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## 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 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.

## 1 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

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## 5 Measurements in the Alabama Forest

Table 1 shows the summary of the ambient concentrations of amines and  $\text{NH}_3$  measured in the Alabama forest in June and July 2013. Temporal variations of amines and  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  over the entire campaign, along with the measured ambient temperatures. C3-amines and  $\text{NH}_3$  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  $\text{NH}_3$  (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  $\text{SO}_2$  and CO plumes.  $\text{SO}_2$  background concentrations were usually less than 1 ppbv, but around 08:00 to 10:00 LT,  $\text{SO}_2$  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  $\text{SO}_2$  and CO plumes, C3-amines and  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$

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were higher during the particle formation events than non-event days. In Kent, there were more abundant amines (C1–C6) and NH<sub>3</sub> 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<sub>2</sub> from the surrounding coal-burning power plants (and hence sulfuric acid production), may explain the frequent new particle formation events reported from this site (Erupe et al., 2010; Kanawade et al., 2012; Yu et al., 2013).

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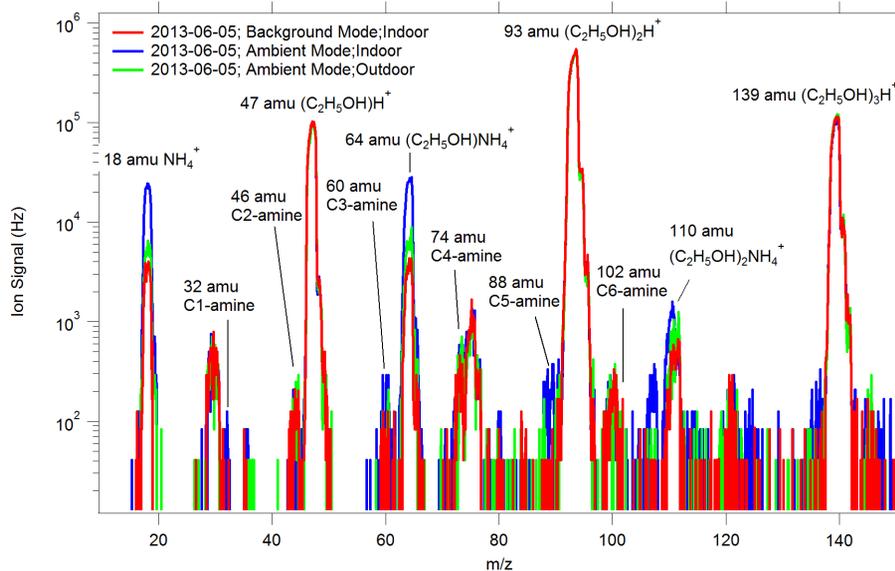
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**Figure 1.** Typical CIMS mass spectra taken under the background (red) and measurement modes, including measurements from the ambient air (green) and indoor air (blue), in the Alabama forest. The y-axis is shown in log scale.

