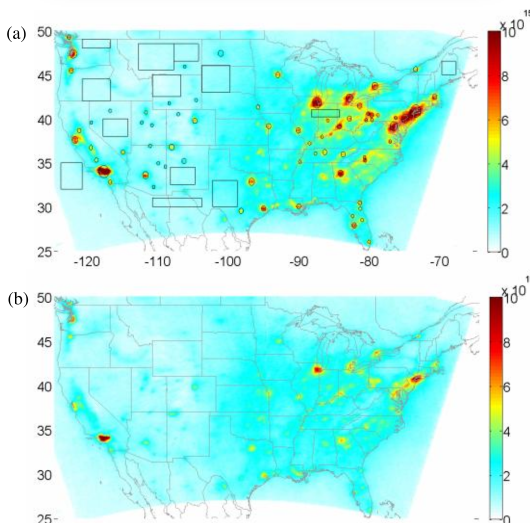
SOAS 2013: Tower & chamber working group

SOAS Coordination Meeting

Paul Wennberg, presenting

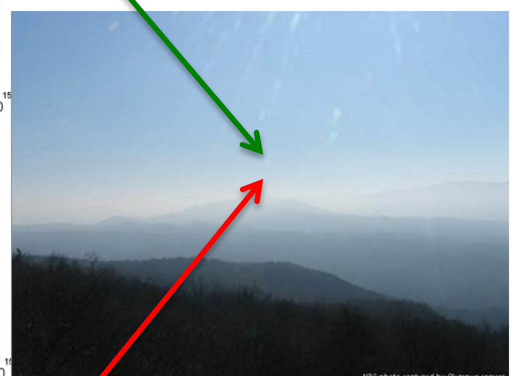
March 13, 2013

Gas-phase chemistry and SOAS



Trends in OMI NO_2 observations over the US: effects of emission control technology and the economic recession

A. R. Russell[1], L. C. Valin[1], and R. C. Cohen[1,2]



Overarching Goal:

Tie the *emissions* of BVOC and NOx to the formation of oxidants & aerosols via development of an *explicit photo-chemical mechanism*

Approach

Combine field and chamber studies to:

- Test existing mechanisms of biogenic VOC oxidation during the day and night via direct observation and appropriate simulations of the abundance of radicals and the multi-generation products of BVOC oxidation.
- Evaluate the impact of these biogenic VOC reactions on ozone, OH, and reactive nitrogen.
- Test hypothesized mechanism that link specific BVOC oxidation products to the formation of secondary organic aerosol.
- Resolve long-standing instrumental and model artifacts/disagreements.
  - Critical for moving the science forward
  - Must be systematically characterized in controlled experiments

Tower Measurements at the Centreville, AL Site

Synergy between tower instruments

Will provide a complete picture of BVOC fate above a forest canopy

- Oxidant budgets (HOx and O_3)
  - OH and HO_2 (Brune; Kim/Guenther)
  - O_3 (Brown; Brune)
- Nitrogen budget
  - Σorg. nitrates, Σ org. peroxynitrates (Cohen)
  - Speciated org. nitrates (Wennberg)
  - NO_3, N_2O_5 (Fry/Brown)
  - NO and NO_2 (Cohen; Brown; Kim/Guenther; Weinheimer)
- BVOC budget and reactivity
  - Concentration (deGouw/Goldstein) and flux (Guenther/Goldstein)
  - Reactivity toward OH (Brune; Guenther/Kim), NO_3 (Thornton), and O_3 (Helmig)
- OVOC budget
  - Org. Peroxides and acids and multifunctional ketones/aldehydes (Wennberg)
  - Formaldehyde and glyoxal (Keutsch)
  - Carbonyls (Guenther/Goldstein)

HO_x and OHR measurements with LIF

William Brune (Penn State)

