

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

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

Y. You<sup>1</sup>, V. P. Kanawade<sup>2</sup>, J. A. de Gouw<sup>3</sup>, A. B. Guenther<sup>4,5</sup>, S. Madronich<sup>6</sup>, M. R. Sierra-Hernández<sup>7</sup>, M. Lawler<sup>6,8</sup>, J. N. Smith<sup>6,8</sup>, S. Takahama<sup>9</sup>, G. Ruggeri<sup>9</sup>, A. Koss<sup>3</sup>, K. Olson<sup>10</sup>, K. Baumann<sup>11</sup>, R. J. Weber<sup>12</sup>, A. Nenes<sup>12,13</sup>, H. Guo<sup>12</sup>, E. S. Edgerton<sup>11</sup>, L. Porcelli<sup>1</sup>, W. H. Brune<sup>14</sup>, A. H. Goldstein<sup>10</sup>, and S.-H. Lee<sup>1</sup>

Discussion Paper

Discussion Paper

Printer-friendly Version

Interactive Discussion



**ACPD** 14, 16411-16450, 2014

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page

**Abstract** 

Introduction

Conclusions

References

**Tables** 

**Figures** 











<sup>&</sup>lt;sup>1</sup>Kent State University, College of Public Health, Kent, Ohio, USA

<sup>&</sup>lt;sup>2</sup>Indian Institute of Technology – Kanpur, Department of Civil Engineering and Center for Environmental Science & Engineering, Kanpur, India

<sup>&</sup>lt;sup>3</sup>National Oceanic and Atmospheric Administration, Chemical Science Division, Boulder, Colorado, USA

<sup>&</sup>lt;sup>4</sup>Pacific Northwest National Laboratory, Richland, Washington, USA

<sup>&</sup>lt;sup>5</sup>Washington State University, Department of Civil and Environmental Engineering, Pullman, Washington, USA

<sup>&</sup>lt;sup>6</sup>National Center for Atmospheric Research, Atmospheric Chemistry Division, Boulder, Colorado, USA

Ohio State University, Byrd Polar Research Center, Columbus, Ohio, USA

<sup>8</sup>University of Eastern Finland, Applied Physics Department, Kuopio, Finland

<sup>9</sup>Ecole Polytechnique Federale de Lausanne, Institute d'Ingenierie de l'Environment, Lausanne, Switzerland

<sup>10</sup>University of California – Berkeley, Department of Environmental Science, Policy and Management, Berkeley, California, USA

<sup>11</sup>Atmospheric Research and Analysis, Inc., Morrisville-Cary, North Carolina, USA

<sup>12</sup>Georgia Institute of Technology, School of Earth and Atmospheric Sciences, Atlanta, Georgia, USA

<sup>13</sup>Georgia Institute of Technology, School of Chemical and Biomolecular Engineering, Atlanta, Georgia, USA

<sup>14</sup>Penn State University, Department of Meteorology, University Park, Pennsylvania, USA

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.

ACPD

14, 16411-16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

I ✓ ▶I

✓ ▶ L

Back Close

Full Screen / Esc



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 SO<sub>2</sub> 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.

#### Introduction

Amines and ammonia (NH<sub>3</sub>) 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<sub>3</sub> include animal husbandry, vegetation, biomass

Paper

Discussion Paper

Discussion Paper

Discussion Paper

**ACPD** 

14, 16411–16450, 2014

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page Introduction **Abstract** 

Conclusions References

> **Figures** Tables

Back Close

Full Screen / Esc

**Printer-friendly Version** 



Back

Full Screen / Esc

**Printer-friendly Version** 

Interactive Discussion



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<sub>2</sub> sequestration technologies also utilize amine solutions and this has become an important source of anthropogenic amines in the atmosphere (Shao and Stangeland, 5 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 NH<sub>3</sub> 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 NH<sub>3</sub>, 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<sub>3</sub> (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 NH<sub>3</sub> on aerosol nucleation (Yu et al., 2012).

Amines and NH<sub>3</sub> 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

## **ACPD**

14, 16411-16450, 2014

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page

Introduction **Abstract** 

Conclusions References

> **Figures Tables**

Close

14, 16411–16450, 2014

**ACPD** 

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page

Introduction **Abstract** Conclusions References **Figures Tables** Back Close Full Screen / Esc **Printer-friendly Version** 

Interactive Discussion

containing compounds also contribute to the formation of light absorbing organic compounds in atmospheric "brown carbon" aerosols (Laskin et al., 2010). Amines and NH<sub>3</sub> 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., 5 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) online 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<sub>3</sub>, and conducted ambient measurements in Kent, Ohio.

In the present study, we report the ambient concentrations of amines and NH<sub>3</sub> 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<sub>3</sub>. This study presents one of the very few simultaneous measurements of am-

**Printer-friendly Version** 

Interactive Discussion



bient amines and NH<sub>3</sub> 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.

#### 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<sup>-1</sup>) and  $SO_2$  (92 000 ton year<sup>-1</sup>) 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<sub>x</sub> and SO<sub>2</sub> 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**ACPD** 

14, 16411–16450, 2014

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page

Introduction **Abstract** 

Conclusions References

> **Figures Tables**

#### Amine-CIMS characterization and calibration

The amines/NH<sub>3</sub> CIMS was described elsewhere (Yu and Lee, 2012). As discussed in detail below, this CIMS detects ambient amines and NH3 at the pptv and tens of pptv level, with a 1 s integration time. The sensitivity ranged between 2-12 Hz pptv<sup>-1</sup> for different amines and NH<sub>3</sub> (for 1 MHz of protonated ethanol reagent ion signals), as determined from in situ calibrations (Table 1).

NH<sub>3</sub> 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):

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

$$(C_2H_5OH)_nH^+ + B \rightarrow BH^+ + nC_2H_5OH$$
 (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. Ethanol also has been used for NH<sub>3</sub> measurements in other CIMS techniques (Nowak et al., 2002, 2006).