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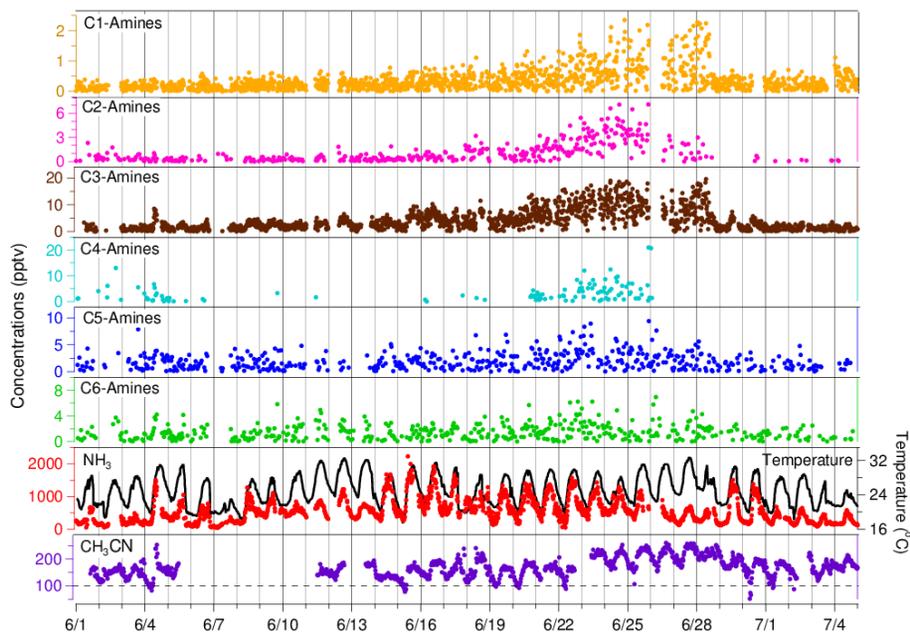
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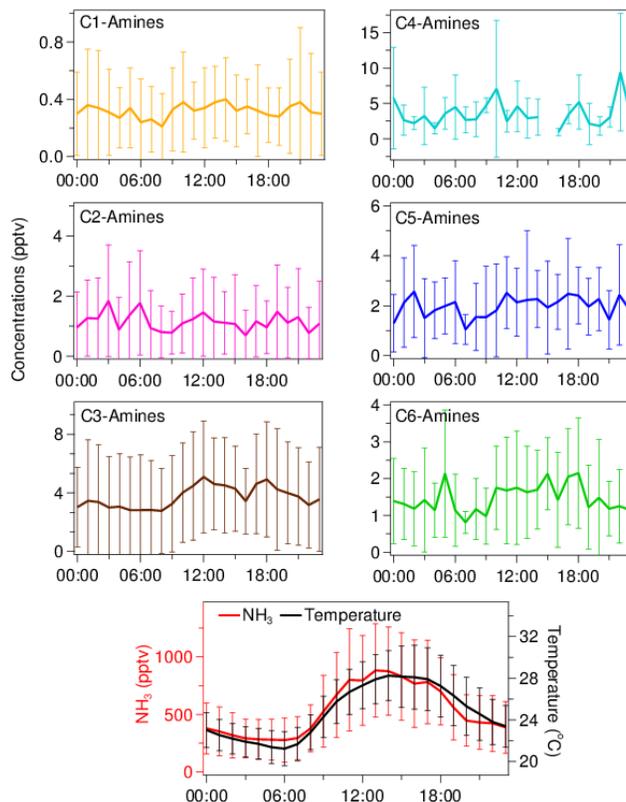


**Figure 2.** Temporal variations of amines,  $\text{NH}_3$ , and  $\text{CH}_3\text{CN}$  along with the ambient temperature measured in the Alabama forest during the entire SOAS field campaign. Vertical grids correspond to times at midnight.

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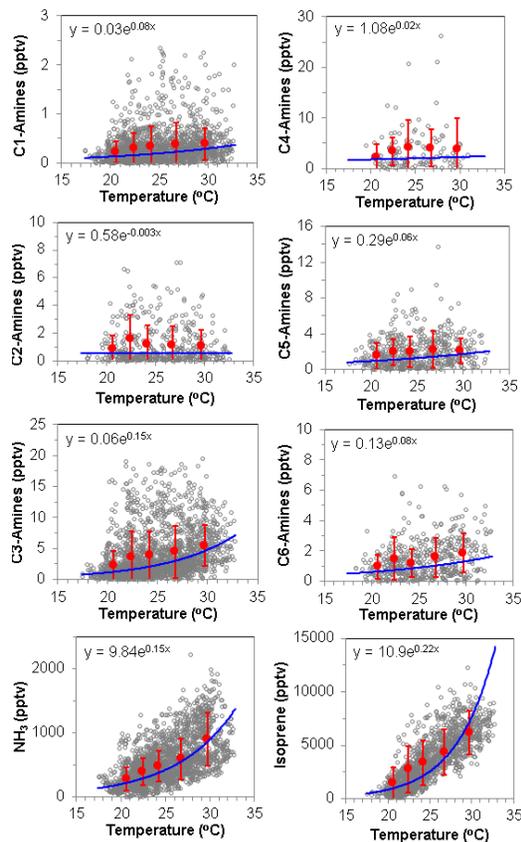
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**Figure 3.** The averaged diurnal variation throughout the entire SOAS campaign for the measured C1- to C6-amines and NH<sub>3</sub> concentrations measured in the Alabama forest during the summer. C4-amines were below the detection limit for most 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<sub>3</sub>.

