Budgets and Modeling of Nighttime Biogenic Hydrocarbon Oxidation from P-3 Night Flights During SENEX

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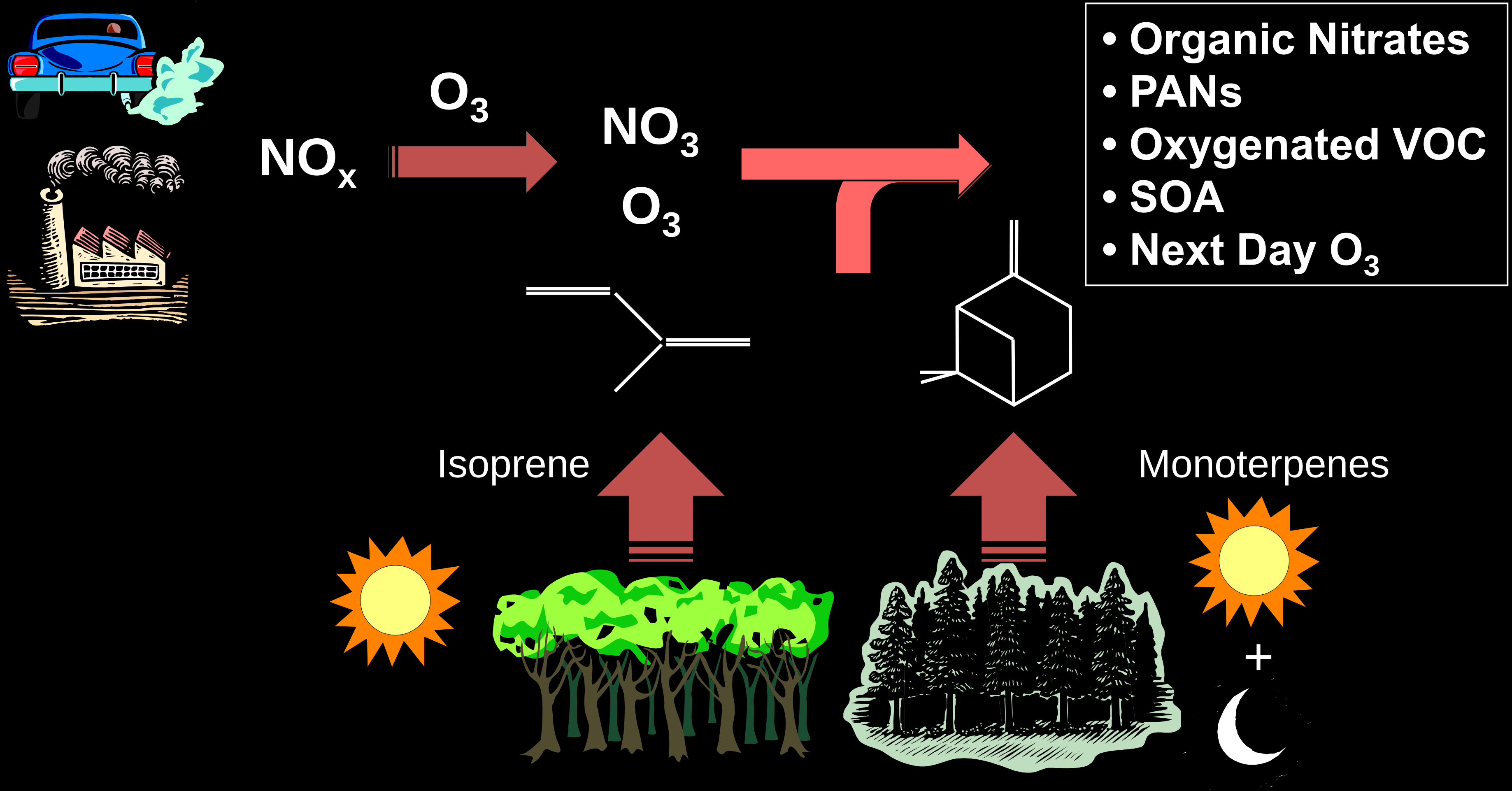
Nighttime BVOC Oxidation

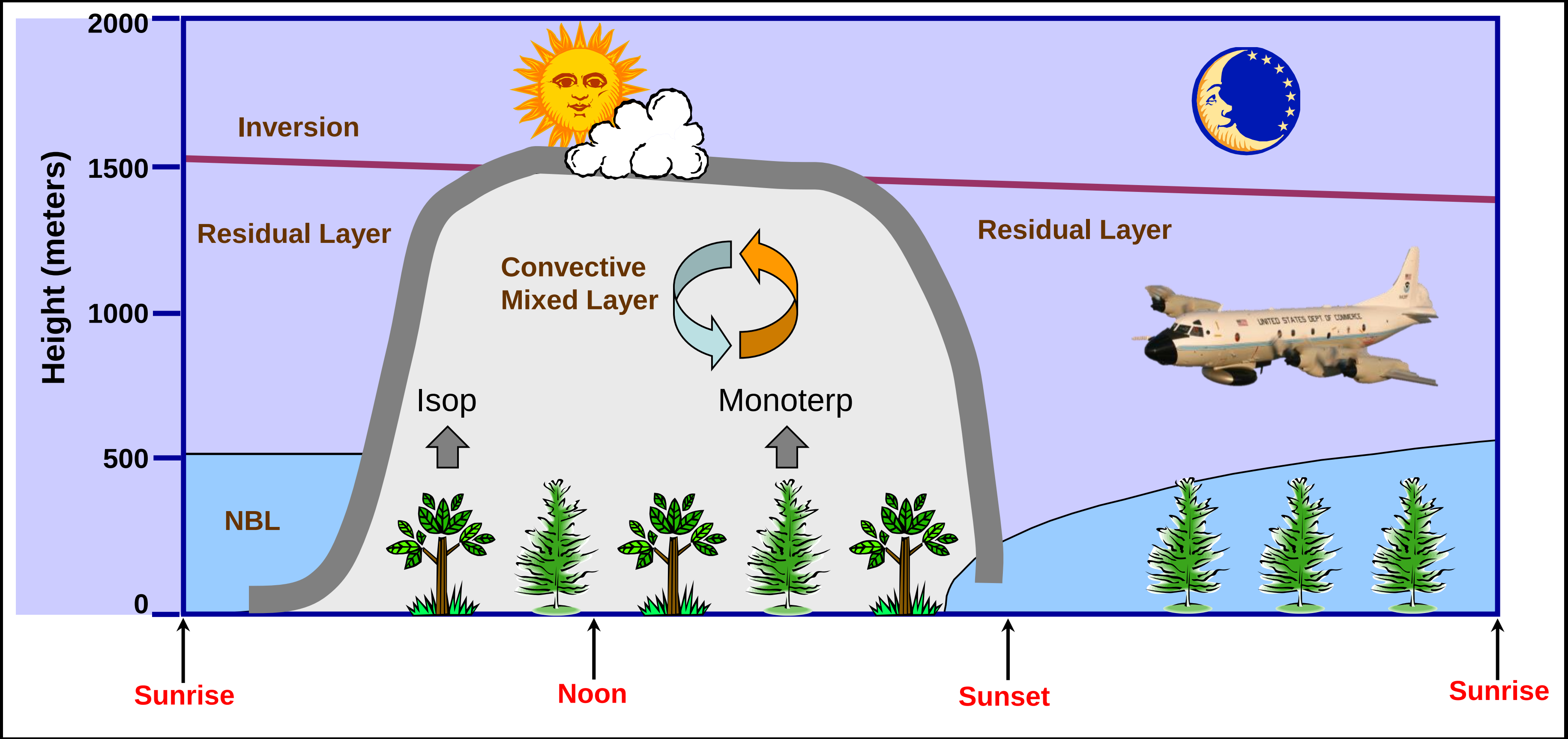


NO_x $\xrightarrow{O_3}$ NO_3, O_3

- Organic Nitrates
- PANs
- Oxygenated VOC
- SOA
- Next Day O_3

- BVOC oxidation by NO_3 is one of the key anthropogenic – biogenic interaction mechanisms (anthropogenic oxidant + biogenic emission)
- Both NO_3 and O_3 react readily with BVOC – How widespread is NO_x, and how does this change the “normal” nighttime oxidation cycle?