Discussion Paper

Discussion Paper

Discussion Pape

14, 16411–16450, 2014

**Atmospheric amines** and ammonia measured with a CIMS

**ACPD** 

Y. You et al.

Title Page

**Abstract** Conclusions

References

**Tables** 

**Figures** 

Introduction



Back



Full Screen / Esc

Printer-friendly Version

Interactive Discussion



16417

**Abstract** Conclusions

References

Introduction

**Figures Tables** 



Back Close

Full Screen / Esc

**Printer-friendly Version** 

Interactive Discussion



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<sub>3</sub> 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<sub>3</sub> (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<sub>3</sub>. 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-

14, 16411–16450, 2014

**ACPD** 

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page







Discussion Paper

References **Figures** 

Close

Introduction





Full Screen / Esc

**Printer-friendly Version** 

Interactive Discussion



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<sub>3</sub> calibration gases were generated from pre-calibrated National Institute and Technology traceable permeation tubes in a temperature- and flow rate-controlled stan-5 dard 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<sub>2</sub>H<sub>5</sub>OH)H<sup>+</sup>, m/z 93 (C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub>H<sup>+</sup> (the highest peak) and m/z 139 (C<sub>2</sub>H<sub>5</sub>OH)<sub>3</sub>H<sup>+</sup>. NH<sub>3</sub> product ions appeared at m/z 18 NH<sub>4</sub><sup>+</sup>, m/z 64 (C<sub>2</sub>H<sub>5</sub>OH)NH<sub>4</sub><sup>+</sup>, and m/z 110 (C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub>NH<sub>4</sub><sup>+</sup>. C1-amine (methylamine) ions were at m/z 32 (CH<sub>3</sub>)NH<sub>3</sub><sup>+</sup>; C2-amines at m/z 46 (e.g., (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup>, dimethylamine;  $CH_3CH_2NH_2^+$ , ethylamine); C3-amines at m/z 60 (e.g.,  $(CH_3)_3NH_2^+$ , trimethylamine); C4-amines at m/z 74 (e.g.,  $(C_2H_5)_2NH_2^+$ , diethyleamine); 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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 1s integration time). Figure S2 shows the calibration curves of amines and NH3 obtained in situ in the Alabama forest. The sensitivity of NH<sub>3</sub> was highly reproducible (Fig. S2), ~ 13 Hz pptv<sup>-1</sup> with 1 MHz of ethanol reagent ions, for the entire SOAS campaign as well as the pre14, 16411–16450, 2014

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page

**Abstract** 

Conclusions

**Tables** 

Back

and post-campaign calibrations. This is an important improvement made over the previous studies (Benson et al., 2010; Yu and Lee, 2012) where NH<sub>3</sub> sensitivities varied on a day-to-day basis. Although the sensitivities of amines were also improved, amine sensitivities were still lower than the NH<sub>3</sub> 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<sup>-1</sup>) than water (697 kJ mol<sup>-1</sup>) (Jolly, 1991), our CIMS only responds to basic compounds that have higher proton affinities (e.g., trimethylamine 945 kJ mol<sup>-1</sup>; NH<sub>3</sub> 854 kJ mol<sup>-1</sup>) 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

ACPD

14, 16411-16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

14 >1

Back Close

Full Screen / Esc

Printer-friendly Version



**Printer-friendly Version** 

Interactive Discussion



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<sub>2.5</sub> 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<sub>2</sub>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<sub>2</sub> 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).

### **ACPD**

14, 16411–16450, 2014

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page Introduction **Abstract Conclusions** References **Figures Tables** Back Close Full Screen / Esc

Table 1 shows the summary of the ambient concentrations of amines and NH<sub>3</sub> measured in the Alabama forest in June and July 2013. Temporal variations of amines and NH<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> over the entire campaign, along with the measured ambient temperatures. C3-amines and NH<sub>3</sub> 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 NH3 (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<sub>2</sub> and CO plumes. SO<sub>2</sub> background concentrations were usually less than 1 ppbv, but around 08:00 to 10:00 LT, SO<sub>2</sub> 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 SO2 and CO plumes, C3-amines and NH<sub>3</sub> 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<sub>3</sub> at this forest site were not associated with the transported sulfur or CO plumes.

14, 16411–16450, 2014

**ACPD** 

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page

Introduction

References

**Figures** 

Close

Back

**Abstract** 

**Conclusions** 

**Tables** 

**Printer-friendly Version** 

Interactive Discussion



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<sub>3</sub>

Discussion Paper

Discussion Paper

Paper

Discussion Paper



Full Screen / Esc

concentrations occurred during this burning event (Fig. 7). Wind direction plots showed that the highest concentrations of C3- to C6-amines and NH<sub>3</sub> 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<sub>3</sub>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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> at the subppbv level (Fig. 2). These results show that wet deposition is one of the important sink processes of amines and NH<sub>3</sub> 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<sub>3</sub> measured in Kent over 20 days in August and September. Figure 8 shows the temporal variation of amines and NH<sub>3</sub> 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<sub>3</sub> up to 6 ppbv. C1- through C3-amines and NH<sub>3</sub> showed very similar temporal variations as the ambient temperature, with higher concentrations in the afternoon, showing

ACPD

14, 16411–16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Title Page

Introduction

Close

Abstract

Conclusions References

Tables Figures

I⁴ ►I

**→** 

Full Screen / Esc

Back

Printer-friendly Version



Discussion

Introduction **Abstract Conclusions** 

References

Title Page

**Figures Tables** 

Back Close

Full Screen / Esc

**Printer-friendly Version** 

Interactive Discussion



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<sub>3</sub> were involved in gas-particle partitioning processes. On the other hand, C4to 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<sub>3</sub> during the summer (Fig. 8), likely due to higher ambient temperatures. NH<sub>3</sub> concentrations reported here are within the same range as those previously reported from the same site (Benson et al., 2010; Erupe et al., 2010).

