Emission, Fate, and Contribution of Biogenic Volatile Organic Compounds to Organic Aerosol Formation in the Presence of Anthropogenic Pollution: Measurements and Modeling during SOAS

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Big science with small aircraft

- Small aircraft typically cruise at lower airspeeds (80-150 knots).

- More maneuverable; can also target the same airspace (e.g., same cloud penetration).

- Order(s) of magnitude less expensive to operate.

- Flexible, albeit limited, payloads and missions.

- Typical max payload (Dutchess, Cozy IV): 350#

- Similar micromet observations available (e.g., 3-D wind measurement at 20Hz)

Turbulence probe

Stony Brook team: Luping Su, Alicia Mullaley, Lani Kai Ritter, Kim Lamont, Fred Wimberley (relief pilot; photographer)

Using the Long EZ aircraft, we measured the vertical distribution of VOCs above the forest canopy at the AABC site and the SEARCH site. 39 flights between June 1 and June 14 using the Whole Air Sample Profiler (WASP) (Mak et al., 2013)

Purdue University Airborne Laboratory for Atmospheric Research

ALAR

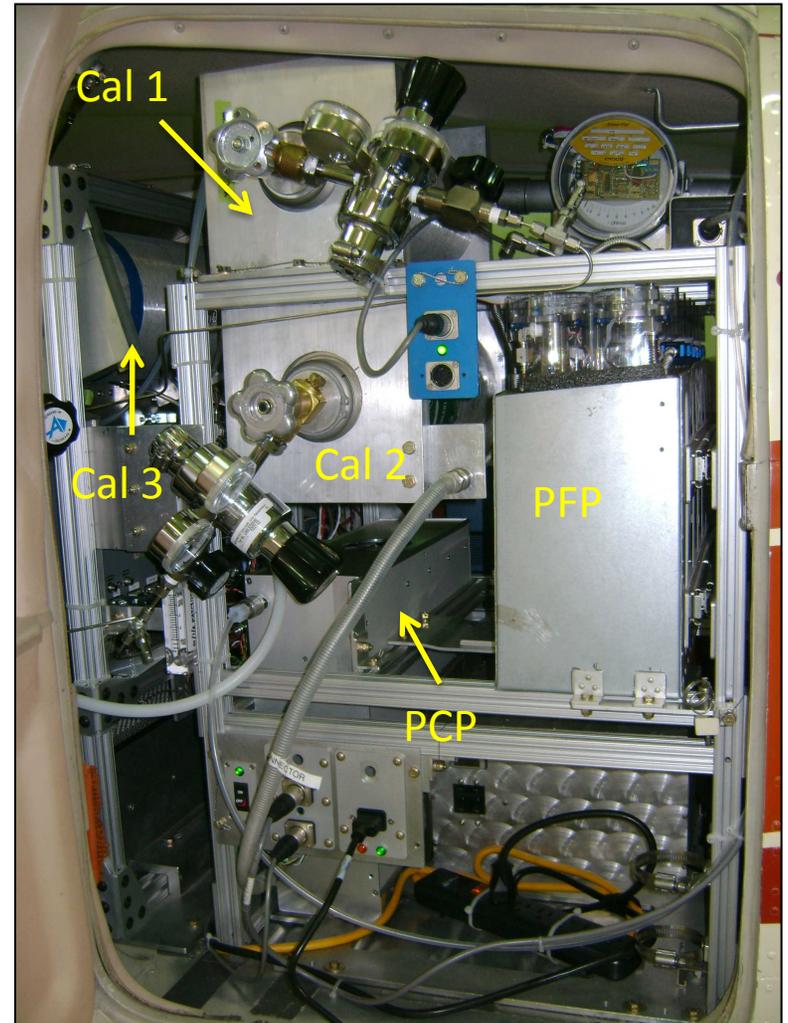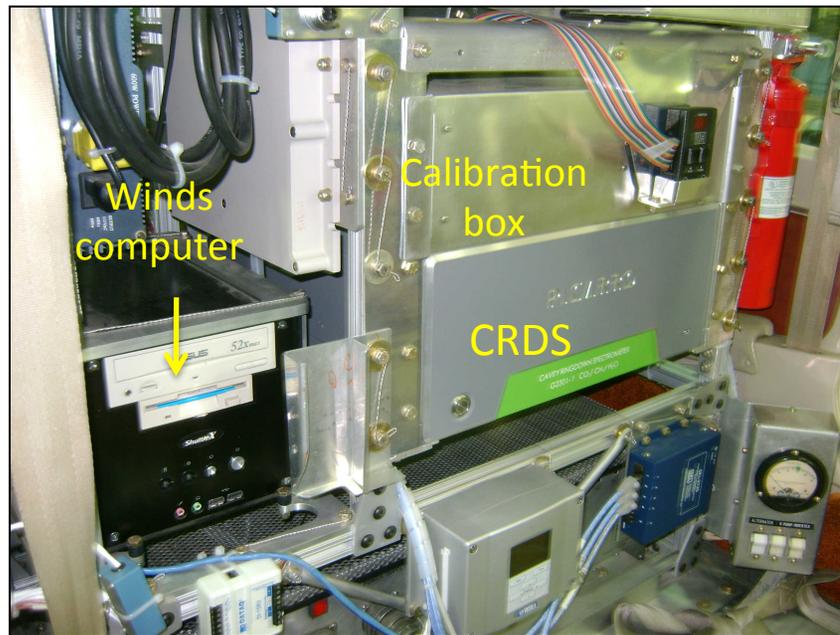**SOAS Sampling Collaboration:** Paul Shepson (Purdue) & Kerri Pratt (Michigan)
Pilot: Paul Shepson (Purdue University)
Aircraft Speed: ~140 knots (160 mph, 72 m/s)

2013 SOAS Flight Days: June 10, 11, 13, 26, 28, 29
Flight Altitude: ~0-3.5 km agl

Experimental Details – Typical Deployment

CO$_2$ and CH$_4$ measurements with +/- 0.05% uncertainty using cavity ring down spectroscopy (Picarro) and 3 NOAA standard cylinders

Turbulence probe
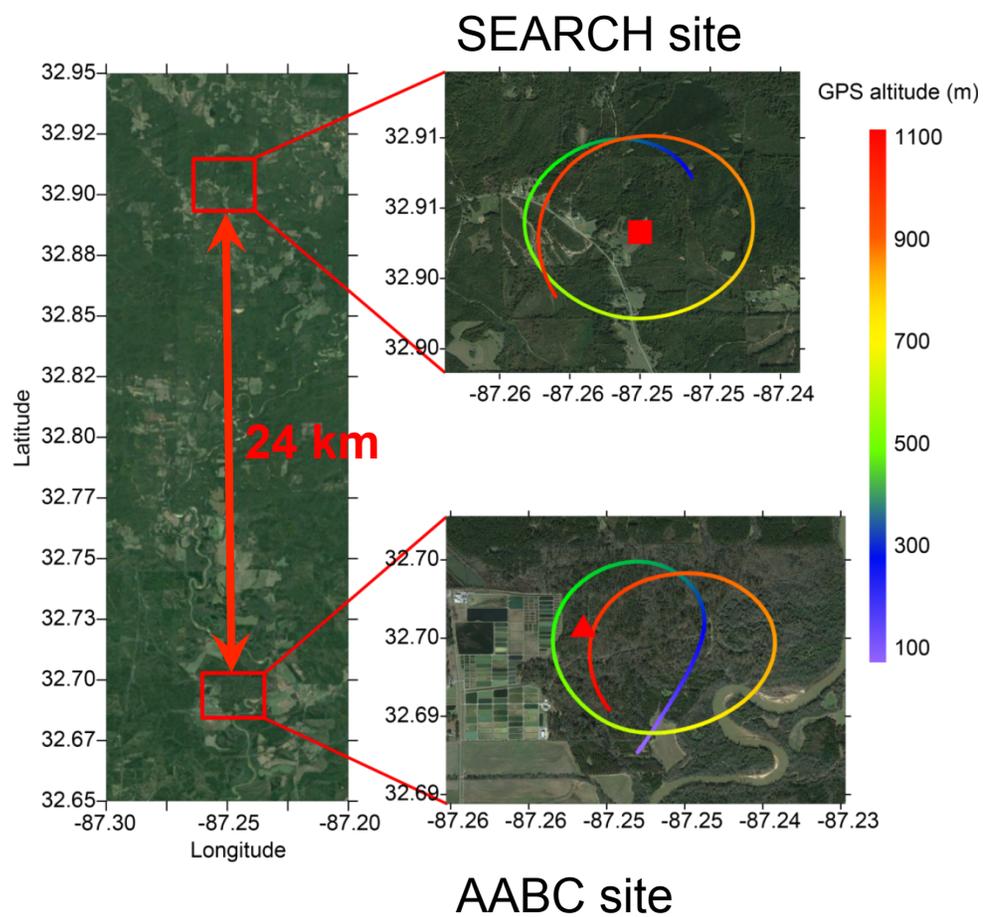
SOAS: *added* O$_3$, Aerosol, & Cloud Water

Cloud water collector:

- O$_3$ (2B Technol.)