Boundary Layer Dynamics & BVOC Emissions



- Daytime: Isoprene, monoterpenes throughout convective mixed layer
- Nighttime: Mainly isoprene, some monoterpenes in residual layer; monoterpene emission and oxidation in nocturnal boundary layer
- P-3 flies mainly in residual layer – study BVOC oxidation mainly from previous day’s emissions
- Periodic low approaches to sample the NBL

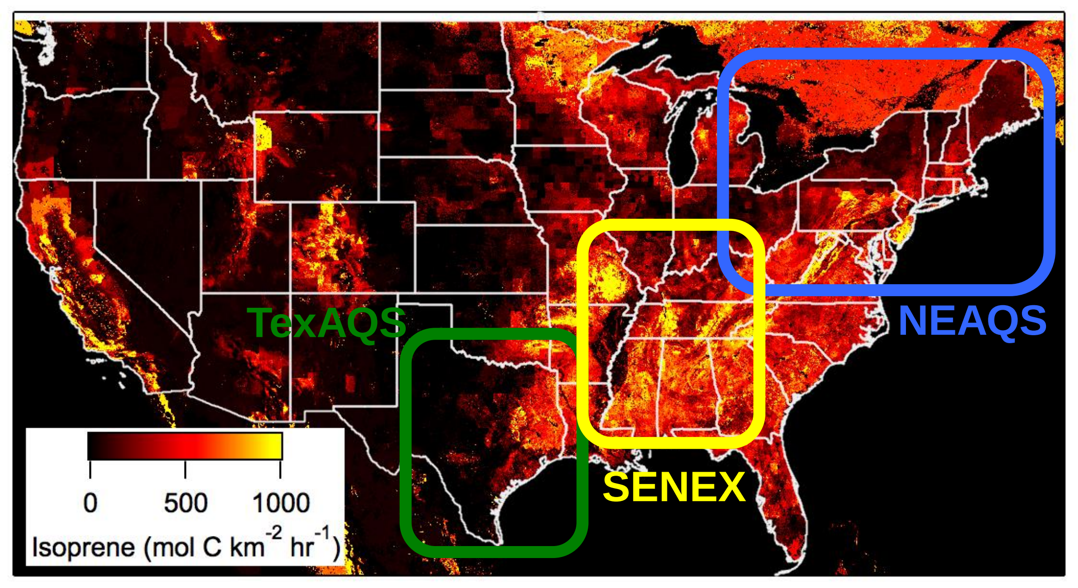
What's Different About SENEX 2013 ?

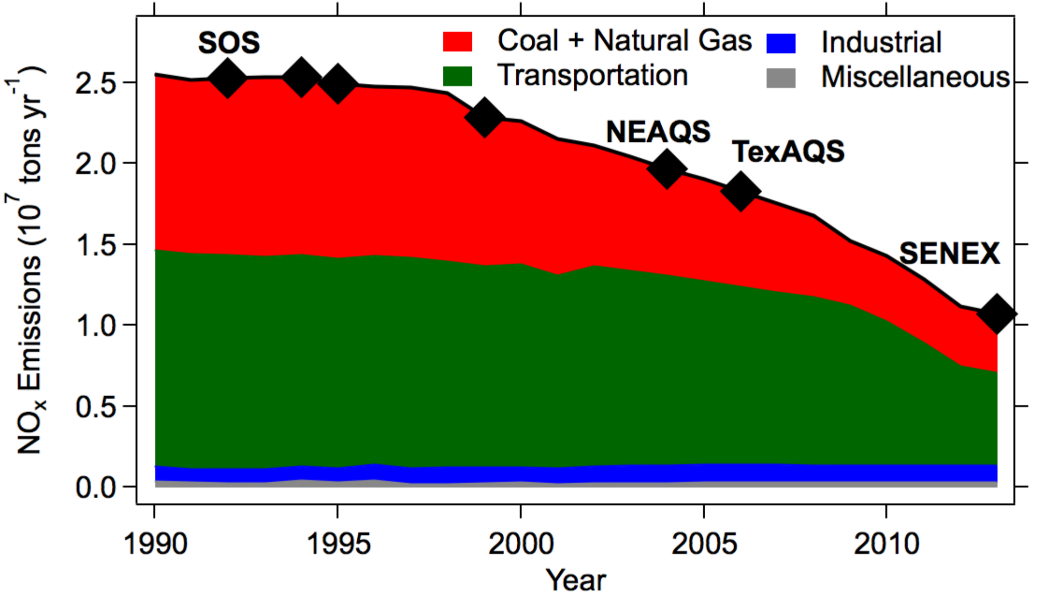
- Prior P-3 campaigns have examined residual layer chemistry
  - New England, 2004
  - Texas, 2006

- Southeast region has much higher biogenic emissions

- NO_x emissions have decreased precipitously over the last decade

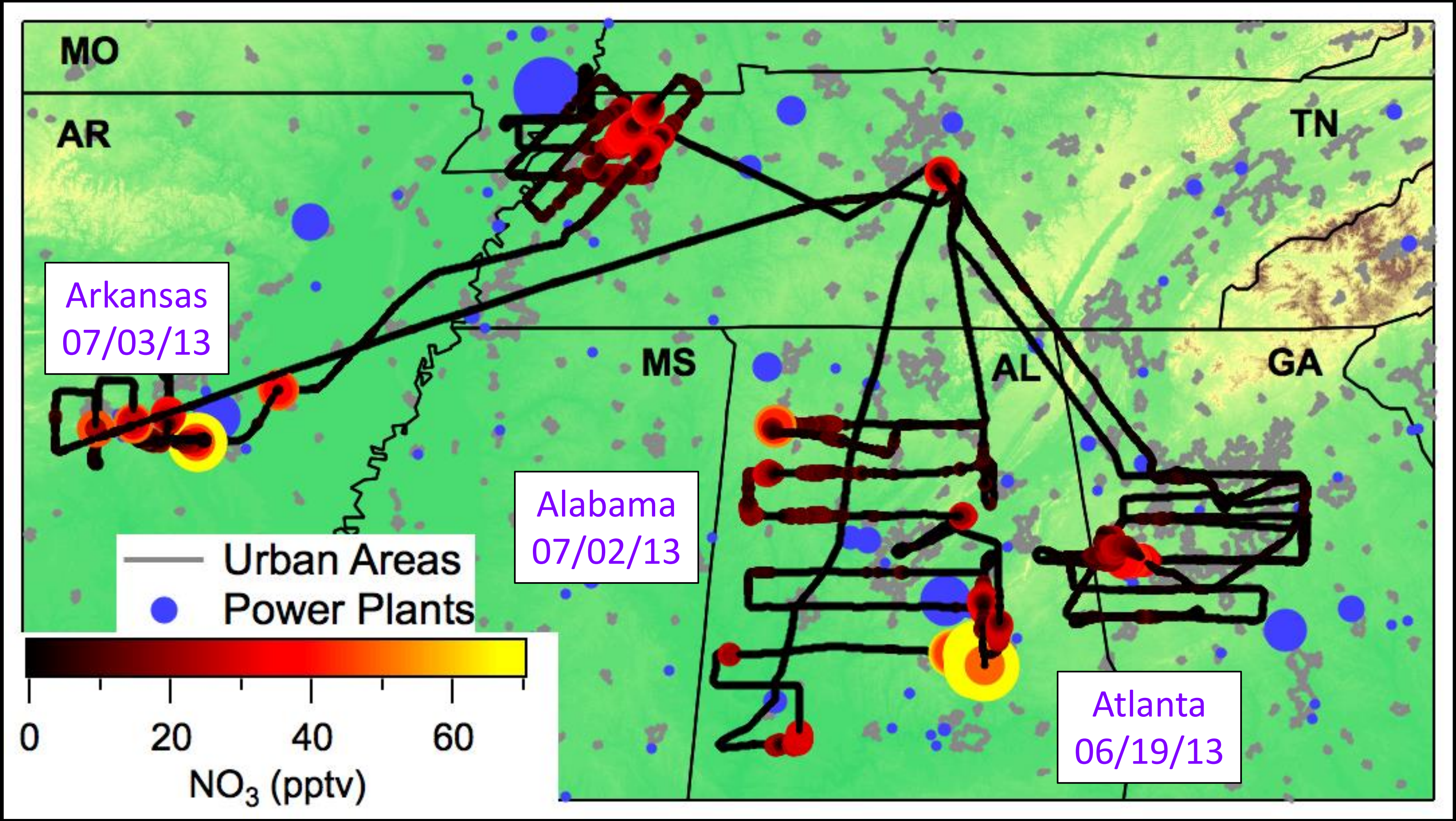
- Instruments to measure key intermediates in the oxidation chemistry (day or night) have improved dramatically since 2004 / 06





SENEX 2013: Observed NO_3 Mixing Ratios

- Observed NO_3 typically low (0 – 3 pptv) outside of discrete plumes (e.g. Power plants or biomass burning).