#### Discussion and conclusions

We have measured amines and NH<sub>3</sub> 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<sub>3</sub> (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<sub>3</sub> (up to 6 ppb) (Table 1). These different NH<sub>3</sub> concentrations measured at these two sites are consistent with EPA-reported annual emission rates of NH3 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

#### 16424

14, 16411–16450, 2014

**ACPD** 

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

14, 16411–16450, 2014

Atmospheric amines and ammonia measured with a CIMS

**ACPD** 

Y. You et al.

Full Screen / Esc

Close

Back

Printer-friendly Version

Interactive Discussion



reduced nitrogen compounds in the atmosphere (Ge et al., 2010b; Nowak et al., 2012). Amines and NH<sub>3</sub> concentrations measured in the Alabama forest were not associated with traffic or with transported anthropogenic SO<sub>2</sub> 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<sub>3</sub> 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<sub>3</sub> 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

Discussion

Paper

**Printer-friendly Version** 

Interactive Discussion



amines efficiently react with atmospheric oxidants such as OH, ozone, and NO<sub>3</sub> in the atmosphere (Finlayson-Pitts and Pitts, 2000; Nielsen et al., 2012, 2011). During the SOAS field campaign, OH concentrations measured with LIF were  $\sim 2 \times 10^6 \, \text{cm}^{-3}$  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<sub>3</sub>, because of their high water solubilities. Henry's Law constants of amines (C1-C6) and NH<sub>3</sub> are  $\sim 10-160\,\mathrm{M\,atm}^{-1}$  and  $\sim 60\,\mathrm{M\,atm}^{-1}$ . 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<sub>3</sub> 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<sub>2.5</sub> aerosols were composed of  $1.8\pm1.1\,\mu\mathrm{g}\,\mathrm{m}^{-3}$  sulfate,  $0.1\pm0.1\,\mu\mathrm{g}\,\mathrm{m}^{-3}$  nitrate,  $0.6\pm0.3\,\mu\mathrm{g}\,\mathrm{m}^{-3}$  ammonium, and 3.2 ± 2.3 µg m<sup>-3</sup> organic components. Aerosol water content ranged from 2-20 µg m<sup>-3</sup> 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

# **ACPD**

14, 16411-16450, 2014

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page

Introduction **Abstract** 

**Conclusions** References

> **Figures Tables**

Back Close

Full Screen / Esc

**ACPD** 

14, 16411–16450, 2014

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page Introduction **Abstract** 

**Conclusions** References

> **Figures Tables**

Back Close

Full Screen / Esc

**Printer-friendly Version** 

Interactive Discussion



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<sub>3</sub> had diurnal variations, with higher concentrations in the afternoon than in the evening (Fig. 2). In Kent, C1- to C3-amines 5 and NH<sub>3</sub> 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 ~ 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<sub>3</sub> and the aerosol-phase  $NH^{4+}$  measured in sub-micron and micron size particles ranged from  $\sim 0.8 \, \mu g \, m^{-3}$  in the evening up to  $\sim 1.6 \, \mu \mathrm{g \, m}^{-3}$  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<sub>3</sub>, when neglecting the transport of NH<sub>3</sub> 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<sub>3</sub> 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 (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).

# 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

Akyüz, M.: Simultaneous determination of aliphatic and aromatic amines in indoor and outdoor air samples by gas chromatography—mass spectrometry, Talanta, 71, 486–492, 2007.

Almeida, J., Schobesberger, S., Kurten, A., Ortega, I. K., Kupiainen-Maatta, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurten, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppa, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petaja, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H.,

**ACPD** 

14, 16411–16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Title Page

Abstract

Conclusions References

Tables

Figures

Introduction

I**4** ▶

•

Back

Full Screen / Esc

Close

Printer-friendly Version



14, 16411-16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Full Screen / Esc

Close

Back

Printer-friendly Version

**Interactive Discussion** 



Simon, M., Sipila, M., Stozhkov, Y., Stratmann, F., Tome, A., Trostl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamaki, H., and Kirkby, J.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere. Nature, 502, 359–363, 2013.

Angelino, S., Suess, D., and Prather, K.: Formation of aerosol particles from reactions of secondary and tertiary alkylamines: characterization by aerosol time-of-flight mass spectrometry, Environ. Sci. Technol., 35, 3130–3138, 2001.

ApSimon, H. M., Barker, B. M., and Kayin, S.: Modelling studies of the atmospheric release and transport of ammonia in anticyclonic episodes, Atmos. Environ., 28, 665–678, 1994.

Benson, D. R., Markovich, A., Al-Refai, M., and Lee, S.-H.: A Chemical Ionization Mass Spectrometer for ambient measurements of Ammonia, Atmos. Meas. Tech., 3, 1075–1087, doi:10.5194/amt-3-1075-2010, 2010.

Berndt, T., Stratmann, F., Sipilä, M., Vanhanen, J., Petäjä, T., Mikkilä, J., Grüner, A., Spindler, G., Lee Mauldin III, R., Curtius, J., Kulmala, M., and Heintzenberg, J.: Laboratory study on new particle formation from the reaction  $OH + SO_2$ : influence of experimental conditions,  $H_2O$  vapour,  $NH_3$  and the amine tert-butylamine on the overall process, Atmos. Chem. Phys., 10, 7101–7116, doi:10.5194/acp-10-7101-2010, 2010.

Bigg, E. K.: Gas emissions from soil and leaf litter as a source of new particle formation, Atmos. Res., 70, 33–42, 2004.

Chang, I.-H., Lee, C.-G., and Lee, D. S.: Development of an automated method for simultaneous determination of low molecular weight aliphatic amines and ammonia in ambient air by diffusion scrubber coupled to ion chromatography, Anal. Chem., 75, 6141–6146, 2003.

Dawson, M. L., Perraud, V., Gomez, A., Arquero, K. D., Ezell, M. J., and Finlayson-Pitts, B. J.: Measurement of gas-phase ammonia and amines in air by collection onto an ion exchange resin and analysis by ion chromatography, Atmos. Meas. Tech. Discuss., 7, 1573–1602, doi:10.5194/amtd-7-1573-2014, 2014.

de Gouw, J. A., Warneke, C., Parrish, D. D., Holloway, J. S., Trainer, M., and Fehsenfeld, F. C.: Emission sources and ocean uptake of acetonitrile (CH<sub>3</sub>CN) in the atmosphere, J. Geophys. Res., 108, 4329, doi:10.1029/2002JD002897, 2003.

De Haan, D., Tolbert, M., and Jimenez, J.: Atmospheric condensed-phase reactions of glyoxal with methylamine, Geophys. Res. Lett., 36, L11819, doi:10.1029/2009GL037441, 2009.

14, 16411-16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Interactive Discussion

16430

- Eisele, F. L.: First tandem mass spectrometric measurements of tropospheric ions, J. Geophys. Res., 93, 716–724, 1988.

