. The mixing ratios of DMSO by AmPMS in a coastal environment are also presented. Ammonia and amine abundances and their correlations are compared and discussed. Also, the linkage between particle formation events and gas-phase amine abundances are presented.

2 Experimental

Home-made permeation tubes (PTs) were constructed using $0.4\,\text{cm}$ ID $\times$ $0.6\,\text{cm}$ OD Teflon (PTFE and FEP) tubing with the ends sealed with glass rods. The seals were made by inserting short lengths of glass rod ($0.5\,\text{cm}$ diameter) into the heated ends of a $\sim 12\,\text{cm}$ length of Teflon tubing, and quenching it in an ice water bath to facilitate the seal. A small amount ($\sim 1\,\text{mL}$) of an amine-water solution was placed in the cooled tubing prior to sealing the second end. Proper end seals were found to be important for stable permeation rates: some tubes had permeation rates that were large and

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variable, believed to be due to poor end seals. There were differences in permeation rates of amines through PTFE and FEP with the general observation that permeation was better through PTFE than FEP.

The PTs were placed inside a ~ 20 cm length of 1/2 inch OD teflon tubing through which N_2 gas flowed, picking up amine vapor. The flow of N_2 was (i) 40–100 cm^3 min^{-1} (STP of 273 K and 1 atm, "sccm") when used with the dynamic dilution system, (ii) up to several 1000 sccm when being used to calibrate AmPMS, and (iii) typically 20 sccm during acid-base titrations. Most experiments were performed with the permeation tube assembly at ambient temperature which generally varied less than 3 °C. Since permeation/diffusion through plastics is known to be temperature dependent (e.g. Brito and Zahn, 2011), a temperature-controlled aluminum enclosure around the permeation tube assembly was used in some experiments.

Ammonia, methyl amine, dimethyl amine and trimethyl amine were in the form of aqueous solutions (methyl, dimethyl, and trimethyl amine were ~ 40 wt% in water, ammonia was ~ 60 wt% in water, Sigma Aldrich and VWR). A permeation tube with dimethyl sulfoxide was also fabricated and its permeation rate was deduced by comparison to signals from a calibrated PTrMS (see Supplement).

2.1 Acid-base titration procedure

Amines were quantified by absorption into an acidified (starting pH of 5 or less) solution. Solutions were prepared using 18.2 MΩ deionized water (Milli-Q) with a small amount of KCl (1 to 10 mM KCl) added to facilitate the pH measurement (VWR sympHony Epoxy, Gel Combination pH electrode or a Beckman–Coulter, Semi-Micro). Buffer solutions of pH 4 and 7 were used to calibrate the probes. Generally, a 40 (±1) mL aliquot of this solution was degassed of CO_2 etc. by bubbling N_2 gas (50–100 sccm) whereupon the initial pH of 5-to-5.5 rose to 7 or higher. In some experiments a short degassing time was used (pH rose to ~ 6) and this had no observable effect on the results. After degassing, the solution pH was lowered to 5 by addition of 0.4 mL of a 1×10^{-3} M HCl solution. Probes and any lines that contacted the solutions were rinsed

thoroughly to reduce the risk of contamination. Occasionally, more of the acid solution (up to an additional 0.5 mL in some runs) was needed to lower the pH to 5 possibly due to small amounts of basic contaminants; however the measured permeation rates were not noticeably affected.

Blank flows without a PT inline were also investigated to check for background base levels (basic contaminants from surfaces etc.) Small increases in pH with time were observed but were not steady indicating an intermittent and decreasing source of base molecules consistent with a surface desorption rate that decreases with time. These pH changes were equivalent to a background rate of 0.1 to 1 pmol s^{-1}. Background rates were observed to be higher than this when the gas-lines, flask and sealing materials (Teflon, silicone, etc.) had been exposed to high levels of amine vapor: several pmol s^{-1} for time periods of an hour after which they decreased to pmol s^{-1} or less. Thorough cleaning of the flask and lines between runs and eliminating elastomers (silicone rubber seals) resulted in the best data, especially for low permeation rate tubes.

To check how well the solution scavenges the base, tandem experiments were carried out with a second flask capturing any base in the effluent from the first flask (see the Supplement). The first flask was sealed (silicone rubber seal on the pH probe) so that the effluent gas from the first solution could be bubbled through the second solution. The pH of both solutions was monitored simultaneously. This tandem titration system verified that more than 95 % of the permeated ammonia was absorbed by the first solution.

2.2 Addition of amines to AmPMS

Amines were introduced into AmPMS' sampling line (a 1/4″ tube between 30 and 100 cm in length) in several ways: (i) by entraining the small flow from the permeation tube into the sample flow, (ii) by placing the permeation tube in line with the sample flow, which is typically 1.2 sLpm, or (iii) by mixing the PT flow into a flow of up to 6 sLpm and sub sampling this flow with AmPMS. Also, when AmPMS was directly attached to the bottom of the nucleation flow reactor, amines were added to the 6 sLpm that was

flowing through the AmPMS detection region (Zollner et al., 2012; Panta et al., 2012). The sample flow was either outdoor air or humidified N_2 (~ 30 % RH, determined from the relative flows of fully humidified and of dry N_2). Note that an additional length of 1/4″ OD tubing of up to 6 m length was needed (inlet line) when sampling outdoor air.

