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Atmospheric amines and ammonia measured with a chemical ionization mass spectrometer (CIMS)

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Abstract. We report measurements of ambient amines and ammonia with a fast response chemical ionization mass spectrometer (CIMS) in a southeastern US forest and a moderately polluted midwestern site during the summer. At the forest site, mostly C3-amines (from pptv to tens of pptv) and ammonia (up to 2 ppbv) were detected, and they both showed temperature dependencies. Aerosol-phase amines measured thermal-desorption chemical ionization mass spectrometer (TDCIMS) showed a higher mass fraction in the evening with cooler temperatures and lower in the afternoon with warmer temperatures, a trend opposite to the gas-phase amines. Concentrations of aerosol-phase primary amines measured with Fourier transform infrared spectroscopy (FTIR) from micron and submicron particles were 2 orders of magnitude higher than the gas-phase amines. These results indicate that gas to particle conversion is one of the major processes that control the ambient amine concentrations at this forest site. Temperature dependencies of C3-amines and ammonia also imply reversible processes of evaporation of these nitrogen-containing compounds from soil surfaces in daytime and deposition to soil surfaces at nighttime. During the transported biomass burning plume events, various amines (C1–C6) appeared at the pptv level, indicating that biomass burning is a substantial source of amines in the southeastern US. At the moderately polluted Kent site, there were higher concentrations of C1- to C6-amines (pptv to tens of pptv) and ammonia (up to 6 ppbv). C1- to C3-amines and ammonia were well correlated with the ambient temperature. C4- to C6-amines showed frequent spikes during the nighttime, suggesting that they were emitted from local sources. These abundant amines and ammonia may in part explain the frequent new particle forma-

tion events reported from Kent. Higher amine concentrations measured at the polluted site than at the rural forested site highlight the importance of constraining anthropogenic emission sources of amines.

1 Introduction

Amines and ammonia (NH_3) are ubiquitous in the atmosphere and they are present in the gas phase, aerosol particles, and rain and fog droplets (Ge et al., 2010b). Atmospheric sources of amines and NH_3 include animal husbandry, vegetation, biomass burning, oceans, waste incinerators, cooking, tobacco smoking, car exhausts, and various industrial processes (Ge et al., 2010a, b; Hertel et al., 2013). Some of the current CO_2 sequestration technologies also utilize amine solutions and this has become an important source of anthropogenic amines in the atmosphere (Shao and Stangeland, 2009). Amines can cause serious health effects (Ge et al., 2010b; Lee and Wexler, 2013), as they can be rapidly oxidized to form carcinogens, such as nitrosamines and isocyanic acid in the atmosphere (Finlayson-Pitts and Pitts, 2000; Nielsen et al., 2011, 2012). The background concentrations of amines are typically at the pptv (parts per trillion in volume mixing ratio) to tens of pptv level in the gas phase (Akyüz, 2007; Chang et al., 2003; Dawson et al., 2014; Grönberg et al., 1992; Hanson et al., 2011; Kieloaho et al., 2013; Schade, 1995; Sellegri et al., 2005b; VandenBoer et al., 2011; Yu and Lee, 2012), whereas NH_3 is typically at the sub-ppbv (parts per billion in volume mixing ratio) to tens of ppbv level (Benson et al., 2010; Erupe et al., 2010; Fountoukis et al., 2009; Nowak et al., 2006, 2007, 2010).

Amines and NH_3, together with sulfuric acid, play critical roles in atmospheric new particle formation processes (Zhang et al., 2012). Quantum chemical calculations suggested that amines can reduce the energy barrier of sulfuric acid nucleation, even more effectively than NH_3 (Kurtén et al., 2008). Laboratory studies showed that amines can substitute ammonium to aminium in charged clusters (Lloyd et al., 2009). Studies of nucleation kinetics showed that amines indeed participate in the sulfuric acid aerosol nucleation at the molecular cluster level (Almeida et al., 2013; Berndt et al., 2010; Karl, 2010; Wang et al., 2010a, 2010b; Yu et al., 2012; Zollner et al., 2012). The enhancement effects of amines on nucleation are dependent on the basicity of amines; there are also synergetic effects of amines and NH_3 on aerosol nucleation (Yu et al., 2012).

Amines and NH_3 participate in secondary organic aerosol (SOA) formation via various pathways including formation of salts (Angelino et al., 2001; Murphy et al., 2007), oxidation reactions (Angelino et al., 2001; Gai et al., 2010; Karl, 2010; Malloy et al., 2009; Murphy et al., 2007; Nielsen et al., 2011; Silva et al., 2008; Updyke et al., 2012; Zahardis et al., 2008) and aqueous phase reactions (De Haan et al.,

2009). These nitrogen containing compounds also contribute to the formation of light absorbing organic compounds in atmospheric "brown carbon" aerosols (Laskin et al., 2010). Amines and NH_3 affect the aerosol acidity (Pankow, 2003; Pratt et al., 2009), a key aerosol property that may control the formation yields of biogenic SOA (Jang et al., 2002; Surratt et al., 2007). Ammonium sulfate and aminium sulfate salts have distinctively different deliquescent relative humidity (RH) points (Qiu and Zhang, 2013) and in turn affect the aerosol phase state (solid vs. liquid); this may have important implications for aerosol processes, such as SOA formation yields (Vaden et al., 2011).

Amines have been measured typically with low time resolution (hours, days or even weeks) online and often with offline analytical methods based on chromatography, mass spectrometry, UV, fluorescence or electrochemical detectors (Ge et al., 2010b; Yu and Lee, 2012). These methods are not suitable for capturing temporal variations of atmospheric amines that can rapidly change due to emissions and deposition processes, as well as reactions with oxidants and aerosols. Chemical ionization mass spectrometry (CIMS) has been used for the fast-response online detection of atmospheric amines (Eisele, 1988; Hanson et al., 2011; Sellegri et al., 2005b; Yu and Lee, 2012). Sellegri et al. (2005b) used a proton transfer reaction mass spectrometer (PTR-MS) to measure trimethylamine and other volatile organic compounds (VOCs) in the Finnish boreal forest. Hanson et al. (2011) developed an ambient pressure proton transfer mass spectrometer (AmPMS) technique to measure gas-phase C1- to C6-amines in downtown Atlanta, Georgia. Yu and Lee (2012) developed a CIMS detection method that utilizes ethanol ions as chemical reagent to simultaneously detect amines and NH_3, and conducted ambient measurements in Kent, Ohio.

Measurements of amines in the forested environments are very scarce at present. Schade (1995) suggested that trimethylamine could be the main aliphatic amine compound emitted from vegetation sources. Forest soils also contain dissolved organic nitrogen compounds such as free amino acids and alkylamines, due to biodegradation of proteins and peptides in the forest ecosystem (Bigg, 2004; Yu et al., 2002). An early PTR-MS measurement in the boreal forest by (Sellegri et al., 2005a) reported C3-amines between 30–80 pptv in the spring. Another measurement at the same site with a liquid chromatography technique showed even higher concentrations of reduced nitrogen compounds between May and October, C2- and C3-amines at levels of up to hundreds of pptv, and C4-amines up to tens of pptv, and suggested that amines may be emitted from leaf litters (Kieloaho et al., 2013).