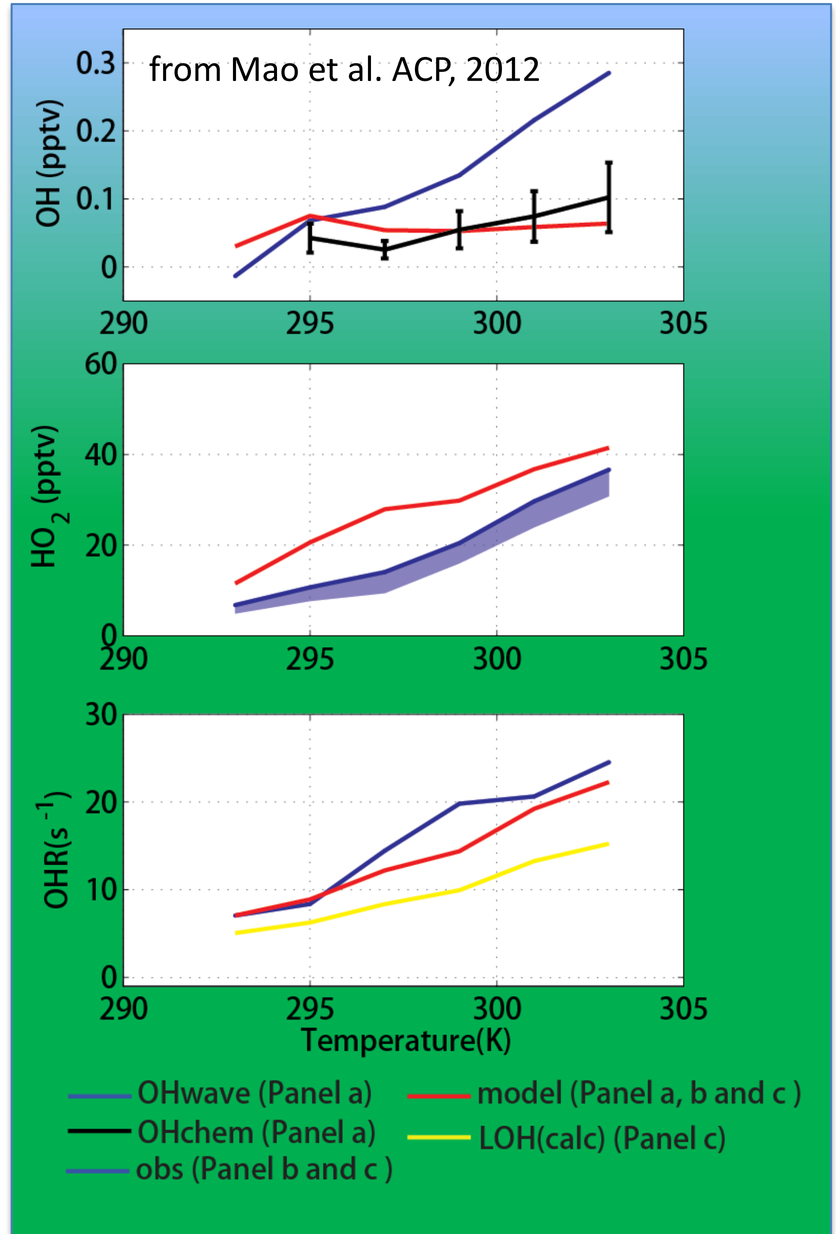
Li Zhang, David Miller, Philip Feiner

Science goals:

- Definitively resolve issues of forest oxidation chemistry
- Test hypothesis that interference (OHwave-OHchem) in the Penn State GTHOS is due to the Criegee Intermediate

Method to achieve goals:

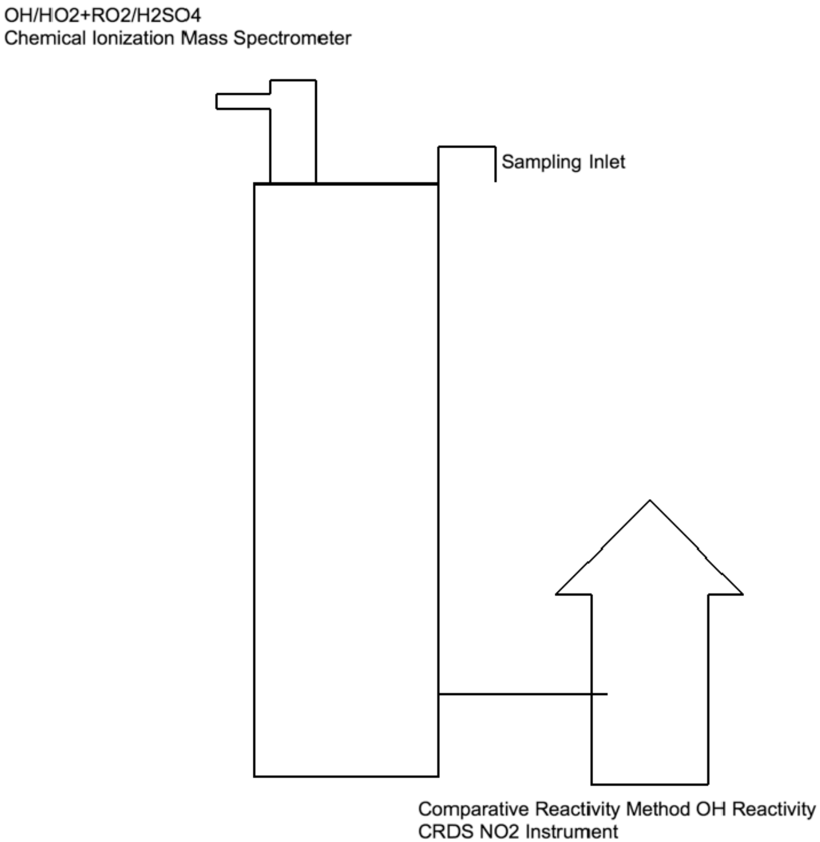
- Do field study in hot, high BVOC Alabama forest and then lab study in Caltech chamber to dissect chemical environment in Alabama
- Measure OH, HO_2, and OH reactivity
- Put GTHOS on top of tower to increase sensitivity
- Compare chemical oxidation models with our measurements



HO_X / H_2SO_4 (CIMS) and NO_2 (CRDS) measurements

Saewung Kim (U.C. Irvine) and Alex Guenther (NCAR) Funded by EPA

- Constrain Photolytic and Recycling Sources of OH during the SOAS Campaign (evaluating oxidation capacity amplification by isoprene)
- Constraining H_2SO_4 Levels in the Southeastern U.S. ($OH+SO_2$ vs Stabilized Criegee $+SO_2$)
- Evaluating new instrumentation (Commercial LGR CRDS NO_2)



