# Formation and Gas-Particle Partitioning of Organic Nitrates: Influence on Ozone Production

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# Importance of Organic Nitrates (ONs)

- ONs regulate oxidant production

  Reactions involving VOCs and $NO_x$ form $O_3$. Also:

  $RO_2 + NO \rightarrow \alpha\, RONO_2 + (1-\alpha)\, RO + NO_2$

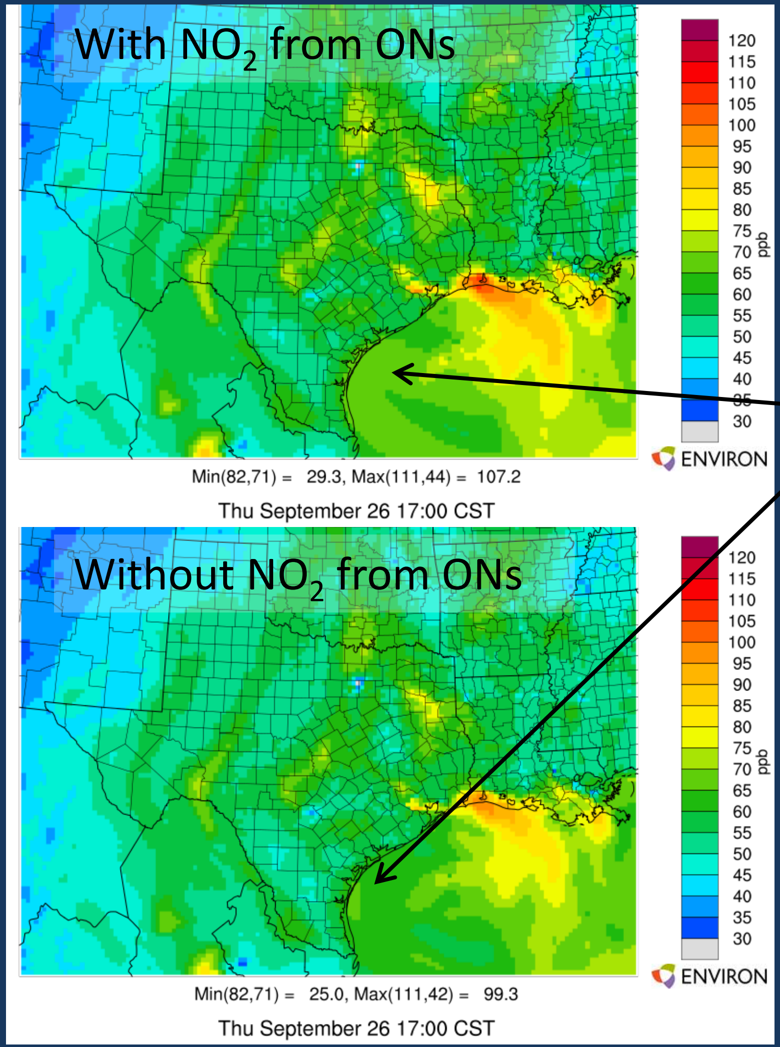
  - sink for both NO and radicals
  - permanent or temporary N-sink?

  $RONO_2 + h\nu/OH \rightarrow \beta\, NO_2 + (1-\beta)\, RONO_2$ → "NOx recycling"

- ONs are an important aerosol constituent
  - Significant fraction of urban OA
  - $RONO_2$ are chromophores
- Interaction between aerosol, ON and oxidants
  - If aerosols sequester and/or destroy ONs they can modulate oxidant production

# Ozone is sensitive to $NO_2$ "recycled" from ONs

**Ozone at 17:00 CST on 9/26/13**




- Outflow of continental air to Gulf of Mexico: ONs react as continental air ages
- $NO_2$ from ONs adds 5 to 10 ppb ozone over western Gulf – inconsistent with low ozone at coastal monitors

# Condensed Mechanisms and Regional Modeling

- Current mechanisms devote only a handful of species/reactions to ONs out of hundreds
- Current regional models (CMAQ, CAMx) do not explicitly model gas/aerosol partitioning for ONs