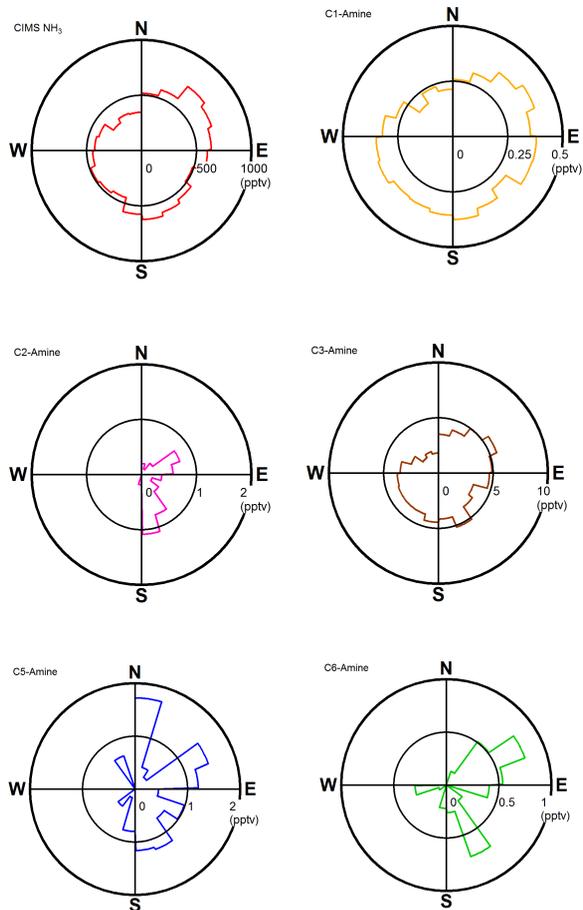
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**Figure 4.** Temperature dependence of amines,  $\text{NH}_3$  and isoprene for the entire SOAS campaign. Gray dots show the measurement data and blue lines show the exponential fitting of the data. Red circles and vertical lines show the mean and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

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**Figure 5.** Wind direction plots of the measured amines and  $\text{NH}_3$ , averaged over the entire SOAS campaign. C4-amines were rarely measured, so are not shown here.

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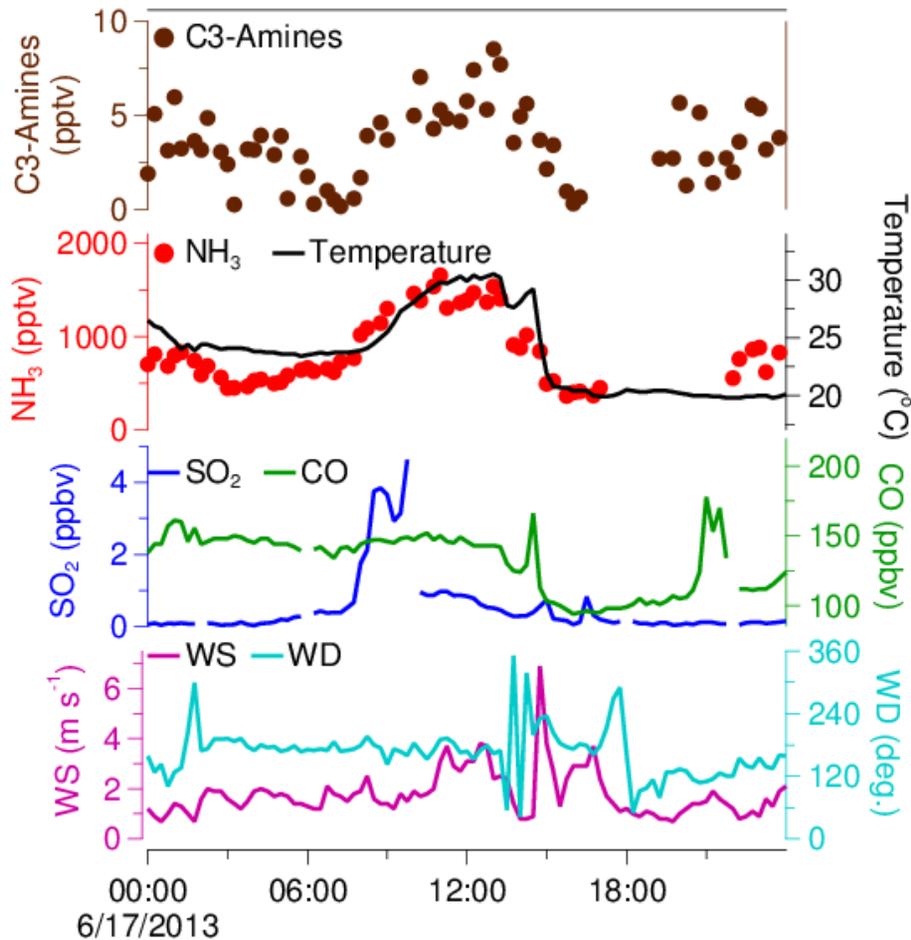
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**Figure 6.** Diurnal variation of C3-amines,  $\text{NH}_3$ , temperature,  $\text{SO}_2$ , CO, wind speed (WS) and wind direction (WD) for 17 June 2013 in the Alabama forest.