In the present study, we report the ambient concentrations of amines and NH_3 measured in an Alabama forest and in Kent, Ohio during the summer of 2013. The Alabama site represents a relatively rural forest environment typical for the southeastern US environments with high biogenic VOCs

emissions, while Kent is located in the Midwest surrounded by large power plants and agricultural activities at the regional scale. Observations at these two relatively contrasting environments can provide information that is helpful to identify emission sources, sinks and the chemistry of atmospheric amines and NH$_3$. This study presents one of the very few simultaneous measurements of ambient amines and NH$_3$ with a fast response CIMS. To our best knowledge, this is the first time that measurements of amines were made in a rural biogenic VOC-dominated environment in the southeastern US.

1.1 Measurement sites

Measurements were made at the Southeastern Aerosol Research and Characterization (SEARCH) Centreville, AL site (near Brent, AL) during the Southern Oxidant and Aerosol Study (SOAS, http://soas2013.rutgers.edu/) from June 1 to 15 July 2013. The main objective of SOAS is to study the atmospheric chemistry and climate-relevant properties of aerosols generated from interactions of biogenic and anthropogenic emissions. Brent (32.94° N, 87.18° W) has a population of less than 5000 inhabitants and is surrounded by mixed deciduous (oak, hickory, and sweetgum) and coniferous (loblolly and shortleaf pine) trees, resulting in high ambient ratios of isoprene to monoterpenes. It is located about 85 km south of Birmingham and 40 km southeast of Tuscaloosa. The measurement site is approximately 30 and 40 km away from the US Interstate Highways 20 and 65, respectively, and is within 5 km of the State Highway 82. Several large emission sources of NO$_x$ (NO + NO$_2$; 17 000 ton year^{-1}) and SO$_2$ (92 000 ton year^{-1}) are located within 100 km of the measurement site. This forest site thus can represent contrasting air masses, where at times atmospheric constituents are mostly of biogenic origin and at other times biogenic air masses are mixed with pollutant NO$_x$ and SO$_2$ emissions.
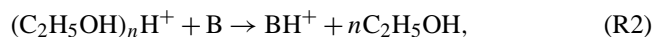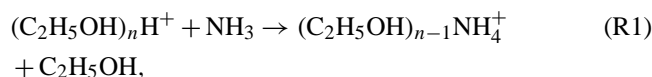
Following the SOAS campaign, subsequent measurements were made in Kent (41.15° N, 81.36° W) over 20 days during August and September 2013. The Kent site was previously described elsewhere (Benson et al., 2010; Erupe et al., 2010; Kanawade et al., 2012; Yu et al., 2013). Kent has a high tree cover fraction, and has a population of about 30 000. It is surrounded by several larger cities: Akron/Canton about 30 km to the southwest, Cleveland about 65 km to the northwest, and Pittsburgh about 160 km to the east. There are two interstate highways near the measurement site, US Interstate 76 about 5 km south of the sampling site and Interstate 80 about 10 km north of the site. There are high emissions of SO$_2$ (http://www.epa.gov/air/sulfurdioxide/) from the large size coal-burning power plants located in the Ohio River valley region. There are also widespread agricultural activities in Northeast Ohio. Kent also represents one of the very few observation sites in the US where long-term measurements of new particle formation were conducted, including aerosol size distributions and key nucleation precursors (sulfuric acid, NH$_3$ and amines) (Benson et al., 2010; Erupe et

al., 2010; Kanawade et al., 2012; Yu et al., 2013). Observations conducted over the past 8 years consistently showed frequent new particle formation events, with the frequency between ∼ 17 % and ∼ 40 %, over different seasons at this site.

2 Amine-CIMS characterization and calibration

The amines/NH$_3$ CIMS was described elsewhere (Yu and Lee, 2012). As discussed in detail below, this CIMS detects ambient amines and NH$_3$ at the pptv and sub-pptv level, with a 1 min integration time. The sensitivity ranged between 2–12 Hz pptv^{-1} for different amine and NH$_3$ for 1 MHz of protonated ethanol reagent ion signals, as determined from in situ calibrations (Table 1).

NH$_3$ and amines (such as methylamine, dimethylamine, ethylamine, trimethylamine, diethylamine, and triethylamine etc. and their isomers, denoted as B below) are ionized using ethanol ions as reagent, via the following ion–molecule reactions (Erupe et al., 2011; Yu and Lee, 2012):

$$(C_2H_5OH)_nH^+ + NH_3 \rightarrow (C_2H_5OH)_{n-1}NH_4^+ \quad (R1)$$
$$+ C_2H_5OH,$$

$$(C_2H_5OH)_nH^+ + B \rightarrow BH^+ + nC_2H_5OH, \quad (R2)$$

where $n = 1, 2$, and 3. A collision dissociation cell (CDC) is used in the CIMS to destroy the weakly bounded clusters, and thus primary ethanol ions typically contain n only up to 3. As shown in the CIMS spectra (Fig. 1), there were ethanol monomer, dimer, and trimmer reagent ions; whereas for product ions there were only BH$^+$ ions. The ethanol ion chemistry for the detection of NH$_3$ was worked out previously by Nowak and colleagues (Nowak et al., 2002), and we have linearly applied the same technique to the detection of amines (Erupe et al., 2011; Yu and Lee, 2012).

The CIMS was located in a trailer at the SOAS ground site. Ambient air was sampled through a 13 cm long perfluoroalkoxy (PFA) Teflon tube (diameter, 1.27 cm) and a subsequent 17 cm long PFA tube (diameter, 0.635 cm) with a flow rate of 10 L min^{-1} (liter per minute) (Fig. S1). The residence time within the sampling inlet prior to the CIMS ionization region was 0.17 s. The sampling inlet was drilled through the wall of the trailer, horizontally, in the direction precisely aligned with the CIMS inlet. Only PFA and polytetrafluoroethylene (PTFE) Teflon material (as opposed to stainless or aluminum) were used to reduce the deposition of ammonium nitrate and NH$_3$ on the inner surfaces of the sampling inlet (Nowak et al., 2007). CIMS background signals were obtained by introducing ambient air through another PFA Teflon tube (inner diameter, 0.635 cm) (Fig. S1). A three-way valve, which was also made of PFA, was used to switch the sampling between the ambient and background measurement modes. Ambient and background measurements were conducted over 15 and 5 min, respectively, within every 20 min period. During the background mode, ambient air
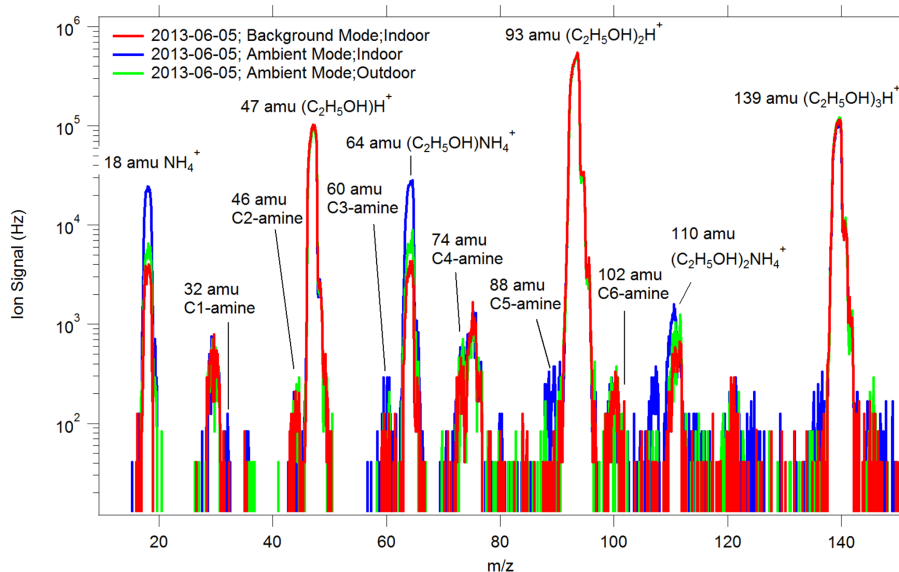
Figure 1. Typical CIMS mass spectra taken under the background (red) and measurement modes, including measurements from the ambient air (green) and indoor air (blue), in the Alabama forest. Y axis is shown in log scale.

