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Amine permeation sources characterized with acid neutralization and sensitivities of an amine mass spectrometer

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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, methylamine, dimethylamine, and trimethylamine 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, using these sensitivities, mixing ratios for ammonia and the alkyl amines are derived from the signals. 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; Yu et al., 2012) 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 highly time-resolved measurements. Recent efforts using mass spectrometry (Eisele, 1988; Sellegri et al., 2005; Hanson et al., 2011; Yu and Lee, 2012; You et al., 2014) show real time capabilities for measuring gas-phase atmospheric amines. The development of mass spectrometry techniques including AmPMS is discussed in Hanson et al. (2011). These types of instruments 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 that was previously only poorly calibrated (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 using the sensitivities determined with the permeation sources. Dimethyl sulfoxide (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 Proton Transfer Mass Spectrometer (PTrMS) (Hanson et al., 2009) and an Ambient pressure Proton transfer Mass Spectrometer

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(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 cm ID × 0.6 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 cm diameter) into the heated ends of a ∼ 12 cm length of Teflon tubing, and quenching it in an ice water bath to facilitate the seal. A small amount (∼ 1 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 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, methylamine, dimethylamine and trimethylamine were in the form of aqueous solutions (methyl, dimethyl, and trimethylamine 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 MW 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 Electrode). 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.). Increases in pH were observed but they were small, unsteady and slowed with time indicating an intermittent and decreasing source of base molecules. These pH changes were equivalent to a background rate of 0.1 to 1 pmol s^{-1}, however, higher background rates were observed when the gas lines, flask and sealing materials (perfluorocarbon adaptors, silicone, etc.) had been exposed to high levels of amine vapor: several pmol s^{-1} for time periods of hours. 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 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 effluent flow was directly exposed to only glass and perfluorocarbon tubing). 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

AmPMS detects high proton affinity compounds by their reaction with water proton clusters, and in the case of amines, ammonium water clusters, e.g.,

$$(CH_3)_2NH + H_3O^+(H_2O)_n \rightarrow (CH_3)_2NH_2{}^+(H_2O)_m + (n-m+1)H_2O, \tag{1a}$$

$$(CH_3)_2NH + NH_4^+(H_2O)_l \rightarrow (CH_3)_2NH_2^+(H_2O)_m + (l-m)H_2O + NH_3. \tag{1b}$$

These reactions are fast (Sunner et al., 1988; Viggiano et al., 1988; Hanson et al., 2011) and water ligands are removed when the ions at ambient pressure are sampled into the 1st stage of the vacuum system (a pressure of about 0.2 Torr). Reagent ions typically have $n = 5$ to 7 in the drift region but AmPMS primarily detects water proton clusters at $n = 1$ and 2 and ammonia and amine clusters with water ligands at 10 % or less. Two more stages of pumping leads to a pressure of 2×10^{-5} Torr in the chamber where the quadrupole mass filter and ion detector are located. The Supplement shows a typical mass spectrum.

Amines were introduced into AmPMS' sampling line (a 1/4″ perfluorocarbon 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).

When used to sample ambient air above the roof of a building, a 3 to 5 m inlet (1/4″ OD Teflon, perfluoroalkoxy (PFA)) was attached to the sampling line to reduce the risk of contamination by interior air that may contain amines at elevated levels. At the end of the inlet was attached a small rain hood of 1/2″ OD Teflon tubing along with a coarse Teflon screen to keep out insects. The screen had become dislodged from the rain hood at some point during the Oklahoma campaign.