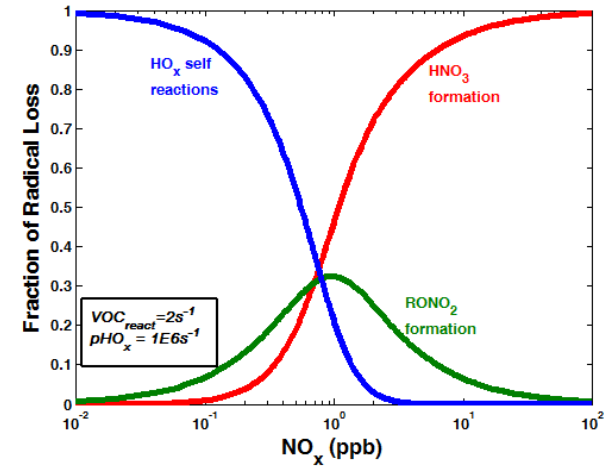
<u>*Expected Deliverables*</u>

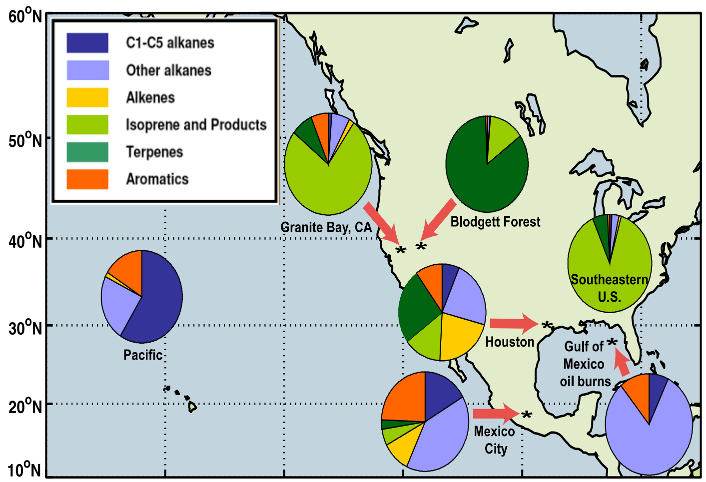
- Highly constrained OH budget with observed P(OH) and L(OH): evaluation of OH 'recyling' in isoprene oxidation.
- Observed H_2SO_4: Nucleation from sulfuric acid both from conventional and newly reported pathways
- Multiple NO_X Observations: Providing confidence in constraining the conventional OH recycling pathway (NO+HO2)

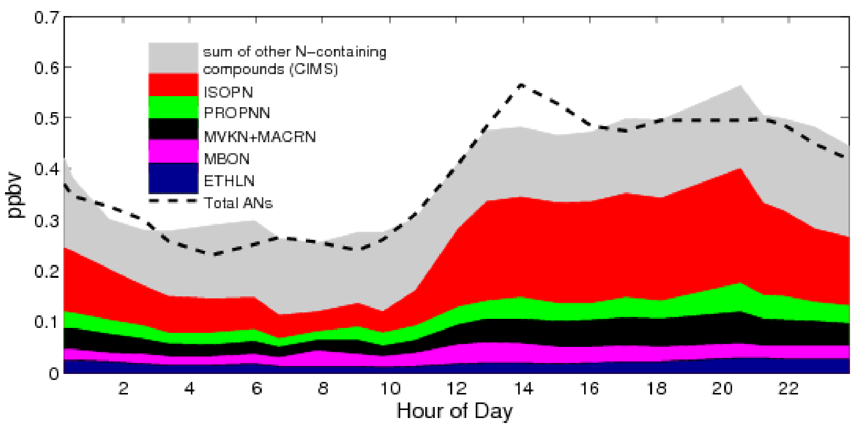
NOx and Alkylnitrates measurements with TDLIF

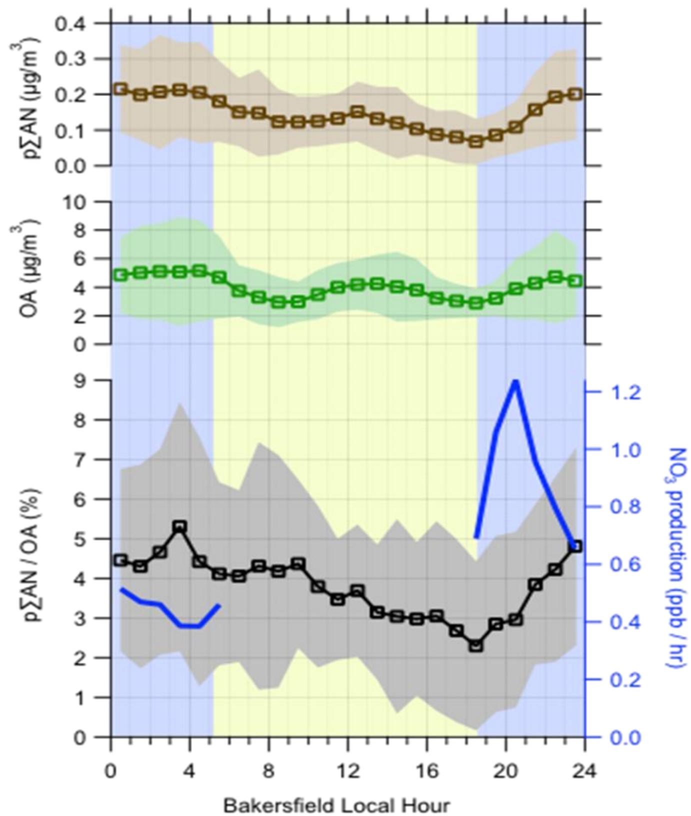
Ron Cohen (Berkeley)

- What are the chemical, physical, and biological sources and sinks of NO_x in the southeast U.S.?
- What were they in preindustrial times?
- Evaluation using measurements of NO, NO_2, total PNs, and total $RONO_2$.