Table 1. The CIMS sensitivities (normalized to 1 MHz ethanol reagent ions) determined by in situ calibrations (Fig. S1), background signals, and detection limits (3 times the standard deviation of background signals, within a 1 min integration time) of amines and NH_3. Typical ambient concentrations measured in the Alabama forest and in Kent are also included (20 min average data).

Basic Compound [a]	Sensitivity [Hz (pptv MHz)$^{-1}$] [b]	Detection Limit, DL	Alabama Forest: Jun–Jul	Kent: Aug–Sep
NH_3 (ppbv)	13	0.035	Up to 1–2	Up to 6
C1-Amine (pptv) (methylamine)	12	0.1	< DL	1–4
C2-Amines (pptv) (dimethylamine)	12	0.5	< DL	< DL
C3-Amines (pptv) (trimethylamine)	8	0.8	1–10	5–10
C4-Amines (pptv) (diethylamine)	4	3.3	< DL	10–50
C5-Amines (pptv)	2	1.9	< DL	10–100
C6-Amines (pptv) (triethylamine)	2	1.4	< DL	< DL

[a] CIMS shows the sum of isomer concentrations. Here, we indicate specific amine compounds used in calibration. For example, for C3-amines, trimethylamine was used for calibration. But for C5-amines, no calibrations were made because permeation tubes are not available and its sensitivity was interpolated between those for C4- and C6-amines.
[b] With regard to the unit of sensitivity (Hz (pptv MHz)$^{-1}$): sensitivity was defined as the change in ion signals (Hz) of a basic compound corresponding to 1 pptv of the calibration gas concentration, then normalized to 1 000 000 Hz of the ethanol reagent ion signal.

passed first through a diffusion drier (DDU 570/H, Particle Instruments) containing silica-gel to remove water vapor, and then through the silicon phosphate scrubbers (AS-200-8-EB, Perma Pure) to remove amines and NH_3 (Yu and Lee, 2012). The drier was used to prolong the lifetime of the scrubber; the scrubber does not efficiently remove basic compounds when it is wet. The drier was needed, especially under high RH conditions in summer in Alabama. Our experiments using ambient air, without applying the drier, have shown that ambient RH did not affect the CIMS background ion signals. We also experimentally confirmed that the application of the drier did not change the background signals. Linear interpolation of background signals was made between two consecutive background measurements. Normalization

of background and ambient signals was made against the total ethanol ion signals including monomer, dimer and trimer cluster ions by assuming the same transmission efficiency for different clusters, to take into account the variation of ethanol ion signals between the background and sampling modes due to fluctuations of the flow and pressure in the ionization cell. The reagent ion signals were typically around 300 kHz, with differences less than 10 % between the two modes (higher during the background than the sampling mode).

In situ calibrations were made for various amines and NH_3. Two separate and independent gas handling systems were built for the calibration and background/ambient mode measurements; this is a different approach than was used for our previous studies (Benson et al., 2010; Yu and Lee, 2012).
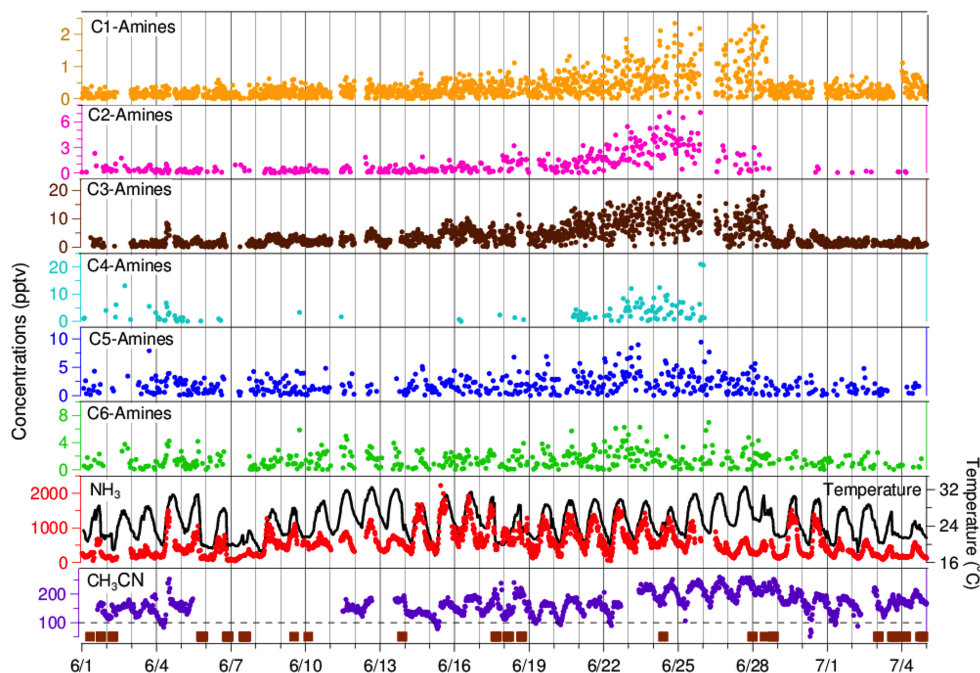
Figure 2. Temporal variations of amines, NH_3, and CH_3CN along with the ambient temperature measured in the Alabama forest during the entire SOAS field campaign. Vertical grids correspond to times at midnight. The brown colored bars in the bottom panel indicate the period of rainfalls. Concentrations of amines and NH_3 data shown here were averaged over 20 min; the same for Figs. 3, 8 and 10.