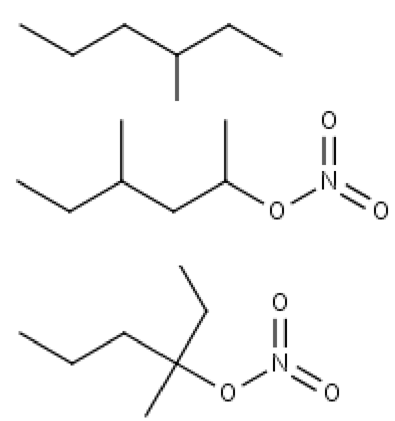
| | CB05 | CB6r1 | SAPRC11 | RACM2 |
|---|---|---|---|---|
| Total rxn/spec | 156/51 | 213/73 | 273/109 | 363/120 |
| ON rxn/spec | 2/1 | 4/3 | 5/2 | 4/3 |
| ON species (comments) | NTR | NTR<br>INTR<br>(isoprene N)<br>CRON<br>(nitrocresols) | RNO3<br>NPHE<br>(nitrophenols) | ONIT<br>ISON<br>(isoprene N)<br>NALD<br>(isoprene N) |

# Chemical aging of ONs

- Photolysis liberates $NO_2$ from ONs
  - 1 week timescale; other processes compete
- OH reaction liberates $NO_2$ from small ONs
  - Have tested propyl and butyl nitrate in a smog chamber
- No conclusive experiments with large ONs
  - Photolysis expected to be similar to small ONs
  - Nitrate group lowers OH rate constant, e.g.
    - OH + 3-Me-hexane: 7.2E-12
    - OH + 3-Me-hexane-2-nitrate: 4.6E-12
    - OH + 3-Me-hexane-3- nitrate: 1.9E-12

    → OH reaction likely to add functional group rather than liberate $NO_2$

    (MCM assumes otherwise)




MCM 3.2

# Summary of CB6r2 Implementation

- ONs are formed from VOC + $NO_x$
- Partition to PM reversibly
- In PM are hydrolyzed to $HNO_3$

→ ON less available for $NO_x$ recycling

Improvements expected for:

- Modeled $O_3$
- Modeled NOy partitioning

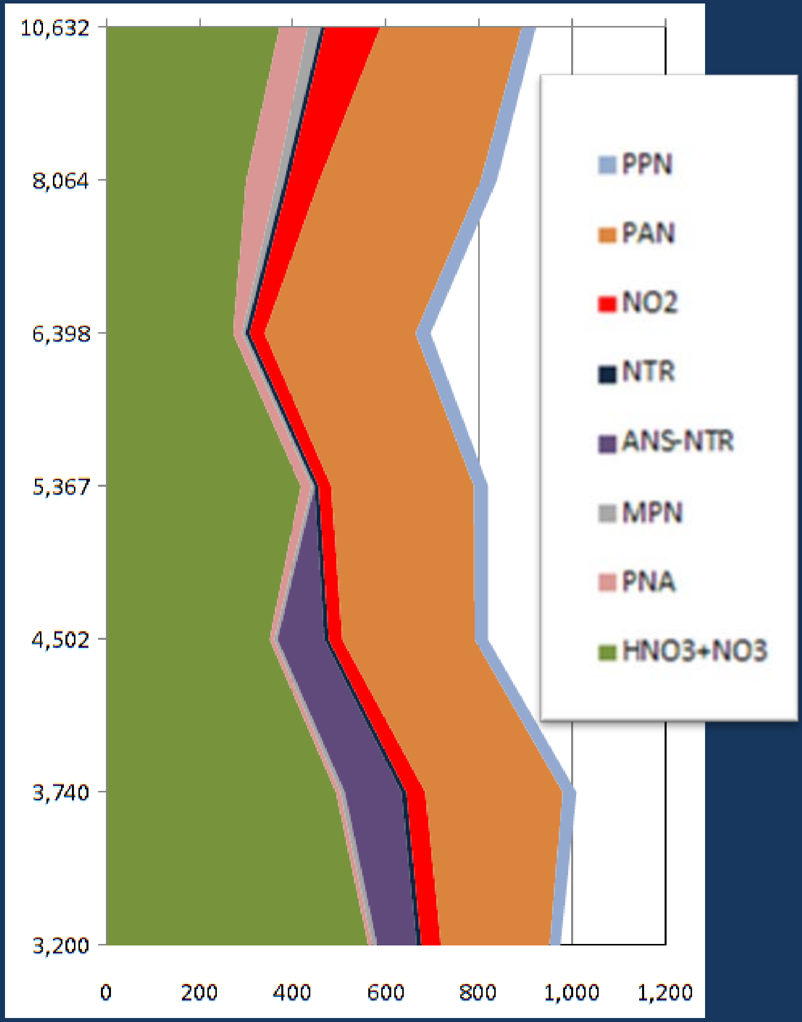
# ONs in Carbon Bond

| CB Species | Rxn | CB05 | CB6 | CB6r1 | CB6r2 (AQRP 12-012) |
|---|---|---|---|---|---|
| NTR | hv | NO2<br>slow | as CB05 | as CB6 | |
| | OH | HNO3<br>slow | HNO3<br>medium | as CB6 | |
| INTR (isoprene) | OH | | NTR/NO2/INTR<br>very fast | as CB6 | NTR2/NO2/INTR<br>very fast |
| NTR1 (alkyl) | hv | | | | NO2<br>slow |
| | OH | | | | NTR2<br>medium |
| NTR2 (multi-functional) | H2O | | | | HNO3<br>fast |

# Testing CB6r2 Improvements

## NOy averages from INTEX-A aircraft flights

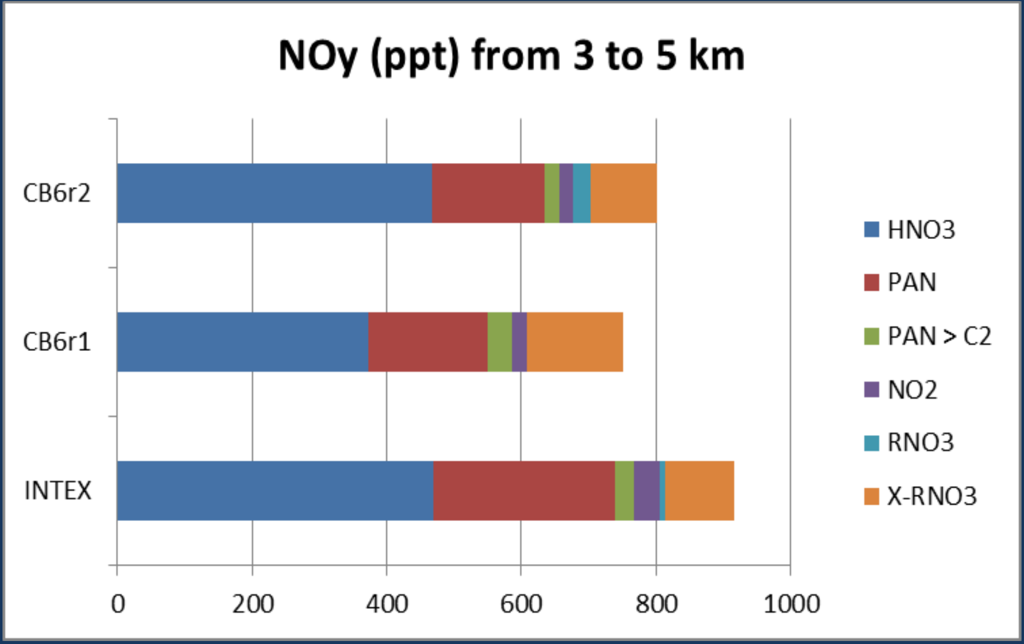
- Data from multiple instruments, some with limited height range
- NTR = sum of alkyl nitrates < C5 speciated by GC
- ANS = sum of all alkyl nitrates by thermal decomposition (below 5 km)
- Focus on height range from 3 to 5 km