Arkansas
07/03/13

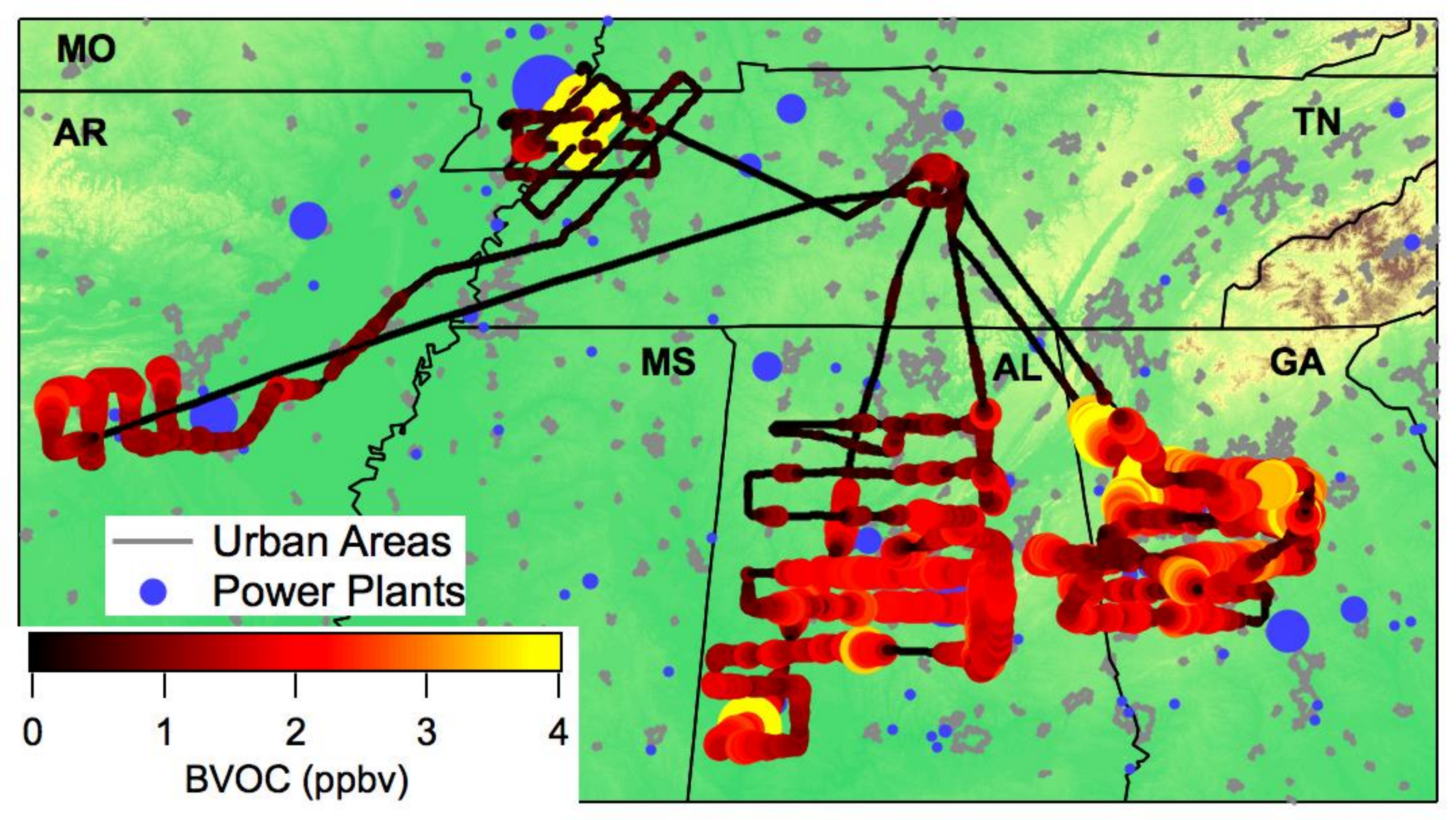
Alabama
07/02/13

Atlanta
06/19/13

NEAQS, TexAQS: NO_3 to 400 pptv in residual layer

SENEX 2013: Observed BVOC Mixing Ratios

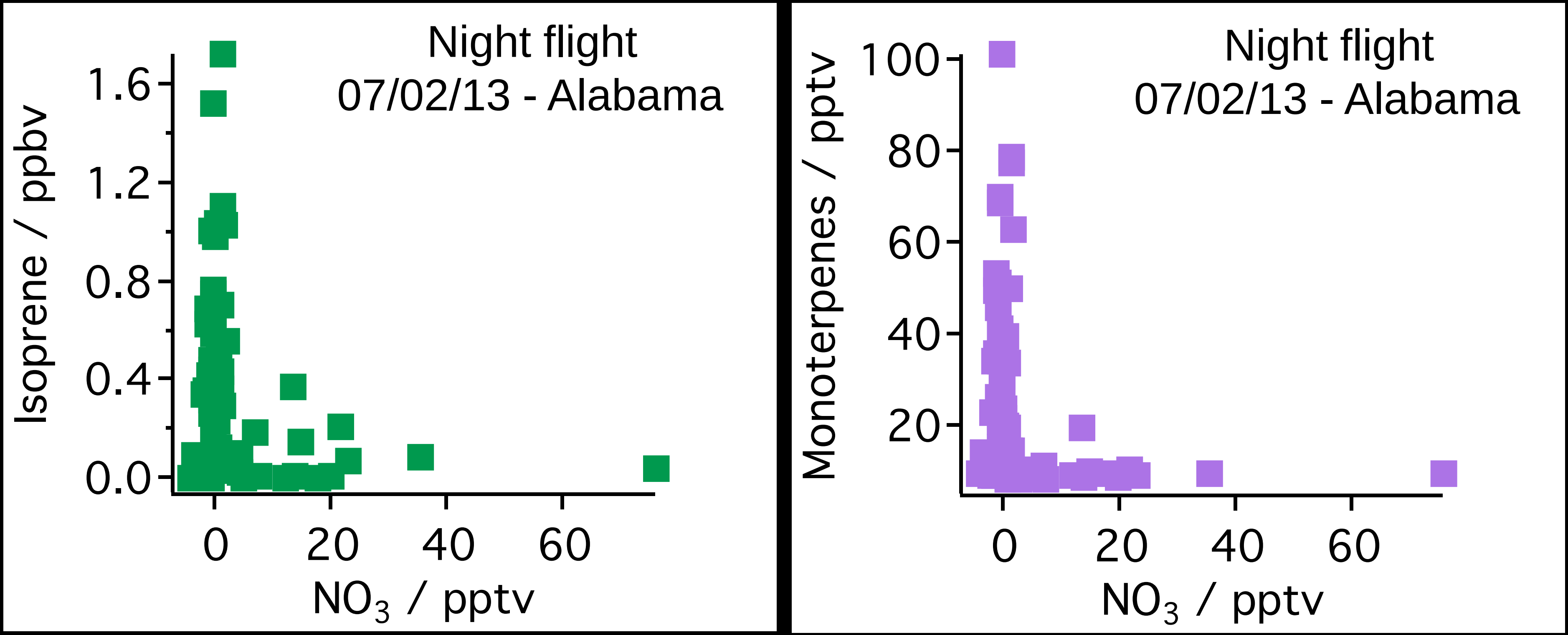
- High observed concentrations of BVOCs during night flights.



Biogenics = Σ(Isoprene + Monoterpenes + Methacrolein + Methyl vinyl ketone)

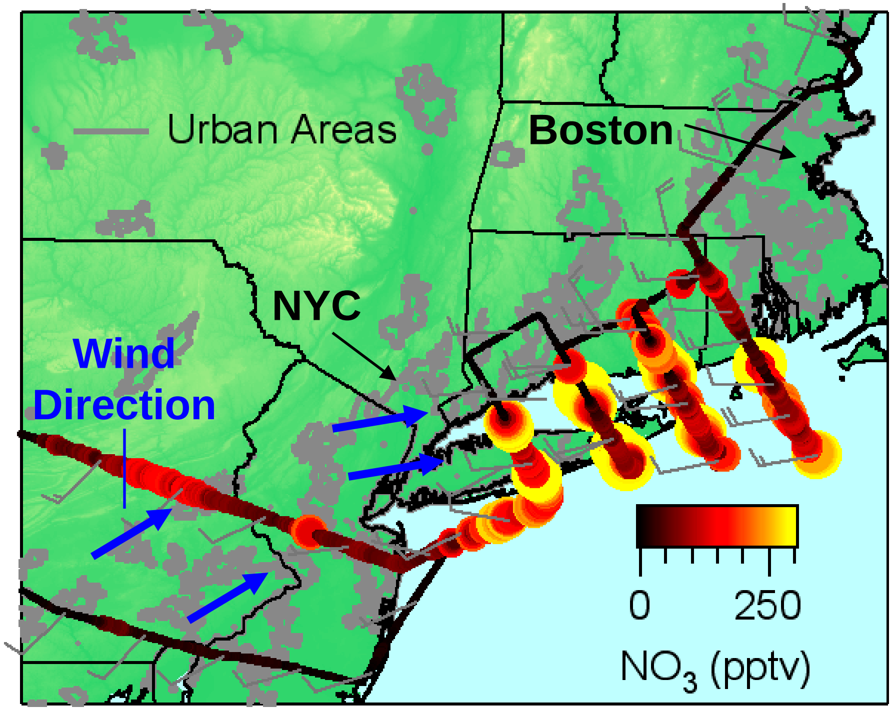
Nighttime NO_3 – BVOC Relationship

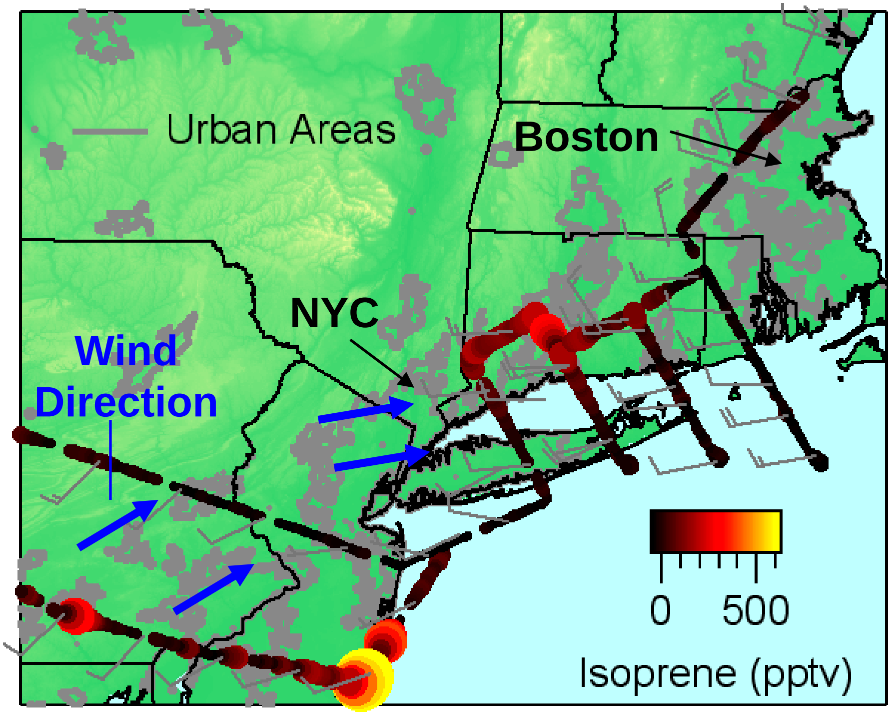
- Anti-correlation observed between NO_3 and BVOCs.