This modification was made to reduce possible contamination of standard calibration gases on the inlet inner surfaces. Amines and NH_3 calibration gases were generated from pre-calibrated National Institute of Standards and Technology (NIST) traceable permeation tubes in a temperature- and flow rate-controlled standard gas generator (491 MB, Kin-Tek). Each standard gas was run continuously for 20 h prior to the calibration to ensure that the vapor was fully stabilized in the oven.

Figure 1 shows the typical CIMS mass spectra taken under the background and measurement modes (for the indoor and ambient air) during the SOAS campaign. Reagent ethanol ion peaks appeared at m/z 47 $(C_2H_5OH)H^+$, m/z 93 $(C_2H_5OH)_2H^+$ (the highest peak) and m/z 139 $(C_2H_5OH)_3H^+$. NH_3 product ions appeared at m/z 18 NH_4^+, m/z 64 $(C_2H_5OH)NH_4^+$, and m/z 110 $(C_2H_5OH)_2NH_4^+$. C1-amine (methylamine) ions were at m/z 32 $(CH_3)NH_3^+$; C2-amines at m/z 46 (e.g., $(CH_3)_2NH_2^+$, dimethylamine; $CH_3CH_2NH_2^+$, ethylamine); C3-amines at m/z 60 (e.g., $(CH_3)_3NH^+$, trimethylamine]; C4-amines at m/z 74 (e.g., $(C_2H_5)_2NH_2^+$, diethylamine]; C5-amines at m/z 88; and C6-amines at m/z 102 (e.g., $(C_2H_5)_3NH^+$, triethylamine). We generally found significantly higher concentrations of amines and NH_3 in the indoor than in the ambient air, indicating direct emissions of nitrogen containing basic compounds from human bodies (e.g., sweat and breath) (Sutton et al., 2000). For example, on the specific day shown in Fig. 1, we estimated that there were NH_3 4.9 ppbv, C1-amine 14 pptv,

C2-amines 20 pptv, C3-amines 30 pptv, C5-amines 183 pptv, and C6-amines 181 pptv in the indoor air; and there were NH_3 0.62 ppbv, C3-amines 16 pptv and C6-amines 73 pptv in the ambient air. The indoor air concentrations were extremely sensitive to the presence of people inside the room.

Table 1 summarizes the CIMS sensitivities of amines and NH_3 obtained from in situ calibrations, background signals, and detection limits (DL, defined as 3 times the standard deviation of the background ion signals, with 1 min integration time). Tables S1 and S2 show detection limits of each amine compound and NH_3 derived for different integration times (1, 5, 10, and 60 s) from measurements made during the SOAS campaign and in Kent, Ohio. In general, detection limits leveled off after 5–10 s. Table S3 shows mean values of background signals measured at the two sites. The background signals were fairly stable over the entire measurement periods. Figure S2 shows the calibration curves of amines and NH_3 obtained in situ in the Alabama forest. The sensitivity of NH_3 was highly reproducible (Fig. S2), $\sim 13\,Hz\,pptv^{-1}$ for 1 MHz of ethanol reagent ions, for the entire SOAS campaign as well as the pre- and post-campaign calibrations. This is an important improvement made over the previous studies (Benson et al., 2010; Yu and Lee, 2012), where NH_3 sensitivities varied on a day-to-day basis. Although the sensitivities of amines were also improved, amine sensitivities were still lower than the NH_3 sensitivity and measurements of amines were also less reproducible (Figs. S2 and Table 1). Lower amine sensitivities were due to loss of amines in the gas-line.
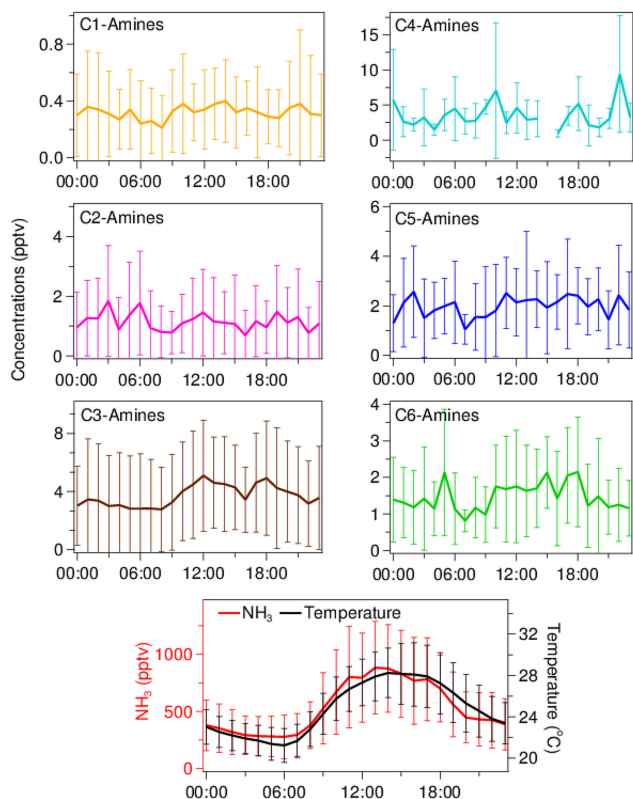
Figure 3. The averaged diurnal variation throughout the entire SOAS campaign for the measured C1- to C6-amines and NH$_3$ concentrations measured in the Alabama forest during the summer for 6 weeks. C4-amines were below the detection limit for most of the time during the campaign, except the burning events (Fig. 2), so are not shown here. The vertical bars indicate one standard deviation of the measurement values, representative of day-to-day fluctuations in ambient concentrations (Fig. 2). The average ambient temperature is also shown, along with NH$_3$.

Figure 4. Temperature dependence of amines, NH$_3$ and isoprene for the entire SOAS campaign. Gray dots show the measurement data and blue lines show exponential fitting of the data. Red circles and vertical lines show the mean and one standard deviation of concentrations of these chemical species, with each bin representing 20 percentile of temperature values.

Consistent with this observation, the measured sensitivities also showed a decreasing trend with the increasing molecular weight of the amine molecule (Table 1). Detection limits were also substantially improved, compared to the previous work (Yu and Lee, 2012). These improvements in the detection limits and sensitivities were achieved because background signals (Table S3) were lower, less variable and independent of ambient RH conditions.