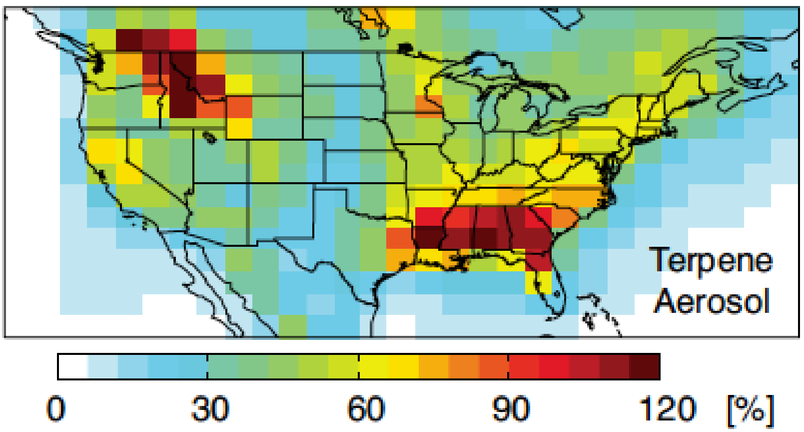




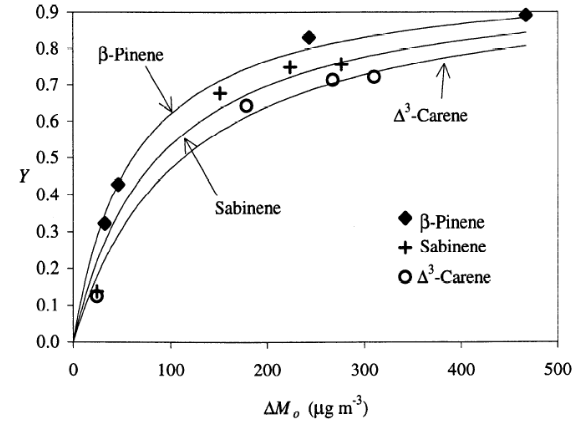
BVOC Oxidation by NO_3: Anthropogenic influence on SOA

Juliane L. Fry (Reed College), Steven S. Brown (NOAA) et al.

The issue: Models show large enhancements in SOA derived from biogenic VOC emissions and oxidation when the nighttime NO_3 pathway is included.



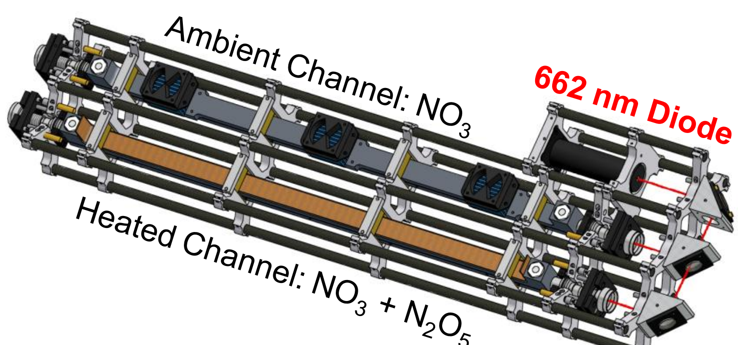
Pye *et al.* ACP 2010: Increase in BVOC-SOA upon inclusion of NO_3 oxidation



Griffin *et al.* JGR 1999: Large chamber SOA yields from NO_3-BVOC reactions are the basis for these model predictions

The experimental approach: Measure ambient NO_3, reactive nitrogen speciation, NO_3-BVOC oxidation products, potential aerosol mass and aerosol composition; Develop a budget for NO_3 production and loss, BVOC emissions and oxidation pathways, and SOA formation.

"RONALD": Cavity ring-down NO_3 and N_2O_5 (direct absorption at 662 nm). Sub pptv detection limits.

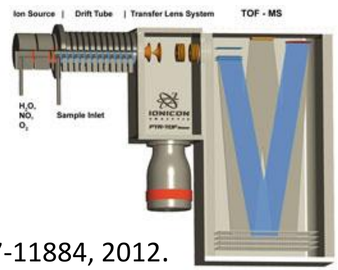


Are NO_3-BVOC reactions a large source term for SOA?

VOC measurements by PTR-ToF-MS and GC-MS

Allen Goldstein (UC Berkeley), Alex Guenther (NCAR), Joost de Gouw (NOAA)

(SRI-)PTR-ToF-MS
operated by
Pawel Misztal (UCB)



Karl, Atmos. Chem. Phys., 12, 11877-11884, 2012.

GC-MS
operated by
Kevin Olson (UCB)
Abby Koss (NOAA)

Measurements of a wide range of speciated VOCs will:

- Provide key constraints on the anthropogenic and biogenic emissions based on primary and secondary tracers and their vertical gradients
- Enable evaluation of the processes controlling oxidation and transformation of biogenic VOCs under anthropogenic influences

Through collaboration with other SOAS / SENEX researchers we aim to:

- Understand the full range of semi-volatile compounds measured by multiple instruments (SV-TAG, TD-PTR-ToF-MS, etc.)
- Determine which oxidation products are most important in producing SOA and under what conditions
- Investigate the role of biogenic and anthropogenic VOCs on climate
- Link our ground-based VOC data to regional measurements on WP-3D (Cans & PTR-MS, de Gouw), C-130 (on-line GC-MS, PTR-ToF-MS VOC fluxes, Guenther) and Long-EZ (vertical profiles, Mak)

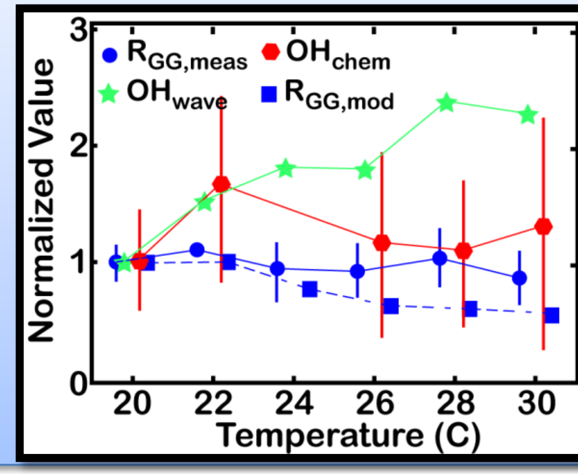
Glyoxal and formaldehyde measurements by LIP/LIF

Frank Keutsch (U.W. Madison)

