

Sulfuric Acid, Ammonia, Amines and New Particle Formation in the Alabama Forest

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Kent State University



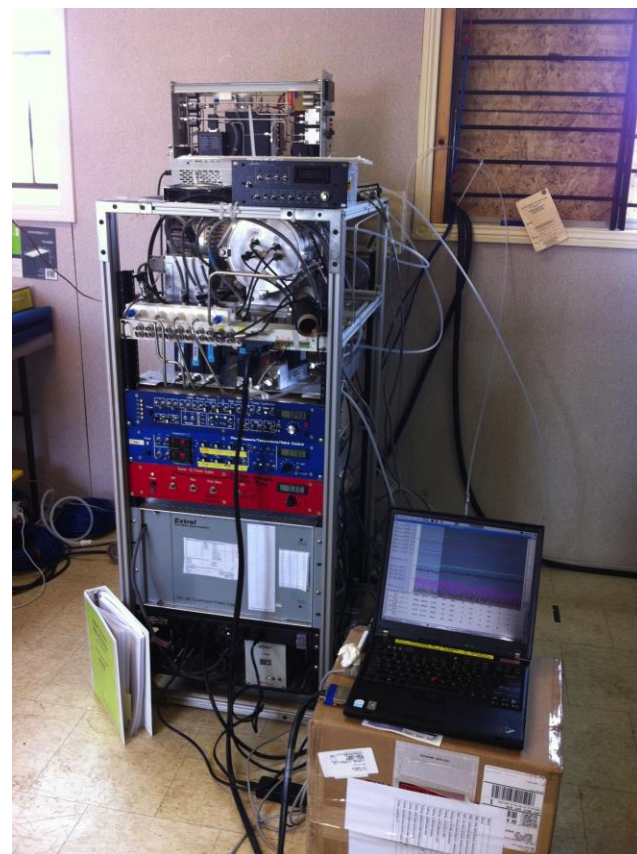
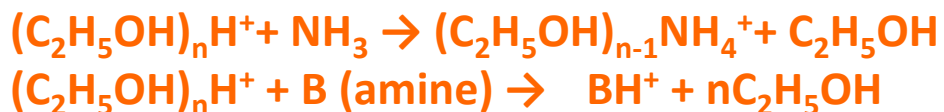
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Amine/ammonia Chemical Ionization Mass Spectrometer (CIMS)

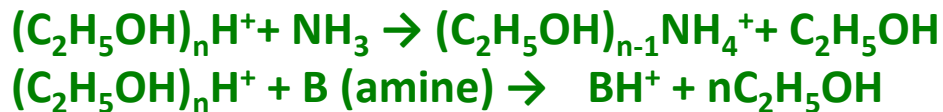
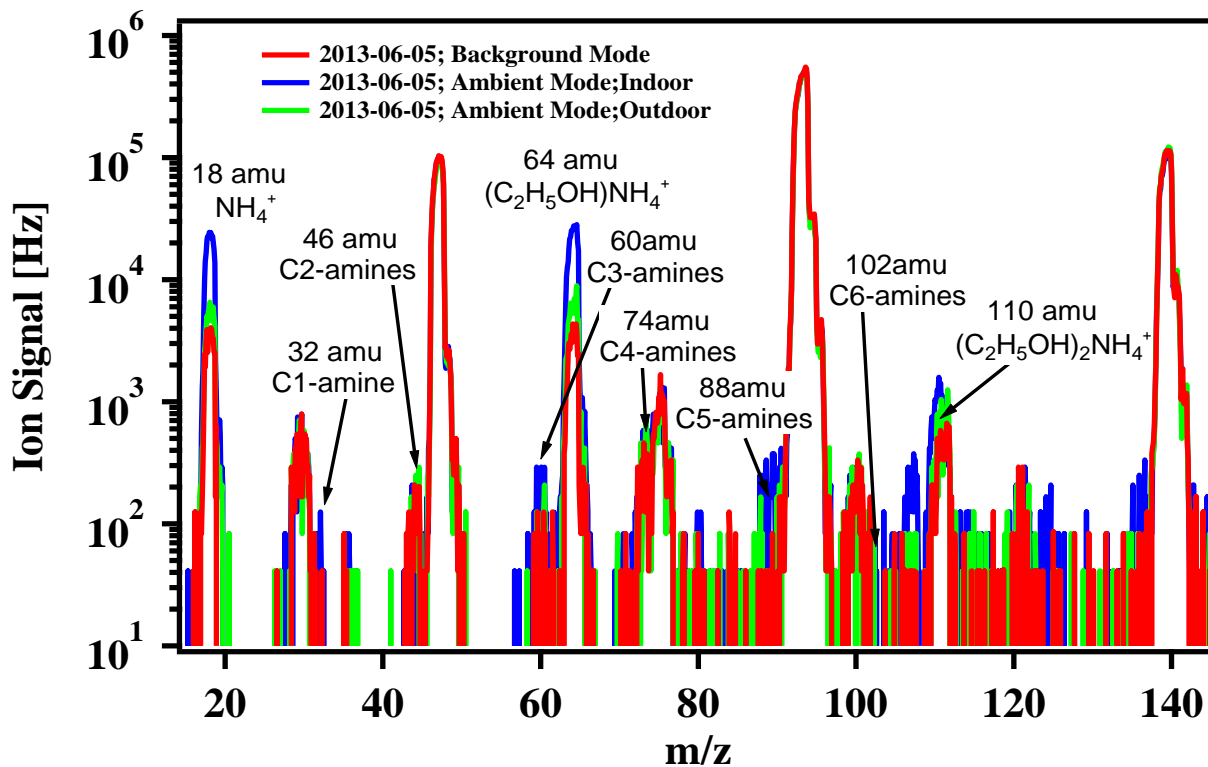
- Measures ammonia and various amines at the pptv level.
- Fast time response, 1 min
- Selective measurements for high proton-affinity base compounds (so, little interferences from other organics)



In SOAS trailer

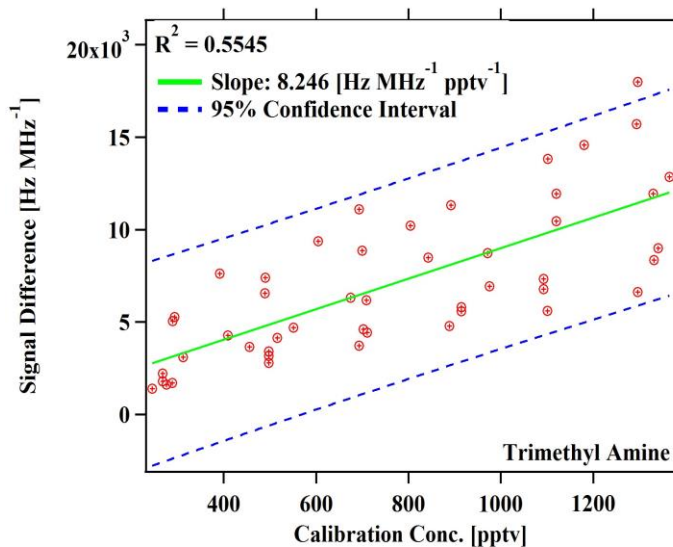
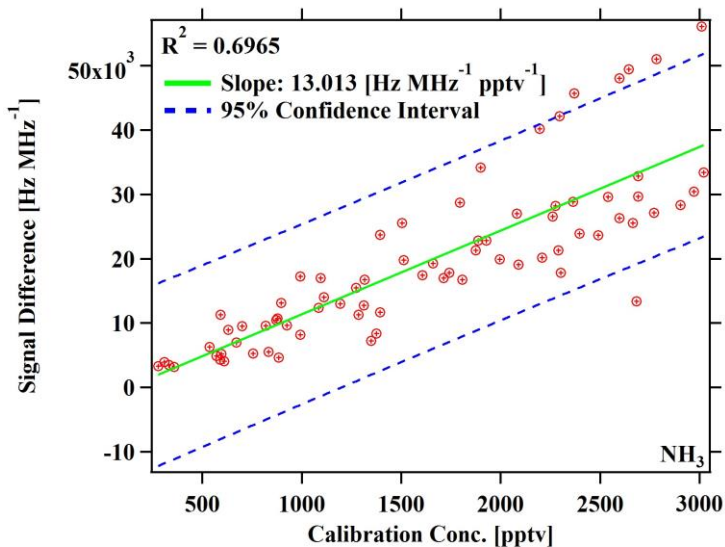
Yu and Lee, Environ. Chem., 2012

Amine/ammonia Chemical Ionization Mass Spectrometer (CIMS)