Amines have been measured with CIMS techniques in other studies, using protonated water ions as reagent (Hanson et al., 2011; Sellegri et al., 2005a). Because ethanol has a higher proton affinity (788 kJ mol^{-1}) than water (697 kJ mol^{-1}) (Jolly, 1991), our CIMS only responds to basic compounds that have higher proton affinities (e.g., trimethylamine 945 kJ mol^{-1}; NH$_3$ 854 kJ mol^{-1}) and hence are selectively detected (via R1 and R2) with little interferences from other VOCs present in the atmosphere. Since most VOCs are detected at odd masses, in general, even masses are good indicators for nitrogen-containing com-
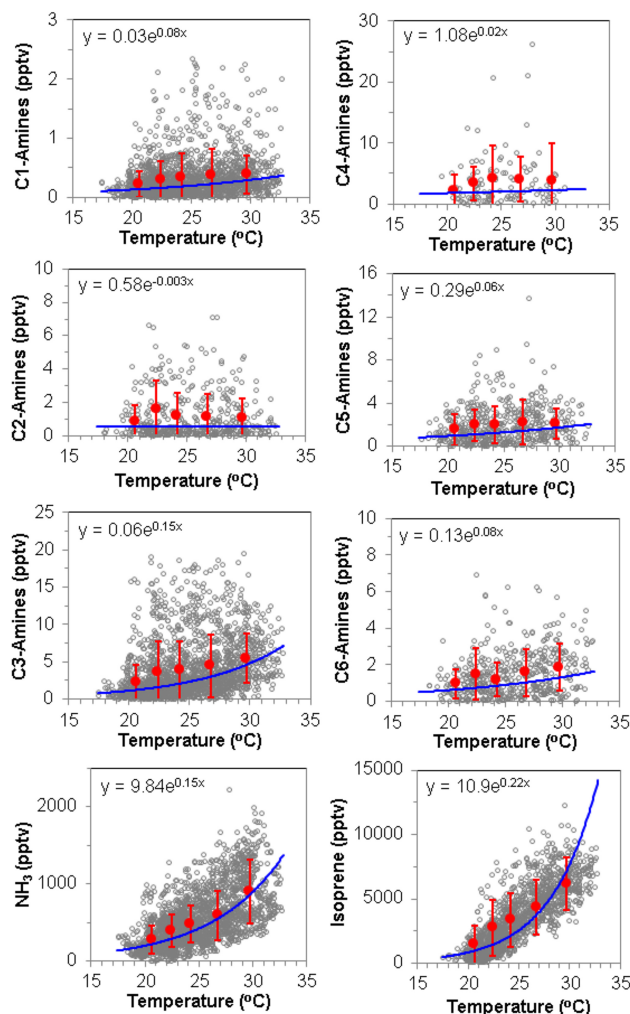
pounds. Background signals were also independent of the ambient temperature and RH in our CIMS. On the other hand, there were some RH dependencies of background signals in the PTR-MS and because of the varying background signals, so the AmPMS did not report NH$_3$ concentrations, simultaneously with amines (Hanson et al., 2011).

3   Supporting measurements during the SOAS campaign

During the SOAS campaign, a large number of state-of-art analytical instruments were deployed for aerosol and trace gas measurements (http://soas2013.rutgers.edu/). Here, we briefly describe specific measurements used in the present
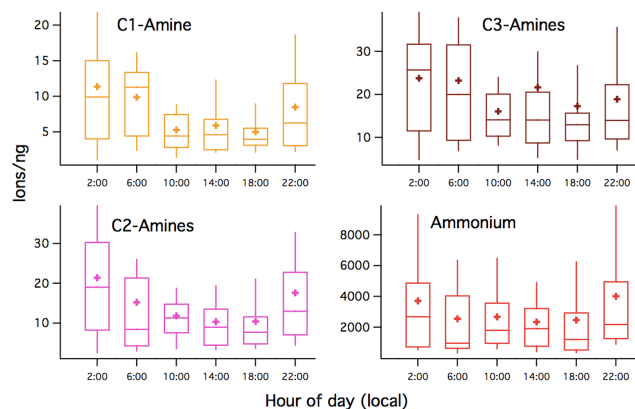
Figure 5. Campaign-averaged, 4-hour-binned C1- to C3-amines and ammonium particle-phase signals from TDCIMS. Line end-points are the 10th and 90th percentile, bottom and top of the box indicates 25th and 75th percentile, horizontal lines are the median and the crosses are the mean. The ion data used were background-corrected, detectable (2-sigma) points from 30 min particle collections and are mass-normalized by the collected particle mass. Collected particle masses ranged from 2–80 ng, and volume mean diameters for collected particles ranged from 40–120 nm.

study. Aerosol-phase amines were measured with two independent methods. First, dried submicron particles were collected on PTFE filters and analyzed with Fourier transform infrared spectroscopy (FTIR) to identify functional groups of chemical components (including primary amines) in the aerosol phases. The samples were collected at either ambient temperature, 50 °C or 70 °C; the analyzed amine concentrations were invariant with temperature so the reported values reflect averaged values between two co-located sampling lines. Additionally, chemical composition of particles in the size range from ∼ 40–120 nm was measured with an online thermal-desorption chemical ionization mass spectrometer (TDCIMS) (Smith et al., 2008; Smith et al., 2010). The collected particle masses ranged from 2–80 ng, and volume mean diameters for collected particles ranged from 40–120 nm. Thus, the FTIR and TDCIMS measurements represent chemical information of aerosols for different size ranges and for different types of amine compounds. Continuous analysis of $PM_{2.5}$ mass was made with a tapered element oscillating microbalance (TEOM; R&P, Model 1400 a/b). Aerosol pH and particle water content were predicted, based on the ISORROPIA aerosol thermodynamic model (Fountoukis and Nenes, 2007; Nenes et al., 1998) and organic and inorganic anions and cations detected with ion chromatography (Guo et al., 2014). An in situ gas chromatography–mass spectrometry (GC–MS) instrument was used to measure a large suite of VOCs, including isoprene, monoterpenes and their oxidation products, and the biomass burning tracer acetonitrile (CH_3CN). Sample air was drawn from the top of the flux tower at the SOAS ground site, and VOCs were cryo-statically sampled for 5 minutes every half hour.
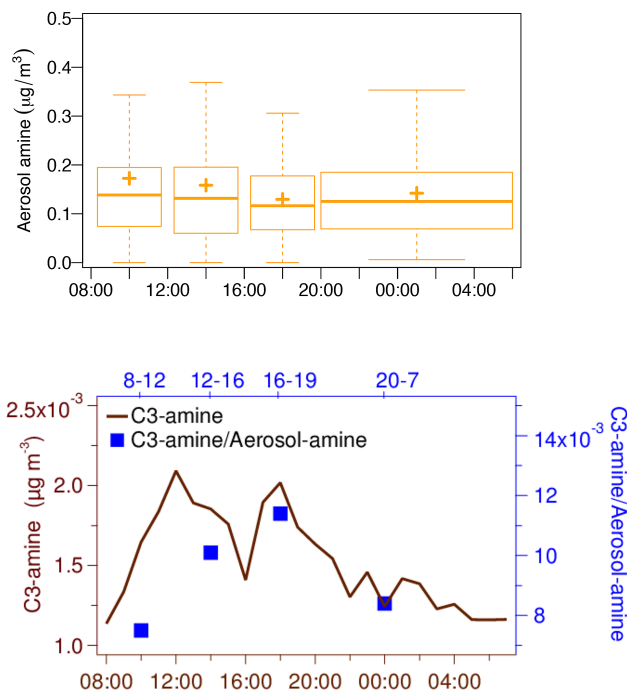

Figure 6. (Upper panel) Average daily variation of aerosol phase concentration ($\mu g\,m^{-3}$) of primary amines in submicron particles collected on PTFE filters and analyzed with FTIR during the SOAS campaign. The horizontal solid lines indicate the median, plus signs indicate the mean, the boxes extend from the 25th to 75th percentile, and the whiskers span the interquartile range. (Lower panel) Temporal variation of the averaged gas-phase C3-amines (brown line) and the ratio of C3-amines over the aerosol-phase aliphatic amines (blue squares) during the SOAS campaign. The unit of gas-phase C3-amine concentrations was converted from pptv to $\mu g\,m^{-3}$ (1 pptv = 0.41 ng m^{-3}) to be compared with aerosol-phase amines. Since C3-amines dominated for most of the SOAS campaign (Figs. 2 and 3), C3-amines can be representative of the total gas phase amine concentrations.