The sampling line arrangement for AmPMS has been changed from its initial deployment (Hanson et al., 2011) so that the sample flow does not go through a three way valve before entering the instrument. Also gas cylinders are not required for field deployment as the ion source flow is taken from a catalytic converter. Details of this arrangement, the zero-ing procedure, and tests of a ~ 4 m long inlet line are presented in the Supplement.

Calibration data was treated by comparing the mixing ratio calculated from the permeation rate and the total sample flow rate to the mixing ratio from AmPMS signals, assuming a high sensitivity. Signals were converted to mixing ratios using:

$$X_{MR} = \ln(1 + s_{XH^+}/s_0)/(N_{1\,ppt}kt) \qquad (1)$$

where s_{XH^+} and s_0 are the signals due to analyte and reagent ions, respectively, when analyte X is present, k and t are the ion-molecule rate coefficient and drift time, respectively, and $N_{1\,ppt}$ is the number density for a mixing ratio of 1 pptv at ambient pressure and temperature. For low values of the ratio s_{XH^+} over s_0, a standard sensitivity for the instrument S_{typ} is given by assuming there is no breakup of the XH^+ ion, and k takes a value of $2 \times 10^{-9}\,cm^3\,s^{-1}$: $S_{typ} = s_0 k t N_{1\,ppt}$ (Sunner et al., 1988; Viggiano et al., 1988; Hanson et al., 2011). The value of t, typically 1 ms, is set by the geometry of the drift region and the electric field. For typical conditions within the instrument, $N_{1\,ppt} = 2.45 \times 10^7\,cm^{-3}\,pptv^{-1}$ and S_{typ} is 5 Hz pptv^{-1} for $s_0 = 10^5$ Hz. At mixing ratios ≤ 1000 pptv, (1) simplifies to the following equation with less than a 5 % error:

$$X_{MR} = s_{XH^+}/(s_0 N_{1\,ppt}kt) = s_{XH^+}/S_{typ} \qquad (2)$$

s_0 contains the signal for the NH_4^+ ion for amines because amines readily react with NH_4^+ (Viggiano et al., 1988; Hanson et al., 2011). These equations can be modified for

mass dependent ion throughput and detection by including a factor in Eqs. (1) and (2) in front of the s_{XH^+} term (Hanson et al., 2011).

3 Results

3.1 Permeation rates

Figure 1 depicts a titration calibration of an ammonia PT showing pH (right axis) and moles H^+ (left axis) over time. Moles H^+ vs. time are well fit by a linear line and the slope of the line is the moles of base per second captured by the solution, which is 31 pmol s^{-1} for the data in Fig. 1. The precision of the slope, assessed by manually altering the fitted line, is a few % for data with pH < 6; most titrations resulted in data well described by a linear relationship with a precision better than ∼ 10 %. A slowdown in the uptake of the base by the solution for pH > 6 was generally observed and the linear fits were restricted to pH < 6. Some titrations yielded poor linear relationships with time; these were due to leaking supply lines or to insufficient time for the PT to reach steady state with the flow over it. Some runs were constricted to pH < 5.5: poor behavior at higher pH was attributed to contaminated KCl. Abrupt changes in pH were occasionally observed possibly due to contaminants introduced with the degas lines or pH probes. Recently, results from runs for pH ≥ 5 have been erratic, and initial acid levels have been increased to pH ∼ 4.3: runs take longer (up to 50 h) but the permeation rates using the pH < 5 data have a lower variability than rates deduced from pH > 5. The better performance may be due to the longer times of the runs but also to the higher acid content which minimizes contaminant problems.

A number of PTs were used to calibrate AmPMS with rates that ranged from 3 pmol s^{-1} for trimethyl amine to 300 pmol s^{-1} for an ammonia PT. Individual PTs with the same compound can have quite different permeation rates, in part due to fabrication differences. Permeation rates were observed to be time dependent and temperature sensitive (discussed in detail in the Supplement) and, to some extent, material

dependent, i.e. FEP vs. PTFE. Typical permeation rates are shown in Table 1. Some ammonia PTs constructed of PTFE had permeation rates up to $300\,\mathrm{pmol\,s^{-1}}$, much higher than the FEP rates in Table 1. FEP PTs with trimethyl and triethyl amine had very low permeation rates.