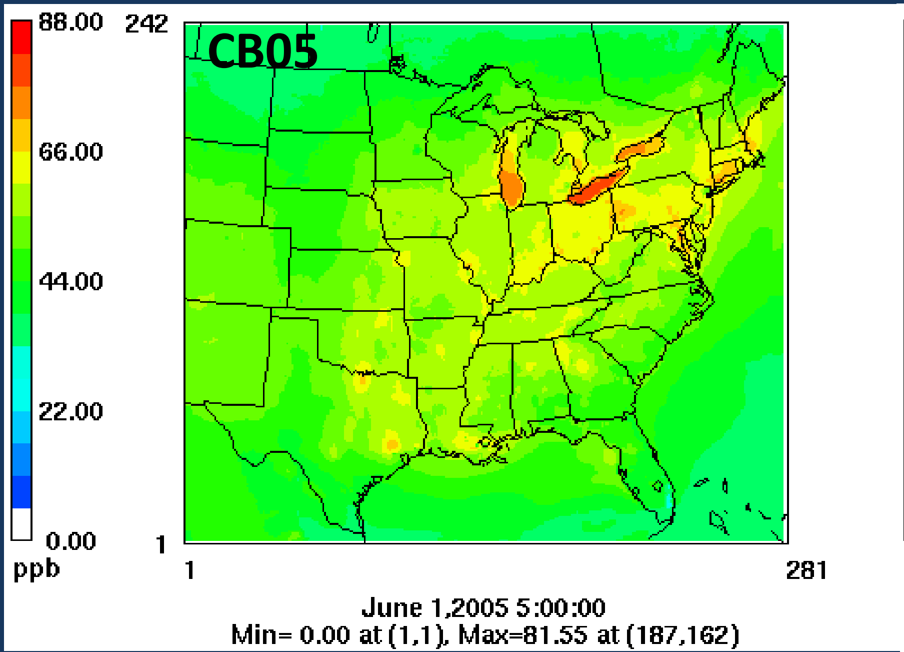


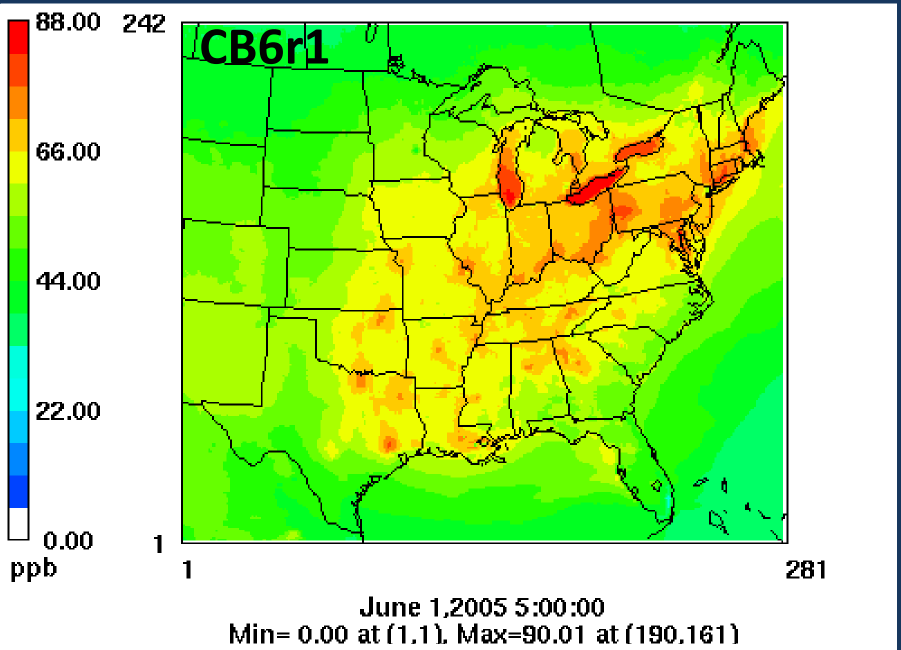

data courtesy of Barron Henderson

# Evaluating NOy Distributions

- CB6r1 combines mono- and multi-functional ONs (RNO3 and X-RNO3)
- CB6r2 resolves mono- from multi-functional ONs and split is consistent with INTEX
- ON hydrolysis in CB6r2 improves HNO3