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 zeroing procedure, and tests of a ~ 4 m length of an 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 the following:

$$X_{\mathrm{MR}} = \ln(1 + s_{\mathrm{XH^+}}/s_0)/(N_{1\,\mathrm{ppt}}kt), \tag{2}$$

where $s_{\mathrm{XH^+}}$ 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 $N_{1\,\mathrm{ppt}}$ is the number density for a mixing ratio of 1 pptv at ambient pressure and temperature. Equation (2) applies when there is no breakup of the $\mathrm{X \cdot H^+}$ ion upon sampling. For X with mixing ratios ≤ 1000 pptv, the ratio $s_{\mathrm{XH^+}}$ over s_0 is about 0.05, and a standard sensitivity for the instrument S_{typ} can be defined: $S_{\mathrm{typ}} = s_0 kt N_{1\,\mathrm{ppt}}$. With k taking a value of $2 \times 10^{-9}\,\mathrm{cm^3\,s^{-1}}$ (Sunner et al., 1988; Viggiano et al., 1988; Hanson et al., 2011), a value for t of typically 1 ms, set by the geometry of the drift region and the electric field, a typical $N_{1\,\mathrm{ppt}}$ of $2.45 \times 10^7\,\mathrm{cm^{-3}\,pptv^{-1}}$, S_{typ} is 5 Hz pptv^{-1} for $s_0 = 10^5$ Hz. Because the sum of all amines rarely exceeds a few ppbv, (2) simplifies to the following equation with less than a 5 % error:

$$X_{\mathrm{MR}} = s_{\mathrm{XH^+}}/(s_0 N_{1\,\mathrm{ppt}}kt) = s_{\mathrm{XH^+}}/S_{\mathrm{typ}}\,. \tag{3}$$

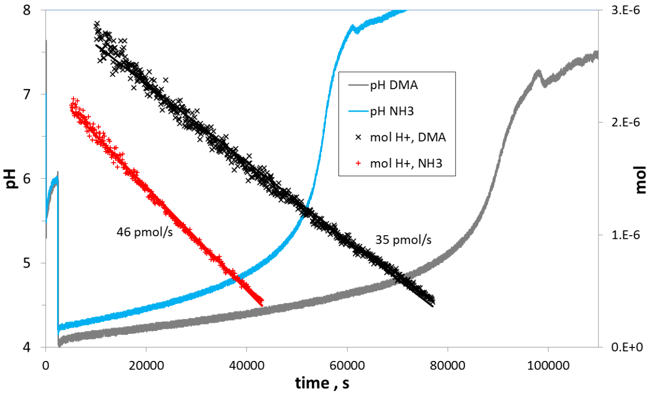

Figure 1. Titration of dimethylamine and ammonia PTs. The gray and light blue lines show the pH of the KCl solutions as they were degassed (0–3000 s), upon addition of HCl (3000 s), and then introduction of the PT effluents at ~ 4000 s. The black and red symbols are the moles of H^+ neutralized by the dissolving base and linear fits to the data for pH < 5 are also shown.

s_0 contains the signal for the $\mathrm{NH_4^+}$ ion for amines because amines readily react with $\mathrm{NH_4^+}$ (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. (2) and (3) in front of the $s_{\mathrm{XH^+}}$ term (Hanson et al., 2011). The sensitivities determined here can provide an evaluation of the ion throughput and detection.

3 Results

3.1 Permeation rates

Figure 1 depicts titration calibrations of ammonia and dimethylamine PTs 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 are 35 and 46 pmol s^{-1} for the two sets of data in Fig. 1. The precision of the slope, assessed by manually altering the fitted line, is a few % for data with pH < 5; 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 > 5.5 was often observed and the linear fits were restricted to pH < 5.5. 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: poor behavior at higher pH was attributed to contaminated KCl. Abrupt changes in pH were occasionally observed when the degas lines or pH probes were introduced,