- Modified 3-stage rotating DRUM impactor, collecting 0.07-2.5 µm particles (Bateman et al. 2009, Phys. Chem. Chem. Phys.)

- Mohnen slotted-rod cloud water collector for cloud droplets > 5.5 µm (Huebert et al. 1988, *J. Atmos. Chem*.)

2 Sampling sites

Flight tracks of Long-EZ aircraft


SEARCH site

AABC site

Photos from Pawel K. Misztal

Vertical profiling of OVOCs

- What happens, chemically and dynamically, above the forest floor/within the forest canopy? To what degree are VOCs oxidized in situ, or are they transported outside of the canopy?

- WASP collection and susbsequent HR-PTRTOFMS analysis allow for high resolution (~3m), fast (~2 minute) vertical profiling of VOCs from above the forest canopy to the top of the CBL(or close to it).
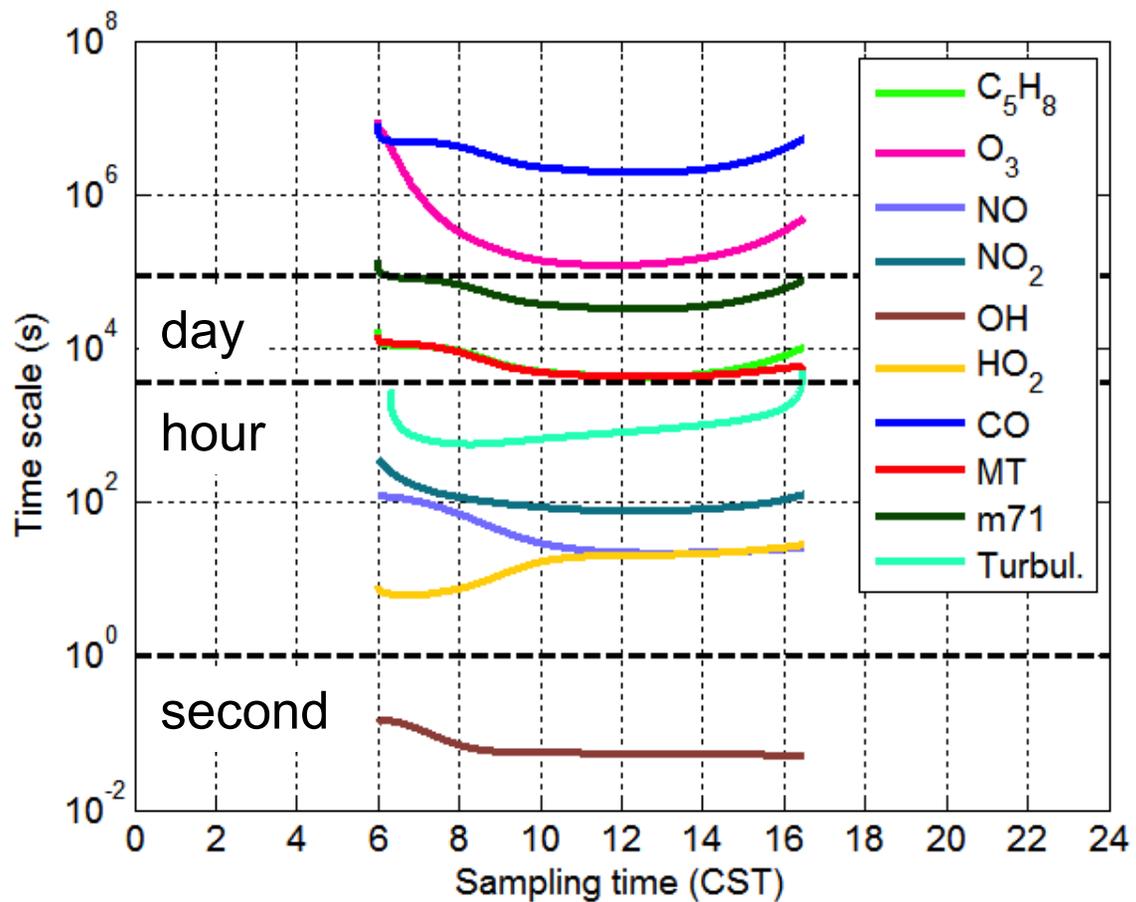
Chemistry versus dynamics (MXLCH).Time scales of selected chemical species and the time scale of turbulence mixing. 'm71' indicates MVK +MACR. Turbul. indicates turbulence.
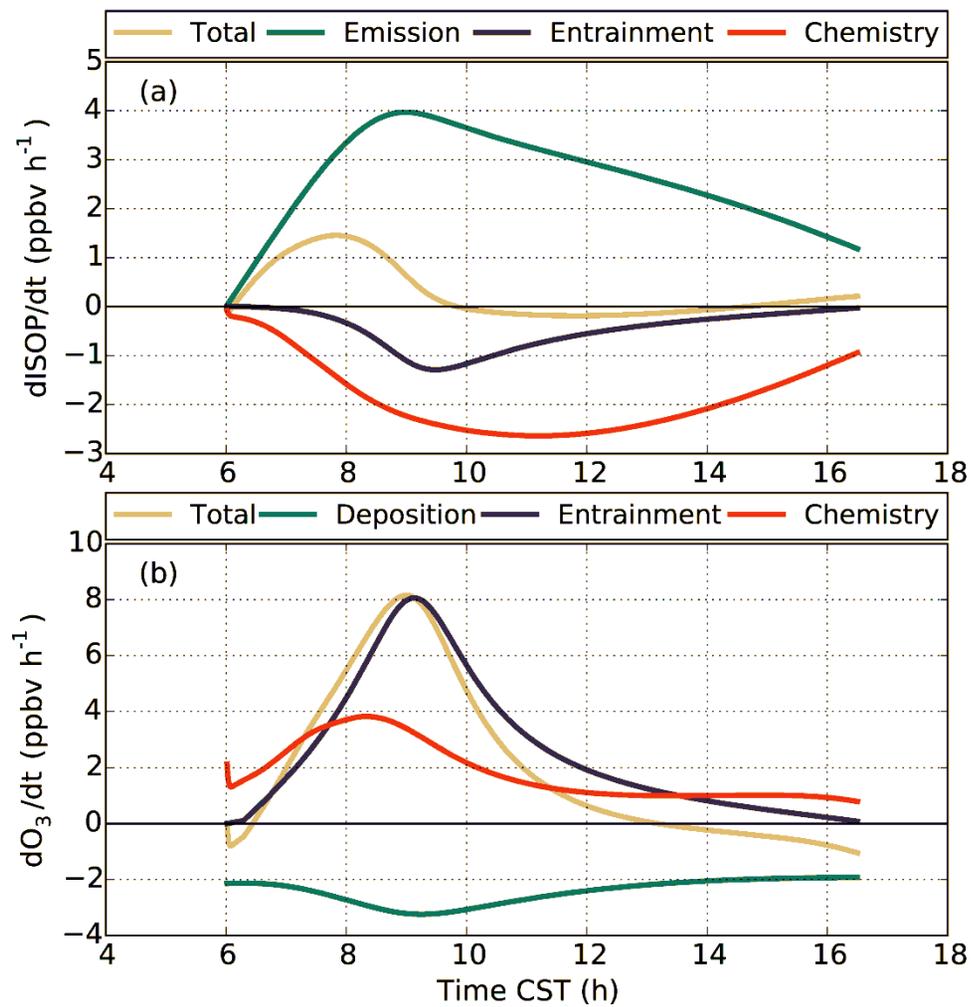
Contribution of dynamics and chemistry to the budgets of (a) isoprene, (b) ozone.

Data Collection (Stony Brook)

- We collected vertical profiles during 5 separate time bins: 8-10am, 10-12, 12-2, 2-4, 4-6pm using the WASP. Samples were analyzed with our HR-PTR-TOFMS, which was located at the AABC site.

- We then looked at representative composites of daytime evolution of vertical profiles.

- We found the diurnal vertical profile structure to be quite similar from day to day (all days were sunny with relatively low winds).

- In addition to vertical profiling we were measuring concentrations and EC fluxes of VOCs at AABC site.