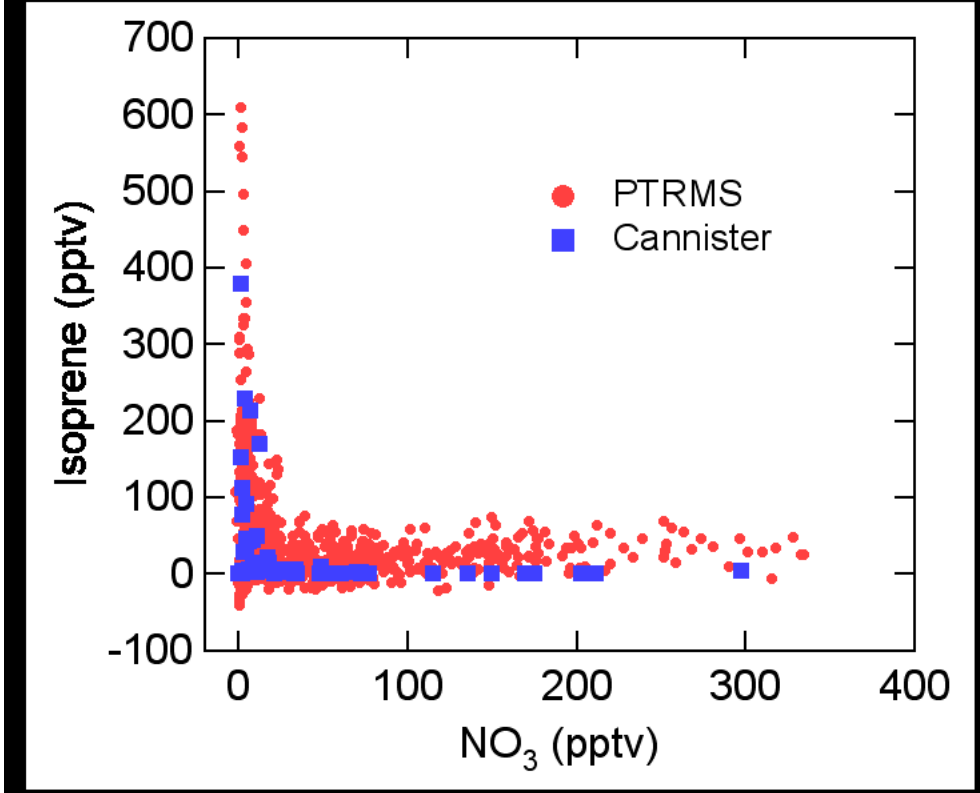


- Previous analysis by Brown *et al.* (2009) shows isoprene/NO_3 anti-correlation due to oxidation, not sampling.
- Sufficient monoterpene concentrations during SENEX to observe similar anti-correlation with NO_3 aloft.