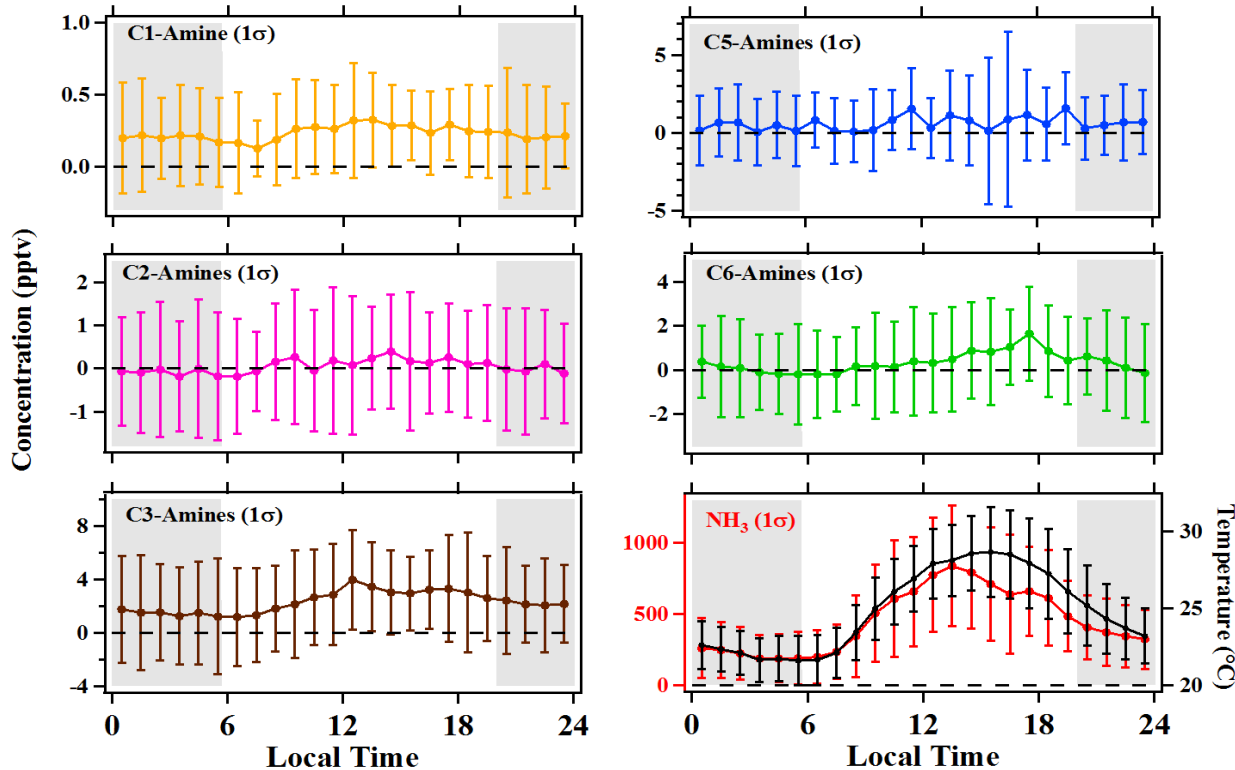


CIMS sensitivity from *in-situ* Calibrations and Detection Limits (1 min integration)

Amine	Sensitivity (Hz/pptv/MHz)	Detection Limit (pptv)
Ammonia	13	54
Methylamine	12	1
Dimethylamine	12	5
Trimethylamine	8	5
Diethylamine	4	23
Triethylamine	2	12



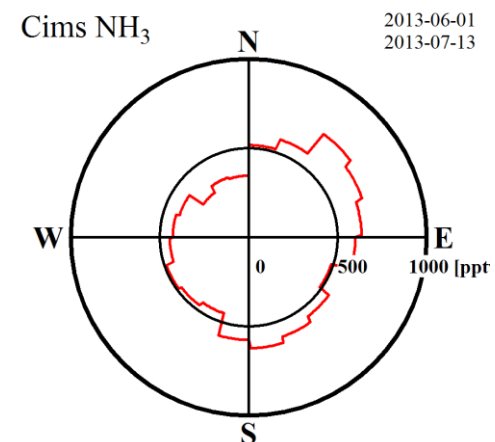
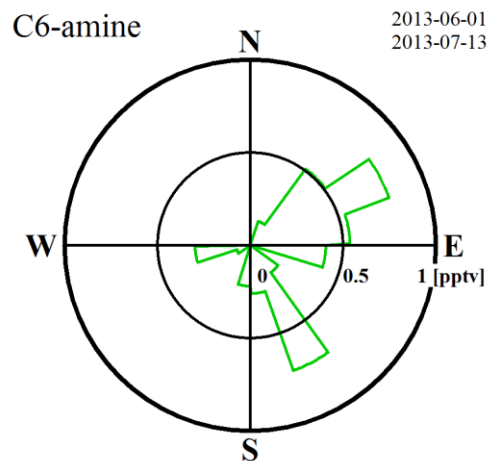
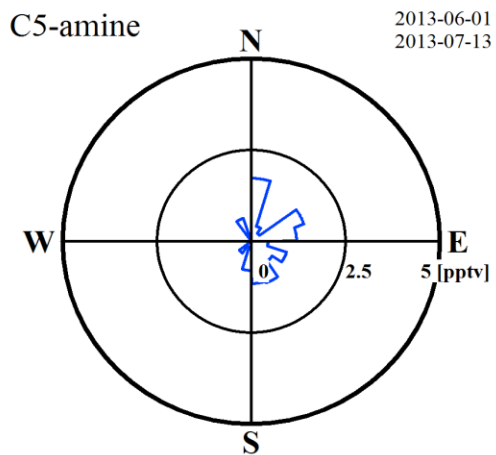
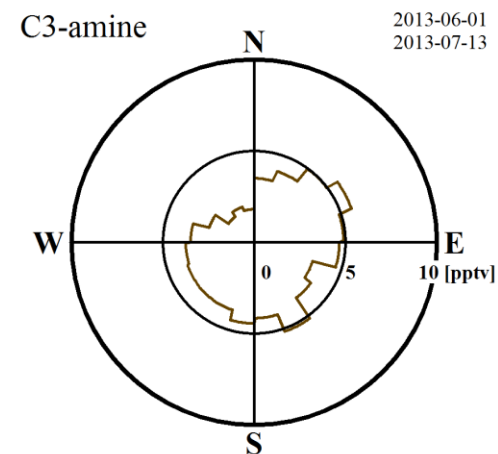
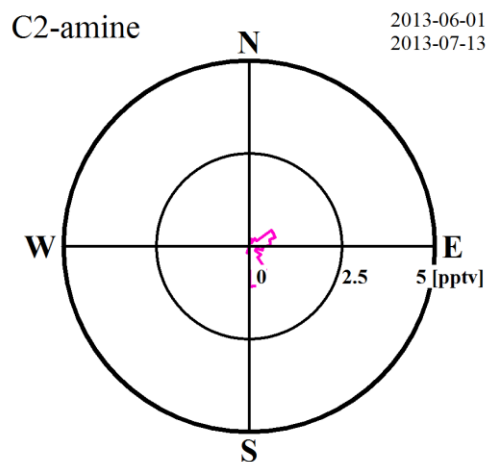
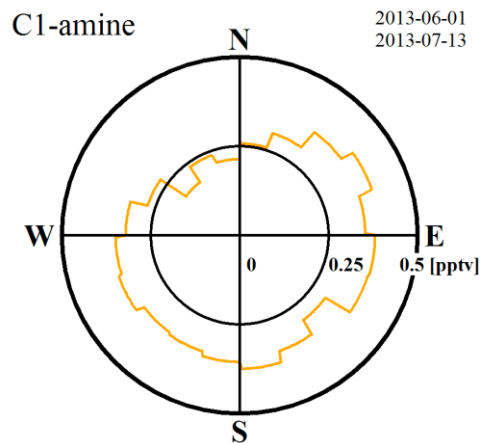
Overall results of 6 weeks: Averaged temporal variation