3. Results: diurnal variation of VOCs profiles
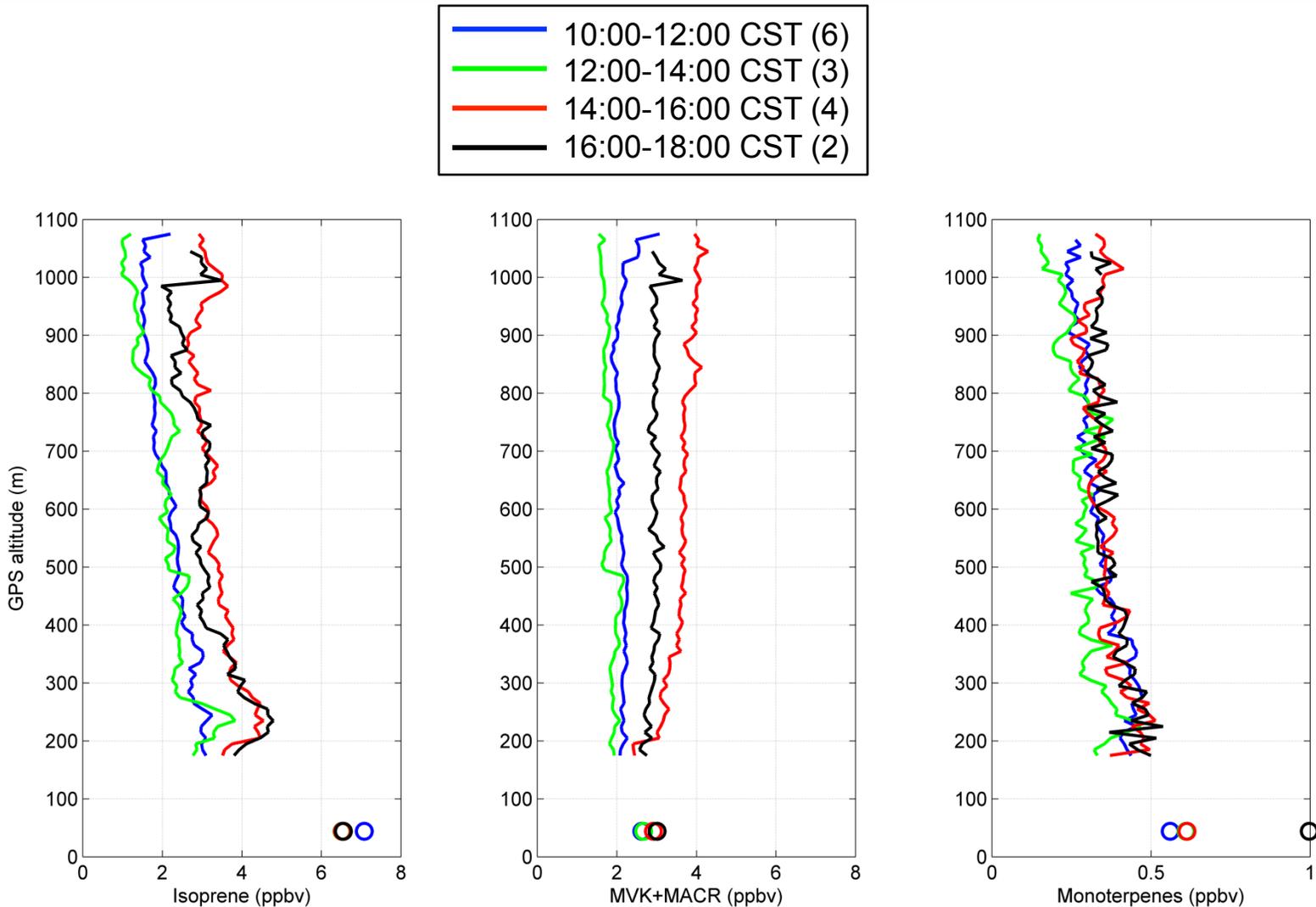
Each solid line is average of all the vertical profiles which fall within the time bin. Each open circle represents the ground measurements at the AABC site during the same time period. Numbers in the parenthesis of the legend indicate the number of RF which fall within this time bin.

5.1 VOC vertical profiles from WASP system
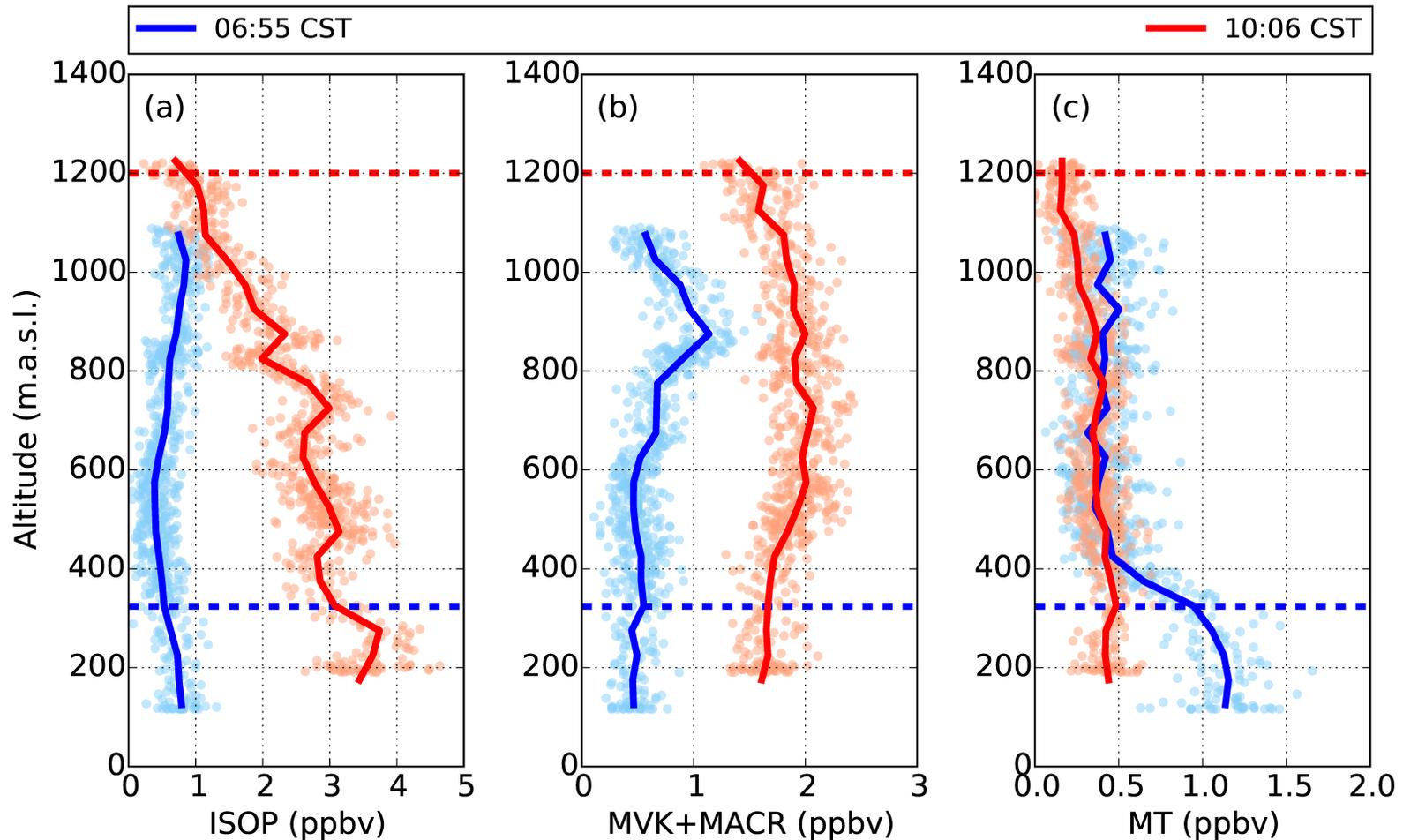
Before sunrise, isoprene and MVK+MACR exhibit lower mixing ratios (< 1.00 ppbv) within and above the CBL. Monoterpenes have a large contrast in mixing ratios within and above the CBL in early morning. During sunlit noontime, observed vertical profiles of isoprene and monoterpenes reveal a vertical gradient within the CBL, with higher mixing ratios near the forest canopy and low values towards the top of the CBL.

4 Model simulation

A MiXed Layer CHemistry (MXLCH) model (J. Vila, E. Patton) is used to reproduce the dynamics/chemistry during the SAS campaign.