3.2 Addition to AmPMS

Shown in Fig. 2 is the gross AmPMS mixing ratio for NH_3 calculated from the signals using the typical sensitivity, S_{typ} (background signal was not subtracted.) An addition of NH_3 was initiated at $\sim 0.05\,\mathrm{h}$ using a single stage dynamic dilution where 40 sccm of the 50 sccm flow over the PT was discarded and replaced by a flow of 40 sccm clean N_2 (push) and then this flow was introduced into the sample line. AmPMS was sampling at $2.1\,\mathrm{sL\,min^{-1}}$ which, considering dilution, contained NH_3 at a mixing ratio of 3700 pptv. The signal rises to a net detection of about 3200 pptv at $\sim 0.3\,\mathrm{h}$ whereupon NH_3 addition was terminated by setting the entire NH_3 perm tube flow to be discarded (the "push" gas remained). Degassing of NH_3 from surfaces (dilution system, sampling lines, and ion drift region) is apparent. The dilution system was taken off the sampling tee at about 1.4 h. For this calibration, the original configuration for AmPMS was used and sample gas passed through a three way valve before entering the ionization region which may adversely affect response times and surface displacement issues. See the Supplement for more on response times.

Figure 3 is a plot of mixing ratio vs. time for an addition of dimethyl amine to AmPMS using the new sampling configuration (see the Supplement) first used for the Lewes campaign. The amine was introduced by placing a $13\,\mathrm{pmol\,s^{-1}}$ permeation tube in a flow of $6\,\mathrm{sL\,min^{-1}}$ clean N_2 at 15.2 h. AmPMS subsampled this flow at $\sim 1.5\,\mathrm{L\,min^{-1}}$, and it contained 2700 pptv dimethyl amine. After rising steadily for about 0.5 h, the net dimethyl amine mixing ratio reached 2500 pptv. A rise in the ammonia mixing ratio of about 700 pptv is also apparent – displacement of ammonia on surfaces by dimethyl amine is possible or the changes in s_0 could lead to artificial changes in the ammonia background level. The permeation tube was removed from the clean air line at 16 h and

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the mixing ratio declines to the 15 h level in about a half hour with about a 10 min decay constant. The instrument had not been cleaned after the Lewes campaign which is the likely reason for the slow response.

Tests with dimethyl and trimethyl amine were performed after the instrument was cleaned following the Oklahoma campaign and AmPMS showed a much quicker response. Plots of two of these calibrations are shown in the Supplement and decays of the signal after the amines were removed were dominated by a ~ 20 s time constant. Also shown in the Supplement are experiments were methyl and trimethyl amines were added to outdoor air upstream of a ~ 4 m length of the sample tube used in the field deployments. These experiments showed that there was a significant interaction of the amines with the sample tube surfaces which tended to smooth out temporal variations in amine concentrations. Also shown in the Supplement are amine additions that show this interaction decreases significantly after cleaning the line.

Calibrations of AmPMS for ammonia, methyl-, dimethyl-, and trimethyl amines show that the sensitivity is high for all of them. Shown in Table 2 is the signal-based mixing ratio (Eq. 1) assuming a typical sensitivity (S_{typ}) and the mixing ratio calculated from the permeation rate and the dilution factors. The last column is the ratio of the former to the latter. Note that $s_0 = s_{NH_4^+} + \sum_n s_{(H_2O)nH_3O^+}$ for the amines as they react with NH_4^+ (plus hydrates) as well as the water proton clusters; s_0 for calculating the NH_3 mixing ratio is the sum over only the water proton clusters signals. The results for NH_3 and the amines are consistent with the following assumptions: (i) a collisional ion molecule reaction rate coefficient of 2×10^{-9} cm^3 s^{-1}, (ii) an ion-molecule interaction time of about 1 ms, and (iii) little ion breakup or mass discrimination effects for the instrument.

DMSO is very efficiently detected by AmPMS. DMSO has a large dipole moment (Nelson et al., 1967) and proton affinity (Hunter and Lias, 1998) and the collisional rate with large water proton clusters could be significantly higher than the 2×10^{-9} cm^3 s^{-1} used for S_{typ}. There could be an enhanced mass spectrometer throughput for ions near 80 u. Tests for mass discrimination are planned by adding C4 (74 u) and C5 (88 u) amines to AmPMS when reproducible PTs for them become available. However, it is

likely that the permeation rate of the DMSO tube was significantly underestimated (see the Supplement) and thus the Lewes data is presented using the S_{typ} value to report mixing ratios.

Collisional dissociation during sampling of the ions was investigated and the signals for protonated amines were relatively insensitive to ion energy for typical conditions. For example, a triethyl amine permeation tube was used to deliver triethyl amine to AmPMS while it was sampling outdoor air and the orifice and octopole bias voltages on AmPMS were varied. For typical conditions (30 and 12 V, respectively, at a pressure of ~ 0.25 torr) there was little evidence for ion breakup processes and even at a $V_{orifice}$ of 70 V significant signal at $M \cdot H^+ = 102$ u was still observed. We conclude that the alkyl amines are detected without significant breakup for normal ion sampling conditions, consistent with the high sensitivity for detecting the alkyl amines at $M \cdot H^+$ discussed above.