NO_3 & Isoprene during NEAQS 2004







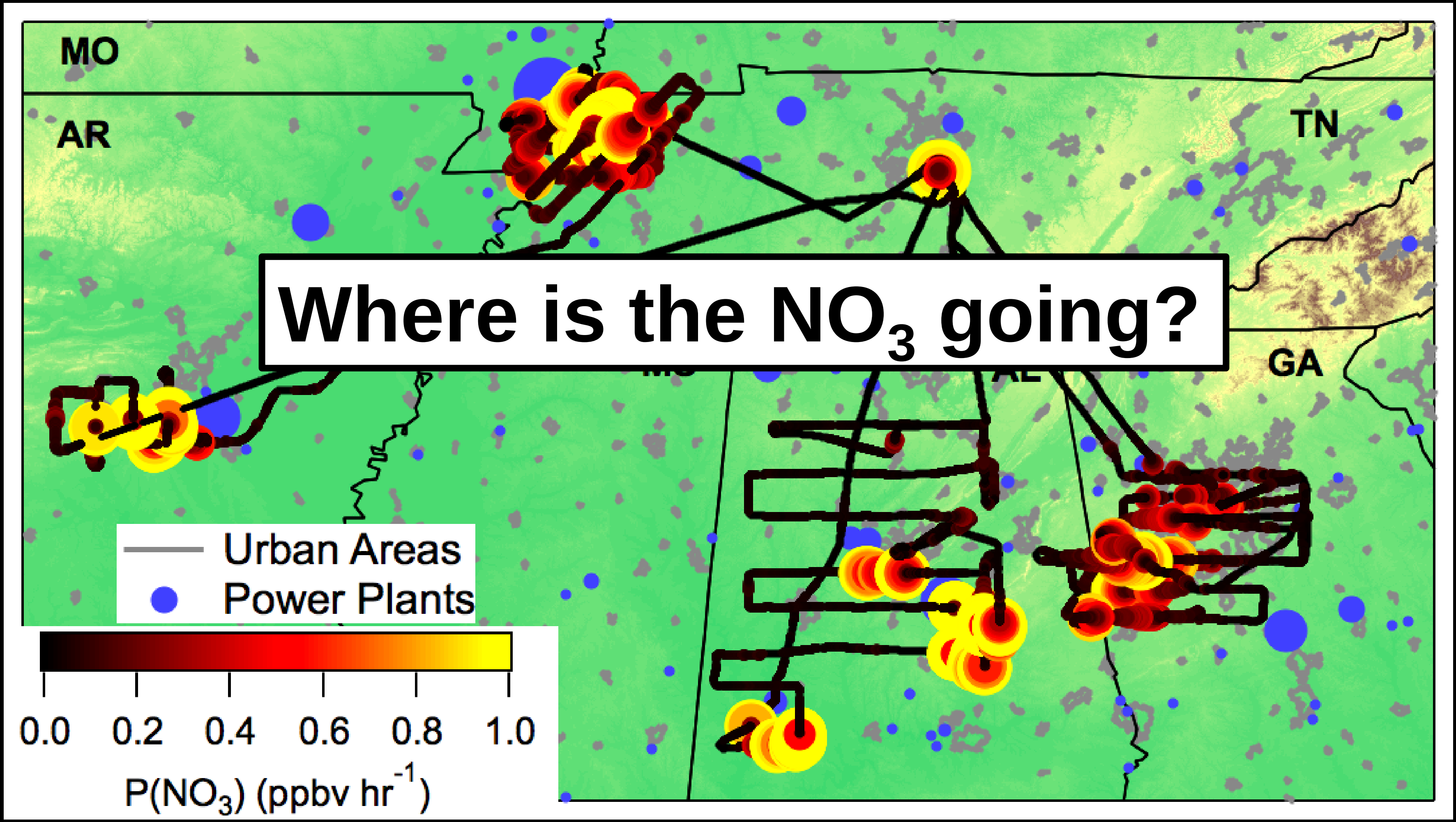
NO_3: Cavity ring-down spectroscopy

PTRMS Isoprene:
Joost de Gouw &
Carsten Warneke

WAS Isoprene:
Eliot Atlas &
coworkers

SENEX 2013: Nitrate Radical Production Rates

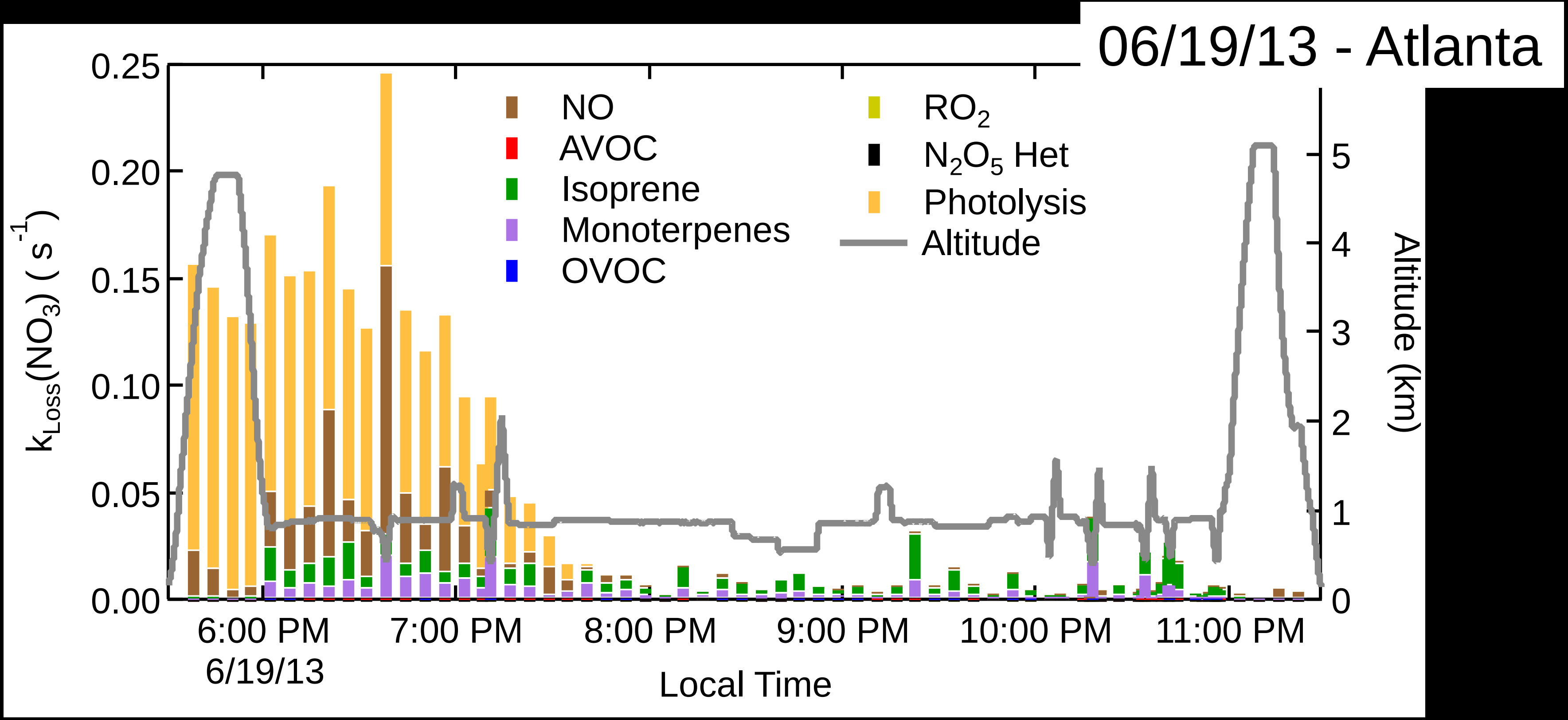
- Despite the low NO_3 concentrations, NO_3 production ($P(NO_3)$) > 0.5 ppb hr^{-1} in many regions.



Where is the NO_3 going?

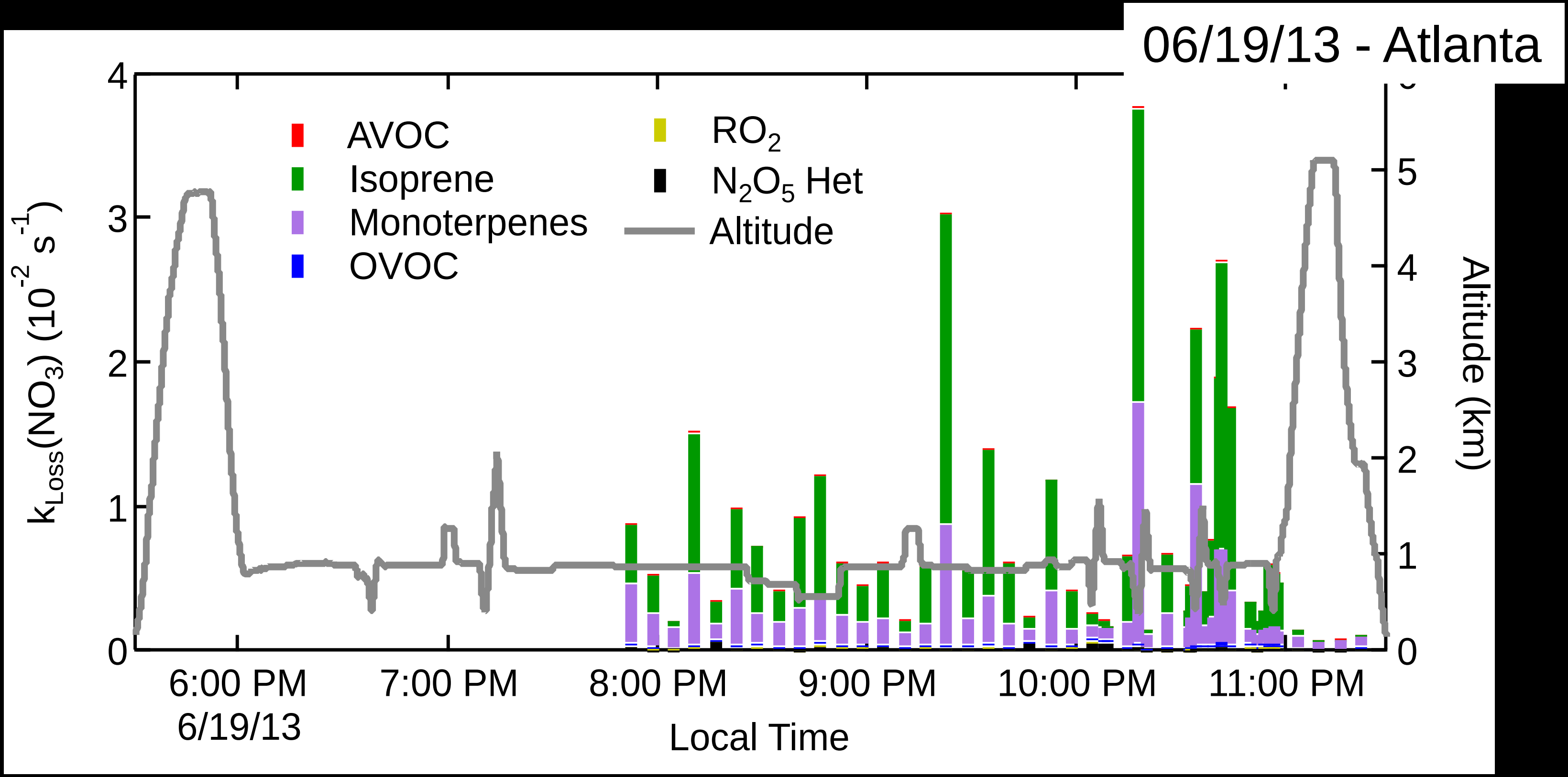
$$P(NO_3) = k_{NO2 + O3} [O_3][NO_2]$$

Budgets for Nitrate Radical Loss



- Calculate NO_3 loss budget using measured VOCs, NO_x, aerosol surface area and calculated photolysis rates.
- Calculated NO_3 loss rates show biogenics to remove as much as 20% of the NO_3 produced during the day.