- Observations from days with low cloud coverage (June 5, 6, 8, 10-13) are averaged and used to guide the model initial conditions;

- Surface heat flux and VOC flux are prescribed based on observations;

- The model is coupled to a new isoprene scheme, which includes recently updated isoprene chemistry.

https://github.com/classmodel/mxlch
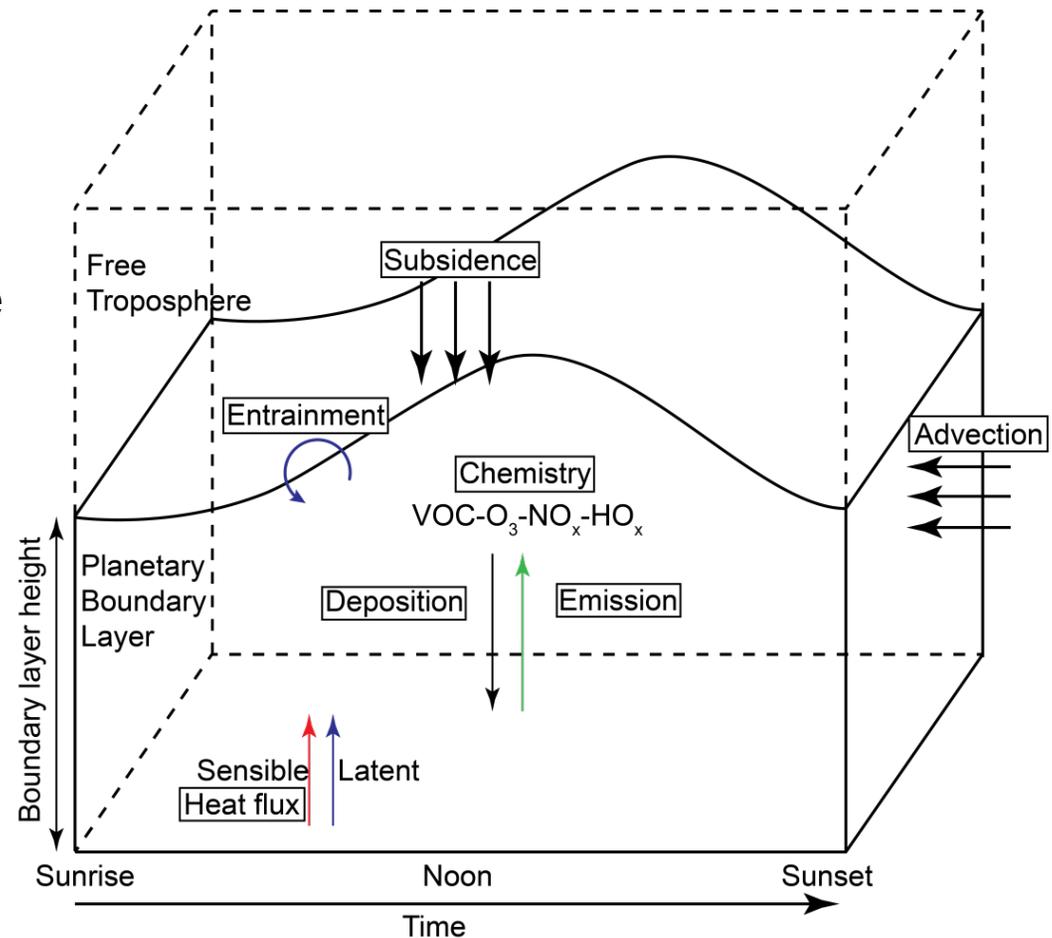
3 Observations

| Parameter	Platform	Instrument	Days used	Institute
VOC	Airborne (Long-EZ)	Whole Air Sample Profiler (WASP) system, Proton Transfer Reaction Time of Flight Mass Spectrometer (PTR-TOF-MS)	June 5, 6, 8, 10-13	Stony Brook University
VOC	Airborne (C130)	Proton Transfer Reaction Mass Spectrometer (PTR-MS)	06/12, 06/14	NCAR, NOAA
VOC flux	AABC tower	PTR-TOF-MS, Sonic anemometer	June 5, 6, 8, 10-13	Stony Brook University, NCAR
O_3, NO_x	Airborne (C130)	chemiluminescence instrument	June 5, 6, 8, 10-13	NCAR
O_3, NO_x	SEARCH tower	ThermoScientific 49i, 42i	June 5, 6, 8, 10-13	ARA
HO_x	SEARCH tower	LIF	June 5, 6, 8, 10-13	Pennsylvania State University
Surface heat flux	AABC tower	Integrated Surface Flux System (ISFS)	June 5, 6, 8, 10-13	NCAR
Potential temperature specific humidity	AABC tower	ISFS	June 5, 6, 8, 10-13	NCAR
Potential temperature specific humidity	Airborne (C130)	onboard sensor	06/12, 06/14	NCAR
Boundary layer height	SEARCH	Ceilometer, sounding	June 5, 6, 8, 10-13	ARA, NCAR