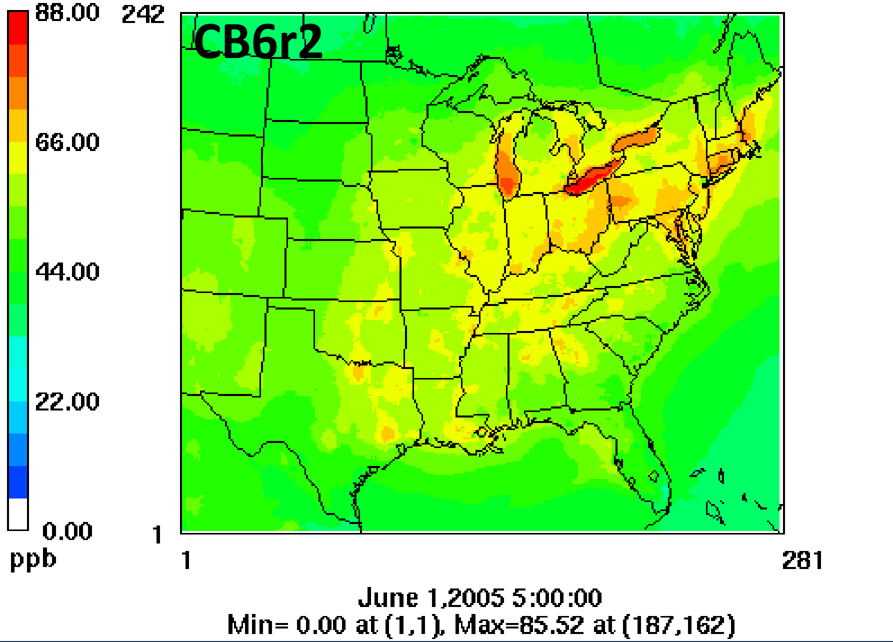



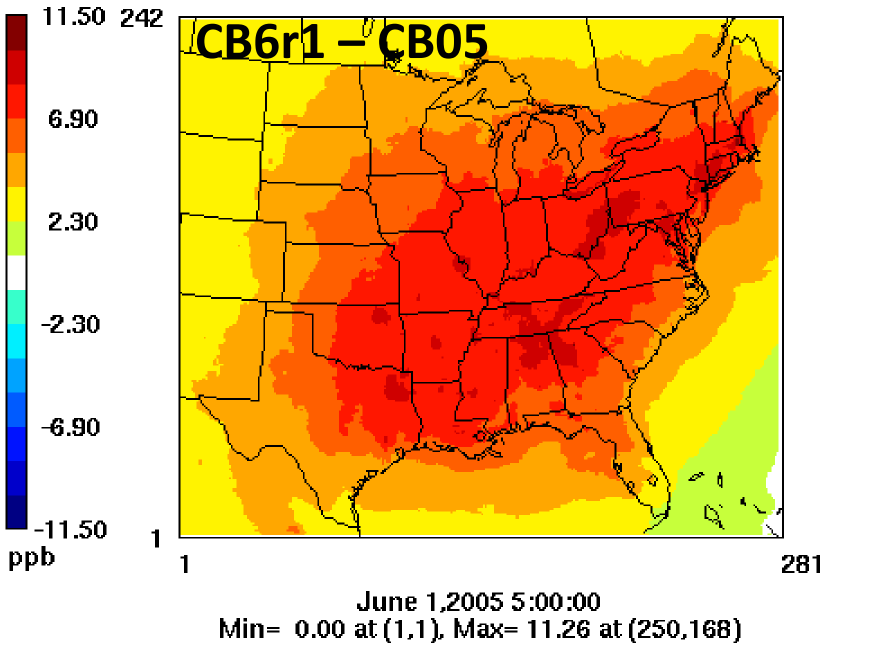

## Evaluating Ozone

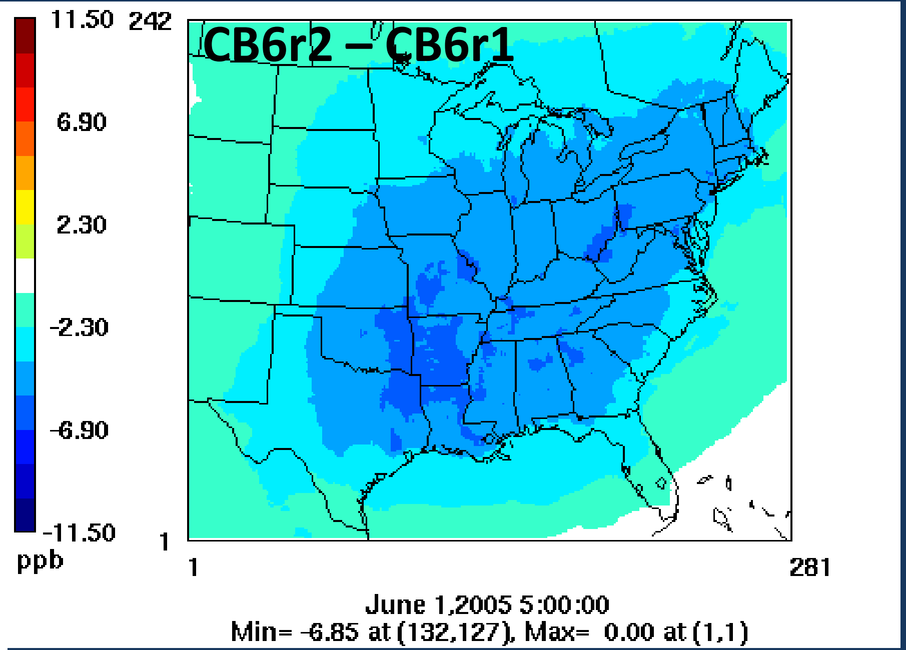