Budgets for Nitrate Radical Loss

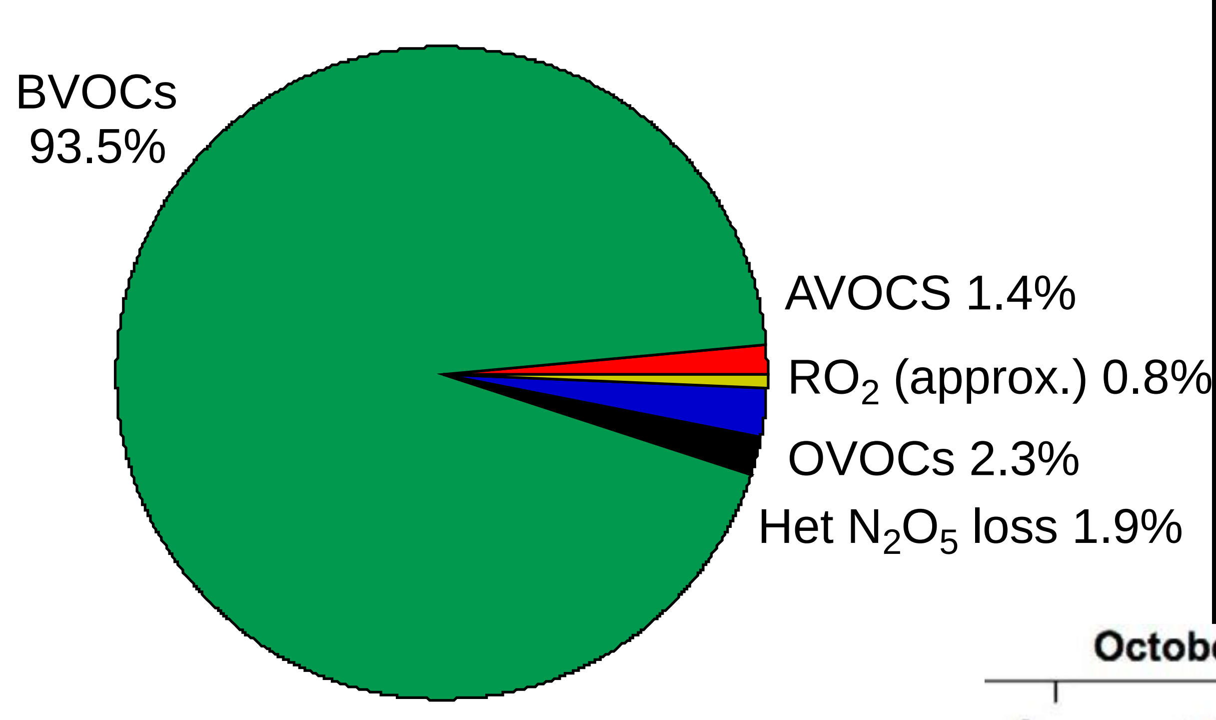


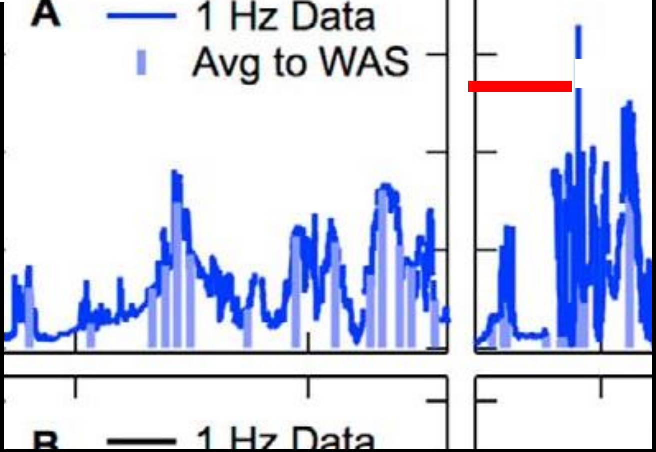
06/19/13 - Atlanta

- Biogenics dominate loss of NO_3 during the night.
- ©$_{N2O5}$ = 0.02 for this budget: likely an upper limit.

Budgets for Nitrate Radical Loss

06/19/13 - Atlanta

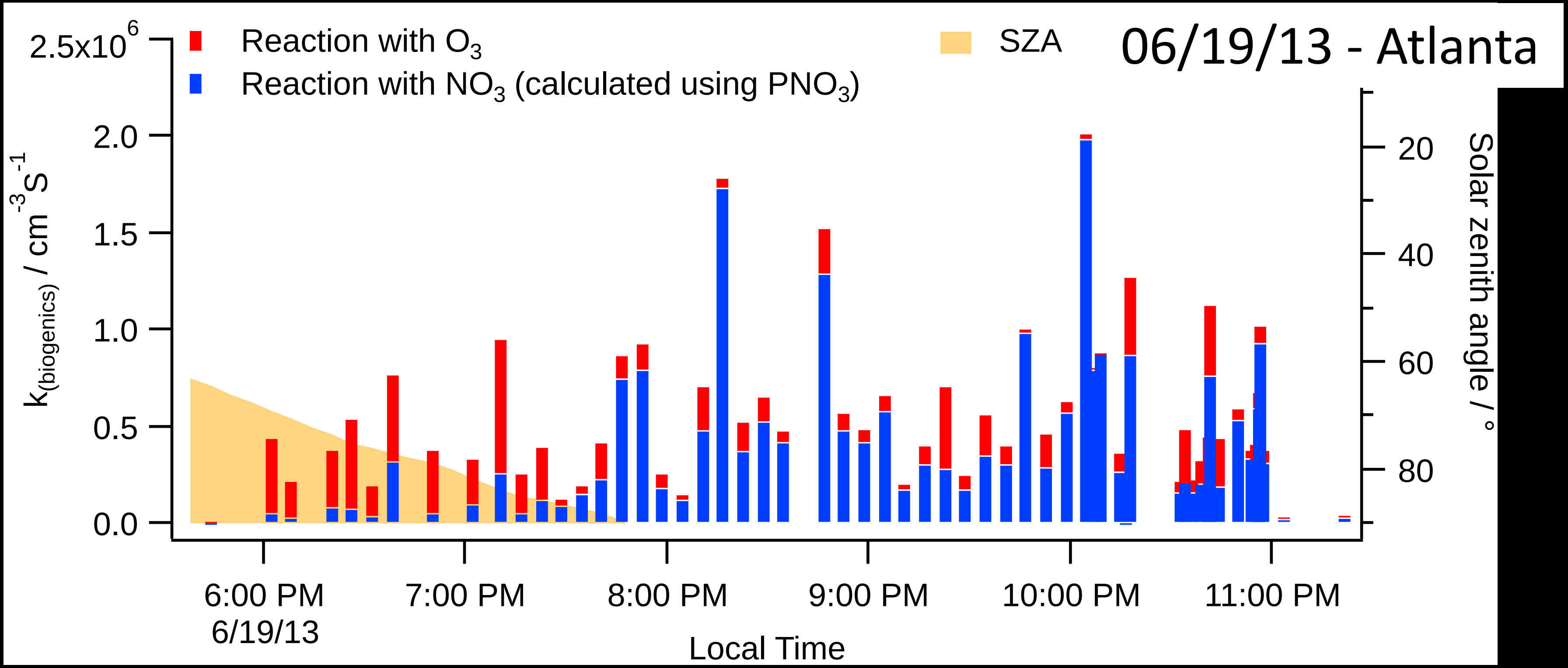




Houston Ship Channel - Texas

Brown *et al*. 2011

Is O_3 or NO_3 the Dominant Nighttime Oxidant ?



- Despite the low observed [NO_3], comparing the rates of reaction of the observed BVOCs with NO_3 and O_3 shows:
  - Nighttime reaction with NO_3 is a more significant sink for BVOCs than O_3.
  - During daytime NO_3 can still compete with O_3 for reaction with biogenics (but neither O_3 nor NO_3 can compete with OH!).

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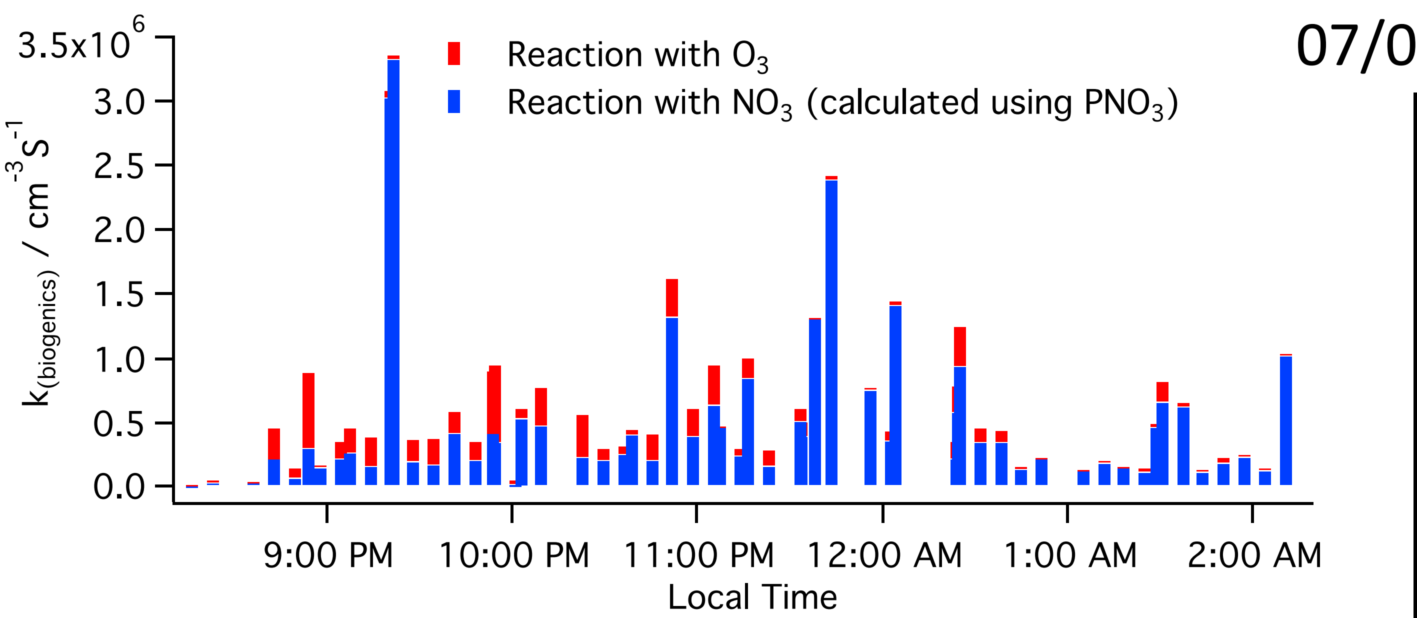
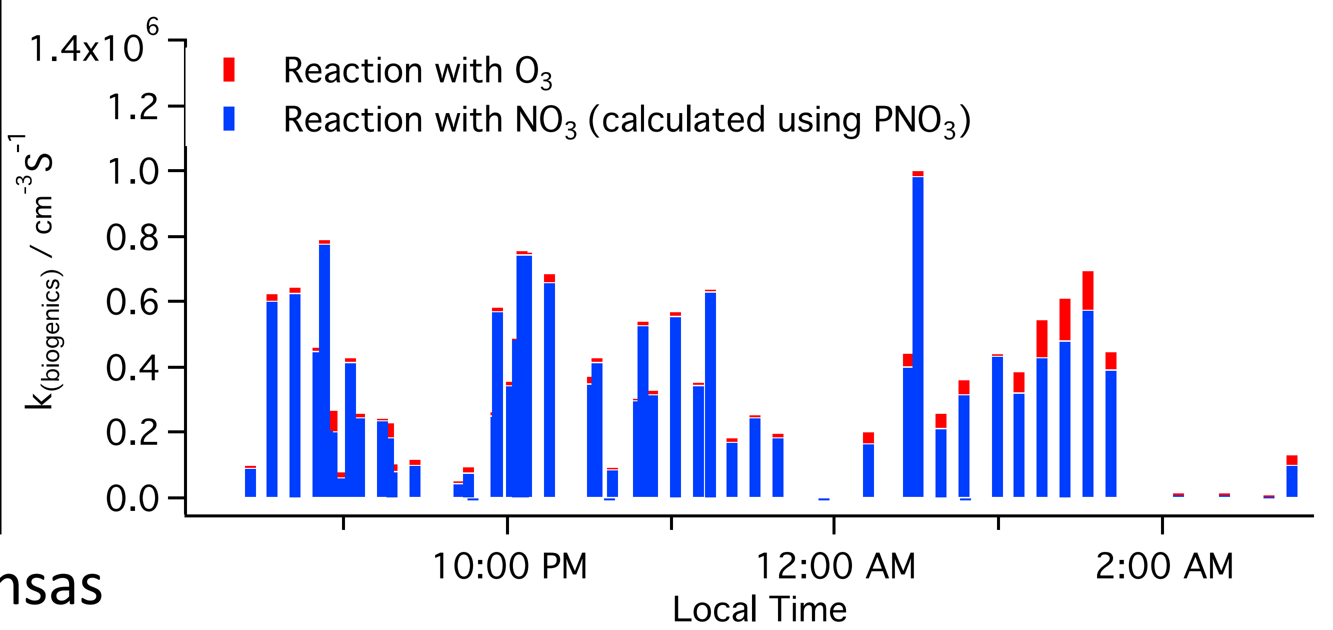