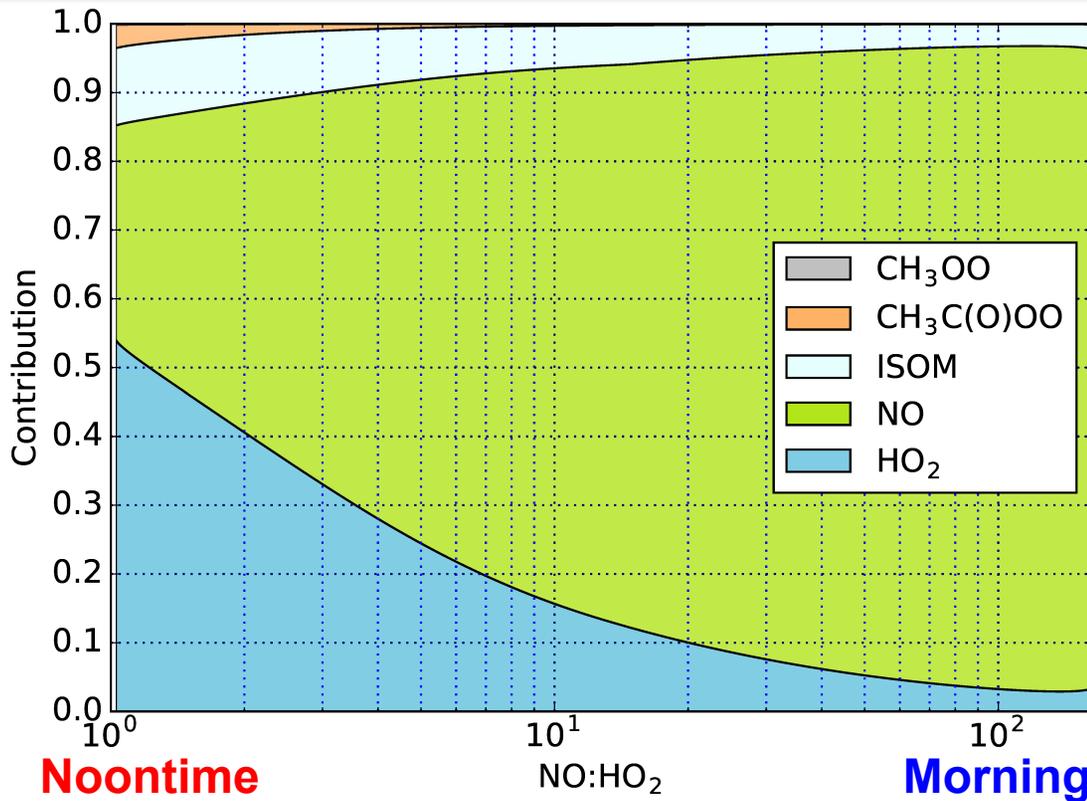# 5.2 Model outputs vs. observations
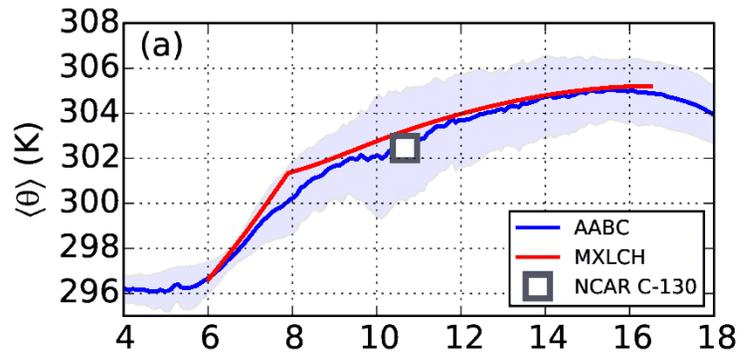
MXLCH is able to reproduce the boundary layer dynamics (potential temperature, specific humidity, boundary layer height) during the sunlit daytime.
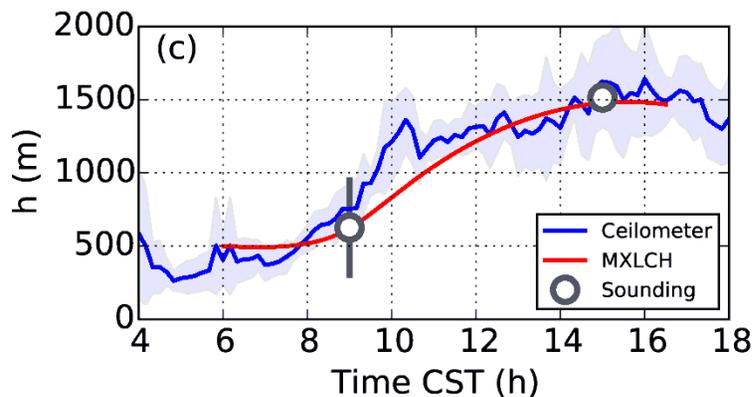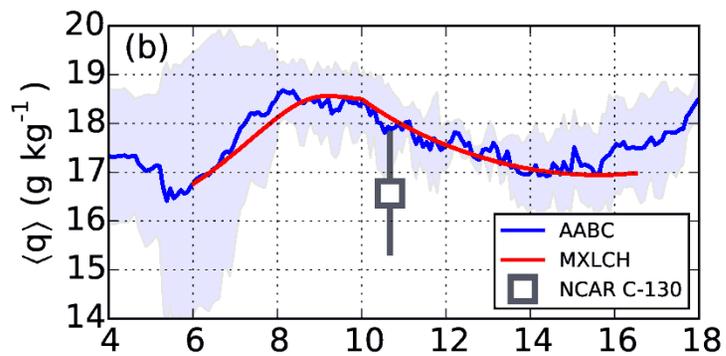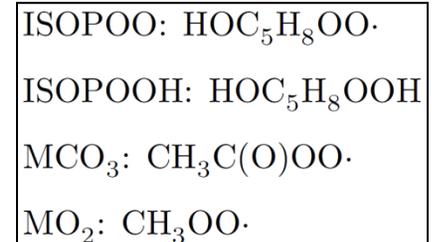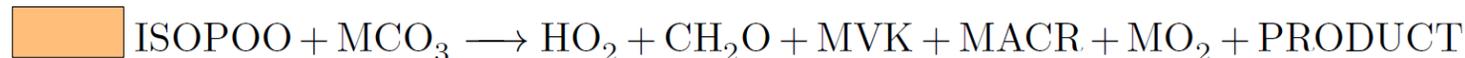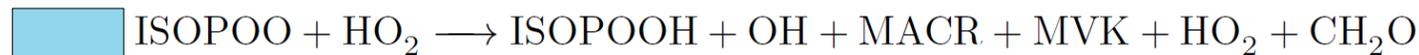
5.2 Model outputs vs. observations
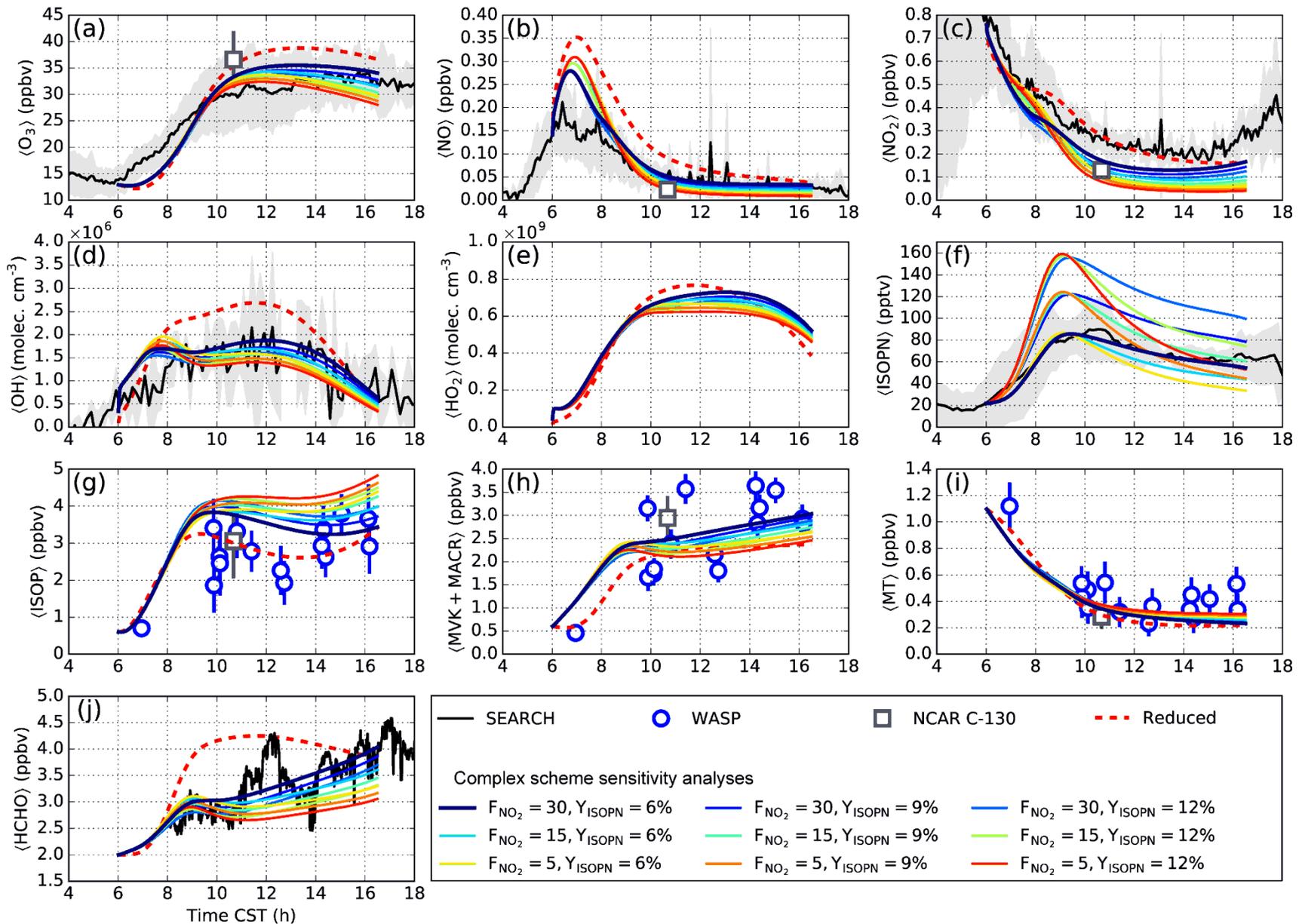
5.4 Fate of ISOPOO radicals under different NO:HO$_2$

HO_2 pathway contributes to 1% of ISOPOO loss in early morning (NO:HO_2 = 163), and gradually increases to 54% during noontime (NO:HO_2 = 1);

Similar results shown in chamber and model simulation under NO:HO_2 = 32.5 (Liu *et al.*, 2013).

Noontime   NO:HO$_2$ **Morning**

ISOPOO + HO$_2$ $\longrightarrow$ ISOPOOH + OH + MACR + MVK + HO$_2$ + CH$_2$O

ISOPOO + NO $\longrightarrow$ NO$_2$ + CH$_2$O + MVK + MACR + PRODUCT

ISOPOO $\xrightarrow{isomerisation}$ HO$_2$ + CH$_2$O + OH + PRODUCT

ISOPOO + MCO$_3$ $\longrightarrow$ HO$_2$ + CH$_2$O + MVK + MACR + MO$_2$ + PRODUCT