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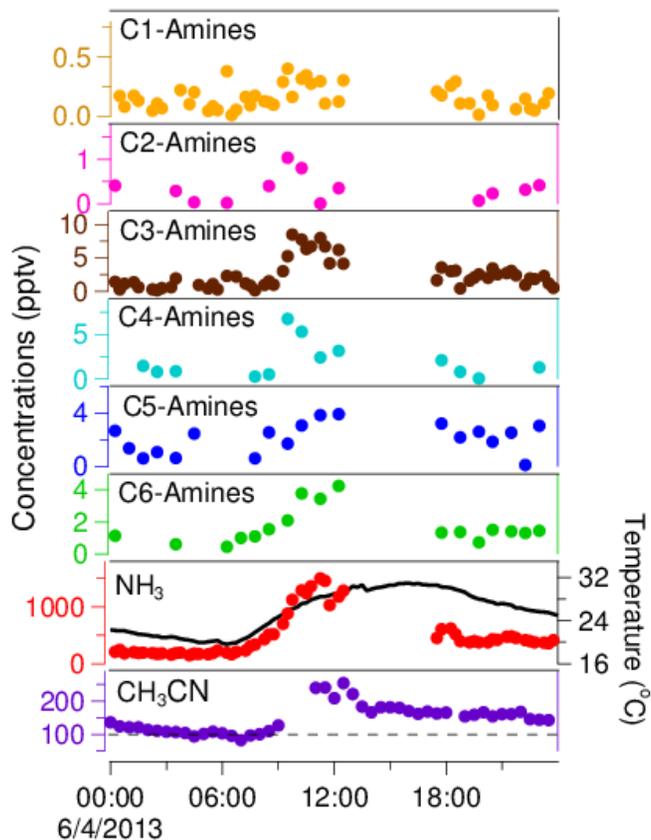
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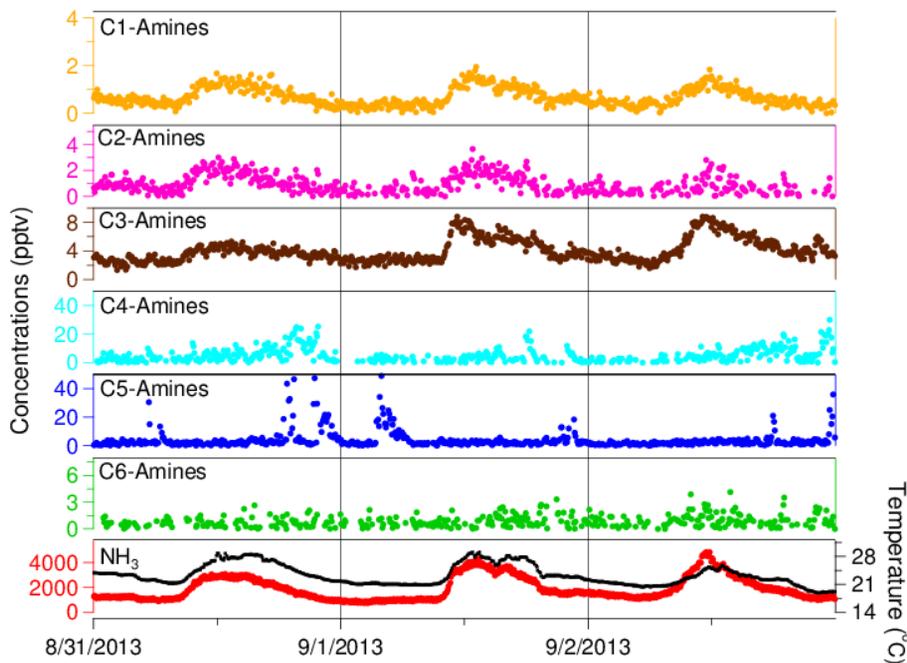