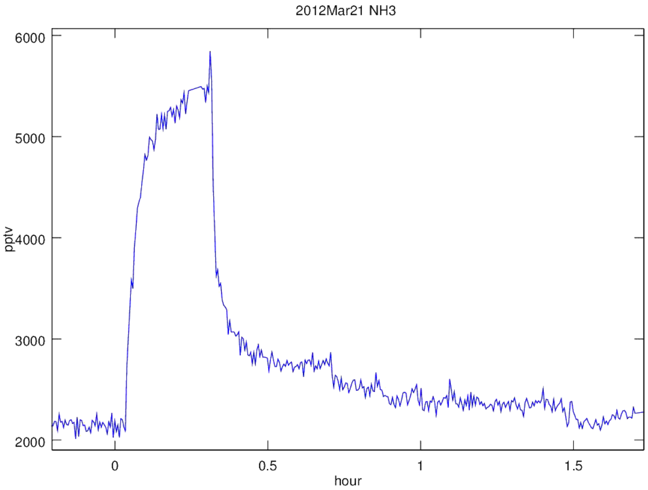

Figure 2. NH_3 mixing ratio measured with AmPMS plotted versus time. Addition of NH_3 at 0.05 h followed by its removal at 0.35 h. Gross signals were used to calculate mixing ratio using S_{typ}; no background subtraction was done. The NH_3 was introduced into the sample flow from a 30 pmol s^{-1} NH_3 permeation tube with single stage dilution. AmPMS was in its original configuration where sample gas first passes through a three-way solenoid valve.

possibly due to dust contamination. Very recently, results from runs for pH ≥ 5 became erratic, and therefore 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 particular permeation tube had measured permeation rates that had an overall variability in rates of up to ±30 % yet for extended time periods (weeks) the variability could be much less than this, on the order of the 10 % precision of the measurement. The variability of measured permeation rates with time and temperature are discussed in the Supplement. The uncertainty in the rates is taken to be the observed overall variability in the measurements, ±30 %. Uncertainty in the calibrations of AmPMS and other uses of the PTs as amine sources can be better than this if rates are determined for a PT just before and just after its use.

A number of PTs were used to calibrate AmPMS with rates that ranged from 3 pmol s^{-1} for trimethylamine 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 of 300 pmol s^{-1}, considerably higher than the FEP rates in Table 1. FEP PTs with trimethyl and triethylamine had very low permeation rates.

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.

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 ∼ 0.05 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 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 ∼ 0.3 h whereupon NH_3 addition was terminated by setting the entire NH_3 PT 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 dimethylamine to AmPMS using the new sampling configuration (see Supplement) first used for the Lewes campaign. The amine was introduced by placing a 13 pmol s^{-1} permeation tube in a flow of 6 sL min^{-1} clean N_2 at 15.2 h. AmPMS subsampled this flow at ∼ 1.5 L min^{-1}, and it contained 2700 pptv dimethylamine. After rising steadily for about 0.5 h, the net dimethylamine 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 dimethylamine 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 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.

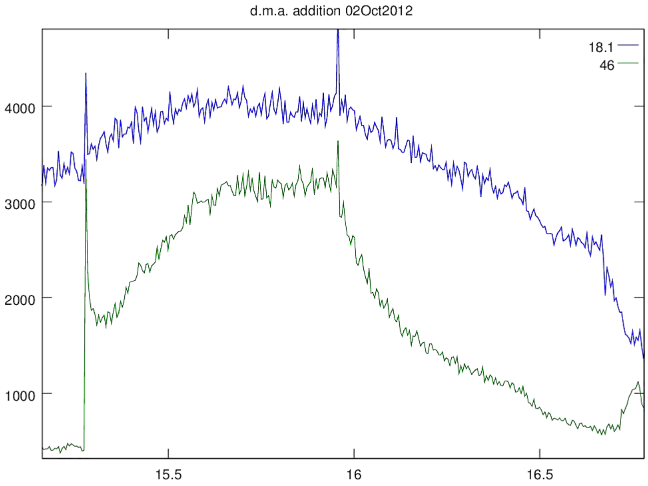

Figure 3. Temporal plot (h) of dimethylamine ($M\cdot H^+$ at 46 u) and ammonia (18 u) mixing ratios before, during and after addition of dimethylamine to AmPMS. The drift region had not been cleaned after the Lewes campaign. A zero was initiated at 16.45 h and AmPMS began to sample another stream of air beginning at 16.7 h.

