Atmospheric amines and ammonia measured with a Chemical Ionization Mass Spectrometer (CIMS)


¹Kent State University, College of Public Health, Kent, Ohio, USA
²Indian Institute of Technology – Kanpur, Department of Civil Engineering and Center for Environmental Science & Engineering, Kanpur, India
³National Oceanic and Atmospheric Administration, Chemical Science Division, Boulder, Colorado, USA
⁴Pacific Northwest National Laboratory, Richland, Washington, USA
⁵Washington State University, Department of Civil and Environmental Engineering, Pullman, Washington, USA
⁶National Center for Atmospheric Research, Atmospheric Chemistry Division, Boulder, Colorado, USA
⁷Ohio State University, Byrd Polar Research Center, Columbus, Ohio, USA
Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Received: 27 May 2014 – Accepted: 9 June 2014 – Published: 20 June 2014

Correspondence to: S.-H. Lee (slee19@kent.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.
Abstract

We report ambient measurements of amines and ammonia with a fast response chemical ionization mass spectrometer (CIMS) in a southeastern US forest in Alabama and a moderately polluted Midwestern site during the summer. In the Alabama forest, mostly C3-amines (from pptv to tens of pptv) and ammonia (up to 2 ppbv) were detected on a daily basis. C3-amines and ammonia showed similar diurnal trends and temperature and wind direction dependences, and were not associated with transported CO and SO₂ plumes. Consistent with temperature dependences, amine and ammonia in the gas and aerosol phases showed opposite diurnal trends, indicating gas-to-particle partitioning of amines and ammonia. Temperature dependences also imply reversible processes of amines and ammonia evaporation from soil surfaces in daytime and deposition of amines and ammonia to soil surfaces at nighttime. Various amines (C1–C6) at the pptv level were observed in the transported biomass burning plumes, showing that biomass burning can be a substantial source of amines in the Southeast US. At the moderately polluted Kent site, higher concentrations of amines (C1–C6, from pptv to tens of pptv) and ammonia (up to 6 ppbv) were detected. Diurnal variations of C1- to C3-amines and ammonia were correlated with the ambient temperature. C4- to C6-amines showed abrupt increases during the nighttime, suggesting that they were emitted from local sources. These abundant amines and ammonia may in part explain the frequent new particle formation events reported from Kent. Lower amine concentrations at the rural forested site highlight the importance of constraining anthropogenic sources of amines.

1 Introduction

Amines and ammonia (NH₃) 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 NH₃ 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 CO₂ 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; Freshour 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 NH₃ 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., 2007, 2010, 2006).

Amines and NH₃, 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 NH₃ (Kurtén et al., 2008). Laboratory studies showed that amines can substitute ammonium to aminium in charged clusters (Lloyd et al., 2009). Nucleation kinetics studies 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, b; 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 NH₃ on aerosol nucleation (Yu et al., 2012).

Amines and NH₃ 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). 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 or longer) on-line or often off-line analytical methods, based on chromatography, mass spectrometry, UV, fluorescence or electrochemical detectors (Ge et al., 2010b; Yu and Lee, 2012). Chemical ionization mass spectrometry (CIMS) has been used for the fast-response on-line 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 the 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.

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 am-
bient 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.

2 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 1 June 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 measure-
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 tens of pptv level, with a 1 s integration time. The sensitivity ranged between 2–12 Hz pptv$^{-1}$ for different amines 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):

\[
(C_2H_5OH)_n H^+ + NH_3 \rightarrow (C_2H_5OH)_{n-1}NH_4^+ + C_2H_5OH \tag{R1}
\]
\[
(C_2H_5OH)_n H^+ + B \rightarrow BH^+ + nC_2H_5OH \tag{R2}
\]