ISOPOO + MO$_2$ $\longrightarrow$ HO$_2$ + CH$_2$O + MVK + MACR + PRODUCT

ISOPOO: HOC$_5$H$_8$OO·
ISOPOOH: HOC$_5$H$_8$OOH
MCO$_3$: CH$_3$C(O)OO·
MO$_2$: CH$_3$OO·

5.5 Variation of VOCs under different NO:HO$_2$
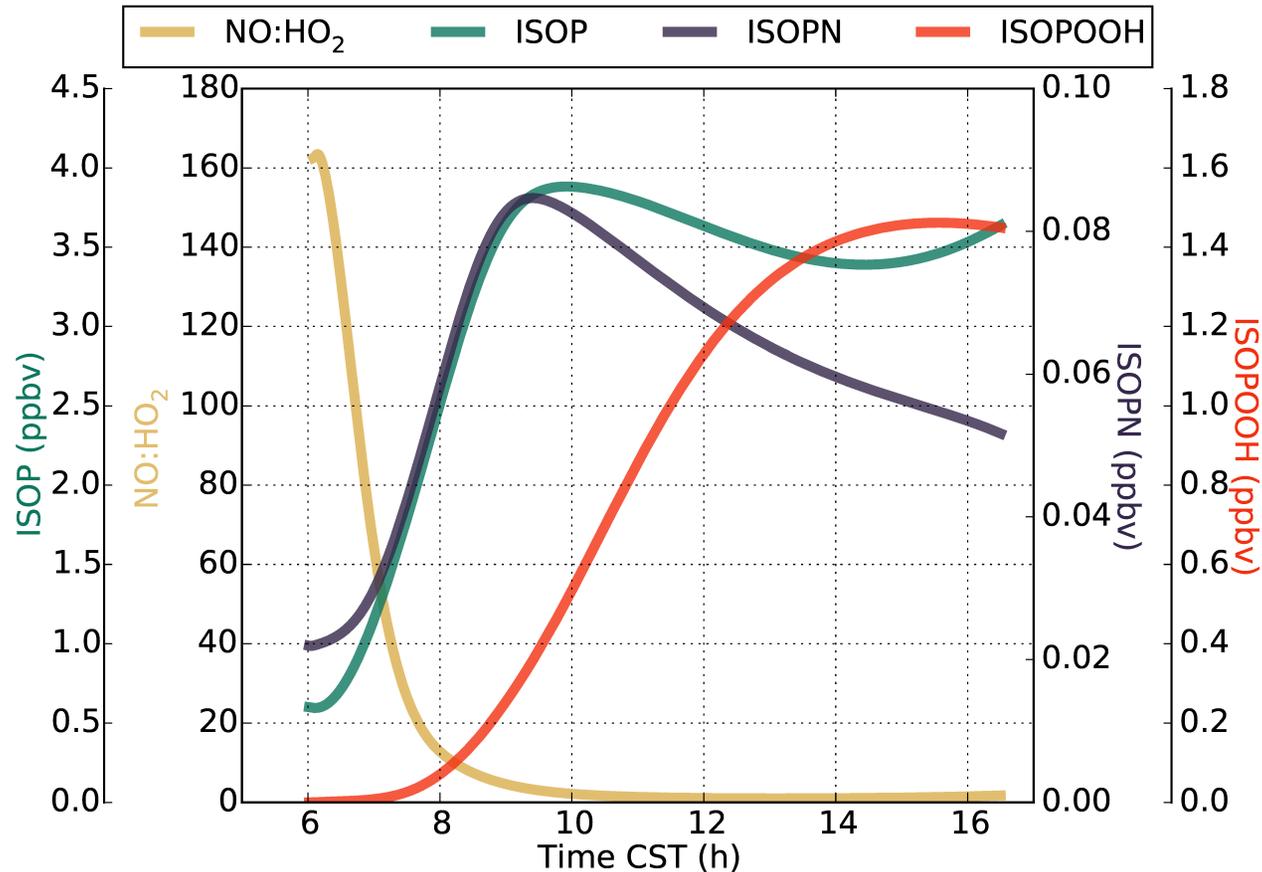
ISOPN production is constrained by isoprene before 09:00 CST. The mixing ratio of ISOPN decreases after 09:00 CST due to its short lifetime (2 h) and limited NO availability. ISOPOOH is inversely correlated with NO:HO$_2$. Model outputs significantly overestimate ISOPOOH mixing ratios in the late afternoon when comparing with ground-based observation (0.40 ppbv), with implications for missing sinks of ISOPOOH.

4. Conclusions

- Isoprene chemistry is strongly influenced by $NO:HO_2$. This is reflected through the fate of ISOPOO radicals, which shifts from NO-dominant (93%) to $NO-HO_2$-balanced (54%) condition from early morning ($NO:HO_2 = 163$) to noontime ($NO:HO_2 = 1$).

- Airborne and ground-based VOC measurements combined with simple mixed layer chemistry model (coupled to updated isoprene scheme) enable better interpretation of the evolution of chemical species inside convective PBL.

The Bidirectional Exchange of VOCs between a Mixed Forest and the Atmosphere in the Southeast US

Pawel Misztal and Allen Goldstein, UC Berkeley, leads

Acknowledgements

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Oxidation of organics
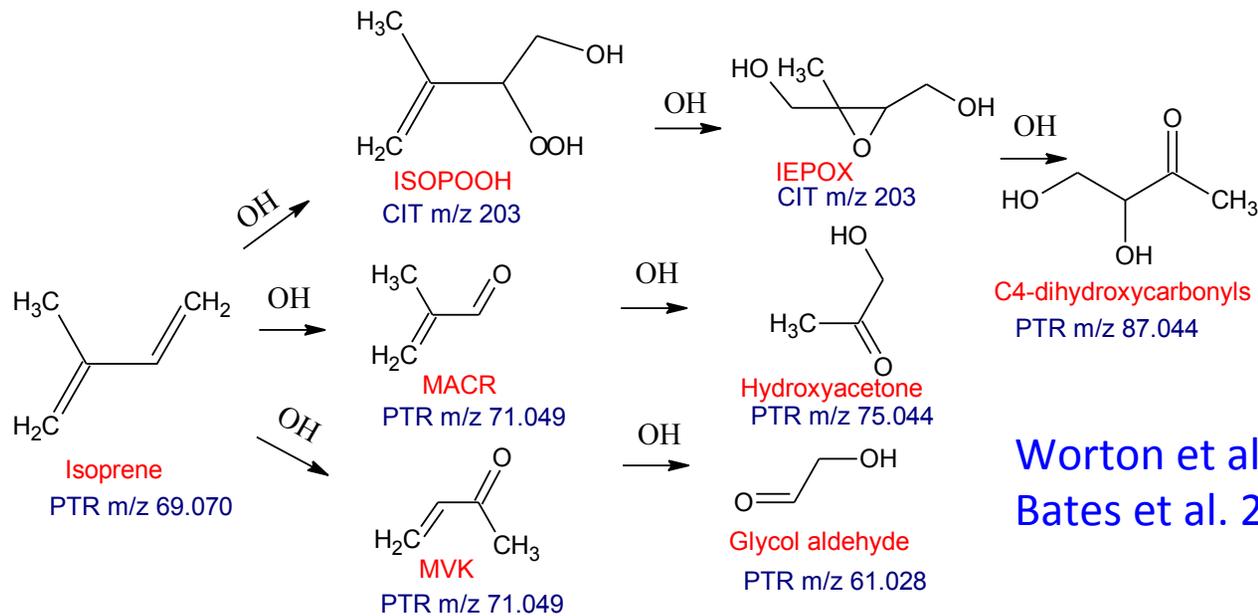
Different yields of oxidation products depending on the hydroperoxide or NO/NO2 oxidation channel which occur simultaneously at different proportions changing diurnally.
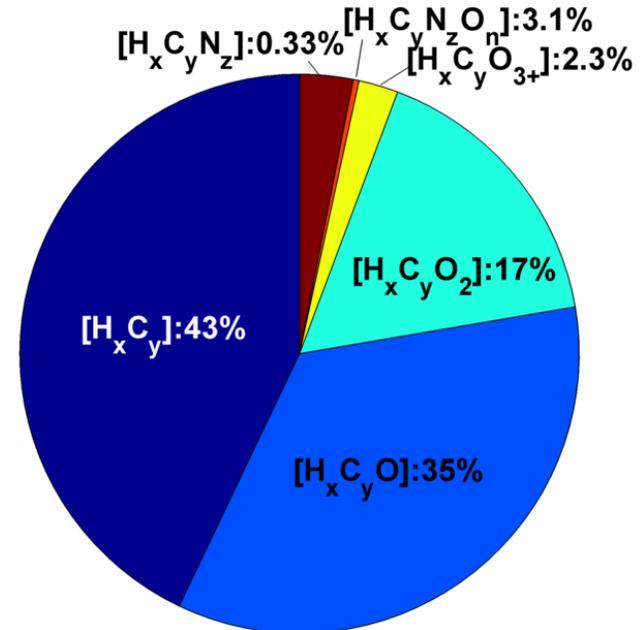
Conversions of peroxides/epoxides to carbonyls observed in instrument in the lab but not characterized in the field (long inlet, relatively low concentration of ISOPOOH).
(Liu et al. IGAC 2014; Rivera-Rios et al. 2014)