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.

Tests with dimethyl and trimethylamine 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 where methyl and trimethylamines 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 is a significant interaction of methylamine with the inlet but a much smaller interaction was observed for trimethylamine. Also shown in the Supplement are plots that show much quicker responses to methylamine additions after cleaning the 4 m line. The presence of ammonia in ambient air may help decrease the amount of sticking of amines to the inlet, consistent with the finding that ammonia decreased the memory effects of amines in gas chromatography work of Groneberg et al. (1992).

Calibrations of AmPMS for ammonia, methyl-, dimethyl-, and trimethylamines 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 $s_0 = s_{\mathrm{NH}_4^+} + \sum_n s_{\mathrm{H_3O+(H_2O)}n}$ 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 $2\times10^{-9}\,\mathrm{cm^3\,s^{-1}}$, (ii) an ion-molecule interaction time of about 1 ms, and (iii) little ion breakup or mass discrimination effects for the instrument.

Dimethyl sulfoxide (DMSO) is very efficiently detected by AmPMS. Dimethyl sulfoxide has a large dipole moment (Nelson Jr. 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 $2\times10^{-9}\,\mathrm{cm}^3\ {}^{-1}$ 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 by varying the voltage across the first vacuum chamber (V_{orifice}, the exit of the chamber is at ground) and the bias voltage of the octopole ion guide in this chamber. The signals for protonated amines were relatively insensitive to ion energy for typical conditions. For example, a triethylamine permeation tube was used to deliver triethylamine 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. Little or no breakup is 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

The instrument was deployed at the University of Delaware's Lewes, DE, site in the summer of 2012 and at the US Department of Energy's Southern Great Plains site in the spring of 2013. At both of these sites, an extensive suite of particle instrumentation was deployed (e.g., as in Atlanta, GA, Jiang et al., 2011 and Bzdek et al., 2013). The Lewes site is at the Hugh R. Sharp campus of the University of Delaware which is situated between the Delaware Bay, a salt marsh, and the outskirts of Lewes. A large motorway, a few miles to the east, and other anthropogenic factors, such as a coal fired power plant and poultry operations, can influence the air at the site. The Oklahoma site is next to pasture land with a local herd of cattle. These are surrounded by many miles of fields some of which are actively under cultivation. About 10 miles to the east is interstate 35 and 30 miles to the east is a petroleum refinery. Urban influences are believed to be small. More information on these two sites can be found in Bzdek et al. (2013) and at the DOE (Department of Energy) website (Southern Great Plains DOE site, Lamont, Oklahoma http://www.arm.gov/campaigns/sgp2013npfs). AmPMS also was used to sample ambient air at a level of ∼ 2 m above the roof of the Science building at Augsburg College in Minneapolis, MN.

As mentioned previously and detailed in the Supplement, the sampling arrangement and zeroing procedure was changed from the Atlanta, GA 2009 (NCCN) campaign (Hanson et al., 2011). There were also slight differences in the sampling arrangement between these two campaigns which are believed to not significantly affect the sensitivity of AmPMS nor the zeroing procedure to obtain background signals. Also, the ion drift region was heated to ∼ 40 °C for the Lewes campaign to eliminate condensation; this was not necessary in Oklahoma due to the low atmospheric water vapor content. The zeroing procedure to obtain instrument backgrounds at the masses of interest is discussed in detail 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).

There is a concern about the instrument's capability to detect low levels of amines given the long inlet and the surfaces within the instrument (sampling line, zeroing tee and the drift region). The stickiness within the inlet was shown (see the Supplement) to be important for methylamine and ammonia but interestingly sticking in the inlet was found to be very low for trimethylamine. Also discussed in the Supplement, sluggishness in the zeroing procedure for ammonia and most of the alkyl amines observed for the Oklahoma data and a small portion of the Lewes data points to interactions with surfaces downstream of the inlet, i.e., within the sampling line, zeroing tee and glass drift region of the instrument.