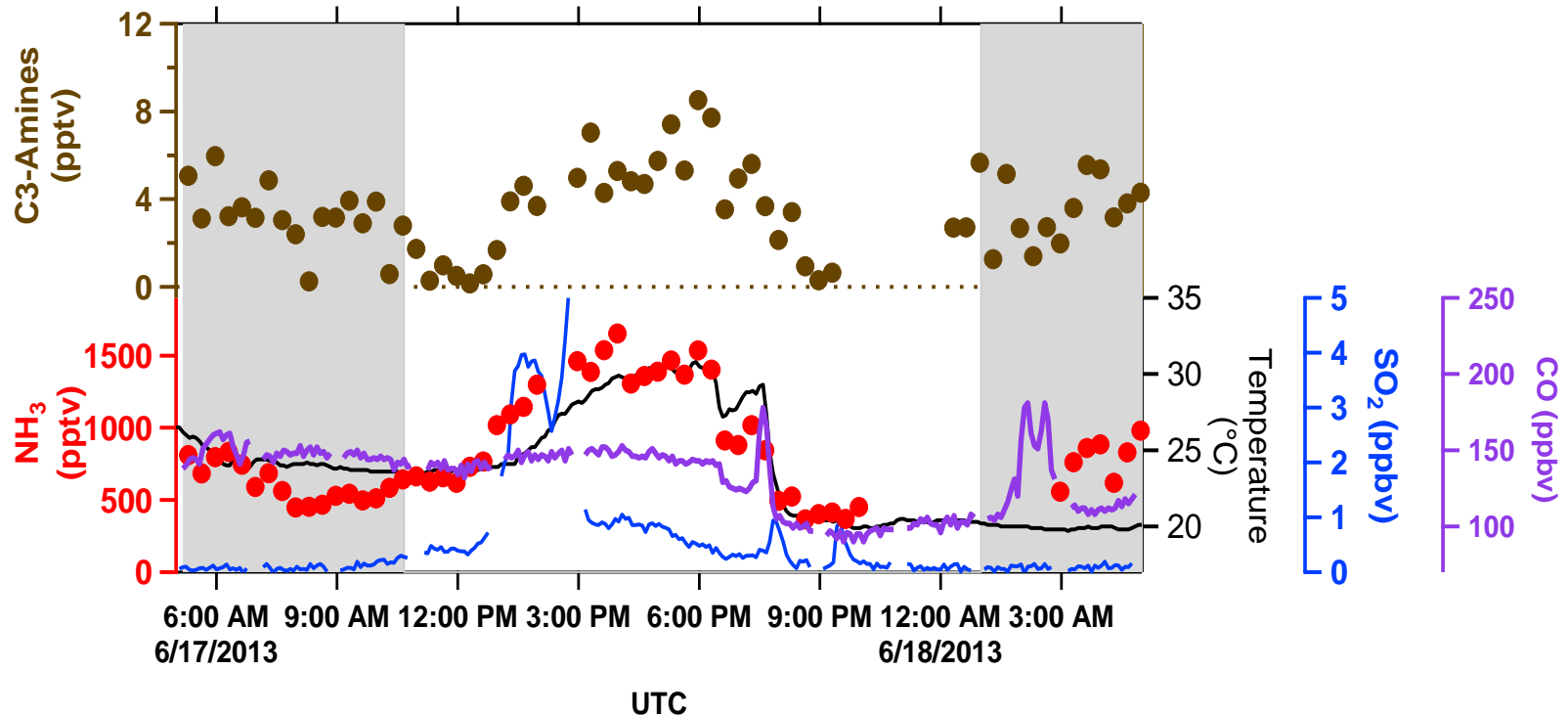
Temperature from ARA

- Trimethylamine shows a similar diurnal trend as NH₃, higher during the afternoon, indicating similar (soil) emission sources of these two base compounds at this site.
- Temperature dependence indicates gas-to-particle conversion processes. Or, reversible processes between deposition and evaporation.

Wind direction dependence of amines for the entire campaign (Wind direction from ARA)



No anthropogenic emissions of amines and ammonia in the Alabama forest

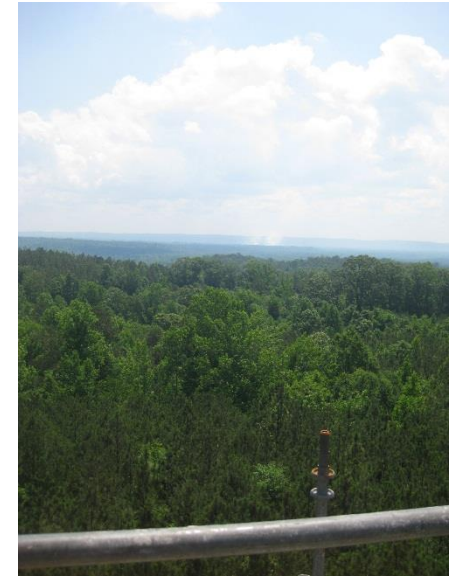
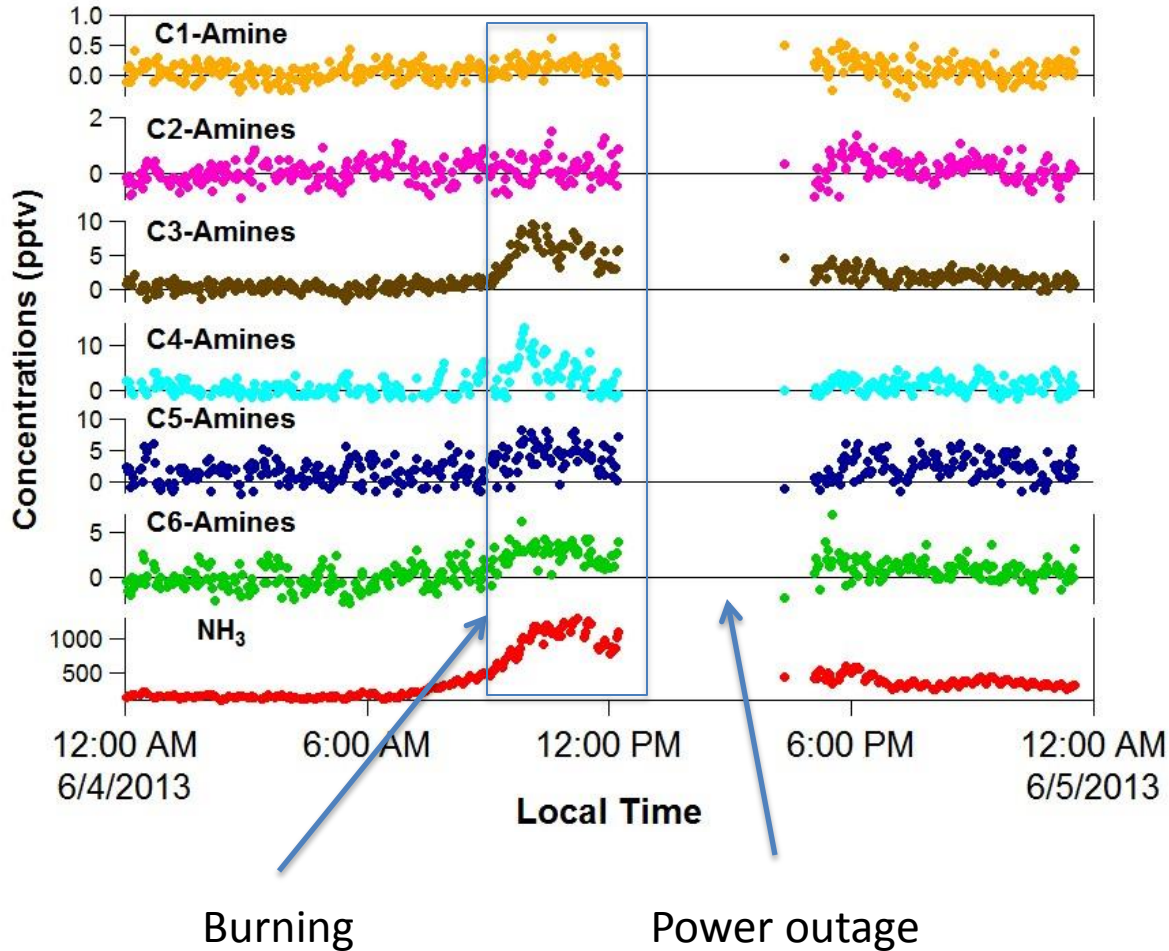


- SO₂ plumes did not affect the measured amines and ammonia.
- CO did not show rush hour dependences and did not affect amines and ammonia.