A detailed description of the instrument can be found elsewhere (Gilman et al., 2010). OH radicals were detected with the laser induced fluorescence (LIF) technique (Mao et al., 2012). Ozone was measured with a pressure and temperature compensated UV absorption instrument TEI-49i (Thermo Scientific). SO_2 was measured by pulsed UV fluorescence (model TEI 43C-TL). Ambient temperature and RH were monitored with the Met4 Measurement System (Paroscientific Inc.). Wind speed and direction were measured with an ultra-sonic anemometer (R. M. Young, model 81000).

4 Measurements in the Alabama forest

Table 1 shows the summary of the ambient concentrations of amines and NH_3 measured in the Alabama forest in June and July 2013. Temporal variations of amines and NH_3 are shown for the 6 weeks of the entire SOAS campaign period (Fig. 2).
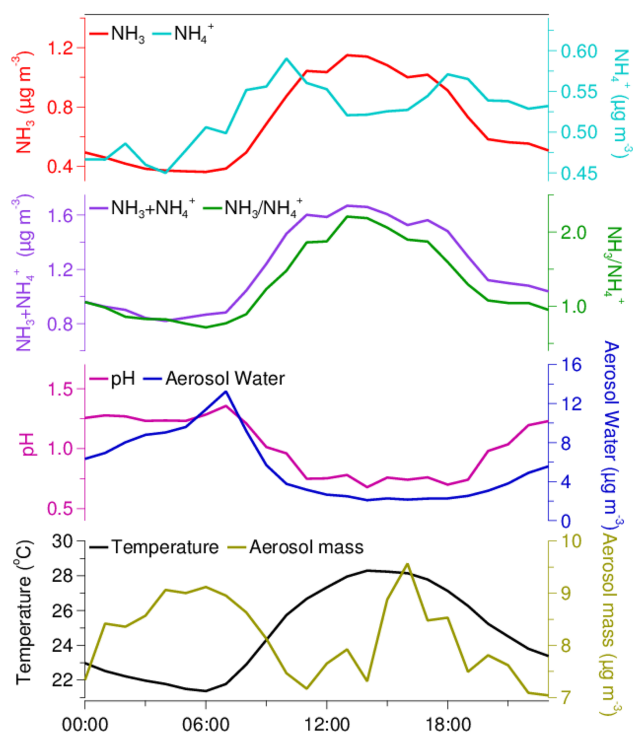
Figure 7. The average diurnal variation of the gas phase NH_3 (red), aerosol-phase ammonium (NH_4^+, cyan) measured with ion chromatography (IC), the sum of NH_3 and NH_4^+ (purple), the ratio of NH_3 to NH_4^+ (green), ISORROPIA-predicted aerosol pH (magenta), ISORROPIA-predicted aerosol water content (blue), ambient temperature (black), and aerosol mass (yellow) for the entire SOAS campaign period. The unit of gas-phase NH_3 concentrations was converted from ppbv to $\mu g\,m^{-3}$ ($1\,ppbv = 1.3\,\mu g\,m^{-3}$) to be compared with aerosol-phase NH_4^+.

Figure 8. Amines, NH_3 and CH_3CN concentrations measured on 4 June 2014 in the Alabama forest. The measured ambient temperature is also shown. There was a local trash burning event starting around 10 a.m. The blank period of amines and NH_3 in the afternoon was due to a power outage in the trailer where the CIMS was located.

Typically, there were pptv or tens of pptv levels of C3-amines and ppbv or sub-ppbv levels of NH_3 for most days. Other amines (C2- and C4- to C6-amines) were below the CIMS detection limits for most of the time. Figure 3 shows the averaged diurnal variation of amines and NH_3 over the entire campaign, along with the measured ambient temperatures. C3-amines and NH_3 showed distinctive diurnal variations with higher concentrations in the warmer afternoon temperatures and lower concentrations during the cooler night and the early morning temperatures. Thus, there were temperature dependencies of C3-amines and NH_3 (Fig. 4). These temperature dependencies show that these basic compounds may be lost by deposition at night and then partition back to the atmosphere in the morning when the surface heating increased.

These temperature dependencies also indicate that these basic compounds were driven by the thermodynamic partitioning between the gas and aerosol phases. The thermodynamic effects can be more important for small molecular weight amine compounds, compared to larger amines, as the
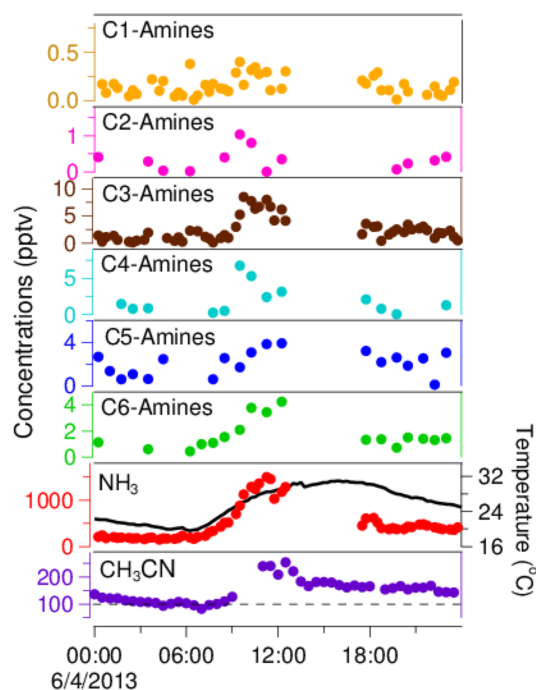
vapor pressure exponentially decreases with the increasing molecular weight (NIST, 2005). During SOAS, the TDCIMS measured various amines in particles in the size range from ~ 40–$120\,nm$. The particle amine fractions showed diurnal variations (Fig. 5) opposite to the gas-phase amines (Fig. 3). There were higher fractional levels of aerosol-phase amines (C1–C3) during the night and in the early morning and lower levels from the late morning until the end of the day. These results indicate active gas to particle conversion of amines at this site. Consistent with these conclusions, the measured aerosol-phase aliphatic primary amine concentrations measured with FTIR from micron and submicron particles were nearly 2 orders of magnitude higher than gas phase amines (in this case, mostly C3-amines) (Fig. 6). These results show that aliphatic amines were primarily present in the aerosol phases, rather than gas phase, at this forest site. On the other hand, the sum of the NH_3 and the aerosol-phase NH_4^+ measured in particles ranged from $\sim 0.8\,\mu g\,m^{-3}$ in the evening up to $\sim 1.6\,\mu g\,m^{-3}$ in the afternoon (Fig. 7).