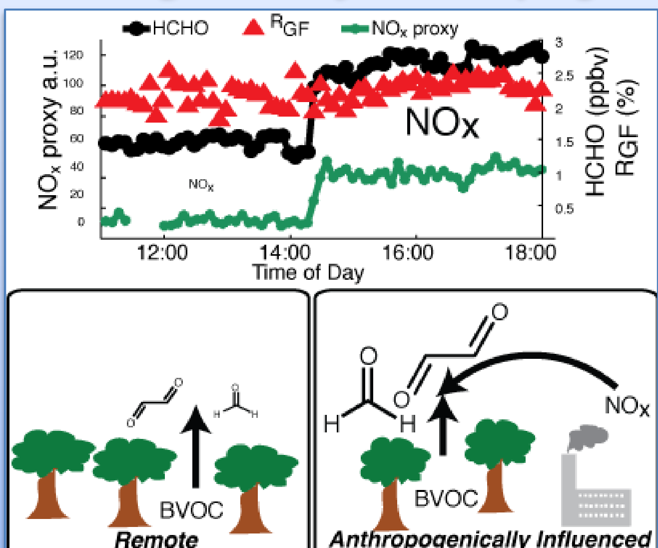
Observational assessment of oxidative capacity

Expand use of ratio of glyoxal to glycolaldehyde as metric for OH

Investigate anthropogenic (NO_x) effect on OH



Investigation of anthropogenic influence on VOC oxidation product distribution



Use ratio of glyoxal to formaldehyde to indicate anthropogenic influence

Use aldehyde measurements to evaluate and improve satellite retrievals and regional models

Assess impact of glyoxal produced in BVOC oxidation on SOA at the rural/urban interface.

Test models of VOC oxidation, esp. the product distribution, as function of anthropogenic influence

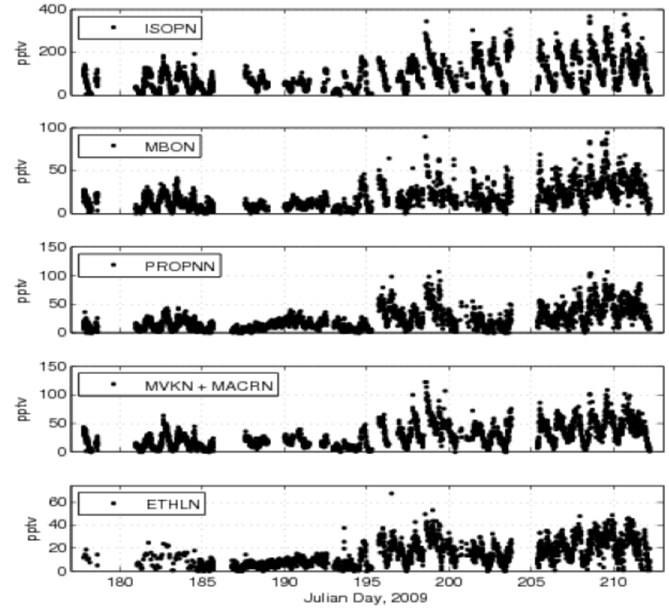
Synergy SENEX and modeling efforts

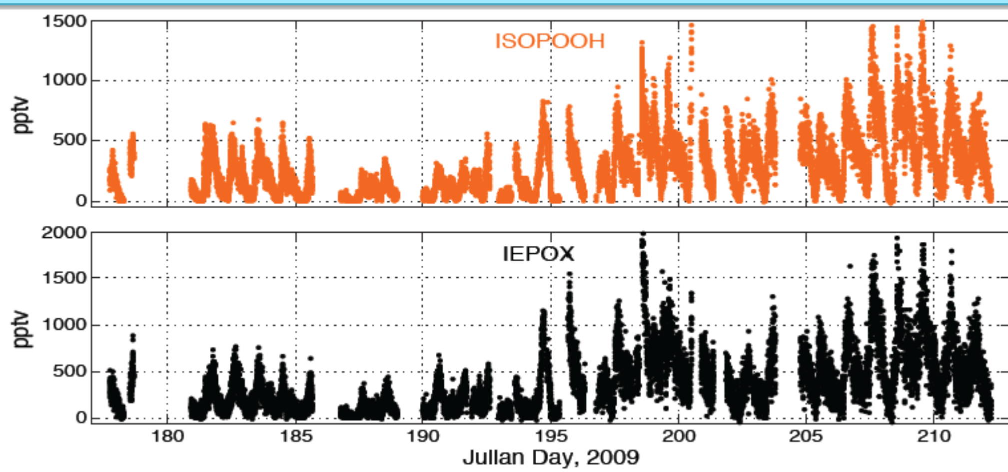
OVOC measurements with CIMS

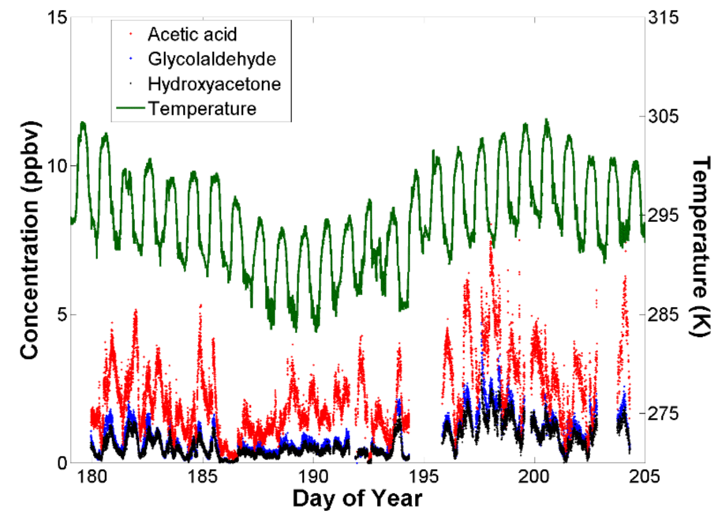
Paul Wennberg(Caltech)

Tran Nguyen, Jason St.Clair, John Crounse, Alex Teng, Kelvin Bates

- **SOAS Goal:** Determining the fate of RO_2 formed in the oxidation of BVOC.
  - Particularly studying the effect of NOx
- **Approach:** Synthesis and In situ detection of acids, peroxides, and organic nitrates
  - H_2O_2, MHP, HMHP, ISOPOOH, etc.
  - HNO_3, formic acid, acetic acid, etc.
  - Speciated $RONO_2$