SO₂, CO and temperature from ARA

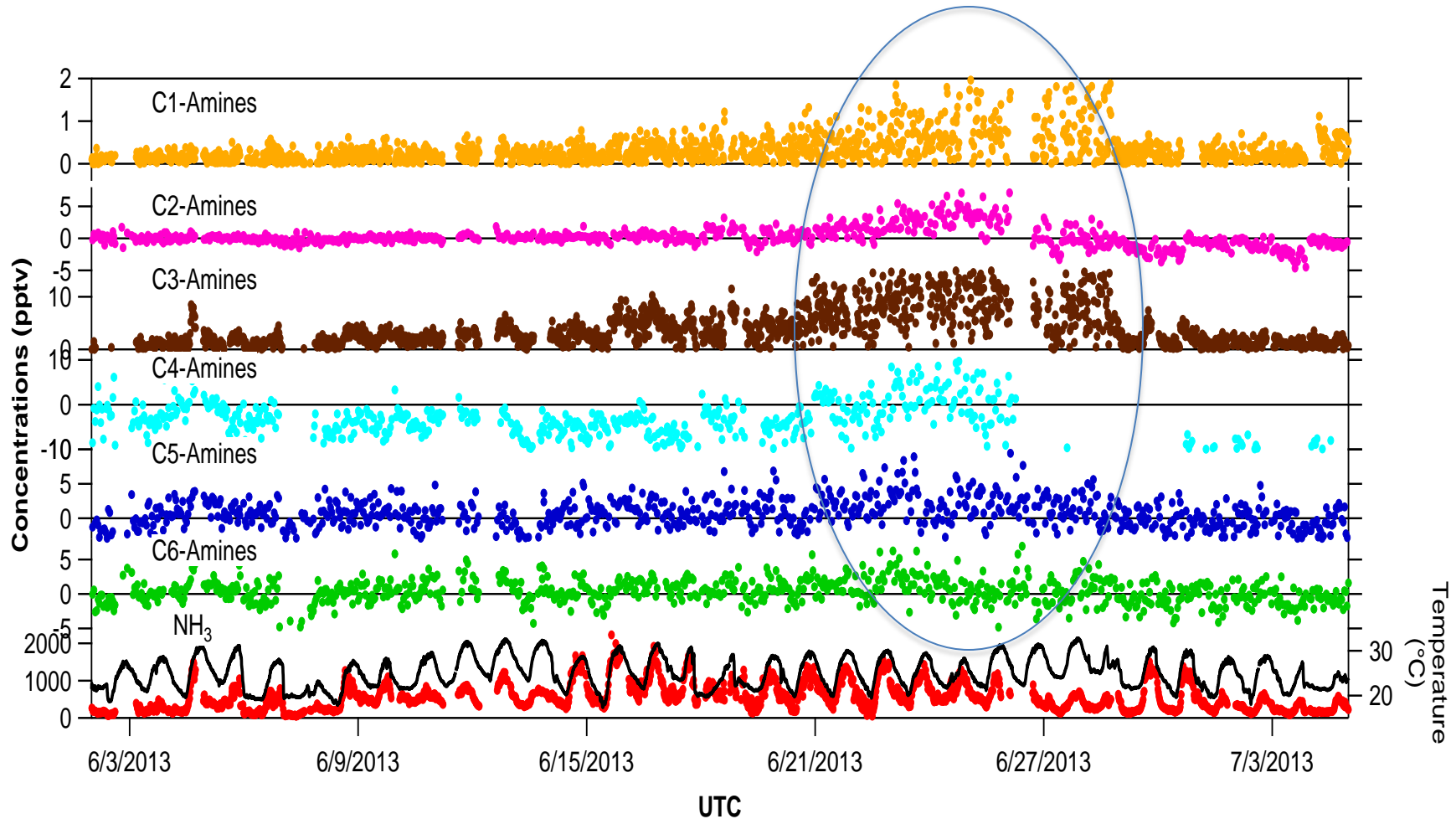
Biomass burning: June 4, 2013

C3- to C6-amines and ammonia are detected



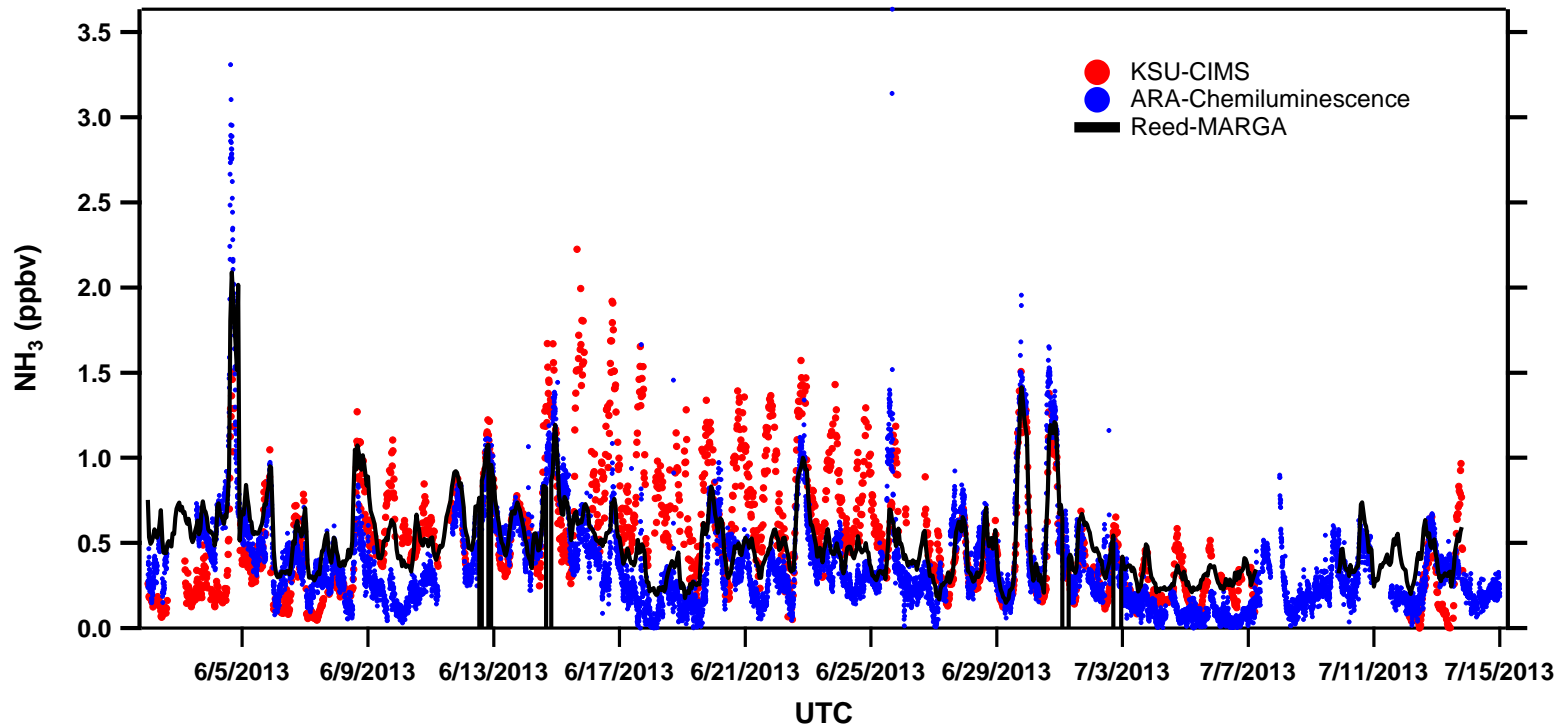
Trash burning by locals, we could see the plume from the tower (white smoke)

Alabama C0...C6 amines and ammonia



- Last week of June, various amines were measured when influenced by biomass burning plumes (high acetonitrile – measured by NOAA CSD, not shown here).

Ammonia inter-comparison at SOAS: KSU CIMS, ARA Chemilunescence, Reed MARGA



- Good agreement in diurnal trends – considering generally extremely poor consistencies between different ammonia instruments reported in literatures.
- High confidence for ammonia measurements.

Amines in the Alabama Forest

➤ **Low concentrations of amines are due to:**

(1) Wet deposition – due to high solubility (10-160 M/atm) and high RH;

(2) Dry deposition under conditions with high aerosol loading, strong aerosol acidity ($\text{pH} < 3$) and high aerosol water contents (GTI Hongyu Guo's poster);

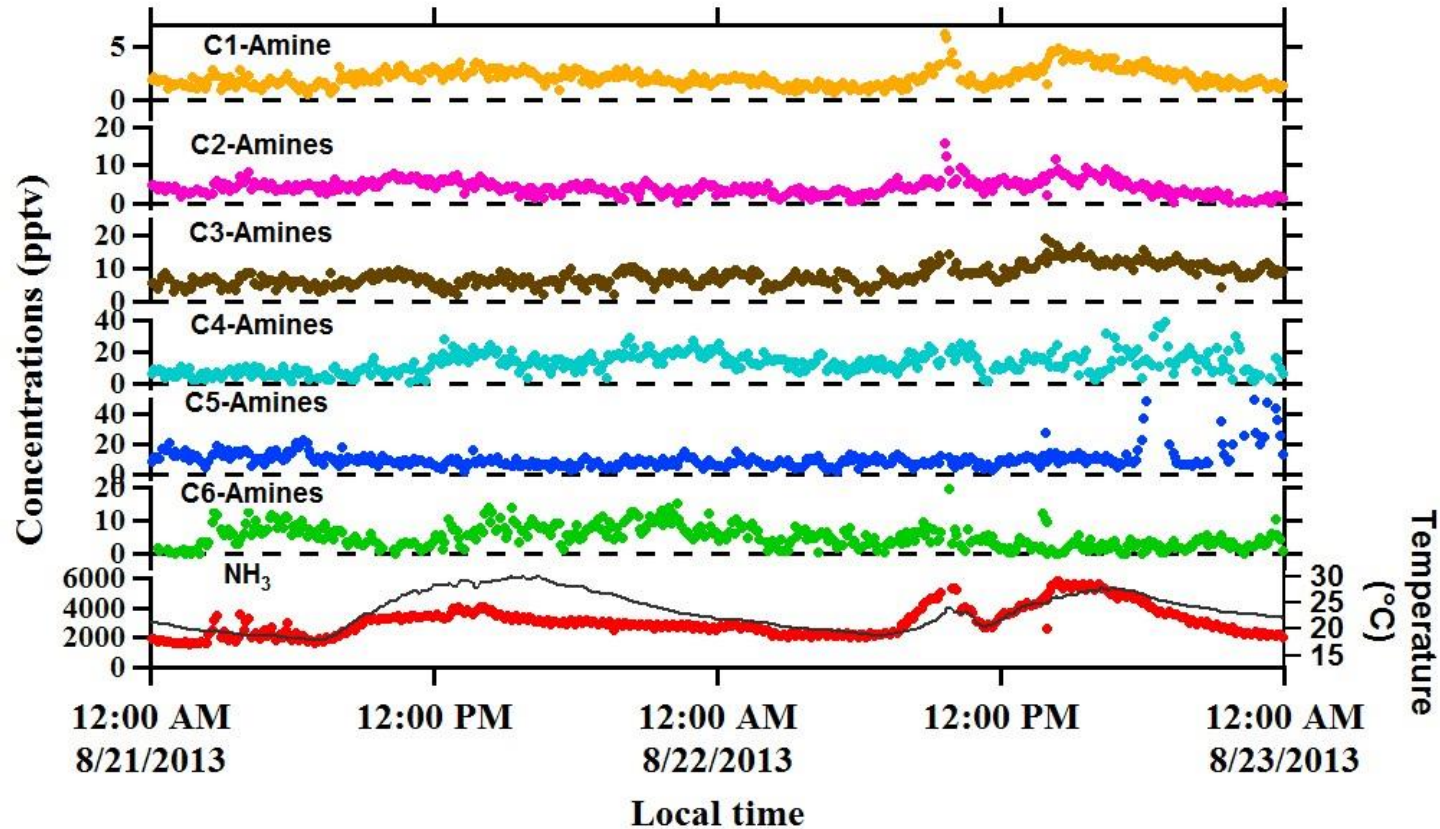
(3) Photodegradation under high OH and ozone concentrations (lifetime several hours only).