Nonetheless, AmPMS data indicate that alkyl amines at levels as low as single digit pptv were detected. The nature of the surface interactions is not known and will be investigated in future work. For now, the ion signals are treated with the assumptions that the time delay in the amine arriving at the ion beam does not depend on the level of amine and that any amines that adhere to surfaces are released later. Therefore, we propose that the nature of the sticking of the amines to surfaces leads to amine mixing ratios that are a "lagging" average. The amines were monitored for ∼ 0.5 s every 20 s and the ambient data were initially averaged over 5 min as was done in Atlanta, GA, in 2009 (Hanson et al., 2011). Because of issues with the determination of background signals the data were averaged over a long time period, either 1 or 2 h (the ammonia, methylamine (MA), and dimethylamine (DMA) data in Lewes were averaged for 4 or 8 h).

Because of these issues, a potential systematic uncertainty in the ambient data from these two campaigns of +100 and −50 % is conservatively assigned. Evidence presented in the Supplement indicates that it is reasonable to conclude that sticking in the inlet was not significant for most of the amines. However, periods of sluggish background determinations in Oklahoma show that sticking within the instrument could be at times a potential source of systematic error. Rapid changes in relative humidity in Lewes led to potential systematic error in interpolating background signals (see Supplement). With future experimentation directed at better understanding the behavior of the instrument, this potential systematic uncertainty might be significantly relaxed. Adding the systematic uncertainty to the uncertainty in the calibrations (±30 %), the overall uncertainty in the ambient data is +150 and −60 %.

3.3.1 Lewes, DE

Shown in Fig. 4 are the 1 to 2 h averages of the C3 to C7 amines and DMSO, and 4 to 8 h averages for ammonia, methylamine and dimethylamine. The longer averaging interval for the smaller amines was instituted because they had large background levels and fast changes in relative humidity resulted in changes in the background signal levels that were not tracked well with the 1 to 2 h zeroes. Also shown in the bottom plot are 5 min data for temperature and relative humidity (divided by 3). The first 2 weeks of the campaign are shown in Fig. 4, and the last 2 weeks are shown in the Supplement.

Levels of ammonia and alkyl amines were generally low in the semi-rural marine environment of Lewes, DE compared to the urban and continental sites (Atlanta, GA (Hanson et al., 2011) and OK, see Fig. 5). The semi-rural environment of Lewes had a 5-day period early in the campaign (1–5 August, Fig. 4) where methyl- and dimethylamines (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. Trimethylamine 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 dimethylamines decreased to less than a few pptv and < 10 pptv, respectively. On the other hand, trimethylamine (TMA) levels re-established at