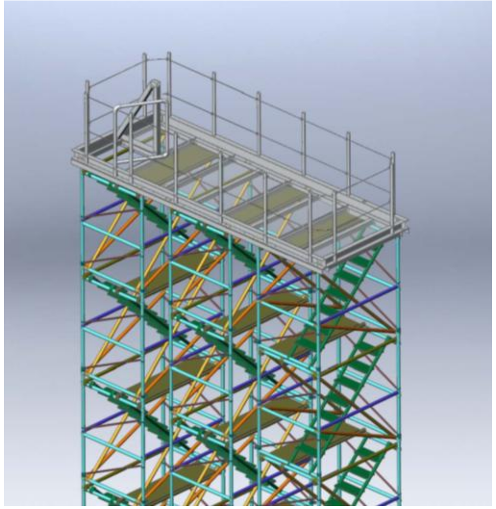






The Alabama CTR SEARCH Site

- 54’ EOL/ISF multi-tower platform
  - Canopy height 30 – 45’

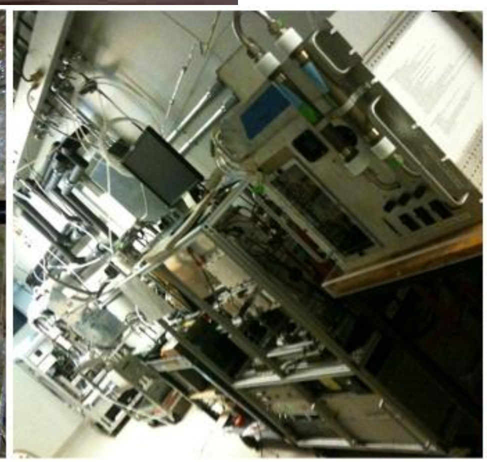


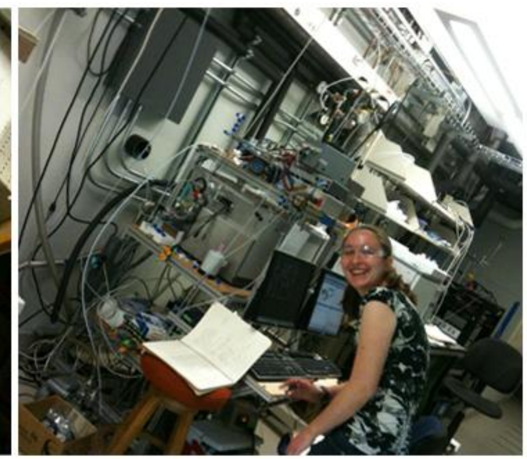
- The geography and tower height are not ideal for flux measurements

- Site provides a mixture of anthropogenic and bio-genic emissions necessary to evaluate the photo-chemistry

Immediate goals at SEARCH

- Concentrations of key species above the canopy
  - Decoupled from surface effects (e.g., deposition)
- The vertical direction of flux
- Limited NOy vertical gradient, and only for NO_2 and $\Sigma RONO_2$
  - Shorter trees (30’ vs. 100’) = 2 levels of measurements
- NOx-influenced measurements