Outlook:

Develop a box model that is constrained by the atmospheric measurements, to identify the emission sources, sink, photochemical and heterogeneous reaction processes of amines and ammonia.

August 21-23 in Kent

All 6 amines and ammonia were measured at daily base continuously in August and September:
More abundant than in Alabama



- C1- to C3-amines and ammonia follow the ambient temperature.
- C4- to C6-amines may be from some local emission sources.

Amines in Alabama and Ohio: Summer 2013

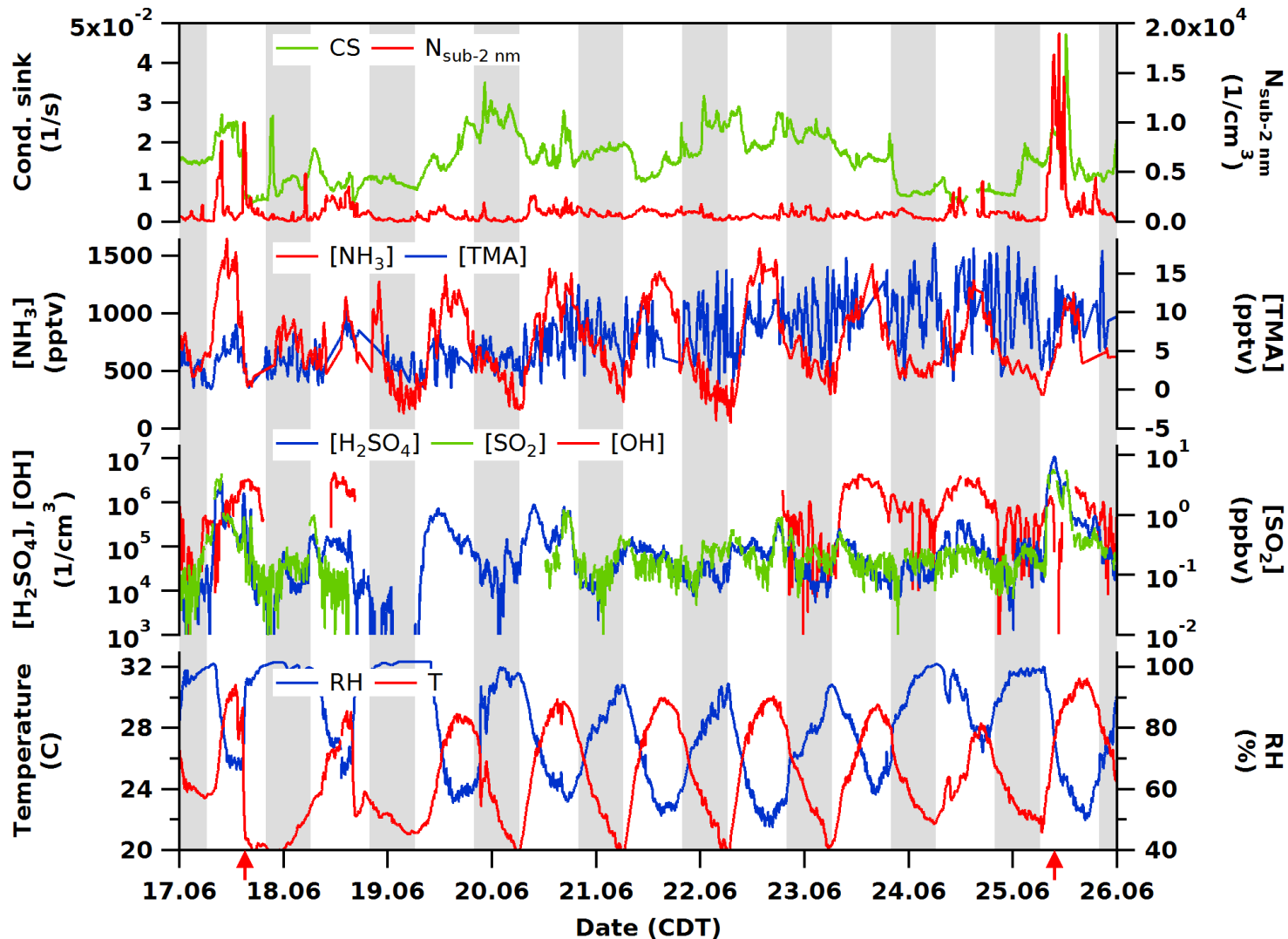
Base Compound	Sensitivity* [Hz/(ppt•MHz)]	Detection Limit (ppt)	Brent, Alabama	Kent, Ohio
NH ₃	13	54	1–2 ppb	1–5 ppb
C1-Amine	12	1	< DL	2-4 ppt
C2-Amines	12	5	< DL	5–10 ppt
C3-Amines	8	5	1-10 ppt	5-10 ppt
C4-Amines	4	23	< DL	10-20 ppt
C5-Amines	2	17	< DL	10-20 ppt
C6-Amines	2	12	< DL	5 ppt

- Higher concentrations of ammonia and amines in Kent indicate that these are emitted from anthropogenic sources (e.g., coal-burning power plants and car exhaust).
- This indicates that urban polluted environments may have abundant amines – regionally and globally important source.

DL = detection limit

Absence of Biogenic New Particle Formation

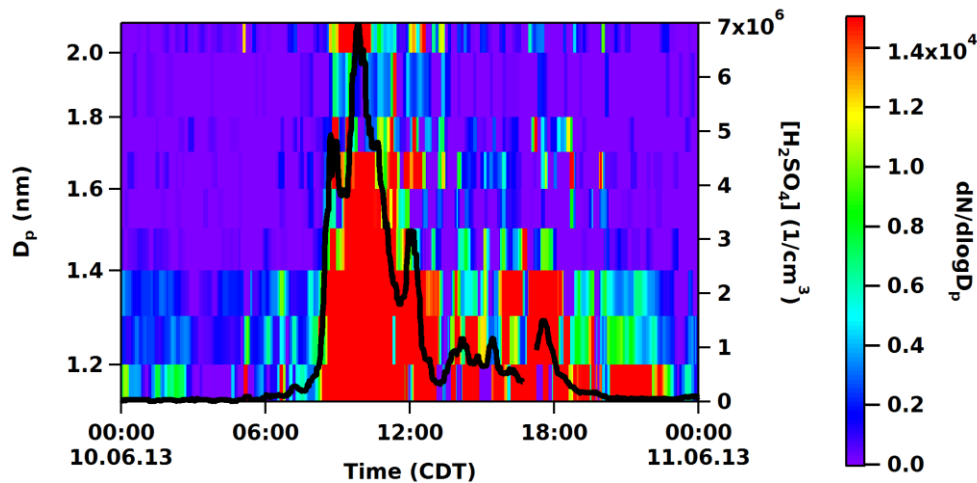
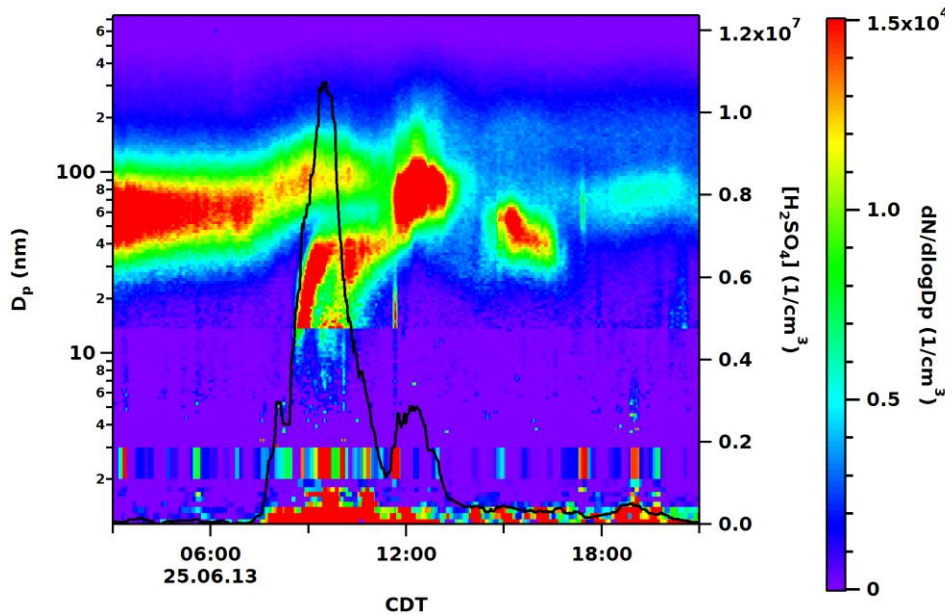
Overview of measurements