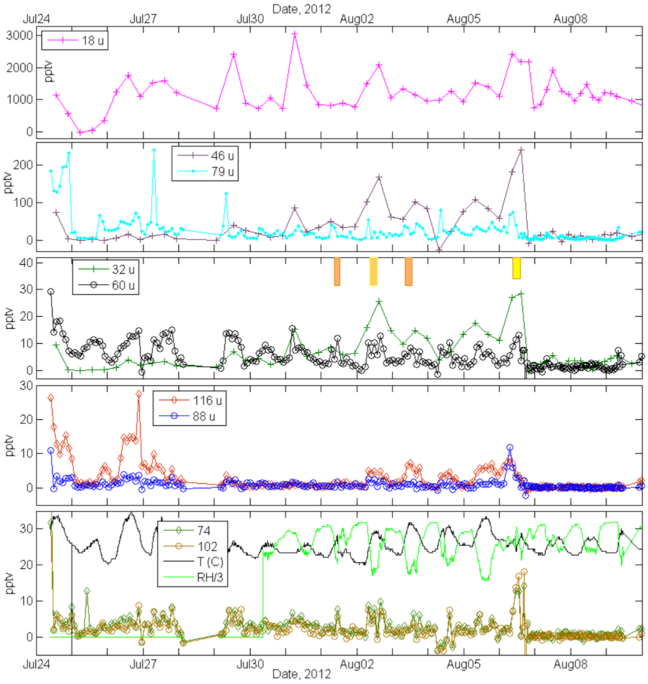

Figure 4. Time series of ammonia (18 u, $M \cdot H^+$) and alkyl amines (32, 46, 60, 74, 88, 102, 116 u) in Lewes, DE in the summer of 2012. DMSO abundances (79 u) are also shown. Particle formation events are indicated at the top of the 3rd plot with color indicating the intensity (yellow, orange, and dark orange). Temperature (°C) and relative humidity (%) are also shown in the bottom plot see Supplement Fig. S10a for more ambient data from this campaign.

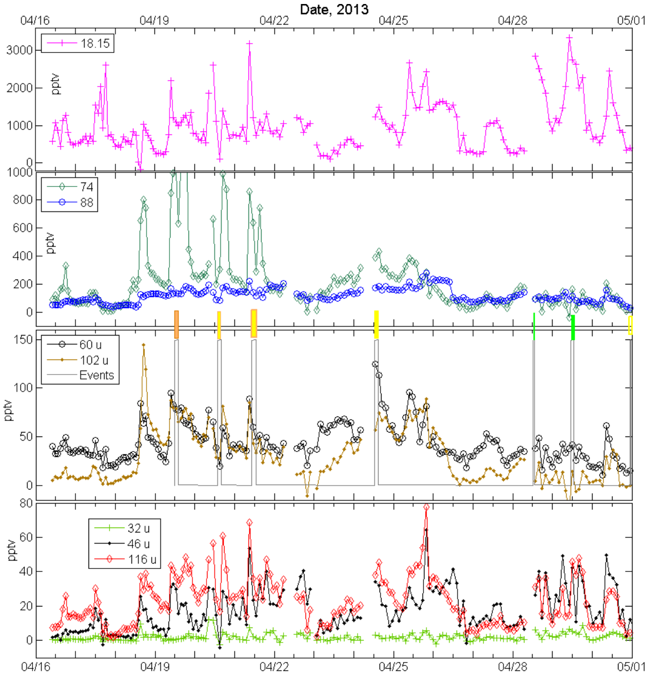

Figure 5. Concentration of ammonia and various amines (pptv) detected by AmPMS in Lamont, OK in 2013. Particle formation events are shown in the second and third plots and the squares indicate the intensity of the event increasing from green to yellow, to orange, and finally to red. From top to bottom: 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 both dimethylamine (46 u) and mass 116 (C7 amines) could be up to 50 pptv (10 to 20 pptv, sustained). See Fig. S10b for more ambient data from this campaign.

~ 10 pptv after 11 August and it was generally the most abundant alkyl amine during the day (see the Supplement). Like the small amines, ammonia mixing ratios from the 9th to the 25 August had 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 ($M \cdot H^+ = 79$ 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 trimethylamine suggesting that a source of DMSO is linked to one that also emits trimethylamine.

3.3.2 Lamont, OK

AmPMS was deployed in Oklahoma at the atmospheric Radiation Measurement (ARM) facility between 16 April and 21 May 2013. Figure 5 shows the 2 h average mixing ratios of ammonia and the alkyl amines for the first 2 weeks of the campaign (the second 2 weeks are shown in the Supplement). The most abundant amines were the 4 and 5 carbon compounds at 74 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 smaller amines were relatively low: methylamine was generally a few pptv or less while dimethylamine and trimethylamine abundances were typically 20 and 50 pptv, respectively.