3.3 Results from AmPMS field campaigns in Lewes, DE and Lamont, OK

3.3.1 Lewes, DE

Ammonia, alkyl amines, and DMSO were monitored by AmPMS in field campaigns conducted at Lewes, Delaware in July–August 2012 (see Bzdek et al., 2013) and at Lamont, Oklahoma in April–May 2013 (Southern Great Plains DOE site; http://www.arm.gov/campaigns/sgp2013npfs). As mentioned previously and detailed in the Supplement, the sampling arrangement and zeroing procedure was changed from the Atlanta 2009 (NCCN) campaign (Hanson et al., 2011). There were also slight differences in the sampling arrangement between these two campaigns: none of these changes significantly affected the sensitivity of AmPMS but they do affect the zeroing procedure to obtain background signals. Also, the ion drift region was heated to $\sim 40\,^\circ$C for the Lewes campaign to eliminate condensation which was not necessary in Oklahoma due to the lower atmospheric water content. The zeroing procedure to obtain instrument backgrounds at the masses of interest is also detailed in the Supplement.

Note that AmPMS does not distinguish isomers or isobaric species. Abundances derived from a signal at a given mass is assigned to a specific amine, however, keep in mind that this could include other species such as amides, which have been shown to be detected efficiently by AmPMS in chamber experiments (Hanson et al., 2011).

Levels of ammonia and alkyl amines were generally low in the semi-rural marine environment of Lewes (DE), Fig. 4 (~ hourly averages), compared to the urban and continental sites (Atlanta (Hanson et al., 2011) and OK, see Fig. 5). The semi-rural environment of Lewes had a five day period early in the campaign (1–5 August, Fig. 4) where methyl- and dimethyl-amines (averaging ~ 20 and ~ 100 pptv, respectively) were much higher than those observed at the urban and rural continental sites. A few poultry operations are within ~ 30 miles of the Lewes site. Trimethyl amine was in the 10 to 15 pptv range while the C4 and C5 amines were generally 5 ptv or less. After a few significant rain events (7–10 August), the weather changed with temperatures generally cooler and humidity higher than the preceding week: methyl and dimethyl amines decreased to less than a few pptv and < 10 pptv, respectively. On the other hand, TMA levels rose after 11 August and it was generally the most abundant alkyl amine at ~ 10 pptv during the day. Like the small amines, ammonia mixing ratios from the 9th of August on decreased significantly from those earlier in the campaign, perhaps also due to changes in the weather patterns.

Specific to Delaware is the detection of large amounts of DMSO ($MH^+ = 79$ u). Marine plankton is known (Hines et al., 1993) to produce dimethyl sulfide (DMS), which in the atmosphere is oxidized to DMSO. Other DMSO sources have been postulated (Nowak et al., 2001). Note that the DMSO data in Fig. 4 was calculated using S_{typ} due to the uncertainty in the DMSO permeation rate. Spikes in DMSO occurred frequently and often at low tide and/or sunrise. The spikes in DMSO on 19, 22, 23, and 24 August were also accompanied by spikes in trimethyl amine suggesting that a source of DMSO is linked to one that also emits trimethyl amine.

3.3.2 Lamont, OK

AmPMS was deployed in Oklahoma at the Atmospheric Radiation Measurement (ARM) facility between 16 April 2013 and 21 May 2013. Figure 5 shows the 2 h average mixing ratios of ammonia and the alkyl amines detected in the spring of 2013 in Oklahoma. The most abundant amines were the 4 and 5 carbon compounds at 74 u and 88 u (or the isobaric amides.) These two sets of species often reached levels of several hundred pptv and spikes on 74 u reached ∼ 1 ppbv. Even the C6 and C7 amines (or amides, possibly oxidation products of the C4 and C5 amines) reached 50 pptv. On the other hand, the abundances of the smaller amines were relatively low: methyl amine was generally a few pptv or less while dimethyl amine and trimethyl amine abundances were typically 20 and 50 pptv, respectively.

Occasionally, amines with high background signals had artifact spikes (see the negative values) when abundances were small compared to backgrounds and uncertainties in backgrounds were high. The Supplement presents details on how the background data was obtained during these times. This procedure was instigated to address sticking to surfaces within the system and the zeroing tubing. Also shown in the Supplement are amine specific time lags of ∼ 10-to-60 min due to the 4 to 6 m inlet line. Therefore the Lewes and Oklahoma data are rendered as 1 or 2 h averages, which is the interval between background determinations. Note that for the Lewes data there was little difference in the results from the two zeroing procedures and the normal procedure was used most of the time. The Oklahoma data was split about even between the two procedures and a possible bias due to insufficient time for AmPMS to reach background levels is discussed in the Supplement. This potential under-measurement error is estimated to be 30 % or less and applies to data obtained with the alternate procedure.