07/02/13 - Alabama



07/03/13 – Arkansas

NO_x Dependence of Nighttime BVOC Oxidation

- Nighttime BVOC oxidation occurs predominantly via reaction with NO_3 and O_3 such that:

$$-\frac{d[BVOC]}{dt} = k_{O_3}[O_3][BVOC] + k_{NO_3}\boxed{[NO_3]}[BVOC]$$

- When [BVOC] large, NO_3 in approximate steady state between production from NO_2 + O_3 and loss to NO_3 + BVOC.

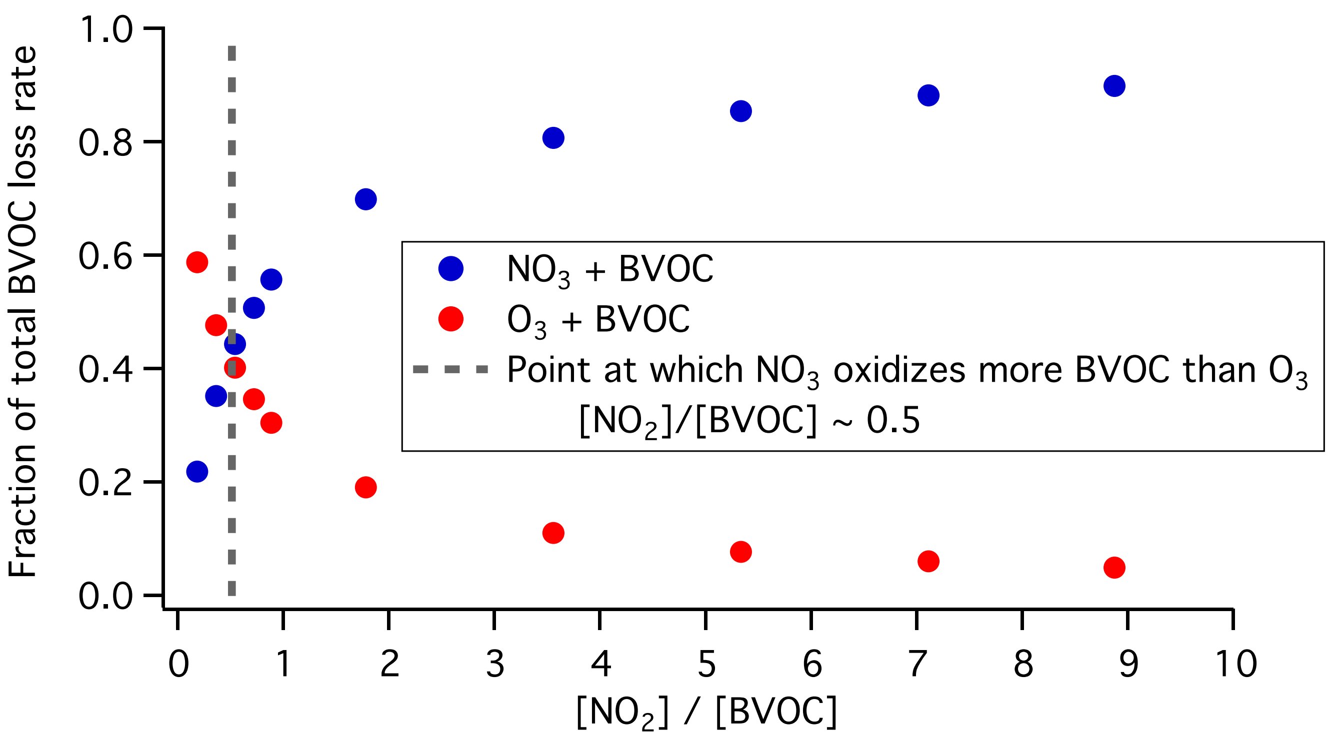
$$[NO_3] \text{»} \frac{k_{NO_2+O_3}[NO_2][O_3]}{k_{NO_3}[BVOC]}$$

- The concentration of NO_2 relative to BVOC determines competition between nitration and ozonolysis.

$$-\frac{d[BVOC]}{dt} \text{»} \left(k_{O_3}[BVOC] + k_{NO_2+O_3}[NO_2]\right)[O_3]$$

NO_x Dependence of Nighttime BVOC Oxidation

- Box model calculations, using a range of NO_2 concentrations and fixed [isoprene], [α-pinene], [β-pinene] and [O_3], illustrate the impact of [NO_2] on nighttime oxidation chemistry.



- Under these BVOC and O_3 concentrations, representative of flight 07/02/13, NO_3 becomes the dominant nighttime oxidant in the model when [NO_2]/[BVOC] > 0.5.

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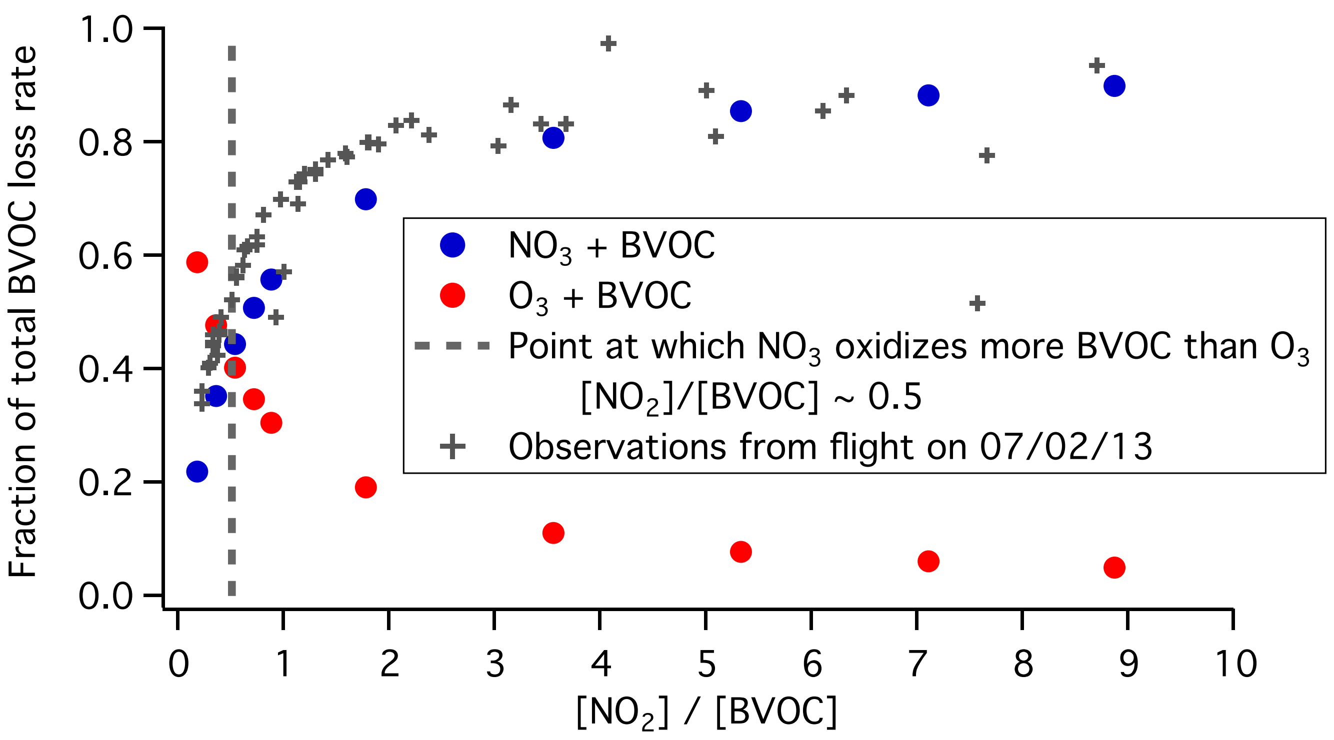