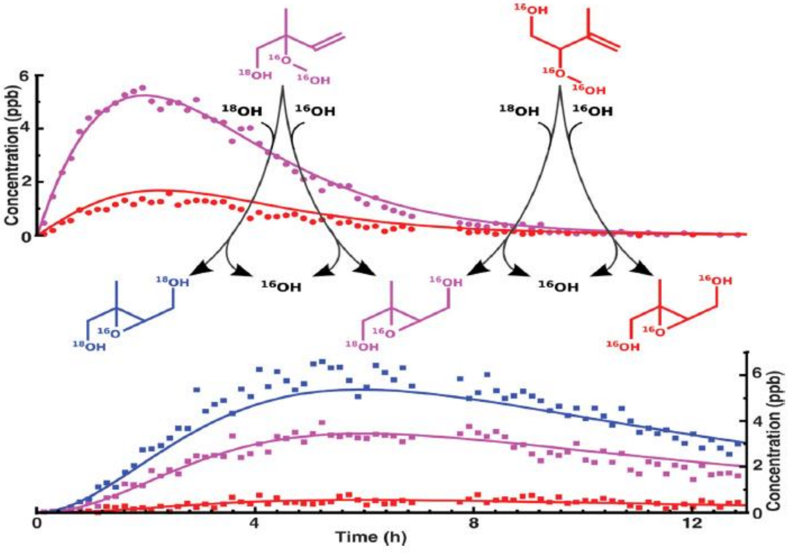




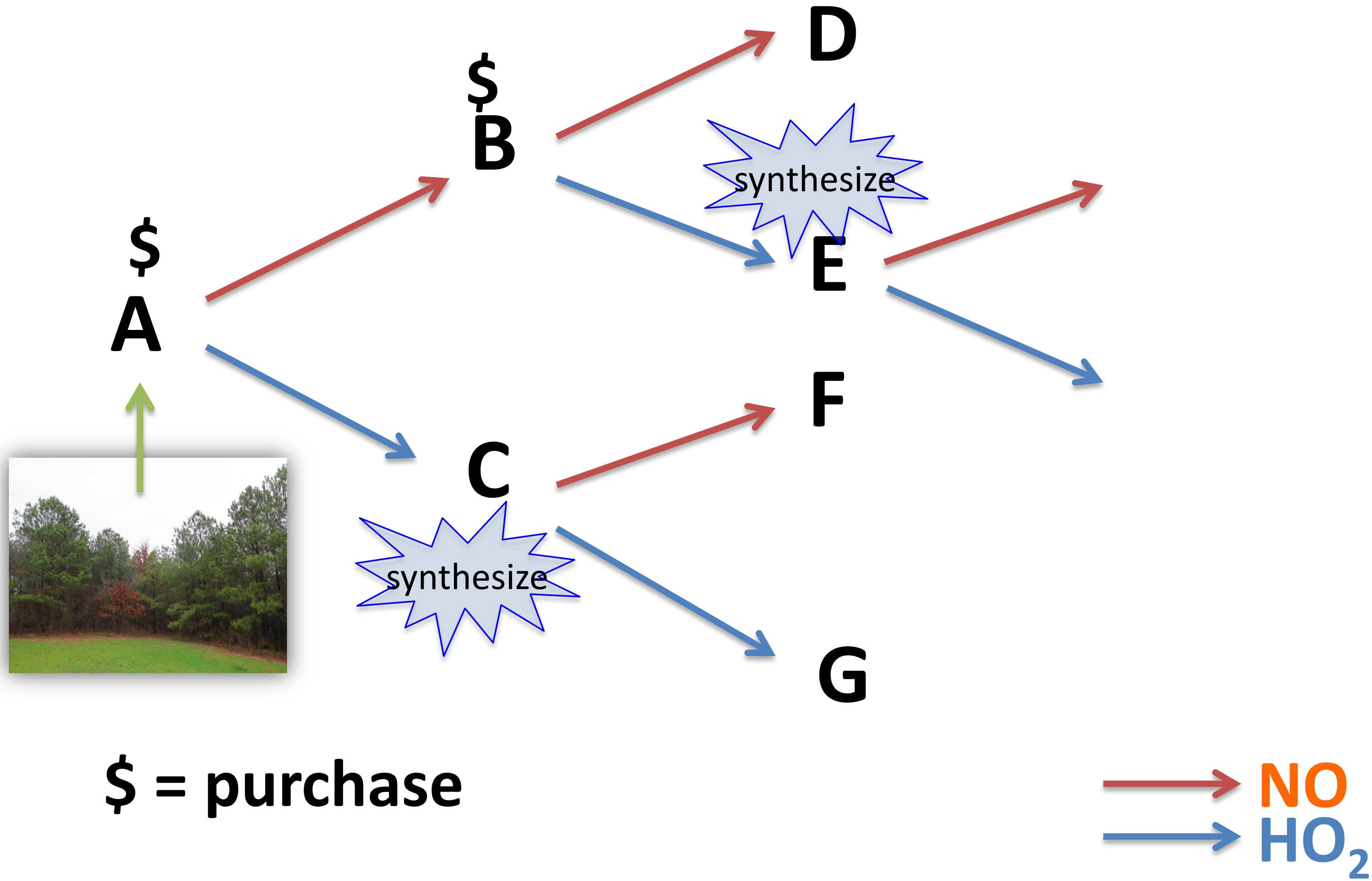
SOAS Chamber Studies

Close coupling of chamber studies to field observations

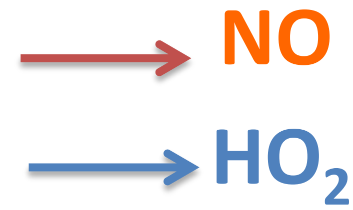
- Provide robust evaluation of field data by:
  - Isolating individual reactions
  - Evaluate hypothesized mechanisms to explain field discoveries
  - Precise inter calibrations using synthesized standards (e.g., IEPOX)