To quantitatively explain this difference, we have performed a simple calculation to determine the likelihood of gas to particle conversion of an amine versus ammonia. In our calculation, we considered only Henry's Law equilibrium and acid dissociation, and neglected salt formation. Henry's Law constants are quite similar for an alkali amine and am-
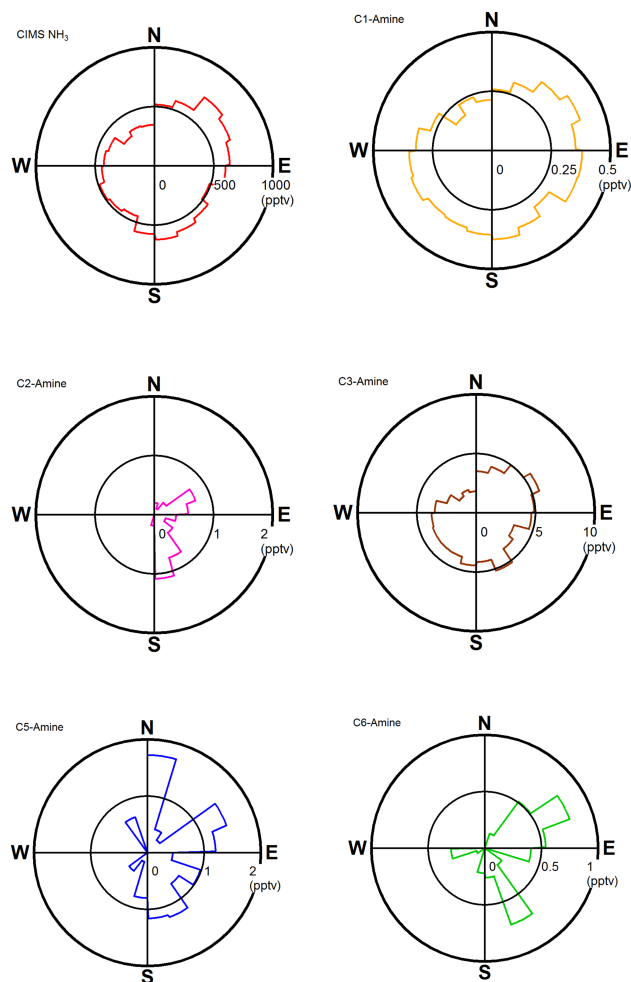
Figure 9. Wind direction plots of the measured amines and NH$_3$, averaged over the entire SOAS campaign. C4-amines were rarely measured, so are not shown here.

monia (Sander, 1999). But their acid dissociation rates (pKa) are different (NIST, 2005). So if we take pKa for a typical alkali amine as -10.8, and pKa for ammonia as -9.2, then the relative gas to particle conversion of an amine compound is nearly 40 times stronger than for ammonia. The ammonia gas to particle ratio was between and 1 and 2 (Fig. 7), so according to our calculation, the gas to particle ratio of an amine should be between 2.5 % and 5 %. Figure 6 shows this ratio was between 0.8 % and 1.2 %, so this is consistent within a factor of 2 with our calculation. These results show that it is reasonable to expect much stronger gas to particle conversion than for ammonia, based on their Henry's Law constants and acid dissociation rates.

Figure 8 shows that amines were emitted from burnings. There was a local trash-burning event that took place near the site around 10 a.m. on 4 June 2013. An abrupt increase of C3- to C6-amines (up to 10 pptv) and NH$_3$ concentrations occurred during this burning event. Wind direction plots showed that the highest concentrations of C3- to C6-amines and NH$_3$ were from the southeast direction (Fig. S3), where the burning took place. Clearly, the detection of such rapid evolution of ambient amines was enabled with the fast response CIMS technique. During the last week of June when the site was affected by the transported biomass burning air masses, as indicated by high concentrations of acetonitrile (CH$_3$CN) (reaching up to 250 pptv), various amines (C1-C6) were also observed at the pptv level (Fig. 2). The global background concentrations of acetonitrile are around 100 pptv (de Gouw et al., 2003; Warneke et al., 2006), so this elevated level indicates the presence of biomass burning emissions. On the other hand, the strong diurnal variation observed in acetonitrile was quite unusual and may indicate the importance of nighttime surface deposition. Compared to the other days where mostly C3-amines and NH$_3$ were measured, these higher concentrations of various amines indicate that biomass burning is an important emission source of amines in the southeastern US.

Wind direction analysis showed that these basic compounds originated from a similar direction (mostly northeast, Fig. 9) during the campaign period. Three-way catalytic converters have been used in automobile engines and power plants in the recent years and they have become an important source of anthropogenic reduced nitrogen compounds in the atmosphere (Ge et al., 2010b; Nowak et al., 2012). We made systematic analysis for each day of the entire campaign, and we found that regardless of wind direction, time of the day (e.g., rush hours) or day in the week, amines and NH$_3$ concentrations measured were not associated with SO$_2$ and CO plumes (e.g., Fig. S4). Therefore, it is unlikely that the power plants, traffic, and industry activities were a direct source of amines in this relatively rural forest.

Concentrations of C3-amines and NH$_3$ detected in the Alabama forest showed some exponential dependencies on the ambient temperature, like isoprene (Fig. 4). Such exponential temperature dependencies, as typically found for BOVCs emitted from trees (Guenther et al., 1995), may suggest some biogenic sources of C3-amines. But there is also caveat in this interpretation, because the temperature dependence was also simply due to the dominant gas-to-particle conversion process, as discussed above.

Throughout the SOAS campaign, amines and NH$_3$ concentrations dropped considerably during rain events, as a general trend. For example, in July with a long period of rain, C3-amines were only at the pptv and NH$_3$ at the subppbv level (Fig. 2). These results show that wet deposition is one of the important sink processes of amines and NH$_3$ in the atmosphere.
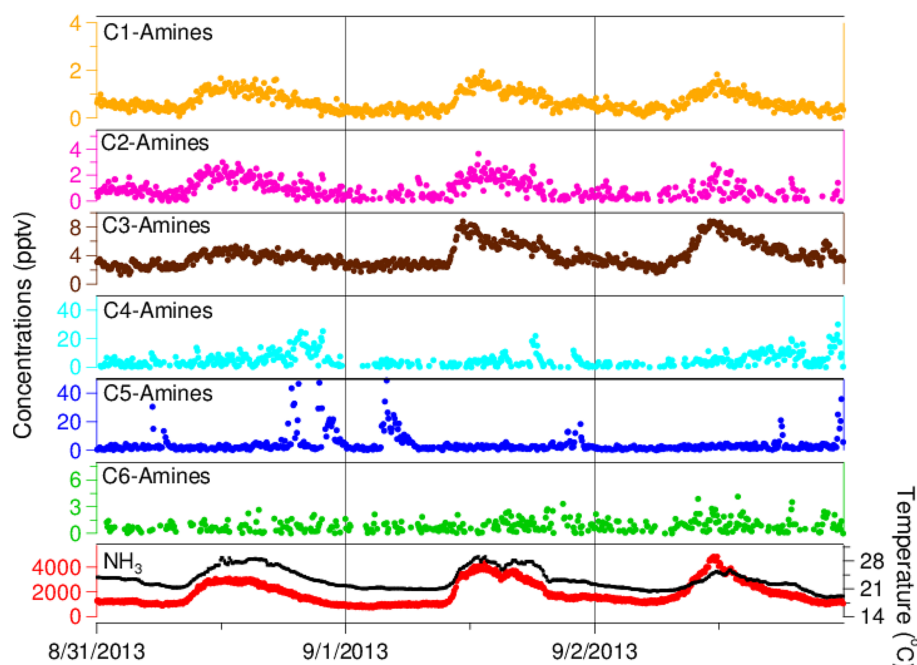
Figure 10. A typical 3-day ambient measurement of amines and NH_3 in Kent, Ohio. Ambient temperatures are also included here. Vertical bars show times at midnight.