where $n = 1, 2, \text{ and } 3$. 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. Ethanol also has been used for NH$_3$ measurements in other CIMS techniques (Nowak et al., 2002, 2006).
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 lpm (liter per minute) (Fig. S1). The residence time within the sampling inlet prior to the CIMS ionization region was 0.17 s. 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 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 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 test experiments using the ambient air have shown that the drier did not affect the background ion 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 stud-
ies (Benson et al., 2010; Yu and Lee, 2012). This modification was made to reduce possible contamination of standard calibration gases on the inlet inner surfaces. Amines and NH\textsubscript{3} calibration gases were generated from pre-calibrated National Institute and Technology traceable permeation tubes in a temperature- and flow rate-controlled standard gas generator (491MB, Kin-Tek). Each standard gas was run continuously for over 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\textsubscript{2}H\textsubscript{5}OH)H\textsuperscript{+}, \( m/z \) 93 (C\textsubscript{2}H\textsubscript{5}OH)\textsubscript{2}H\textsuperscript{+} (the highest peak) and \( m/z \) 139 (C\textsubscript{2}H\textsubscript{5}OH)\textsubscript{3}H\textsuperscript{+}. NH\textsubscript{3} product ions appeared at \( m/z \) 18 NH\textsubscript{4}\textsuperscript{+}, \( m/z \) 64 (C\textsubscript{2}H\textsubscript{5}OH)NH\textsubscript{4}\textsuperscript{+}, and \( m/z \) 110 (C\textsubscript{2}H\textsubscript{5}OH)\textsubscript{2}NH\textsubscript{4}\textsuperscript{+}. C1-amine (methylamine) ions were at \( m/z \) 32 (CH\textsubscript{3})NH\textsubscript{3}\textsuperscript{+}; C2-amines at \( m/z \) 46 (e.g., (CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2}\textsuperscript{+}, dimethylamine; CH\textsubscript{3}CH\textsubscript{2}NH\textsubscript{2}\textsuperscript{+}, ethylamine); C3-amines at \( m/z \) 60 (e.g., (CH\textsubscript{3})\textsubscript{3}NH\textsubscript{+}, trimethylamine); C4-amines at \( m/z \) 74 (e.g., (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}NH\textsubscript{2}\textsuperscript{+}, diethyleamine); C5-amines at \( m/z \) 88; and C6-amines at \( m/z \) 102 (e.g., (C\textsubscript{2}H\textsubscript{5})\textsubscript{3}NH\textsubscript{+}, triethylamine). We generally found significantly higher concentrations of amines and NH\textsubscript{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\textsubscript{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\textsubscript{3} 6.2 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\textsubscript{3} obtained from in situ calibrations, background signals, and detection limits (DL, defined as three times the standard deviation of the background ion signals, within a 1 s integration time). Figure S2 shows the calibration curves of amines and NH\textsubscript{3} obtained in situ in the Alabama forest. The sensitivity of NH\textsubscript{3} was highly reproducible (Fig. S2), \( \sim 13 \text{ Hz pptv}^{-1} \) with 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 (Fig. S2 and Table 1). Lower amine sensitivities were due to loss of amines in the gas-line system. Consistent with this observation, the measured sensitivities also showed a decreasing trend with the increasing molecular weight of the amine compound (Table 1). Detection limits were also improved, compared to the previous work (Yu and Lee, 2012). For example, detection limits of 7 pptv and 15 pptv were previously reported for C1- and C3-amines (with 1 s integration time), but in the present study they were reduced to 1 pptv and 6 pptv.

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 Reactions 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 compounds. Background signals were independent of the ambient temperature and RH in our CIMS, whereas there were some RH dependences of background signals in the AmPSMS (Hanson et al., 2011).

4 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 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 temperatures so the reported values reflect averaged values between two colocated sampling lines. Additionally, chemical composition of particles in the size range from ~40–120 nm was measured with an on-line 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$_3$CN). Sample air was drawn from the top of the flux tower at the SOAS ground site, and VOCs were cryo-statically sampled for 5 min every half hour. 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 81 000).
5 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). 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 within (or 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 dependences of C3-amines and NH$_3$ (Fig. 4). Wind direction analysis showed that these basic compounds originated from a similar direction (mostly northeast, Fig. 5) during the campaign period.

Figure 6 shows a specific day where the site was influenced by advected SO$_2$ and CO plumes. SO$_2$ background concentrations were usually less than 1 ppbv, but around 08:00 to 10:00 LT, SO$_2$ concentrations rapidly increased up to 5 ppbv. The background CO concentrations were around 100 ppbv for most of the time, but there were two episodes of high CO concentrations (150–200 ppbv) around 3 p.m. and 9 p.m. on the same day. The high concentrations of CO did not occur during rush hours, indicating these CO peaks were not related to traffic activities. Despite clear SO$_2$ and CO plumes, C3-amines and NH$_3$ concentrations were still higher in the afternoon with higher temperatures than in the cooler early morning and evening, similar to the days without plume influences (Fig. 3). Similar analysis was also made for other days and the results all consistently show that amines and NH$_3$ at this forest site were not associated with the transported sulfur or CO plumes.

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 (Fig. 7). 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. 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 only measured, these higher concentrations of various amines indicate that biomass burning could be an important emission source of amines in the southeastern US.