VOC oxidation products at SOAS SEARCH

SOAS

O:C Ratio vs mz

Ox State SOAS

Avg Oxidation State vs Number of Carbons
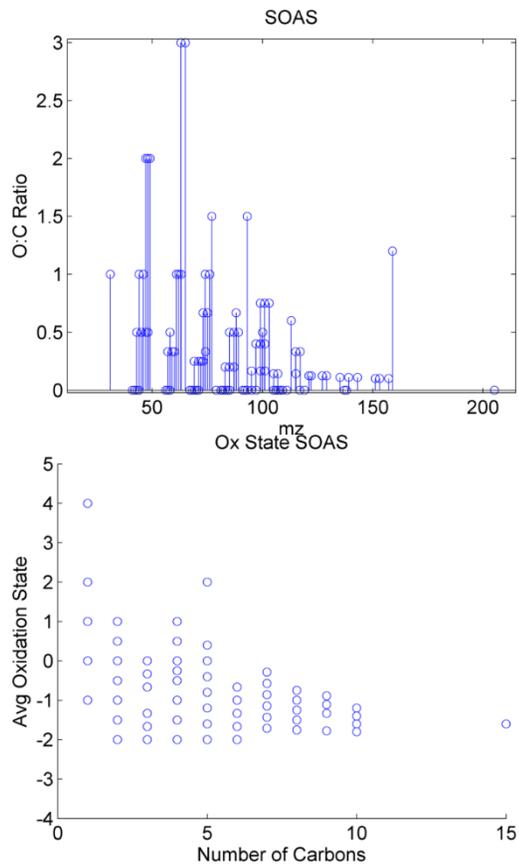
Mass Concentration VOCs at SOAS-SEARCH

$[H_xC_yN_z]$:0.33% $[H_xC_yN_zO_n]$:3.1%
$[H_xC_yO_{3+}]$:2.3%
$[H_xC_yO_2]$:17%
$[H_xC_y]$:43%
$[H_xC_yO]$:35%

Concentration in the field were significantly lower than in the chamber (FIXCIT). Pure hydrocarbons were dominated by isoprene then monoterpenes, while hydrocarbons containing oxygen were dominated by both primary compounds (mainly methanol, acetone and acetaldehyde) and isoprene and monoterpene oxidation products. Line losses of stickier semi-volatile compounds can be responsible for relatively small fraction of O_{2+} (or greater than 2) compounds actually being observed.

Eddy covariance flux methods used at SEARCH

$$F = \overline{w' \, c'}$$

Two independent flux methods:

1. **Fast Fourier Transform (FFT)** – was used to provide conventional fluxes averaged over 30 minutes. Typically ~40% of data are removed due to non-stationarity (Fares et al., 2013)

$$S_a(f) = \int_{-\infty}^{\infty} F_a(t) e^{2\pi \cdot i \cdot t \cdot f} \, dt$$

2. **Continuous Wavelet Transformation (CWT)** - was used for the first time with ground data to derive VOC fluxes (adapted from Misztal et al., 2014; Karl et al., 2013). This method allows for reconstruction of the nonstationary fluxes at higher temporal resolution, enabling observation of shorter-term events and investigations of mechanisms at higher time scales.
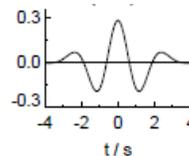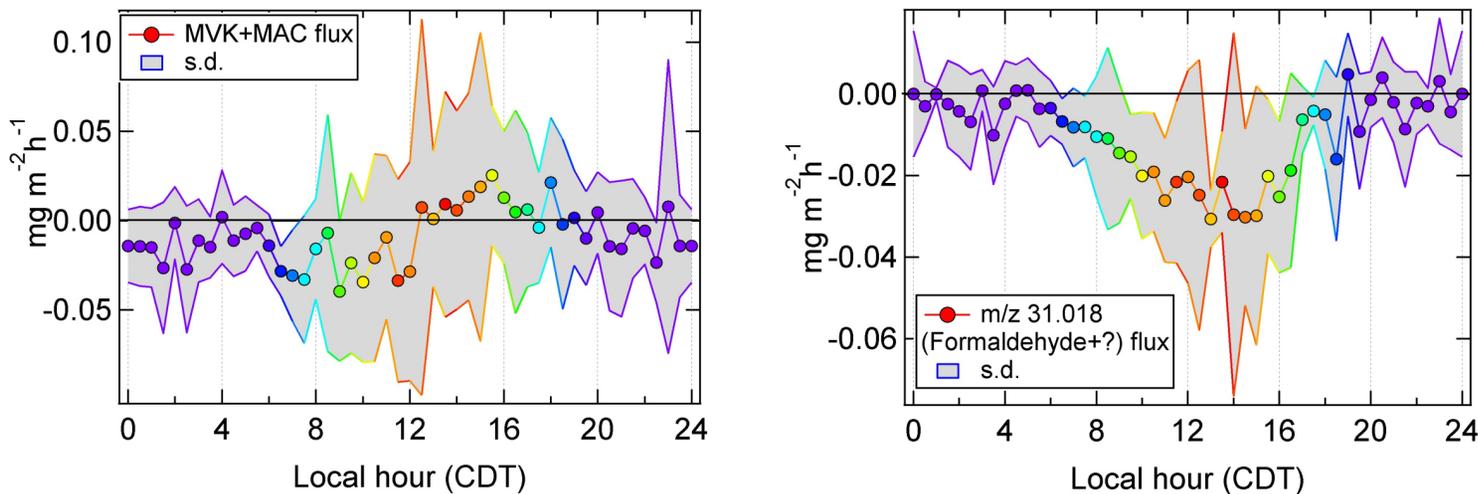

$$\psi_0 = \pi^{-1/4} e^{i\varpi_0 \eta} e^{-\eta^2/2}$$
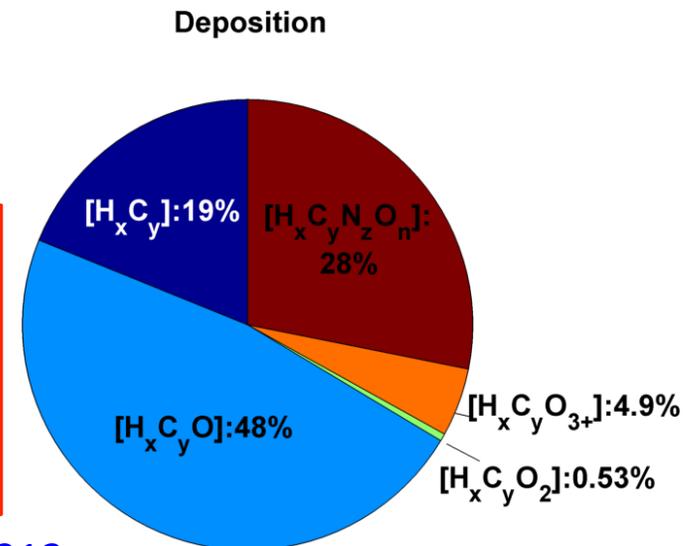
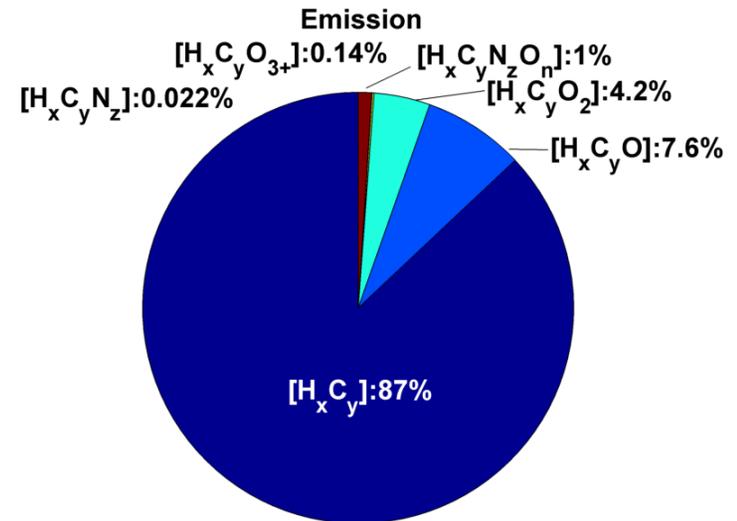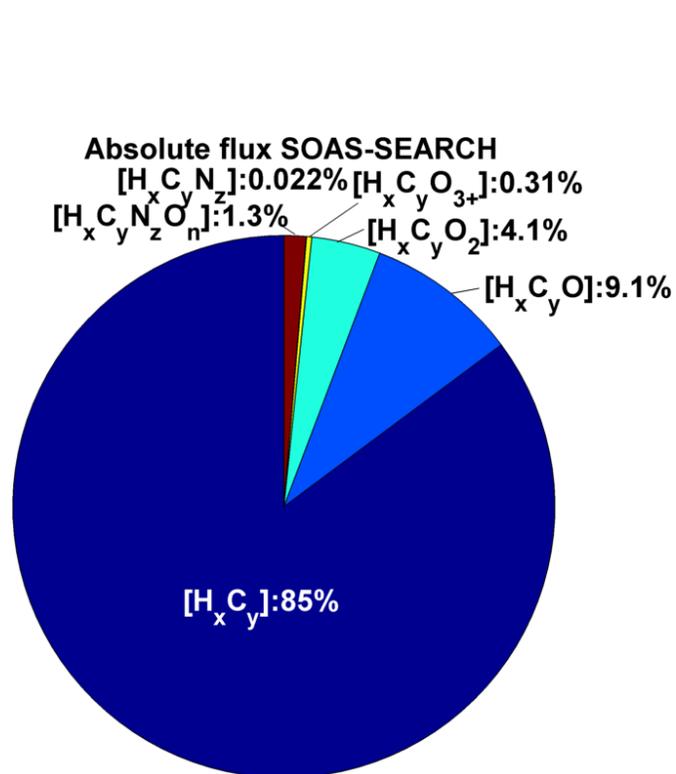# Bidirectional exchange of VOCs at SEARCH
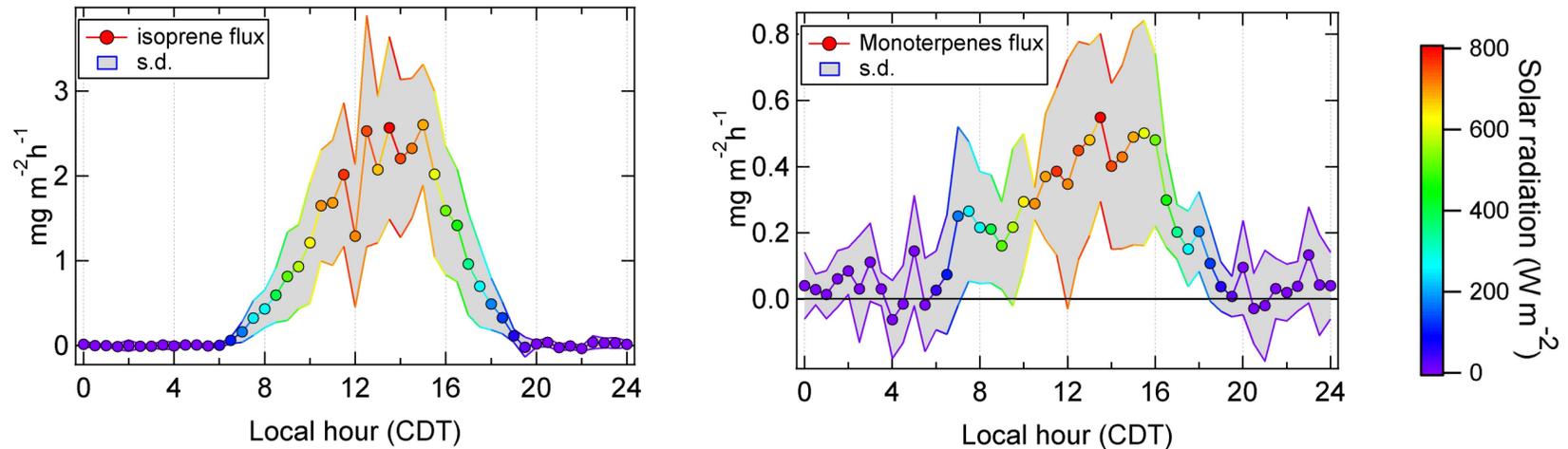
Isoprene and monoterpenes were strongly emitted during the day, constituting approx. 48% of the total net fluxes. Data shown are 2 week average.