**Figure 7.** Amines, NH<sub>3</sub> and CH<sub>3</sub>CN concentrations measured on 4 June 2014 in the Alabama forest. The measured ambient temperature is also shown. There was a local trash burning event starting around 10 a.m. The blank period of amines and NH<sub>3</sub> in the afternoon was due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

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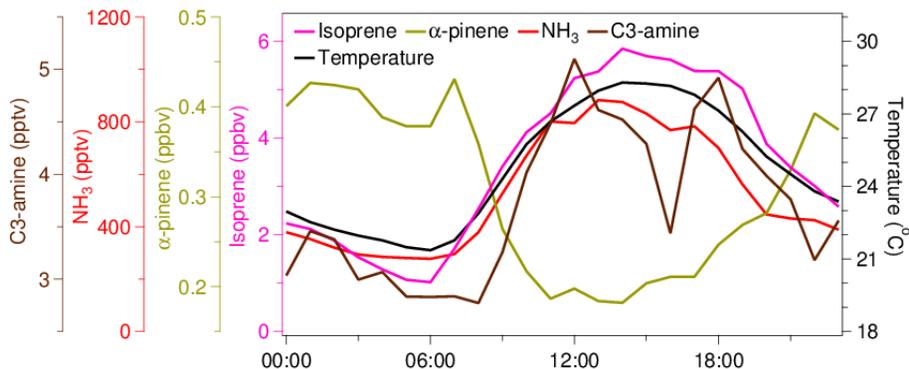
**Figure 8.** A typical 3 day ambient measurement of amines and  $\text{NH}_3$  in Kent, Ohio. Ambient temperatures are also included here. Vertical bars show times at midnight.

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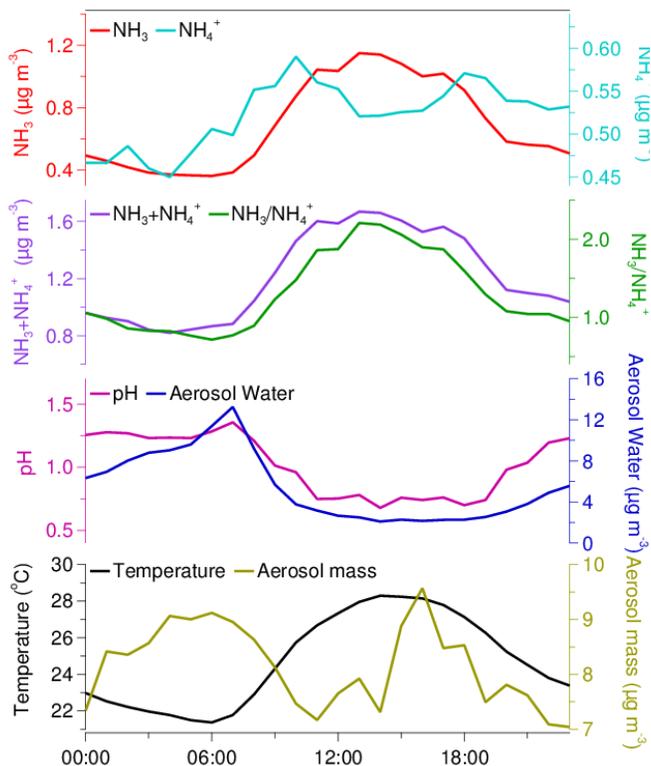