OH from Penn State

RH, temperature and SO₂ from ARA

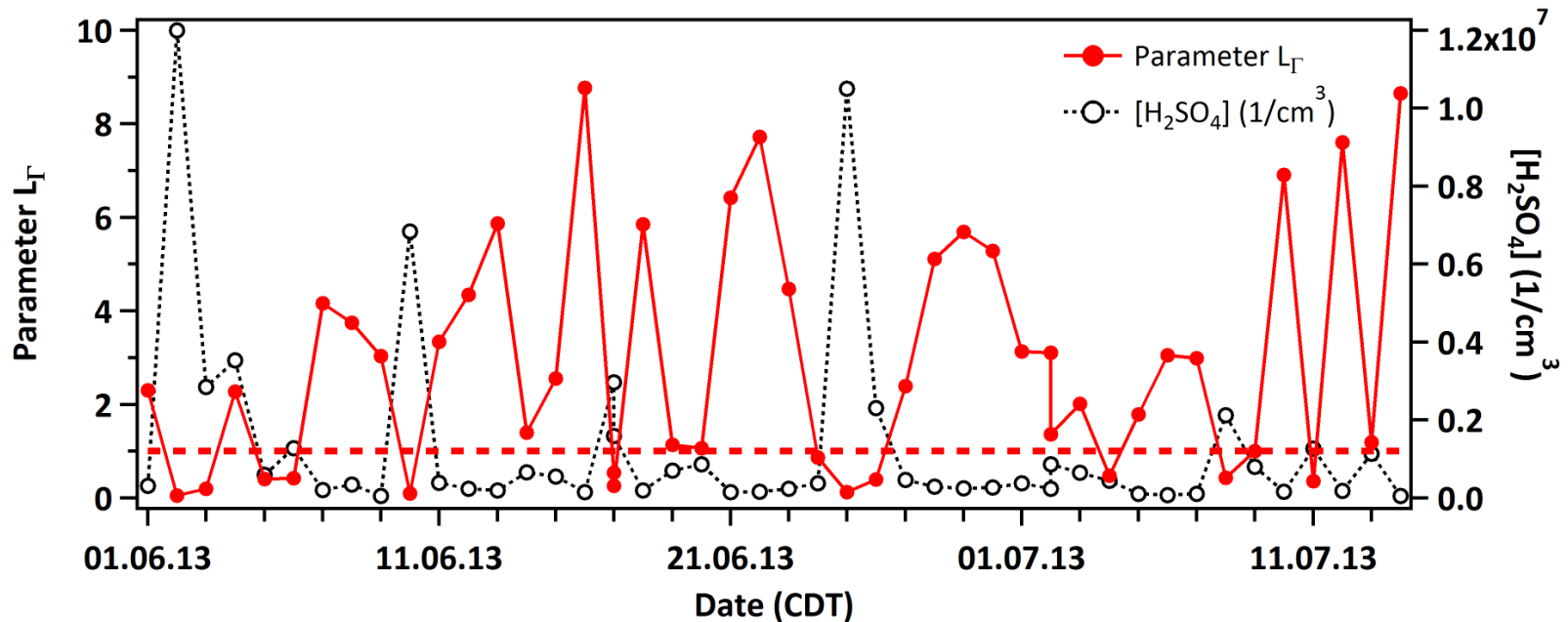
Only two particle growth events: No growth of clusters to > 3 nm



- June 25th
- **No continuous growth 3 nm \rightarrow 8 nm (not an instrument effect)**
- **Not local NPF – long range transport of \sim 8 nm particles**

- June 10th: highest cluster concentration (45000 cm^{-3})
- **Strong correlation between $[H_2SO_4]$ and sub-2 nm particle concentration**
- **No constant pool of sub-2 nm particles (typical background: 200 cm^{-3})**
- **Cluster formation did not lead to new particle formation**

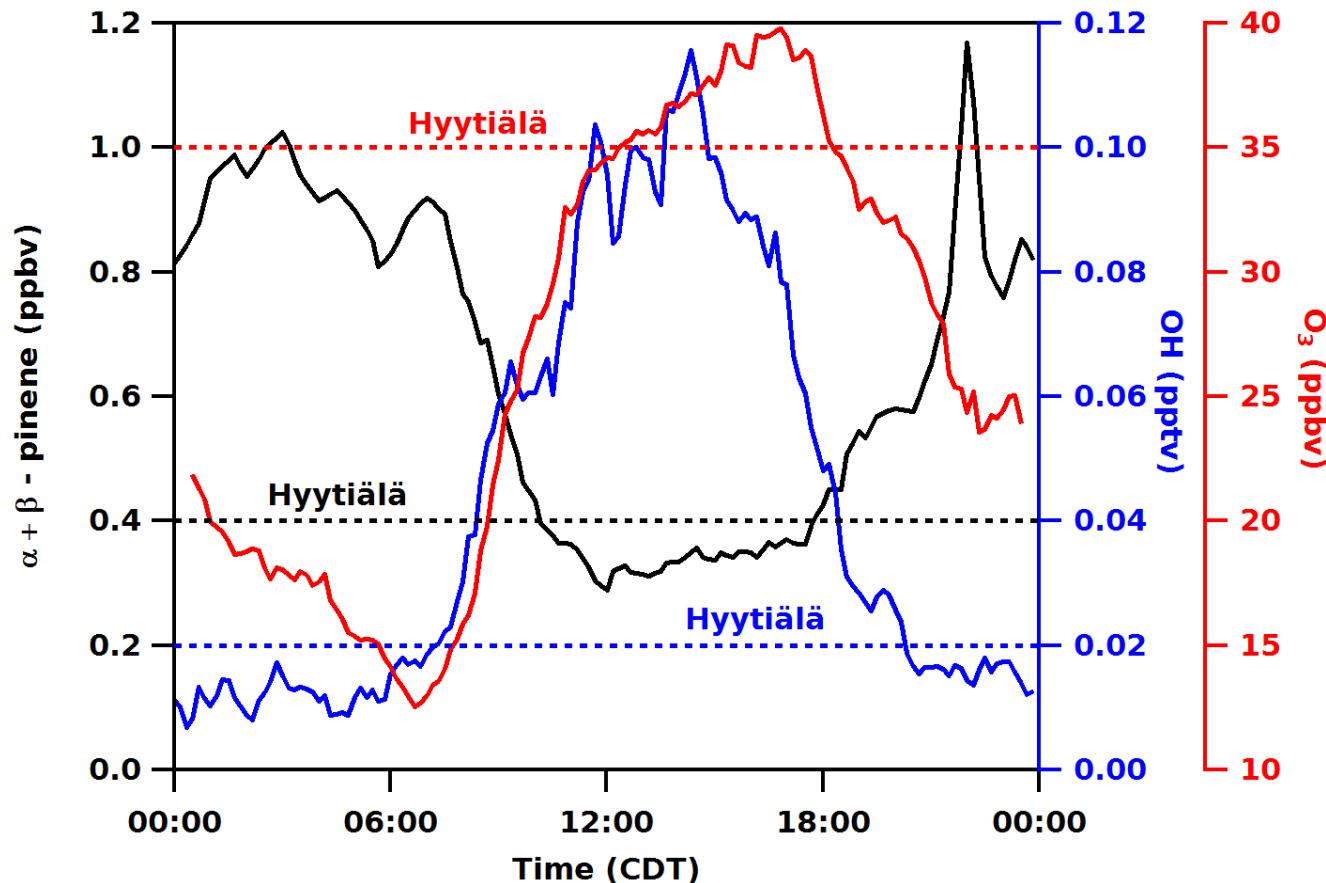
Γ = ratio of condensation sink vs. coagulation growth rate of nucleation species (sulfuric acid and organics)



- For 70% of the period: $\Gamma > 1$, NPF would unlikely occur.
- For 30% of the period: $\Gamma < 1$, NPF should occur.