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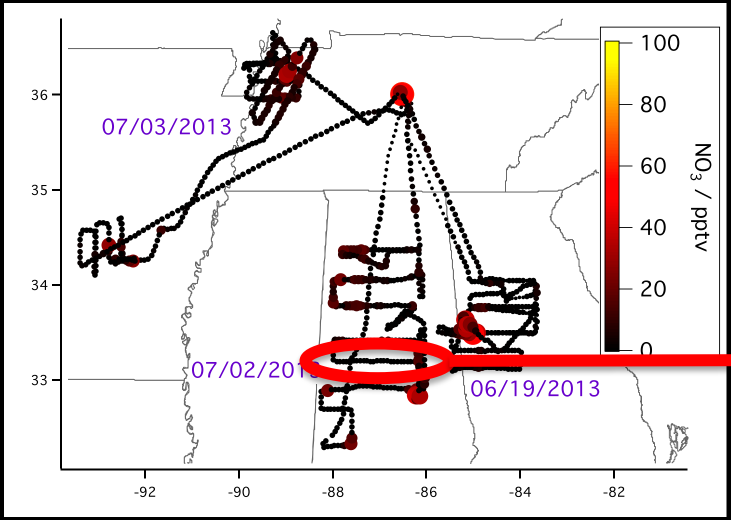
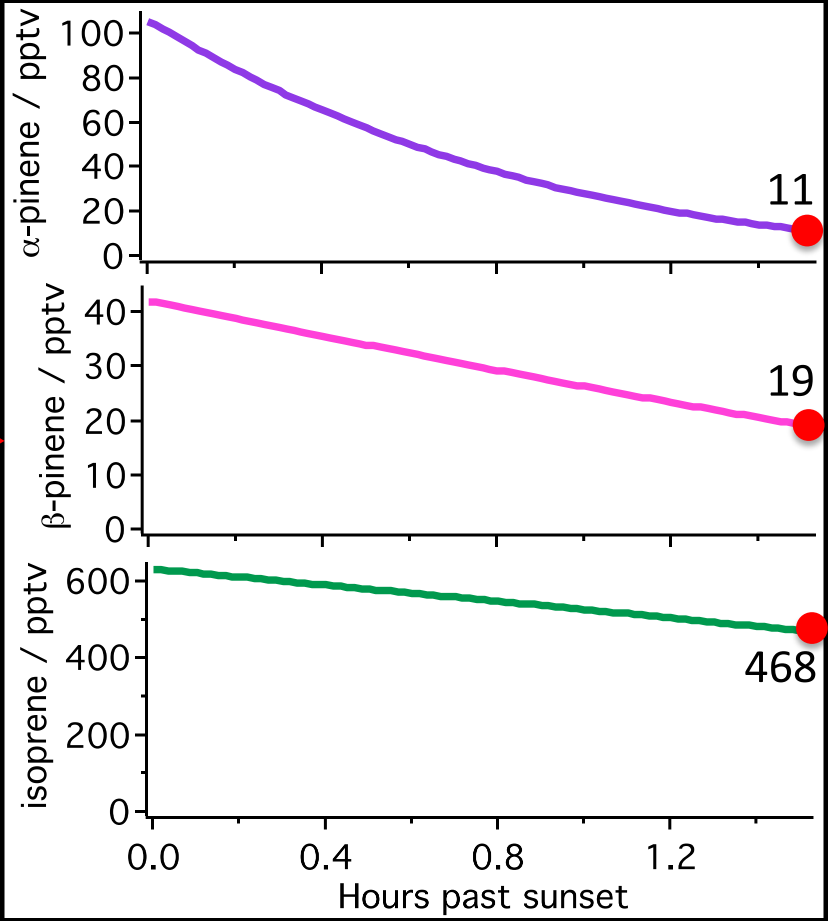
Nighttime BVOC Oxidation

- Box model analysis to calculate mass of emitted BVOC consumed by nighttime oxidation.





- Calculate [BVOC] at sunset from observed [O_3], [NO_2] and [BVOC] at time *t* after sunset.
- 0.7 μg m^{-3} hr^{-1} of BVOC oxidized between sunset and sampling.
- 70% by NO_3.

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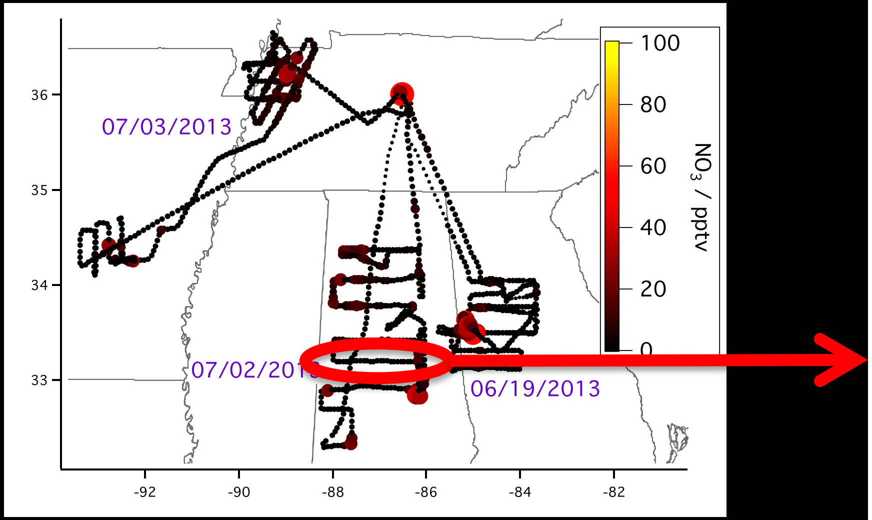

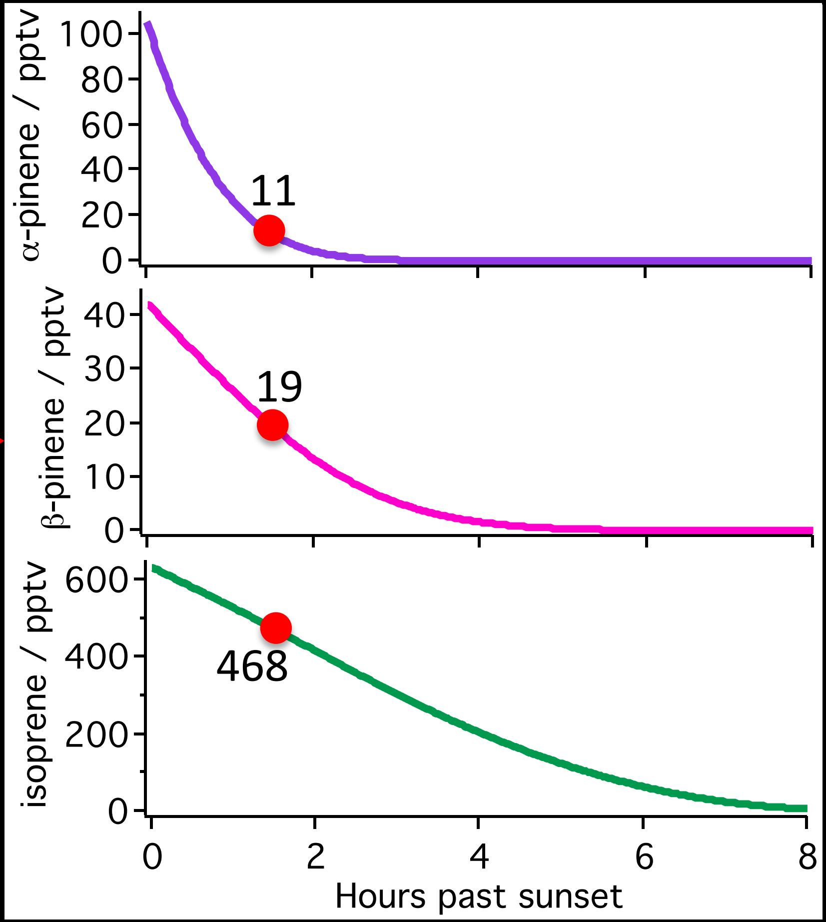

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- 0.7 μg m^{-3} hr^{-1} of BVOC oxidized between sunset and sampling.
- 70% by NO_3.
- 2.56 μg m^{-3} BVOC oxidized over 8 hr night.

Conclusions

- Generally low NO_3 (< 3 pptv), but moderate NO_3 production rates, indicating moderate, NO_x-driven nighttime oxidation.
- Nighttime NO_3 loss dominated by reaction with BVOC.
- NO_3 consistently more effective nighttime oxidant than O_3, but dependent on the $[NO_2]$ / [BVOC] ratio.

Future Work

- Calculate nighttime BVOC oxidation budgets & SOA formation potential for all nighttime flight legs.
- Analysis of vertical profiles and comparisons with surface sites to differentiate NBL from Residual Layer.
- Analysis of nighttime NO_x chemistry in power plant plumes.
- Compare with 1990s SOS data to understand how nighttime oxidation has changed with reductions in NO_x emissions