m/z 71.0485 (mostly MVK+MAC) had bidirectional exchange (see Results). ~35% of observed VOCs had net deposition during mid-day, and the total observed deposition was equal to about 5% of total emissions.

Bidirectional exchange of VOCs at SEARCH

Absolute flux SOAS-SEARCH
$[H_xC_yN_z]$:0.022% $[H_xC_yO_{3+}]$:0.31%
$[H_xC_yN_zO_n]$:1.3%
$[H_xC_yO_2]$:4.1%
$[H_xC_yO]$:9.1%
$[H_xC_y]$:85%

Emission
$[H_xC_yO_{3+}]$:0.14% $[H_xC_yN_zO_n]$:1%
$[H_xC_yN_z]$:0.022%
$[H_xC_yO_2]$:4.2%
$[H_xC_yO]$:7.6%
$[H_xC_y]$:87%

Deposition
$[H_xC_y]$:19% $[H_xC_yN_zO_n]$: 28%
$[H_xC_yO]$:48%
$[H_xC_yO_{3+}]$:4.9%
$[H_xC_yO_2]$:0.53%

Primary compounds dominate the midday emission flux, mostly isoprene, then monoterpenes.
Most observed oxidation products had bidirectional flux.
~80% of net deposited compounds contained at least one O, and 28% contained N.

Data shown in pie charts are 10am-2pm, 20 June 2013, when fetch was over forest.

Flux observations of isoprene oxidation products above forests point to potential role of leaf-surface reactions
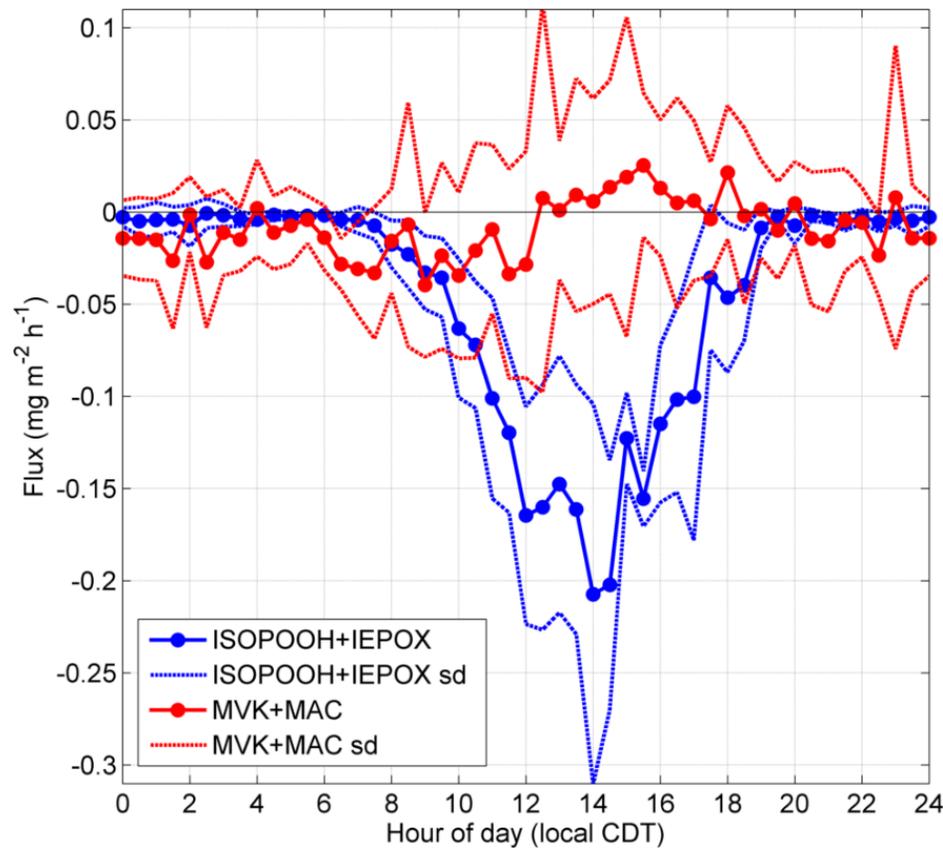
Observed m/z 71.049 (MVK+MACR) flux (PTRToFMS) is different than m/z 203 (ISOPOOH+IEPOX) flux (CIT-CIMS).

The pattern suggests that MVK+MACR may be produced by ISOPOOH+IEPOX reacting on leaf surfaces. MVK+MACR flux diurnal pattern observed at CTR is consistent with that observed at multiple other sites (Karl et al Science 2011), McKinney et al AGU 2013 (Harvard Forest), the AABC site, and Jardine et al from the Amazon.

When NO is high in the morning we observe deposition when (ISOPOOH+IEPOX)/(MVK+MACR) ratio should be low, but in afternoon (lower NO) we see emission which is inconsistent with an earlier hypothesis that ISOPOOH+IEPOX may be dominating m/z 71.049 flux.

Conclusions

- Isoprene and monoterpenes constitute the largest fraction of mass concentration and emission flux observed at SOAS field campaign in Alabama.

- Comparison of smog chamber experiments with field measurements shows similarities in the composition of specific VOCs but reveals challenges related to different conditions such as humidity, surface effects, turbulent mixing and losses in the lines.

- Vast majority of observed organic ions have bidirectional exchange, and ~1/3 of observed organic ions had net deposition.

- The unique diurnal pattern of MVK+MAC depositing in the morning (coinciding with elevated NO) then being emitted in afternoon is consistent with flux observation in other forested areas and implies that MVK+MAC may be formed from ISOPOOH and IEPOX depositing at the surface.

Thank you!