It was consistent throughout the SOAS campaign that amines and NH$_3$ concentrations dropped considerably during rain events. For example, in the first two weeks of July with a long period of rain, C3-amines were only at the pptv and NH$_3$ at the sub-ppbv level (Fig. 2). These results show that wet deposition is one of the important sink processes of amines and NH$_3$ in the atmosphere.

6 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 8 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 dependences (Fig. S4) 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. 8), 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).

7 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 are consistent with EPA-reported annual emission rates of NH$_3$ from various sectors in Alabama and Ohio states (Fig. 9). 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). This 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 7).

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). Amines and NH$_3$ concentrations measured in the Alabama forest were not associated with traffic or with transported anthropogenic SO$_2$ and CO plumes (Fig. 6). Thus it is more likely that they were emitted from natural sources (such as soils and vegetation) and/or transportation from agricultural areas.

Concentrations of C3-amines and NH$_3$ detected in the Alabama forest were well correlated with the measured isoprene (Fig. 10) and all of these compounds showed some exponential dependences on the ambient temperature (Fig. 4), as expected for isoprene emissions from trees (Guenther et al., 1995). This provides some evidence for biogenic emissions of amines and NH$_3$ in the Alabama forest. At the same time, the similar diurnal variations could also be coincidental; isoprene was lower at night without emissions, and amines were lower at night because they were possibly deposited on soil surfaces and aerosol particles. 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). Measurements of amines in the forested environments are very scarce at present and the emission pathways of amines in forests are not well understood. 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 were up to hundreds of pptv, and C4-amines up to tens of pptv level, and suggested that amines may be emitted from leaf litters (Kieloaho et al., 2013).

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, photo-degradation is 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., 2012, 2011). 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 $\sim 10–160$ M atm$^{-1}$ and $\sim 60$ M atm$^{-1}$, respectively (NIST, 2011; Sander, http://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 significantly 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. 11). On average, PM$_{2.5}$ aerosols were composed of 1.8±1.1 µg m$^{-3}$ sulfate, 0.1±0.1 µg m$^{-3}$ nitrate, 0.6±0.3 µg m$^{-3}$ ammonium, and 3.2±2.3 µg m$^{-3}$ organic components. Aerosol water content ranged from 2–20 µg 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. Consistent with these conclusions, the measured aerosol-phase aliphatic amine concentrations were nearly two orders of magnitude higher than gas phase amines (in this case, mostly C3-amines) during the SOAS campaign (Fig. 12). These results indicate that aliphatic amines were mostly present in the aerosol phases, rather than gas phase, at this forest site. Therefore, it is also possible that aerosols containing reduced nitrogen compounds formed from polluted regions may have been transported to the rural forest. The high fraction of amines in the aerosol phases compared to the gas phase also may be consistent with
the substitution of ammonium by amines observed in laboratory studies (Lloyd et al., 2009; Zhang et al., 2012).

In the Alabama forest, C3-amines and NH$_3$ had diurnal variations, with higher concentrations in the afternoon than in the evening (Fig. 2). In Kent, C1- to C3-amines and NH$_3$ also showed similar temperature dependences (Fig. 5). These temperature dependences 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 dependences 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, 2011). During the SOAS, the TDCIMS measured various amines concentrations in particles in the size range from $\sim$ 40–120 nm showed diurnal variations (Fig. 13), opposite to gas-phase amines (Fig. 3). There were higher 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. Some amines in particles showed this pattern more strongly than others, especially C1- and C2-amines. Furthermore, the sum of the NH$_3$ and the aerosol-phase NH$_4^+$ measured in sub-micron and micron size particles ranged from $\sim$ 0.8 µg m$^{-3}$ in the evening up to $\sim$ 1.6 µg m$^{-3}$ in the afternoon (Fig. 11). Although this is not a box model simulation, this result hence implies that aerosol uptake can explain about half of the loss of NH$_3$, when neglecting the transport of NH$_3$ from aloft the boundary layer. Thus, the deposition loss on soil surfaces during the night may be comparable to the loss due to aerosol uptake.

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 NH₃ in the summer (Table 1), and even in winter there were C2- and C3-amines (Yu and Lee, 2012). These basic compounds, together with high emissions of SO₂ 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).

The Supplement related to this article is available online at doi:10.5194/acpd-14-16411-2014-supplement.