  Erupe, M. E., Benson, D. R., Li, J., Young, L.-H., Verheggen, B., Al-Refai, M., Tahboub, O., Cun-
- ningham, V., Frimpong, F., Viggiano, A. A., and Lee, S.-H.: Correlation of aerosol nucleation rate with sulfuric acid and ammonia in Kent Ohio: an atmospheric observation, J. Geophs. Res., 115, D23216, doi:10.1029/2010JD013942, 2010.
- Erupe, M. E., Viggiano, A. A., and Lee, S.-H.: The effect of trimethylamine on atmospheric nucleation involving H<sub>2</sub>SO<sub>4</sub>, Atmos. Chem. Phys., 11, 4767–4775, doi:10.5194/acp-11-4767-2011, 2011.
- Finlayson-Pitts, B. J. and Pitts, J. N.: Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications, Academic Press, San Diego, CA, 2000.
  - Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for  $K^+ Ca^{2+} Mg^{2+} NH_4^+ Na^+ SO_4^{2-} NO_3^- CI^- H_2O$  aerosols, Atmos. Chem. Phys., 7, 4639–4659, doi:10.5194/acp-7-4639-2007, 2007.
- Freshour, N. A., Carlson, K. K., Melka, Y. A., Hinz, S., Panta, B., and Hanson, D. R.: Quantifying amine permeation sources with acid neutralization: calibrations and amines measured in coastal and continental atmospheres, Atmos. Meas. Tech. Discuss., 7, 3835–3861, doi:10.5194/amtd-7-3835-2014, 2014.
  - Gai, Y., Ge, M., and Wang, W.: Rate constants for the gas phase reactions of ozone with diethylamine and triethylamine, Acta Physico-Chemica Sinica, 26, 1768–1772, 2010.
  - Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric amines Part II. thermodynamic properties and gas/particle partitioning, Atmos. Environ., 45, 561–577, 2010a.
  - Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric amines Part I. a review, Atmos. Environ., 45, 524–546, 2010b.
- Gilman, J. B., Burkhart, J. F., Lerner, B. M., Williams, E. J., Kuster, W. C., Goldan, P. D., Murphy, P. C., Warneke, C., Fowler, C., Montzka, S. A., Miller, B. R., Miller, L., Oltmans, S. J., Ryerson, T. B., Cooper, O. R., Stohl, A., and de Gouw, J. A.: Ozone variability and halogen oxidation within the Arctic and sub-Arctic springtime boundary layer, Atmos. Chem. Phys., 10, 10223–10236, doi:10.5194/acp-10-10223-2010, 2010.
- Grönberg, L., Lövkvist, P., and Jönsson, J.: Determination of aliphatic amines in air by membrane enrichment directly coupled to a gas chromatograph, Chromatographia, 33, 77–82, 1992.

14, 16411-16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

- Guenther, A. B., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., and Zimmerman, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100, 8873–8892, 1995.
- Guo, H., et al.: Predicting particle water and pH in the southeast by ISORROPIA: Results from SOAS and beyond, a manuscript in preparation, 2014.
  - Hanson, D. R., McMurry, P. H., Jiang, J., Tanner, D., and Huey, L. G.: Ambient pressure proton transfer mass spectrometry: detection of amines and ammonia, Environ. Sci. Technol., 45, 8881–8888, 2011.
- Hertel, O., Reis, S., Skjøth, C. A., Bleeker, A., Harrison, R., Cape, J. N., Fowler, D., Skiba, U., Simpson, D., Jickells, T., Baker, A., Kulmala, M., Gyldenkærne, S., Sørensen, L. L., and Erisman, J. W.: Nitrogen processes in the atmosphere, Philos. T. Roy. Soc., 368, 177–207, 2013.
  - Jang, M., Czoschke, N. M., Lee, S., and Kamens, R. M.: Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions, Science, 298, 814–817, 2002.
  - Jolly, W. L.: Modern Inorganic Chemistry, 2nd edn., McGraw-Hill, New York, 1991.
  - Kanawade, V., Benson, D. R., and Lee, S.-H.: Statistical analysis of 4 year measurements of aerosol sizes in a semi-rural US continental environment, Atmos. Environ., 59, 30–38, 2012.
  - Karl, M.: Atmospheric Degradation of Amines (ADA) Amines in aerosol a Review, Norwegian Institute for Air Research, Kjeller, Norway, 2010.
  - Kieloaho, A.-J., Hellén, H., Hakola, H., Manninen, H. E., Nieminen, T., Kulmala, M., and Pihlatie, M.: Gas-phase alkylamines in a boreal Scots pine forest air, Atmos. Environ., 80, 369–377, 2013.
  - Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagne, S., Ickes, L., Kurten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R. C., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E. R., Makhmutov, V., Mathot, S., Mikkila, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petaja, T., Schnitzhofer, R., Seinfeld, J. H., Sipila, M., Stozhkov, Y., Stratmann, F.,
    - Tome, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H., Weingartner, E., Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U., and Kulmala, M.:

Disc

14, 16411-16450, 2014

**ACPD** 

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

© BY

Interactive Discussion

Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, Nature, 476, 429–433, 2011.

Kurtén, T., Loukonen, V., Vehkamäki, H., and Kulmala, M.: Amines are likely to enhance neutral and ion-induced sulfuric acid-water nucleation in the atmosphere more effectively than ammonia, Atmos. Chem. Phys., 8, 4095–4103, doi:10.5194/acp-8-4095-2008, 2008.

Laskin, J., Laskin, A., Roach, P. J., Slysz, G. W., Anderson, G. A., Nizkorodov, S. A., Bones, D. L., and Nguyen, L. Q.: High-resolution desorption electrospray ionization mass spectrometry for chemical characterization of organic aerosols, Anal. Chem., 82, 2048–2058, 2010.

Lee, D. and Wexler, A. S.: Atmospheric amines – Part III: Photochemistry and toxicity, Atmos. Environ., 71, 95–103, 2013.

Lloyd, J., Heaton, K., and Johnston, M.: Reactive uptake of trimethylamine into ammonium nitrate particles, J. Phys. Chem. A, 113, 4840–4843, 2009.