5 Measurements in a moderately polluted continental environment

Table 1 also shows a summary of the ambient concentrations of amines and NH_3 measured in Kent over 20 days in August and September. Figure 10 shows the temporal variation of amines and NH_3 during the 3 typical days within the measurement period (31 August to 2 September). The concentrations of C1-amine were up to 4 pptv, C2-amines lower than the detection limit (DL), C3-amines up to 10 pptv, C4-amines between 20–50 pptv, C5-amines between 20–100 pptv, C6-amines lower than DL, and NH_3 up to 6 ppbv. C1- through C3-amines and NH_3 showed very similar temporal variations as the ambient temperature, with higher concentrations in the afternoon, showing that they were controlled by the similar emission and loss processes. The strong temperature dependencies (Fig. S5) also imply that these low molecular weight amines and NH_3 were involved in gas-particle partitioning processes. On the other hand, C4- to C6-amines had some abrupt and frequent increases during the night and did not follow the temporal trend of the ambient temperature, suggesting some local emission sources of these amines.

During the winter season, C2- and C3-amines were at the ppbv and tens of ppbv range at the same site (Yu and Lee, 2012). In comparison, there were higher concentrations of amines and NH_3 during the summer (Fig. 10), likely due to higher ambient temperatures. NH_3 concentrations reported here are within the same range as those previously reported from the same site (Benson et al., 2010; Erupe et al., 2010).

6 Discussion and conclusions

We have measured amines and NH_3 during the summer in two different atmospheric environments. In the rural southeastern US forest, there were mostly C3-amines (up to 15 pptv) and NH_3 (up to 2 ppbv), whereas in the moderately polluted Ohio site, there were more abundant amines (C1–C6, pptv and tens of pptv) and NH_3 (up to 6 ppb) (Table 1). These different NH_3 concentrations measured at these two sites in the same summer of the same year are consistent with EPA-reported annual emission rates of NH_3 from various sectors in Alabama and Ohio states (Fig. S6). Atmospheric lifetime of NH_3 is typically several days, so emissions and transport at the regional scale can influence the measured concentrations of NH_3. The amine concentrations measured in the Alabama forest were lower than those reported from an urban environment in the southeastern US (Atlanta, Georgia) (Hanson et al., 2011). The Hanson et al. (2011) study reported C6-amines up to 25 pptv, C3-amines up to 15 pptv, and C1-amine up to 3 pptv. While the concentrations of amines were generally lower in the Alabama forest, various C1- through C6-amines were present at the pptv level when there were transported biomass burning plumes (Figs. 2 and 8).

Currently, very limited information is available for the land-atmosphere emissions and deposition processes of amines (Hertel et al., 2013). However, some qualitative conclusions can be made to explain the generally low background concentrations of amines observed in the Alabama

forest. First, oxidation reactions are an important chemical process for amines in the southeastern US especially during the summer – as amines efficiently react with atmospheric oxidants such as OH, ozone, and NO_3 in the atmosphere (Finlayson-Pitts and Pitts, 2000; Nielsen et al., 2011, 2012). During the SOAS field campaign, OH concentrations measured with LIF were $\sim 2 \times 10^6\,cm^{-3}$ at noontime. Ozone concentrations were 30 ± 12 ppbv during the daytime and 21 ± 10 ppbv during nighttime. Under these high concentrations of oxidants, atmospheric lifetimes of amines can be as short as several hours. Second, wet deposition is an important sink process for amines and NH_3, because of their high water solubilities. Henry's Law constants of amines (C1–C6) and NH_3 are ~ 10–$160\,M\,atm^{-1}$ and $\sim 60\,M\,atm^{-1}$, respectively (NIST, 2005; Sander, www.henrys-law.org/). Wet deposition can occur via rain, cloud and fog droplets, as well as onto the wet forest canopy and soil surfaces, especially under high RH conditions. The measured amines and NH_3 concentrations indeed decreased during the rain events (Fig. 2). Third, dry deposition rates are also expected to be high for chemical compounds that have high Henry's Law constants (and hence small surface residence times) (Hertel et al., 2013). Uptake coefficient of basic compounds is also dependent on the aerosol acidity (ApSimon et al., 1994). During the SOAS campaign, there were high aerosol loadings, high aerosol water content, and strong acidity of aerosol particles (Fig. 7). On average, $PM_{2.5}$ aerosols were composed of $1.8 \pm 1.1\,\mu g\,m^{-3}$ sulfate, $0.1 \pm 0.1\,\mu g\,m^{-3}$ nitrate, $0.6 \pm 0.3\,\mu g\,m^{-3}$ ammonium, and $3.2 \pm 2.3\,\mu g\,m^{-3}$ organic components. Aerosol water content ranged from 2–$20\,\mu g\,m^{-3}$ and the aerosol pH was generally lower than 3 for the entire SOAS campaign period. These factors together provided an ideal condition for strong uptake of semi-volatile basic compounds on aerosol particles.

Amines and NH_3 are thought to be key nucleation precursors (Berndt et al., 2010; Erupe et al., 2011; Kirkby et al., 2011; Yu et al., 2012; Zollner et al., 2012). Previously, Kieloaho et al. (2013) showed there was not a direct correlation between amines (C2- to C4-amines) and new particle formation in the Finnish boreal forest, whereas at the same forest site Sellegri et al. (2005b) showed concentrations of C3-amines were higher during the particle formation events than non-event days. In Kent, there were more abundant amines (C1–C6) and NH_3 in the summer (Table 1), and even in winter there were C2- and C3-amines at pptv or tens pptv level (Yu and Lee, 2012). These basic compounds, together with high emissions of SO_2 from the surrounding coal-burning power plants (and hence sulfuric acid production), may explain the frequent new particle formation events reported from this site (Erupe et al., 2010; Kanawade et al., 2012; Yu et al., 2013).

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