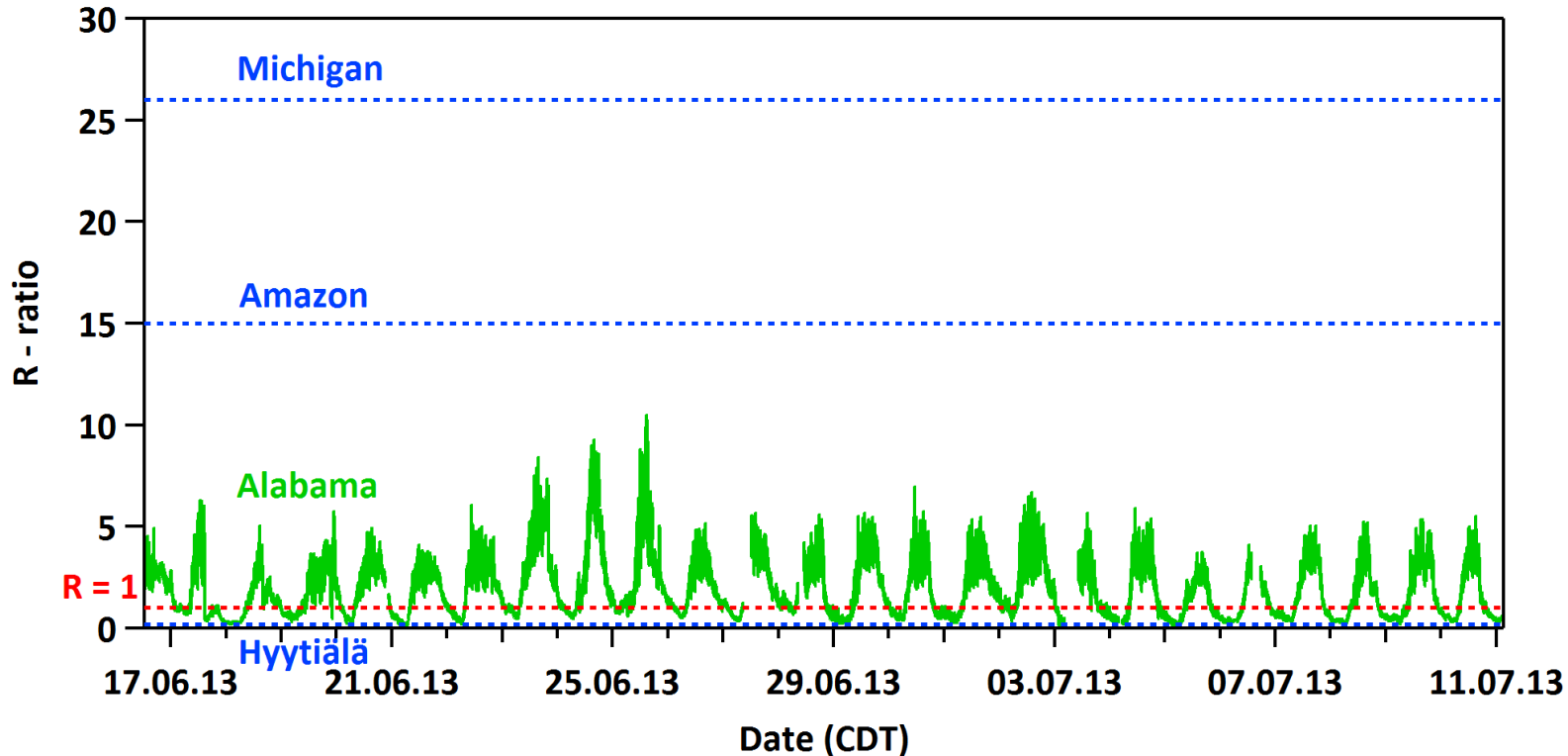
Enough monoterpenes for cluster growth

Data from NOAA



- **MT** (from NOAA) and **OH** (from Penn State) **higher than in Hyytiälä** (Petäjä et al., 2009; Hakola et al., 2012)
- Pinic/pinonic acid: **Alabama 1-70/0.4-20 ng/m³** (by UC Berkley) vs. **Hyytiälä 0.4-20/0.9-70 ng/m³** (Warnke et al., 2006)
- **MT oxidation products** (by Caltech) **at tens pptv range**

The ratio of isoprene and monoterpene carbons – R



- Isoprene in Alabama: **4 - 11 ppbv**, in Hyytiälä: **~0.15** (Hakola et al., 2012)
- **R > 1: NPF suppression range** (Kiendler-Scharr et al., 2009)
- R around 0.2 in Hyytiälä, above 5 in Alabama

Comparison of NPF-related conditions in different forests

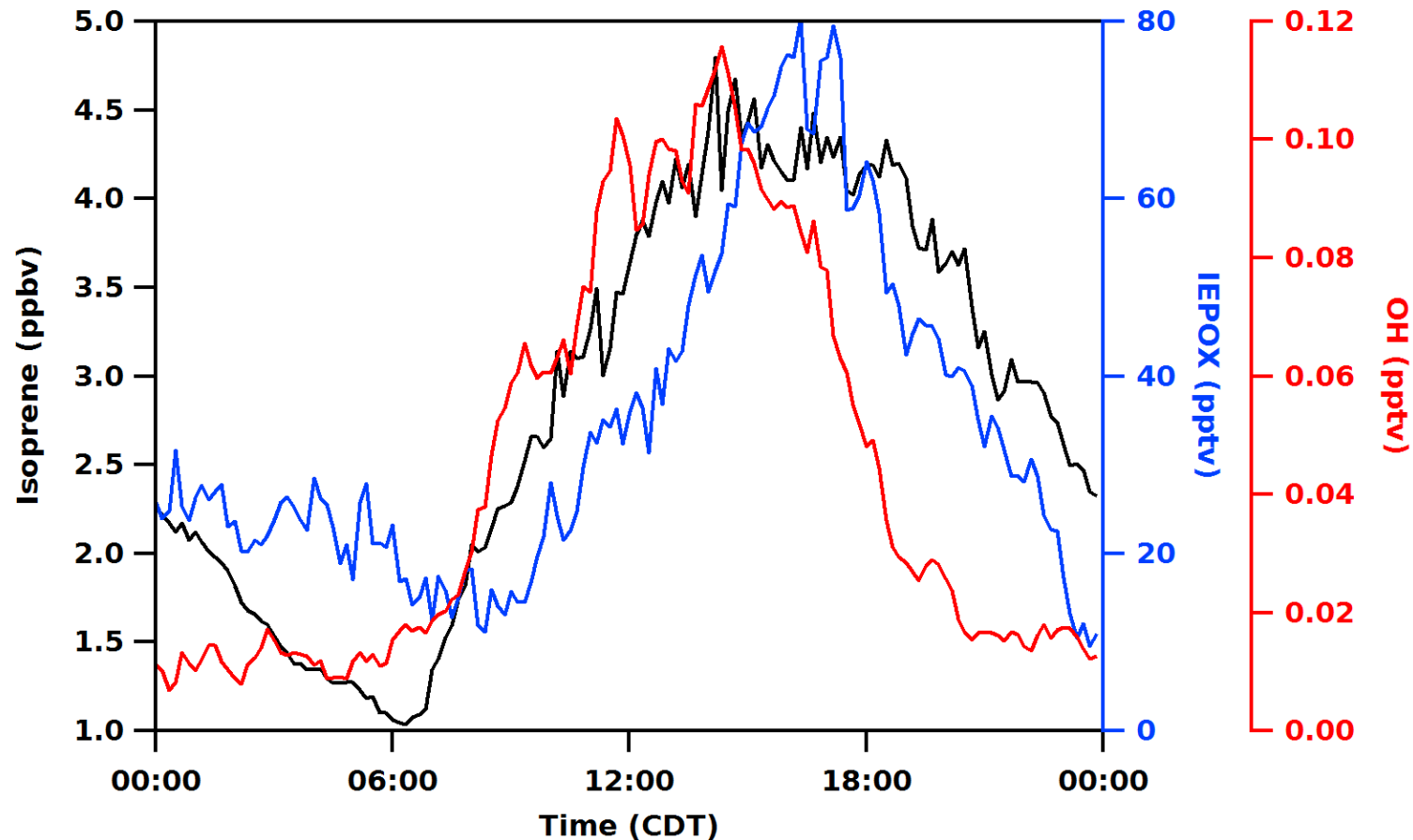
Parameter / Location	No new particle formation			Frequent NPF
	Michigan mixed forest	Amazon rainforest	Alabama mixed forest	Hyytiälä boreal forest
R	26	15	5 - 10	0.2
[OH] (cm ⁻³)	1.5·10 ⁶	5.5·10 ⁶	4·10⁶	5 - 8·10 ⁵
[H ₂ SO ₄] (cm ⁻³)	3·10 ⁶	1 - 5·10 ⁵	1·10⁶	1·10 ⁶
[SO ₂] (ppbv)	0.2 - 4	N/A	0.2 - 9	0.1 - 0.9
CS (s ⁻¹)	0.002	0.9	0.014	0.004
[NH ₃] (ppbv)	1 - 3	0.5 - 1.5	1 - 1.5	0.24
Amines, total (pptv)	N/A	N/A	15	~30 - 90
Temperature (°C)	20 - 25	25 - 30	27 - 33	15 - 20

- Michigan data from Kanawade et al., ACP 2011
- Amazon and Hyytiälä data are from literatures (not shown citations here)
- OH in Alabama from Penn State; SO₂ from ARA

Isoprene suppression of cluster growth

- **Kiendler-Scharr et al., Nature 2009 (chamber study):**
 - OH depletion? – No, OH in Alabama around $2 \times 10^6 \text{ cm}^{-3}$
- **Kanawade, et al., ACP 2010 “Isoprene suppression of biogenic NPF in the mixed deciduous forest”:**
 - Absence of nucleation? – No, frequent cluster formation in Alabama
 - **Absence of growth:** isoprene oxidation products (formaldehyde) reacting with monoterpene-produced Criegee intermediate – Maybe not, enough pinic and pinonic acid and MT oxidation products in Alabama
 - **Absence of growth:** isoprene oxidation products (formic acid) competing with pinic/pinonic acids in clustering with H_2SO_4 – under investigation
- **Surratt et al., PNAS 2010; Lin et al., PNAS 2013**
 - IEPOX – maybe important for growth of acidic clusters

No contribution to NPF by IEPOX (IEPOX from Caltech)



- IEPOX were more likely condensed on pre-existing particles in Alabama, rather than nucleated?