Acknowledgements. We acknowledge funding support from National Science Foundation (NSF, AGS-1137821, AGS 1241498) for SHL; NSF for AN, HG, and RW; Swiss National Science Foundation (SNF 200021_143298) for ST. SHL also thanks Greg Huey, Dave Tanner, Huan Yu and Dave Benson for helpful conversations on CIMS; Janek Uin for assistance on the data reduction; Greg Frost and Charles Blanchard for discussions on ammonia emissions; Jessica Gilman and Brian Lerner for the help with the gas chromatography measurements.

References


Atmospheric amines and ammonia measured with a CIMS

Y. You et al.


Table 1. The CIMS sensitivities (normalized to 1 MHz ethanol reagent ions) determined by in situ calibrations (Fig. S1), background signals, and detection limits (three times the standard deviation of background signals, within a 1 s integration time) of amines and NH$_3$. Typical ambient concentrations measured in the Alabama forest and Kent are also included (20 min average data).

<table>
<thead>
<tr>
<th>Basic Compound</th>
<th>Sensitivity [Hz (pptv MHz)$^{-1}$]$^b$</th>
<th>Detection Limit, DL</th>
<th>Alabama Forest: Jun–Jul</th>
<th>Kent: Aug–Sep</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$ (ppbv)</td>
<td>13</td>
<td>54</td>
<td>Up to 1–2</td>
<td>Up to 6</td>
</tr>
<tr>
<td>C1-Amine (pptv) (methylamine)</td>
<td>12</td>
<td>1</td>
<td>&lt; DL</td>
<td>1–4</td>
</tr>
<tr>
<td>C2-Amines (pptv) (dimethylamine)</td>
<td>12</td>
<td>5</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
</tr>
<tr>
<td>C3-Amines (pptv) (trimethylamine)</td>
<td>8</td>
<td>5</td>
<td>1–10</td>
<td>5–10</td>
</tr>
<tr>
<td>C4-Amines (pptv) (diethylamine)</td>
<td>4</td>
<td>23</td>
<td>&lt; DL</td>
<td>10–50</td>
</tr>
<tr>
<td>C5-Amines (pptv)</td>
<td>2</td>
<td>17</td>
<td>&lt; DL</td>
<td>10–100</td>
</tr>
<tr>
<td>C6-Amines (pptv) (triethylamine)</td>
<td>2</td>
<td>12</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
</tr>
</tbody>
</table>

$^a$ 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 the 1 000 000 Hz of the ethanol reagent ion signal.
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. The y-axis is shown in log scale.
Figure 2. Temporal variations of amines, NH$_3$, and CH$_3$CN along with the ambient temperature measured in the Alabama forest during the entire SOAS field campaign. Vertical grids correspond to times at midnight.
Figure 3. The averaged diurnal variation throughout the entire SOAS campaign for the measured C1- to C6-amines and NH₃ concentrations measured in the Alabama forest during the summer. 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 NH₃.
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 the 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 20th percentile of temperature values.
Figure 5. 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.
**Figure 6.** Diurnal variation of C3-amines, NH$_3$, temperature, SO$_2$, CO, wind speed (WS) and wind direction (WD) for 17 June 2013 in the Alabama forest.
Figure 7. Amines, NH$_3$ and CH$_3$CN 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.
Figure 8. A typical 3-day ambient measurement of amines and NH₃ in Kent, Ohio. Ambient temperatures are also included here. Vertical bars show times at midnight.
Figure 9. EPA-reported annual emission rates of NH$_3$ from various sectors in Alabama (blue) and Ohio (red) in 2011. Data were adopted from the 2011 National Emissions Inventory website: http://www.epa.gov/ttn/chief/net/2011inventory.html.
Figure 10. The averaged diurnal variation of isoprene (magenta), α-pinene (orange), NH₃ (red), C3-amines (brown) and temperature (black) over the entire SOAS campaign period.
Figure 11. The average diurnal variation of the gas phase NH$_3$ (red), aerosol-phase ammonium (NH$_4^+$, cyan) measured with 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 µg m$^{-3}$ (1 ppbv = 1.3 µg m$^{-3}$) to be compared with aerosol-phase NH$_4^+$. 

16448
Figure 12. (Upper panel) Average daily variation of aerosol phase concentration (µg 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 µg 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.
Figure 13. Campaign-averaged, 4 h-binned C1- to C3-amines and ammonium particle-phase signals from TDCIMS. Line endpoints 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. Differences in diurnal trends in Fig. 11 (upper panel) and here are due to different aerosol size ranges and different amine species detected with these two techniques (FTIR and TDCIMS).