Malloy, Q. G. J., Li Qi, Warren, B., Cocker III, D. R., Erupe, M. E., and Silva, P. J.: Secondary organic aerosol formation from primary aliphatic amines with NO<sub>3</sub> radical, Atmos. Chem. Phys., 9, 2051–2060, doi:10.5194/acp-9-2051-2009, 2009.

Mao, J., Ren, X., Zhang, L., Van Duin, D. M., Cohen, R. C., Park, J.-H., Goldstein, A. H., Paulot, F., Beaver, M. R., Crounse, J. D., Wennberg, P. O., DiGangi, J. P., Henry, S. B., Keutsch, F. N., Park, C., Schade, G. W., Wolfe, G. M., Thornton, J. A., and Brune, W. H.: Insights into hydroxyl measurements and atmospheric oxidation in a California forest, Atmos. Chem. Phys., 12, 8009–8020, doi:10.5194/acp-12-8009-2012, 2012.

Murphy, S. M., Sorooshian, A., Kroll, J. H., Ng, N. L., Chhabra, P., Tong, C., Surratt, J. D., Knipping, E., Flagan, R. C., and Seinfeld, J. H.: Secondary aerosol formation from atmospheric reactions of aliphatic amines, Atmos. Chem. Phys., 7, 2313–2337, doi:10.5194/acp-7-2313-2007, 2007.

Nenes, A., Pandis, S., and Pilinis, C.: ISORROPIA: a new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols, Aquat. Geochem., 4, 123–152, 1998.

Nielsen, C. J., D'Anna, B., Karl, M., Aursnes, M., Boreave, A., Bossi, R., Bunkan, A. J. C., Glasius, M., Hallquist, M., Hansen, A.-M. K., Kristensen, K., Mikoviny, T., Maguta, M. M., Müller, M., Nguyen, Q., Westerlund, J., Salo, K., Skov, H., Stenstrøm, Y., and Wisthaler, A.: Atmospheric Degradation of Amines (ADA) Summary Report: Photo-Oxidation of Methylamine, Dimethylamine and Trimethylamine CLIMIT project no. 201604, Norwegian Institute for Air Research, Kieller, Norway, 2011.

- Nielsen, C. J., Herrmann, H., and Weller, C.: Atmospheric chemistry and environmental impact of the use of amines in carbon capture and storage (CCS), Chem. Soc. Rev., 41, 6684–6704, 2012.
- NIST: NIST Standard Reference Database Number 69, edited, National Institute for Standard Technology (NIST) Chemistry Web Book, available at: http://webbook.nist.gov/chemistry/ (last access: 23 September 2013), 2011.
- Nowak, J. B., Huey, L. G., Eisele, F. L., Tanner, D., Mauldin III, R. L., Cantrell, C. A., Kosciuch, E., and Davis, D.: Chemical ionization mass spectrometry technique for the detection of dimethylsulfoxide and ammonia, J. Geophys. Res., 107, 4363, doi:10.1029/2001JD001058, 2002.
- Nowak, J. B., Huey, L. G., Russell, A. G., Tian, D., Neuman, J. A., Orsini, D., Sjostedt, S. J., Sullivan, A. P., Tanner, D. J., Weber, R. J., Nenes, A., Edgerton, E., and Fehsenfeld, F. C.: Analysis of urban gas phase ammonia measurements from the 2002 Atlanta Aerosol Nucleation and Real-Time Characterization Experiment (ANARChE), J. Geophys. Res., 111, D17308, doi:10.1029/2006JD007113, 2006.
- Nowak, J. B., Newman, J. A., Kozai, K., Huey, L. G., Tanner, D., Holloway, J. S., Ryerson, T. B., Frost, G. L., McKeen, S. A., and Fehsenfeld, F. C.: A chemical ionization mass spectrometry technique for airborne measurements of ammonia, J. Geophys. Res., 112, D10S02, doi:10.1029/2006JD007589, 2007.
- Nowak, J. B., Neuman, J. A., Bahreini, R., Brock, C. A., Middlebrook, A. M., Wollny, A. G., Holloway, J. S., Peischl, J., Ryerson, T. B., and Fehsenfeld, F. C.: Airborne observations of ammonia and ammonium nitrate formation over Houston, Texas, J. Geophys. Res., 115, D22304, doi:10.1029/2010jd014195, 2010.
  - Nowak, J. B., Neuman, J. A., Bahreini, R., Middlebrook, A. M., Holloway, J. S., McKeen, S. A., Parrish, D. D., Ryerson, T. B., and Trainer, M.: Ammonia sources in the California South Coast Air Basin and their impact on ammonium nitrate formation, Geophys. Res. Lett., 39, L07804, doi:10.1029/2012gl051197, 2012.
  - Pankow, J. F.: Gas/particle partitioning of neutral and ionizing compounds to single and multiphase aerosol particles, 1. Unified modeling framework, Atmos. Environ., 37, 3323–3333, 2003.
  - Pratt, K., Hatch, L., and Prather, K.: Seasonal volatility dependence of ambient particle phase amines, Environ. Sci. Technol., 43, 5276–5281, 2009.