3.4 Correlations and comparisons of amine measurements

At the OK site methyl amine was usually much lower than trimethyl amine whereas in Lewes, DE, methyl amine often exceeded trimethyl amine. The larger amine

abundances (C3 and greater) in OK were correlated throughout the study (R^2 of ~ 0.4) suggesting they had similar sources while methyl and dimethyl amines were not well correlated to each other ($R^2 = 0.20$) or to other amines. This contrasts with the Lewes data where the relationship between the smallest two amines was pronounced and well correlated ($R^2 = 0.8$); also in Lewes the C4 through C7 amines were somewhat correlated (R^2 ~ 0.3) while trimethyl amine had little correlation with other amines. This suggests different sources for the large vs. small amines in Lewes and probably another source altogether for trimethyl amine. Correlations of the amines with ammonia were generally weak except for the small amines and one large one: in Oklahoma, the largest R^2 was ~ 0.3 for both dimethyl and the C7 amines with ammonia, and in Lewes, the methyl and dimethyl amines were somewhat correlated with ammonia (R^2 of 0.38 and 0.24, resp.)

Ammonia was at the single digit ppbv level (1–2, with occasional spikes to 4 ppbv) at both the OK and DE sites yet there were extended time periods where very little ammonia was present, a few hundred pptv or less. This contrasts with Atlanta measurements where ammonia levels rarely decreased below several hundred pptv (see Nowak et al., 2006, 2007). Signals at 79 u were very small in Oklahoma suggesting very little DMSO was present. Shown in Table 3 are the average amine/amide abundances observed at these three sites as well as in urban air for a three week period in Minneapolis. See Kieloaho et al. (2013) for additional comparisons of amines measured at urban and rural sites.

A significant temperature dependence for trimethyl amine abundances has been reported in earlier studies in the summertime urban Atlanta (Hanson et al., 2011) and in the fall Kent OH boundary layer (Yu and Lee, 2012). In contrast, the spring time Oklahoma measurements show no correlation with temperature for the C3 and larger amines; a weak correlation with temperature for methyl amine and some correlation for dimethyl amine (R^2 values for linear fits against temperature of 0.16 and 0.33 for methyl and dimethyl amines, resp.) The amine abundances in Lewes also showed little or no correlation with temperature (linear fits had R^2 values less than 0.1 for methyl up

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to the C6 amine.) Little or no temperature dependence was also reported for the C2 and C3 amines in the summertime boreal forest (Kieloaha et al., 2013).

Diurnal behavior for the C3 and C6 amines in Atlanta (Hanson et al., 2011) showed late afternoon averages that were about 5 and 8 times early morning averages and most amines in Lewes and Oklahoma also exhibited diurnal behavior but the behavior was weaker than the most abundant amines (C3 and C6) in Atlanta. The behavior of the amines in Oklahoma had the weakest diurnal patterns of the three sites.

In Lewes, all the amines were about a factor of two or three larger from 11:00 to 15:00 LST than their early morning averages (00:00–04:00 LST.) In Oklahoma, daytime hourly means (12:00 to 16:00) for the C3, C5 and C6 amines were about +50, +0 %, +30 % higher, respectively, than the early morning hourly means (00:00 to 04:00 LST). The C1, C2, C4 and C7 amines had somewhat larger variations: they were all about a factor of two larger in the early afternoon than in the early morning, similar to what was observed in Lewes. This set of amines included the least (32 u) and most (74 u) abundant amines.

The diurnal behavior of ammonia in Oklahoma was the most distinct: its hourly median was ~ 500 pptv from midnight to 8 a.m., rose quickly to 1400 pptv by 11 a.m. and dropped slowly to 600 pptv by 10 p.m. Plots of the diurnal behavior (hourly means, medians and select percentiles) of the amines and ammonia for the Oklahoma campaign are presented in the Supplement. Hourly medians showed smaller variations over the course of the day than did the means.

Particle formation events indicated in the figures generally occur in the early afternoon at both sites and they are correlated with amine abundances. More information on the conditions of some of the Lewes events can be found in Bzedek et al. (2013) and details of the Oklahoma events will be presented in forthcoming publications (J. Smith, P. McMurry, personal communications, 2014). In Lewes sulfuric acid levels often reached 2 to 3×10^7 cm^{-3} which contrasts with Oklahoma (J. Zhao, personal communication, 2013) where sulfuric acid levels rarely reached the 10^7 cm^{-3} level and sulfuric acid concentrations were a few times 10^6 cm^{-3} during many of the events.

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The more numerous and generally stronger nucleation events observed in Oklahoma compared to Delaware is apparently driven by the much higher abundance of amines. This highlights the role of amines in particle formation: amines at several hundred pptv levels can induce significant nucleation events even at low sulfuric acid abundances.