Occasionally, net amines had artifact spikes and false negative values when their abundances were small compared to backgrounds. This was attributed to sticking on surfaces within the system and the zeroing tubing. The Supplement presents details on how a lagging background was defined during these times. Also shown in the Supplement are amine specific time lags of ~ 10-to-60 min due to the 4 to 6 m inlet line. The Oklahoma data is rendered as 1 or 2 h averages, the interval between background determinations. Note that

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

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

[a] July/August 2009, Hanson et al. (2011). [b] July/August 2012. [c] Does not exceed hourly detection limit, Table S1 in the Supplement. [d] April/May 2013. [e] October 2012. [f] Nowak et al. (2006).

for the Lewes data there was little difference in net amines from the two zeroing analyses and the normal analysis was used most of the time. The Oklahoma net amines data was split about even between the two analyses. Which analysis to use was determined solely by whichever gave the larger net abundances. A possible bias in the data 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 % and is included in the potential systematic error discussed above.

3.4 Correlations and comparisons of amine measurements

At the OK site methylamine was usually much lower than trimethylamine whereas in Lewes, DE, methylamine often exceeded trimethylamine. 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 dimethylamines 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 ($R^2 \sim 0.3$) while trimethylamine had little correlation with other amines. This suggests different sources for the large vs. small amines in Lewes and probably another source altogether for trimethylamine. 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 dimethylamines were somewhat correlated with ammonia (R^2 of 0.38 and 0.24, respectively).

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, GA 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 3 week period in Minneapolis. See Kieloaho et al. (2013) and You et al. (2014) for additional comparisons of amines measured at urban and rural sites.

A significant temperature dependence for trimethylamine abundances has been reported in earlier studies in the summertime urban Atlanta, GA (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 methylamine and some correlation for dimethylamine (R^2 values for linear fits against temperature of 0.16 and 0.33 for methyl and dimethylamines, respectively). The amine abundances in Lewes showed little or no correlation with temperature (linear fits had R^2 values less than 0.1 for methyl and dimethylamine; trimethylamine had an R^2 value of 0.17). Little or no temperature dependence was also reported for the C2 and C3 amines in the summertime boreal forest (Kieloaha et al., 2013). In measurements in an Alabama forest, You et al. (2014) report little temperature dependence for the C1 and C1 amines and a modest temperature dependence for trimethylamine.

Diurnal behavior for the C3 and C6 amines in Atlanta, GA (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, GA. 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 2 or 3 larger from 11:00 to 15:00 LST than their early morning averages (00:00–04:00 LST). In Oklahoma, daytime hourly mean (12:00 to 16:00) for the C3, C5, and C6 amines were about +50, +0 %, and +30 % higher, respectively, than the early morning hourly medians (00:00 to 04:00 LST). The C1, C2, C4 and C7 amines had somewhat larger variations: they were all about a factor of 2 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 more 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. 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 large 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 abundances 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 cm^{-3}.

In contrast to the other sites discussed here, the Lewes, DE, site had at times methyl and dimethylamines as the most abundant amines; this may be due to nearby poultry operations. Dimethyl sulfoxide was observed at this marine site and spikes in DMSO were accompanied by spikes in trimethylamine 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 methylamine and probably 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 5-minute or shorter time scale. Changes to AmPMS' sampling and ion source configurations are also planned with an aim towards reducing backgrounds and their fluctuations. Changing the configuration of AmPMS more towards how it was deployed in its first field mission (Atlanta, GA 2009, Hanson et al., 2011) will avoid background subtraction anomalies when sampling ambient air in environments where RH changes quickly.

Supporting information

Additional information is available on AmPMS sampling arrangement, zeroing procedures, response times and sampling line issues, calibration with DMSO, other ions of interest, amines diurnal behavior and correlation plots, ion breakup processes, and permeation 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.

The Supplement related to this article is available online at doi:10.5194/amt-7-3611-2014-supplement.

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