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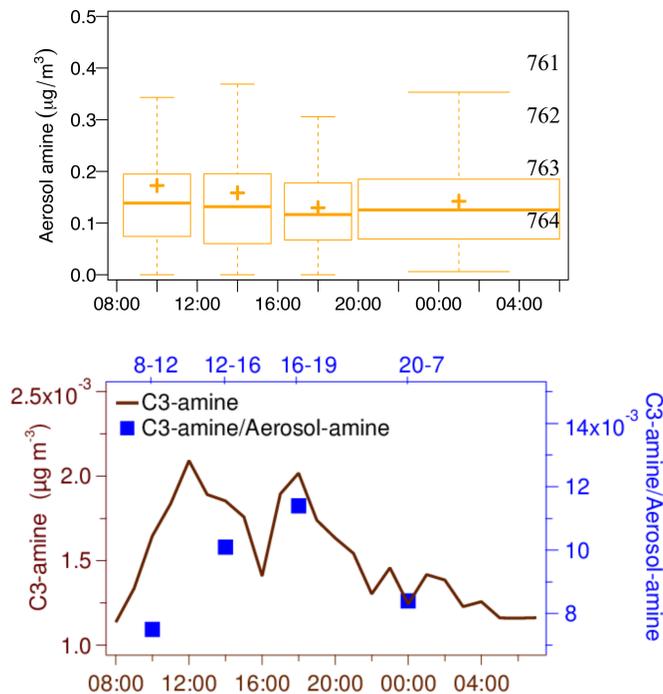
**Figure 10.** The averaged diurnal variation of isoprene (magenta),  $\alpha$ -pinene (orange),  $\text{NH}_3$  (red), C3-amines (brown) and temperature (black) over the entire SOAS campaign period.



**Figure 11.** The average diurnal variation of the gas phase  $\text{NH}_3$  (red), aerosol-phase ammonium ( $\text{NH}_4^+$ , cyan) measured with IC, the sum of  $\text{NH}_3$  and  $\text{NH}_4^+$  (purple), the ratio of  $\text{NH}_3$  to  $\text{NH}_4^+$  (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  $\text{NH}_3$  concentrations was converted from ppbv to  $\mu\text{g m}^{-3}$  (1 ppbv =  $1.3 \mu\text{g m}^{-3}$ ) to be compared with aerosol-phase  $\text{NH}_4^+$ .

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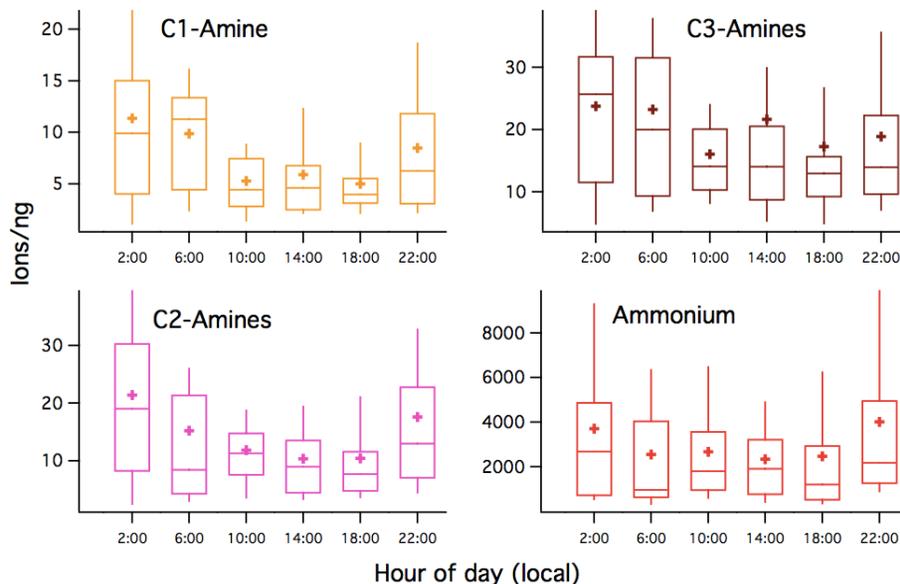


**Figure 12.** (Upper panel) Average daily variation of aerosol phase concentration ( $\mu\text{g}/\text{m}^3$ ) of primary amines in submicron particles collected on PTFE filters and analyzed with FTIR during the SOAS campaign. The horizontal solid lines indicate the median, plus signs indicate the mean, the boxes extend from the 25th to 75th percentile, and the whiskers span the interquartile range. (Lower panel) Temporal variation of the averaged gas-phase C3-amines (brown line) and the ratio of C3-amines over the aerosol-phase aliphatic amines (blue squares) during the SOAS campaign. The unit of gas-phase C3-amine concentrations was converted from pptv to  $\mu\text{g}/\text{m}^3$  ( $1 \text{ pptv} = 0.41 \text{ ng}/\text{m}^3$ ) 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.

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**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).