4   Conclusions

Calibrations of AmPMS for alkyl amines, quantitatively tied to acid-base titrations, show that AmPMS is as sensitive to amines as it has been assumed to be. The results of recent field campaigns show that the abundance of alkyl amines have a wide variability from site to site and temporally: they can range from single digit levels up to 100 s of pptv for some amines. Particle formation events are frequently concomitant with enhanced amine levels (tens to hundreds of pptv) while some events occur at levels as low as single digit pptv, especially when sulfuric acid concentrations exceed $10^7\,\mathrm{cm}^{-3}$.

In contrast to the other sites discussed here, the Lewes, DE, site had at times methyl and dimethyl amines as the most abundant amines; this may be due to nearby poultry operations. DMSO was observed at this marine site and spikes in DMSO were accompanied by spikes in trimethyl amine suggesting a similar cause (low tide) or possibly a similar source.

The 4 to 6 m long sampling lines led to significant delays in the determination of amine levels; for some amines such as methyl amine and ammonia this delay grew to roughly an hour during the extent of the ~ 5 week campaigns. Shortening AmPMS' inlet line and occasional cleansing of it is planned for future deployments. Alternatively, sub-sampling from a large flow, large diameter plenum may help to better determine amines on the five minute or shorter time scale.

Supporting information

Additional information is available on AmPMS sampling arrangement, zeroing proce-
dures, response times and sampling line issues, calibration with DMSO, other ions of
interest, amines diurnal behavior and correlation plots, ion breakup processes, and per-
meation tube and acid-base system diagnostics. AmPMS data from the field studies in
Atlanta, Lewes, and Oklahoma are available upon request (hansondr@augsburg.edu).
The Oklahoma data set will also be available at DOE-ARM archives in late 2014.

Supplementary material related to this article is available online at
http://www.atmos-meas-tech-discuss.net/7/3835/2014/
amtd-7-3835-2014-supplement.pdf.

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Table 1. Typical permeation rates at room temperature.

N-base	Temp. (K)	Rate (pmol s^{-1})
Methylamine[a]	300 ± 3	30–75
Dimethylamine[a]	300 ± 3	10–30
Ammonia[a]	300 ± 3	50–100
Trimethylamine[b]	300	10–15
Triethylamine[b]	300	~ 4

Mature permeation tubes only: older than 1 month, younger than 1 year.
[a] PTs were constructed of FEP.
[b] PT constructed with PTFE.

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Table 2. Laboratory and field (OK)[a] calibrations.

species	Place	mixing ratio, ppbv	signal based, ppbv	ratio[b]
NH_3	Lab	67	55	0.82
NH_3	Lab	3.7	3.2	0.86
CH_3NH_2	Field	15	17	1.1
$(CH_3)_2NH_2$	Lab	2.7	2.5	0.92
$(CH_3)_2NH_2$	Lab	42	33	0.79
$(CH_3)_3NH_2$	Lab	8.3	10	1.2
DMSO	field, lab	2.2-to-7	6.5-to-28	3[c]

[a] Recent deployment to DOE site, Southern Great Plains, Lamont, OK, in spring 2013.

[b] Ratio of sensitivity to S_{typ}.

[c] Permeation rate may be underestimated.

Table 3. Average ammonia and amines/amides (pptv) measured by AmPMS.

site	NH_3	32u	46u	60u	74u	88u	102u	116u
Atlanta[a]	3000[e]	0	1	10	2	4	17	–
Lewes, DE[b]	800	5	28	6	3	1	2	2
Lamont, OK[c]	900	4	14	35	150	98	20	15
Minneapolis[d]	1470	4	42	19	14	20	5	4

[a] July/August 2009 (Hanson et al., 2011).
[b] July/August 2012.
[c] April/May 2013.
[d] October 2012.
[e] Nowak et al. (2006).
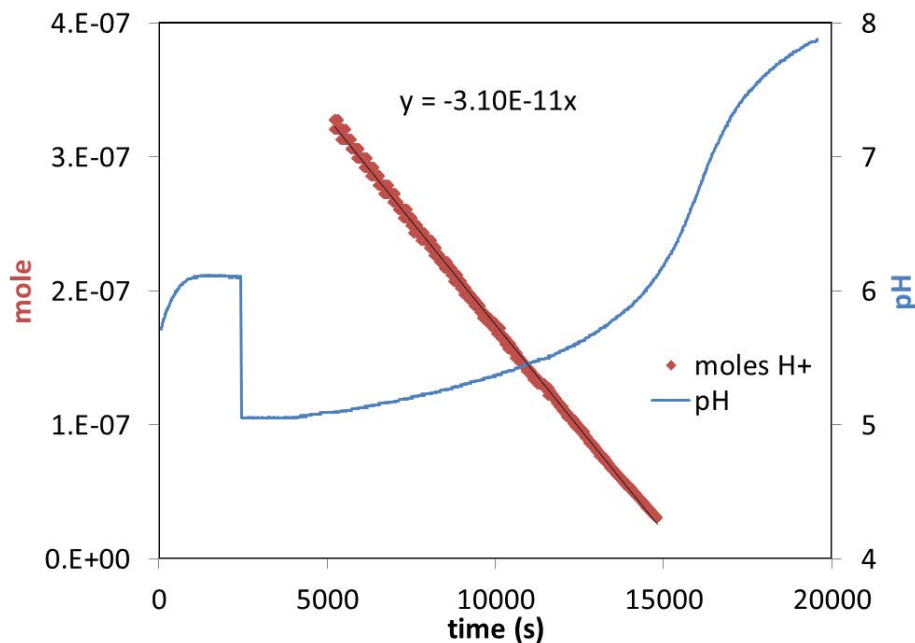
Fig. 1. Titration of an ammonia PT. The blue line shows the pH of the KCl solution as it was degassed (0–2450 s), upon addition of HCl (2450 s), and then introduction of the NH_3 PT effluent at ~ 4000 s. The red diamonds are the moles of H+ neutralized by the dissolving base and show a linear decrease with time for pH < 6.