In conclusion

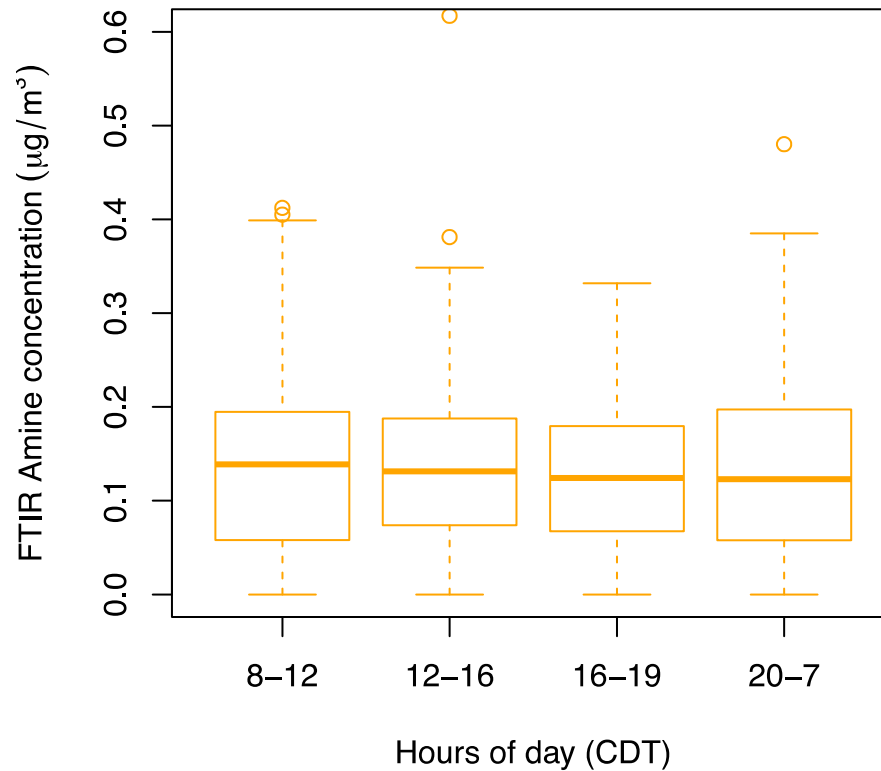
- **Frequent sub-2 nm particle formation in Alabama.** Strongly correlated with sulfuric acid concentration.
- **No persistent presence of sub-2 nm particles during the day and night:** in contrast to results from the boreal forest, Kulmala et al., 2013; but consistent with reports from Kent and Long Island, Yu et al., 2014.
- **No subsequent growth of sub-2 nm particles thus, no NPF:**
 - In parts due to high temperature and condensation sink.
 - Low levels of dimethylamine?
 - Suppression of NPF by high isoprene emission (high R - values), without OH depletion
 - Sufficient MT and MT oxidation products; IEPOX

Amines in the Alabama Forest

- Trimethylamine and ammonia have similar emission sources: they show similar diurnal variations, higher in the afternoon. They show similar temperature and wind direction dependences.
- Temperature dependences also indicate that amine and ammonia are in the thermodynamic equilibrium between gas and aerosol phases.
- There is also reversible process between deposition and evaporation from soil surfaces.
- Biomass burning can be an important source of amines in the Southeastern U.S.
- **Low concentrations of amines are perhaps due to:**
 - (1) Wet deposition – due to high solubility (10-160 M/atm) and high RH;
 - (2) Dry deposition under conditions with high aerosol loading, strong aerosol acidity ($\text{pH} < 3$) and high aerosol water contents (GTI Hongyu Guo's poster);
 - (3) Photodegradation under high OH and ozone concentrations (lifetime several hours only).

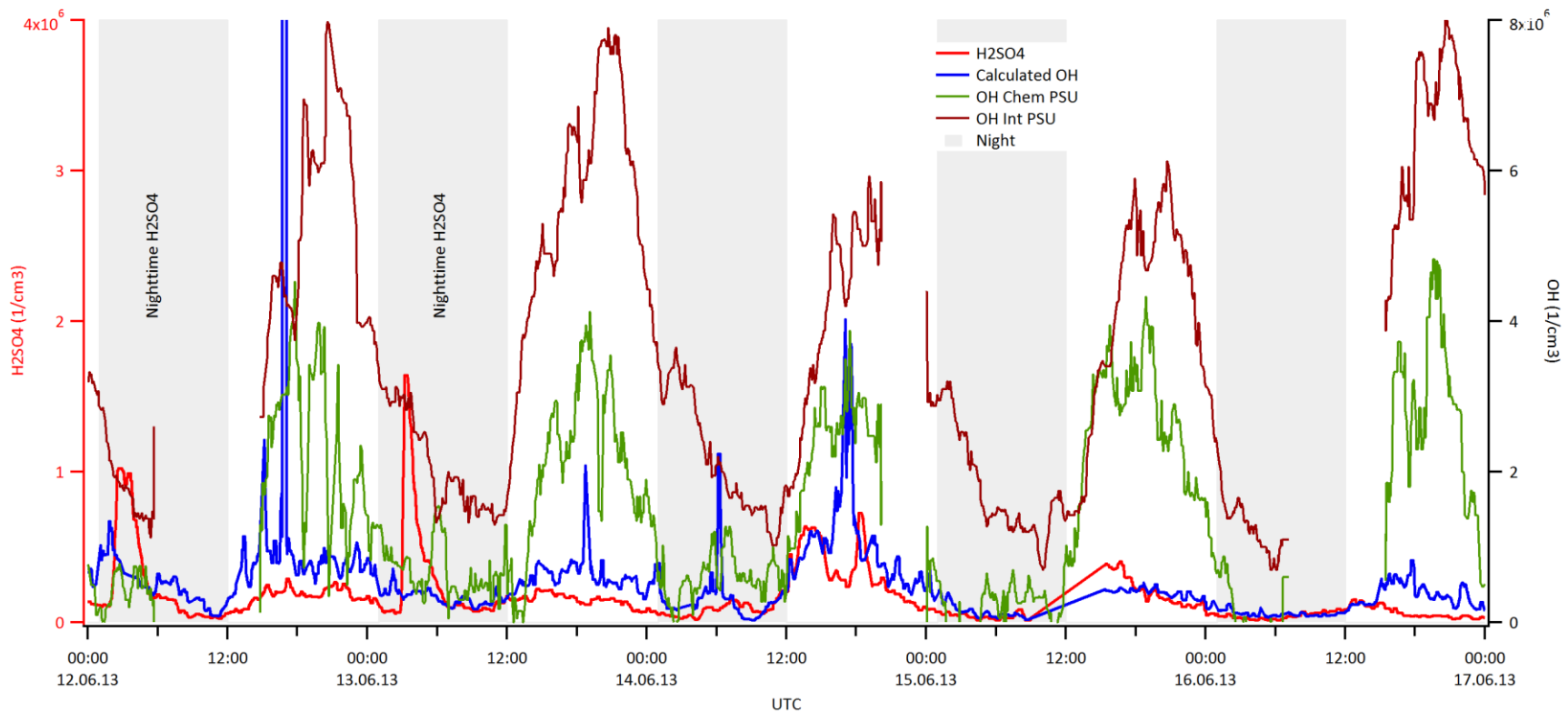
Particle amines by FT-IR

(Satoshi Takahama and Giulia Ruggeri, EPFL)



- Opposite diurnal variations of gas phase and droplets amines: Gas to particle conversion processes.

Nighttime H_2SO_4 formation under high SO_2

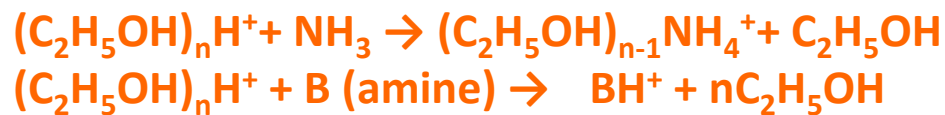


OH from Penn State

Importance of measuring atmospheric amines

- Amines and ammonia play critical roles in new particle formation, via acid-base reactions at the initial stage of aerosol nucleation.
- Important for secondary organic aerosol (SOA) formation, via formation of salts and condensation of amine photo-oxidation products.
- Contribute to the formation of brown organic aerosols.
- Change the acidity and the physical state of aerosols to further affect biogenic SOA yields.
- Amines are currently used to capture atmospheric CO₂ – a new pollution source for amines.
- Amine photochemical reactions produce nitrosamines, nitramines, and isocyanic acid: carcinogens.

Amine/ammonia CIMS



Yu and Lee, Environ. Chem., 2012