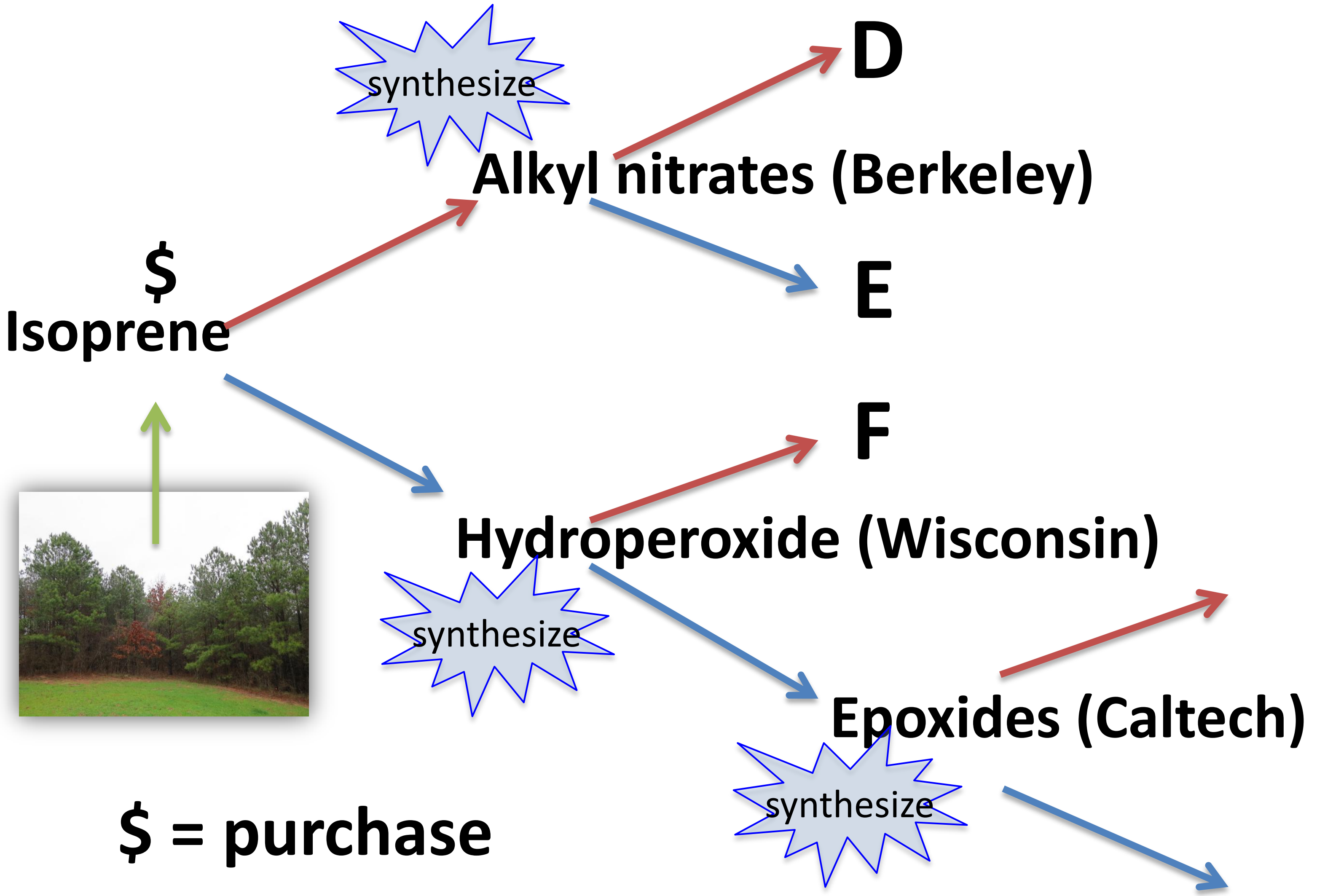


Follow the photochemical cascades



Example: Isoprene

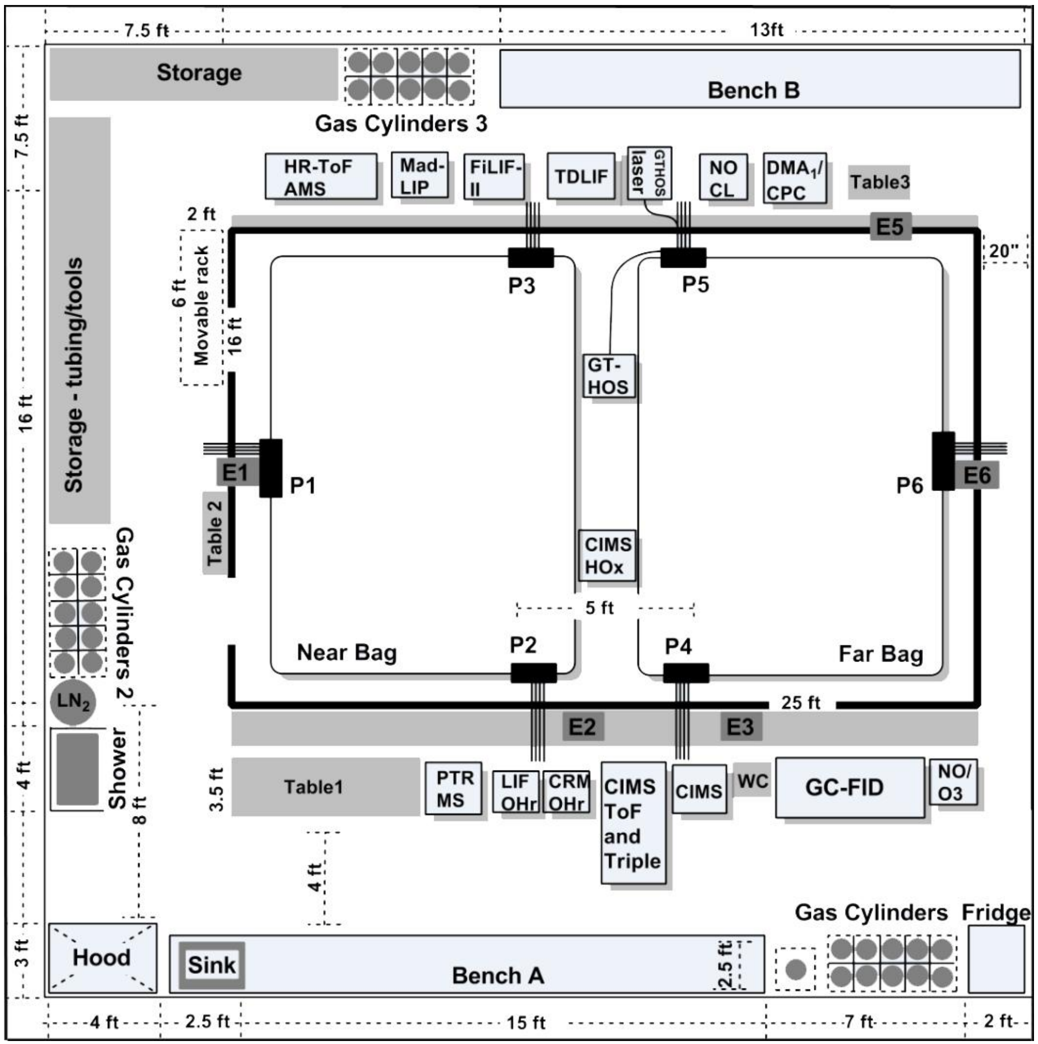




Post-SOAS 6-wk chamber study

- We have developed an experimental plan that:
  - Recreates field conditions in the laboratory
  - Provides similar NOx/VOC ratio, RH, T, etc. to field
  - Makes available unique synthetic products of BVOC oxidation
- Example studies:
    - The yield and fate of the organic nitrates
    - The yield and fate of hydroxy-hydroperoxides (e.g. isoprene hydroxy hydroperoxides)
    - The yield and fate of hydroperoxyaldehydes
    - The yields of SOA precursors (e.g. IEPOX, MPAN)
    - The fate of Criegee radicals and their influence on HOx instrumentation.

Tower instruments @ Caltech



- <u>Confirmed PIs:</u>
  Brune, Cohen, Keutsch, Kim, Guenther, Seinfeld, Tyndall, Weinheimer and Wennberg
- <u>Possible Pis:</u>
  Shepson
- Same instruments deployed at SOAS
  - direct comparison against field data