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2012Mar21 NH3
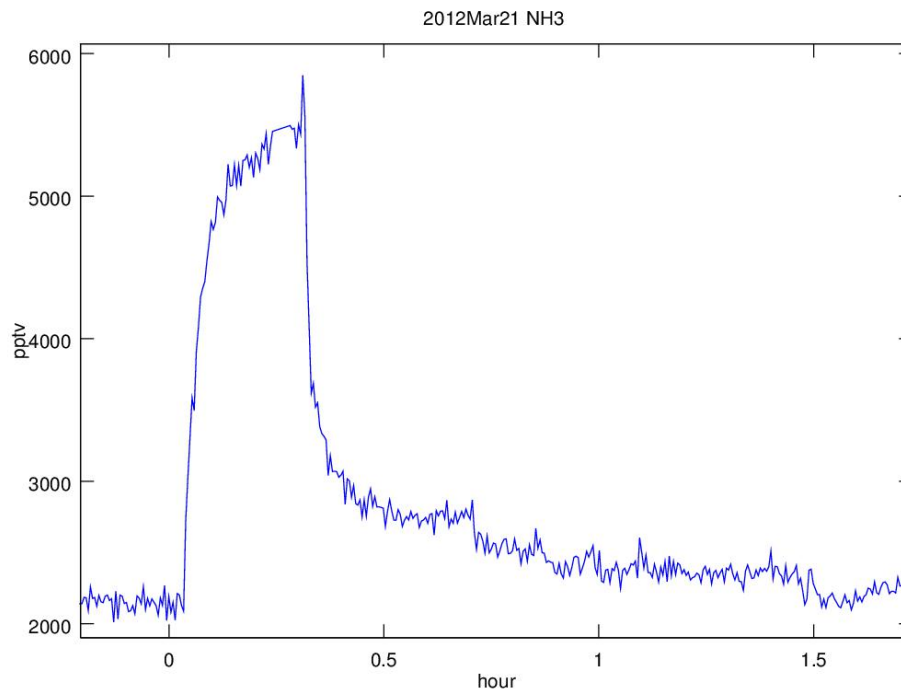
Fig. 2. NH$_3$ mixing ratio measured with AmPMS plotted vs. time. Addition of NH$_3$ at 0.05 h followed by its removal at 0.35 h. Gross signals were used to calculate mixing ratio using S_{typ}; no background subtraction was done. The NH$_3$ was introduced into the sample flow from a 30 pmol s^{-1} NH$_3$ permeation tube with single stage dilution. AmPMS was in its original configuration where sample gas first passes through a three-way solenoid valve.
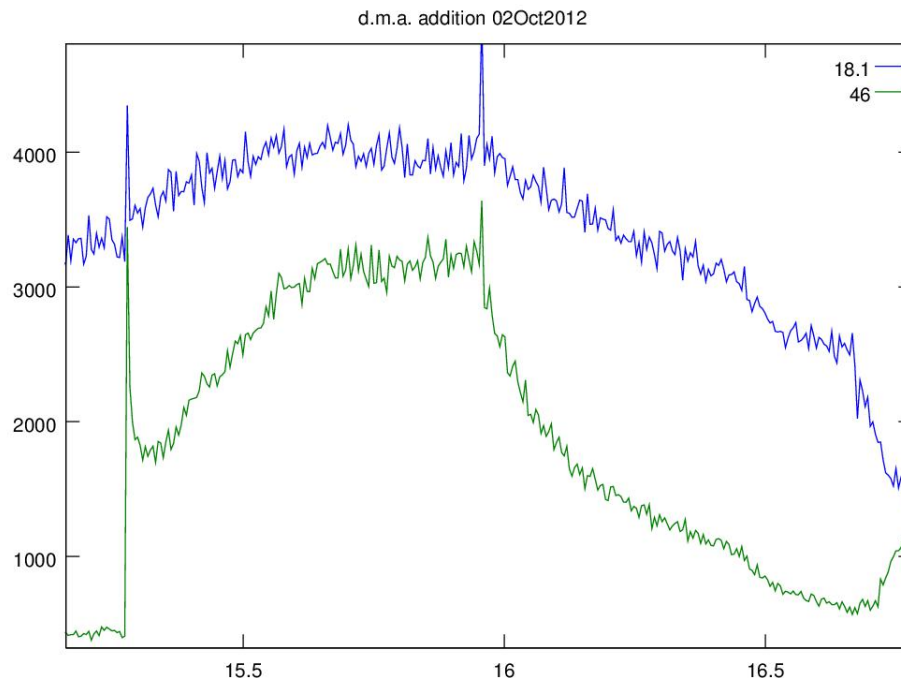
Fig. 3. Temporal plot (h) of dimethyl amine ($M \cdot H^+$ at 46 u) and ammonia (18 u) mixing ratios before, during and after addition of dimethyl amine to AmPMS. The drift region had not been cleaned after the Lewes campaign. A zero was initiated at 16.45 h and AmPMS began to sample another stream of air beginning at 16.7 h.
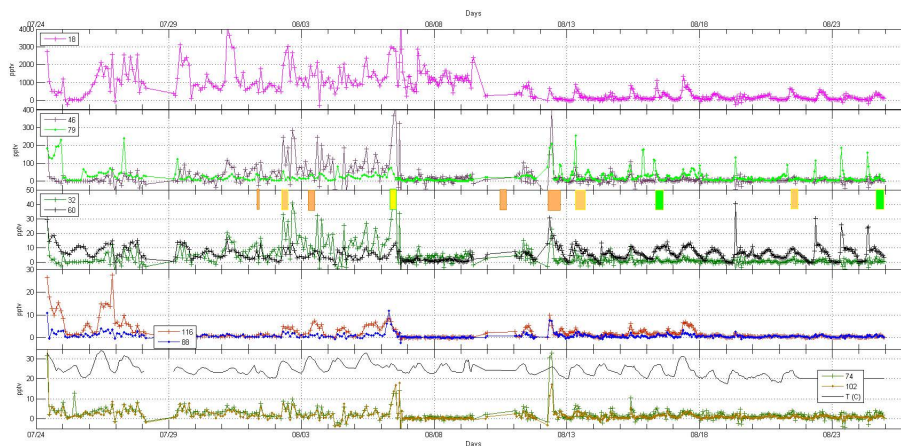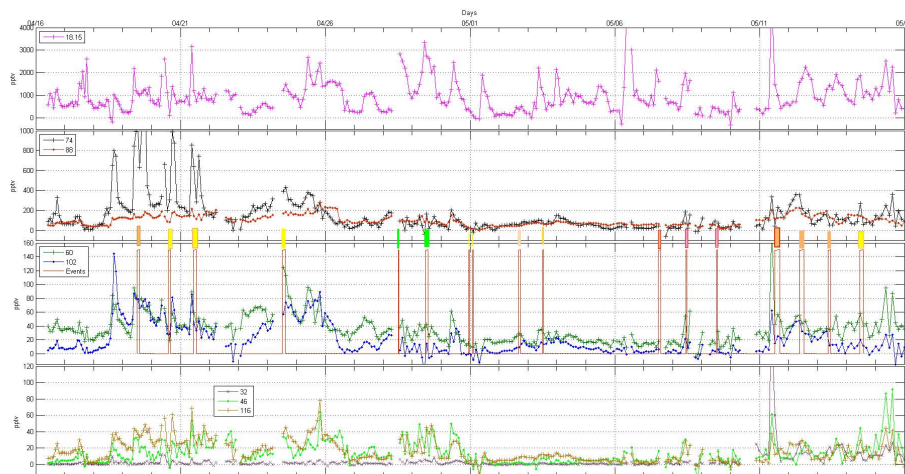
Fig. 4. Time series of ammonia (18u, M·H⁺) and alkyl amines (32, 46, 60, 74, 88, 102, 116 u) in Lewes, DE in the summer of 2012. DMSO abundances (79 u) are also shown. Particle formation events are shown between the 2nd and 3rd plot with color indicating the intensity (green, yellow, orange.) Temperature is also shown in the bottom plot (°C).

Fig. 5. Concentration of ammonia and various amines (pptv) detected by AmPMS in Lamont, OK (DOE-SGP) in 2013. Particle formation events are shown in the second and third plots and the squares indicate the intensity of the event increasing from green- yellow-orange-red. From top to bottom: ammonia (18 u) detection was frequently in the 1000–2000 pptv range; species detected at masses 74 and 88 u (e.g. C4 and C5 amines, resp. or amides) had at times an unusually high presence, reaching sustained levels of 500 pptv; both trimethylamine (60 u) and 102 (C3 and C6 amines) were present in the many tens of pptv range; finally, methylamine (32 u) was generally quite low, while dimethylamine (46 u) and mass 116 (C7 amines) both could be up to 50 pptv (10 to 20 pptv, sustained).