**ACPD** 

14, 16411–16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

**→** 

Close

Back

Full Screen / Esc

Printer-friendly Version



- Qiu, C. and Zhang, R.: Multiphase chemistry of atmospheric amines, Phys. Chem. Chem. Phys., 15, 5738–5752, 2013.
- Sander, R.: Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry, available at: http://www.henrys-law.org/ (last access: 20 September 2013), 1999.
- Schade, G. W. and Crutzen, P. J.: Emissions of aliphatic amines from animal husbandry and their reactions: potential source of N<sub>2</sub>O and HCN, J. Atmos. Chem., 22, 319–346, 1995.
- Sellegri, K., Umann, B., Hanke, M., and Arnold, F.: Deployment of a ground-based CIMS apparatus for the detection of organic gases in the boreal forest during the QUEST campaign, Atmos. Chem. Phys., 5, 357–372, doi:10.5194/acp-5-357-2005, 2005a.
- Sellegri, K., Hanke, M., Umann, B., Arnold, F., and Kulmala, M.: Measurements of organic gases during aerosol formation events in the boreal forest atmosphere during QUEST, Atmos. Chem. Phys., 5, 373–384, doi:10.5194/acp-5-373-2005, 2005b.
- Shao, R. J. and Stangeland, A.: Amines Used in CO<sub>2</sub> Capture, edited, Bellona Report, Oslo, Norway, 2009.
- Silva, P., Erupe, M., Price, D., Elias, J., Malloy, Q., Li, Q., Warren, B., and Cocker III, D.: Trimethy-lamine as precursor to secondary organic aerosol formation via nitrate radical reaction in the atmosphere, Environ. Sci. Technol., 42, 4689–4696, 2008.
- Smith, J. N., Dunn, M. J., VanReken, T. M., Iida, K., Stolzenburg, M. R., McMurry, P. H., and Huey, L. G.: Chemical composition of atmospheric nanoparticles formed from nucleation in Tecamac, Mexico: evidence for an important role for organic species in nanoparticle growth, Geophys. Res. Lett., 35, L04808, doi:10.1029/2007GL032523, 2008.
- Smith, J. N., Barsanti, K. C., Friedli, H. R., Ehn, M., Kulmala, M., Collins, D. R., Scheckman, J. H., Willians, B. J., and McMurry, P. H.: Observations of amonium salts in atmospheric nanoparticles and possible climatic implications, P. Natl. Acad. Sci. USA, 107, 6634–6639, 2010.
- Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for organosulfates in secondary organic aerosol, Environ. Sci. Technol., 41, 517–527, 2007.
- Sutton, M. A., Dragosits, U., Tang, Y. S., and Fowler, D.: Ammonia emissions from non-agricultural sources in the UK, Atmos. Environ., 34, 855–869, 2000.

**ACPD** 

14, 16411-16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

l∢ ≻l

Back Close

Full Screen / Esc

Printer-friendly Version



**ACPD** 

14, 16411–16450, 2014

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page Introduction **Abstract Conclusions** References Tables **Figures** Back Close Full Screen / Esc Printer-friendly Version

Interactive Discussion

16435

- Updyke, K. M., Nguyen, T. B., and Nizkorodov, S. A.: Formation of brown carbon via reactions of ammonia with secondary organic aerosols from biogenic and anthropogenic precursors,
- Vaden, T. D., Imre, D., Beránek, J., Shrivastava, M., and Zelenyuk, A.: Evaporation kinetics and phase of laboratory and ambient secondary organic aerosol, P. Natl. Acad. Sci. USA, 108, 2190-2195, 2011.

Atmos. Environ., 63, 22-31, 2012.

- VandenBoer, T. C., Petroff, A., Markovic, M. Z., and Murphy, J. G.: Size distribution of alkyl amines in continental particulate matter and their online detection in the gas and particle phase, Atmos. Chem. Phys., 11, 4319-4332, doi:10.5194/acp-11-4319-2011, 2011.
- Wang, L., Lal, V., Khalizov, A., and Zhang, R.: Heterogeneous chemistry of alkylamines with sulfuric acid: implications for atmospheric formation of alkylaminium sulfates, Environ. Sci. Technol., 44, 2461-2465, 2010a.
  - Wang, L., Khalizov, A., Zheng, J., Xu, W., Ma, Y., Lal, V., and Zhang, R.: Atmospheric nanoparticles formed from heterogeneous reactions of organics, Nat. Geosci., 3, 238–242, 2010b.
- Warneke, C., Gouw, J. A. d., Stohl, A., Cooper, O. R., Goldan, P. D., Kuster, W. C., Holloway, J. S., Williams, E. J., Lerner, B. M., McKeen, S. A., Trainer, M., Fehsenfeld, F. C., Atlas, E. L., Donnelly, S. G., Stroud, V., Lueb, A., and Kato, S.: Biomass burning and anthropogenic sources of CO over New England in the summer 2004, J. Geophys. Res., 111, D23S15, doi:10.1029/2005JD006878, 2006.
- Yu, H. and Lee, S.-H.: A chemical ionization mass spectrometer for the detection of atmospheric amines, Environ. Chem., 9, 190-201, 2012.
  - Yu, H., McGraw, R., and Lee, S.-H.: Effects of amines on formation of sub-3 nm particles and their subsequent growth, Geophys. Res. Lett., 39, L02807, 2012.
  - Yu, H., Kanawade, V. P., You, Y., Hallar, A. G., Mccubbin, I. B., Chirokova, G., Sedlacek, A. J., Springston, S. R., Wang, J., McGraw, R. L., Mikkila, J., and Lee, S. H.: Sub-3 nm particles observed at the coastal and continental sites in the United States, J. Geophys. Res., 119, 860-879. doi:10.1029/2013JD020841. 2014.
  - Yu, Z., Zhang, Q., Kraus, T. E. C., Dahlgren, R. A., Anastasio, C., and Zasoski, R. J.: Contribution of amino compounds to dissolved organic nitrogen in forest soils, Biogeochemistry, 61, 173–198, 2002.
  - Zahardis, J., Geddes, S., and Petrucci, G. A.: The ozonolysis of primary aliphatic amines in fine particles, Atmos. Chem. Phys., 8, 1181-1194, doi:10.5194/acp-8-1181-2008, 2008.

Discussion Paper

Discussion Paper

Discussion Paper

**ACPD** 

14, 16411-16450, 2014

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page

**Abstract** Introduction Conclusions References **Tables Figures** I₫  $\triangleright$ **Back** Close Full Screen / Esc **Printer-friendly Version** 



Interactive Discussion

Sulfuric acid nucleation: power dependencies, variation with relative humidity, and effect of

bases, Atmos. Chem. Phys., 12, 4399-4411, doi:10.5194/acp-12-4399-2012, 2012.

in the atmosphere, Chem. Rev., 112, 957-2011, 2012.

5

**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<sub>3</sub>. Typical ambient concentrations measured in the Alabama forest and Kent are also included (20 min average data).

Basic Compound <sup>a</sup>	Sensitivity $[Hz (pptv MHz)^{-1}]^b$	Detection Limit, DL	Alabama Forest: Jun–Jul	Kent: Aug-Sep
NH <sub>3</sub> (ppbv)	13	54	Up to 1-2	Up to 6
C1-Amine (pptv) (methylamine)	12	1	< DL	1–4
C2-Amines (pptv) (dimethylamine)	12	5	< DL	< DL
C3-Amines (pptv) (trimethyleamine)	8	5	1–10	5-10
C4-Amines (pptv) (diethylamine)	4	23	< DL	10-50
C5-Amines (pptv)	2	17	< DL	10-100
C6-Amines (pptv) (triethylamine)	2	12	< DL	< DL

<sup>&</sup>lt;sup>a</sup> 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.

14, 16411-16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

I∢ ≻I

Close

**→** 

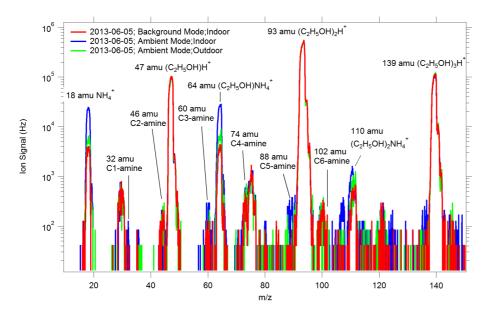
Full Screen / Esc

Back

Printer-friendly Version



<sup>&</sup>lt;sup>b</sup> With regard to the unit of sensitivity [Hz (pptv MHz)<sup>-1</sup>]: 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.

14, 16411-16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Title Page

Abstract Introduction

Conclusions References

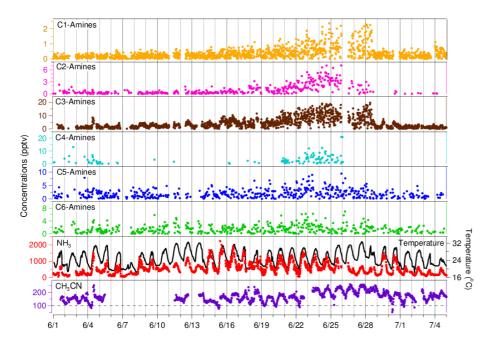
Tables Figures

I ◀ ▶I

Back Close

Full Screen / Esc





**Figure 2.** Temporal variations of amines, NH<sub>3</sub>, and CH<sub>3</sub>CN along with the ambient temperature measured in the Alabama forest during the entire SOAS field campaign. Vertical grids correspond to times at midnight.

14, 16411-16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Title Page

Abstract

Introduction References

Conclusions

[■

Figures

Tables





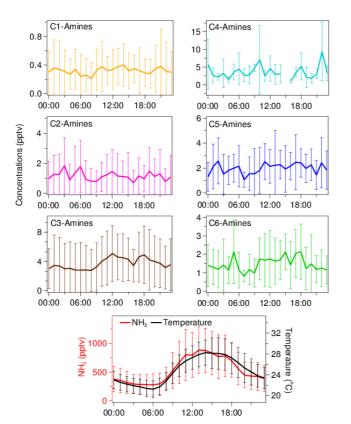
Back



Full Screen / Esc

Printer-friendly Version





**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. 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  $NH_3$ .

**ACPD** 

14, 16411–16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Back

Figures



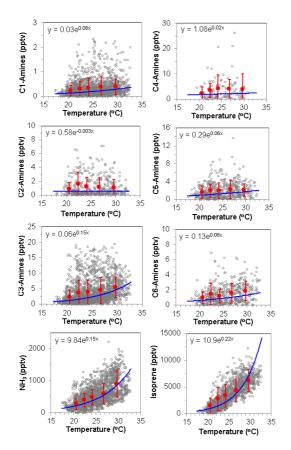




Full Screen / Esc

Printer-friendly Version





**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.

14, 16411-16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I∢



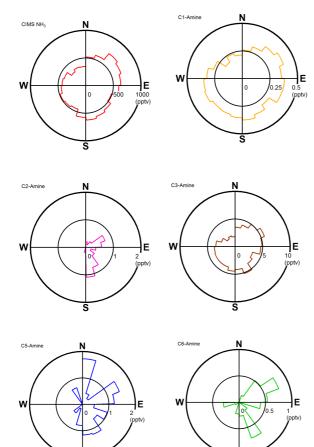




Full Screen / Esc

Printer-friendly Version





**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.

14, 16411-16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures











Printer-friendly Version





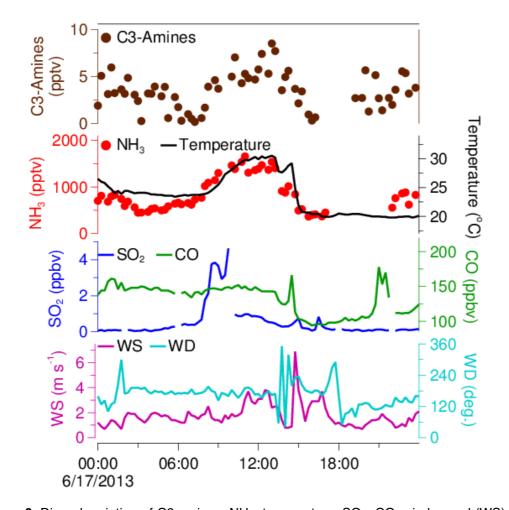


Figure 6. Diurnal variation of C3-amines, NH<sub>3</sub>, temperature, SO<sub>2</sub>, CO, wind speed (WS) and wind direction (WD) for 17 June 2013 in the Alabama forest.

**ACPD** 

14, 16411-16450, 2014

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page

**Abstract** Introduction

Conclusions References

> **Tables Figures**

 $\triangleright$ 

 $\blacktriangleright$ Back Close

Full Screen / Esc

**Printer-friendly Version** 



Discussion Paper



**Printer-friendly Version** 

Interactive Discussion



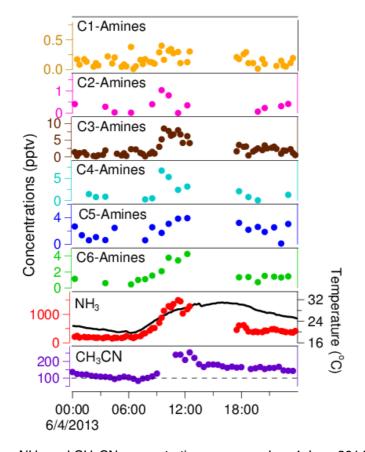


Figure 7. Amines, NH<sub>3</sub> and CH<sub>3</sub>CN concentrations measured on 4 June 2014 in the Alabama forest. The measured ambient temperature is also shown. There was a local trash burning event starting around 10 a.m. The blank period of amines and NH<sub>3</sub> in the afternnon was due to a power outage in the trailer where the CIMS was located.

14, 16411-16450, 2014

**ACPD** 

# **Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page

Introduction

References

Figures

 $\triangleright$ 

Þ

**Abstract** 

Conclusions

**Tables** 



Close Back

Full Screen / Esc

**Printer-friendly Version** 

Interactive Discussion



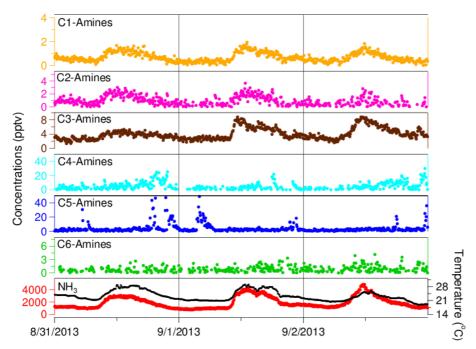


Figure 8. A typical 3 day ambient measurement of amines and NH<sub>3</sub> in Kent, Ohio. Ambient temperatures are also included here. Vertical bars show times at midnight.

14, 16411-16450, 2014

**ACPD** 

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page

Introduction

References

**Figures** 

 $\triangleright$ 

 $\blacktriangleright$ 

**Abstract** 

**Tables** 



**Discussion Paper** 

■ AL ■ OH

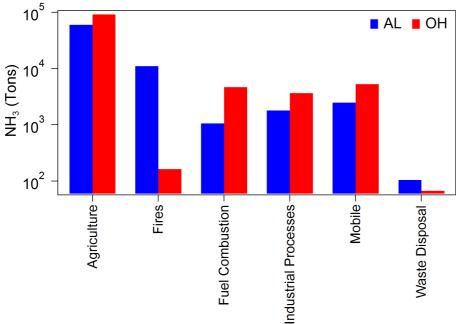


Figure 9. EPA-reported annual emission rates of NH<sub>3</sub> from various sectors in Alabama (blue) and Ohio (red) in 2011. Data were adopted from the 2011 National Emissions Inventory website: http://www.epa.gov/ttn/chief/net/2011inventory.html.

# **ACPD**

14, 16411-16450, 2014

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page

**Abstract** 

Back

Conclusions References

> **Tables Figures**

Introduction

 $\triangleright$ 

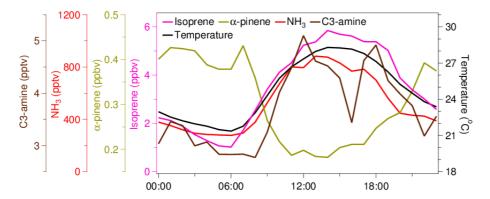
Close



Full Screen / Esc

Printer-friendly Version





**Figure 10.** The averaged diurnal variation of isoprene (magenta),  $\alpha$ -pinene (orange), NH<sub>3</sub> (red), C3-amines (brown) and temperature (black) over the entire SOAS campaign period.

14, 16411-16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

I∢ ≻I

**■** Back Close

Full Screen / Esc

Printer-friendly Version





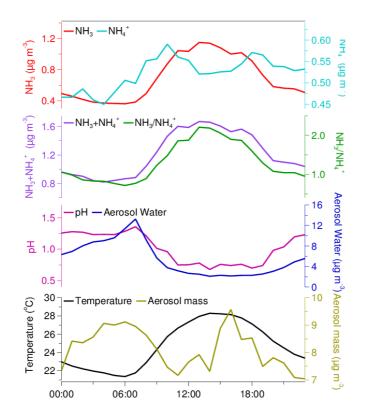


Figure 11. The average diurnal variation of the gas phase NH<sub>3</sub> (red), aerosol-phase ammonium (NH<sub>4</sub><sup>+</sup>, cyan) measured with IC, the sum of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> (purple), the ratio of NH<sub>3</sub> to NH<sub>4</sub><sup>+</sup> (green), ISORROPIA-predicted 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  $\mu g m^{-3}$  $(1 \text{ ppbv} = 1.3 \,\mu\text{g m}^{-3})$  to be compared with aerosol-phase NH<sub>4</sub><sup>+</sup>.

**ACPD** 

14, 16411-16450, 2014

**Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.

Title Page Introduction **Abstract** Conclusions References

> **Figures Tables**

Þ Close Back

Full Screen / Esc



# 14, 16411-16450, 2014

**ACPD** 

# **Atmospheric amines** and ammonia measured with a CIMS

Y. You et al.



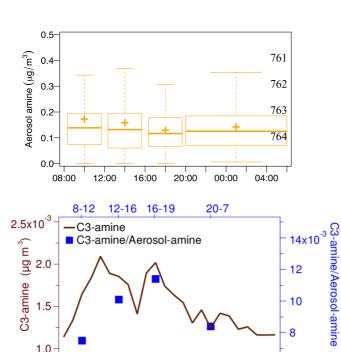
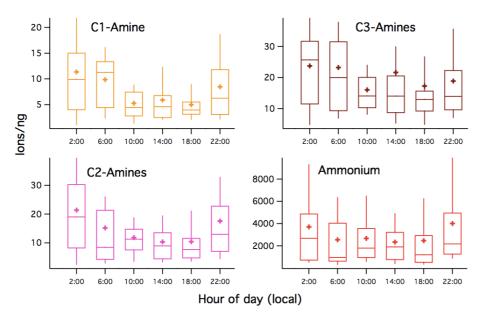


Figure 12. (Upper panel) Average daily variation of aerosol phase concentration (µq m<sup>-3</sup>) of primary amines in submicron particles collected on PTFE filters and analyzed with FTIR during the SOAS campaign. The horizontal solid lines indicate the median, plus signs indicate the mean, the boxes 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  $\mu q m^{-3}$  $(1 \text{ pptv} = 0.41 \text{ ng m}^{-3})$  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.

12:00 16:00 20:00 00:00 04:00



**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).

14, 16411-16450, 2014

Atmospheric amines and ammonia measured with a CIMS

Y. You et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

14



Back



Full Screen / Esc

Printer-friendly Version