**June 2005 average MDA8 $O_3$**

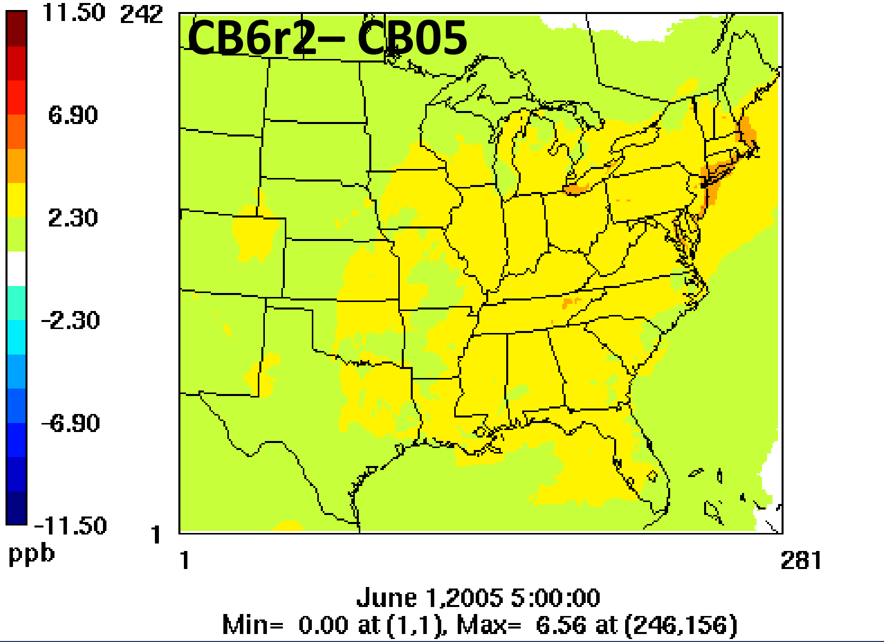
EPA CSAPR modeling database

- Includes ozone and PM
- MM5; NEI; MEGAN; CAMx6





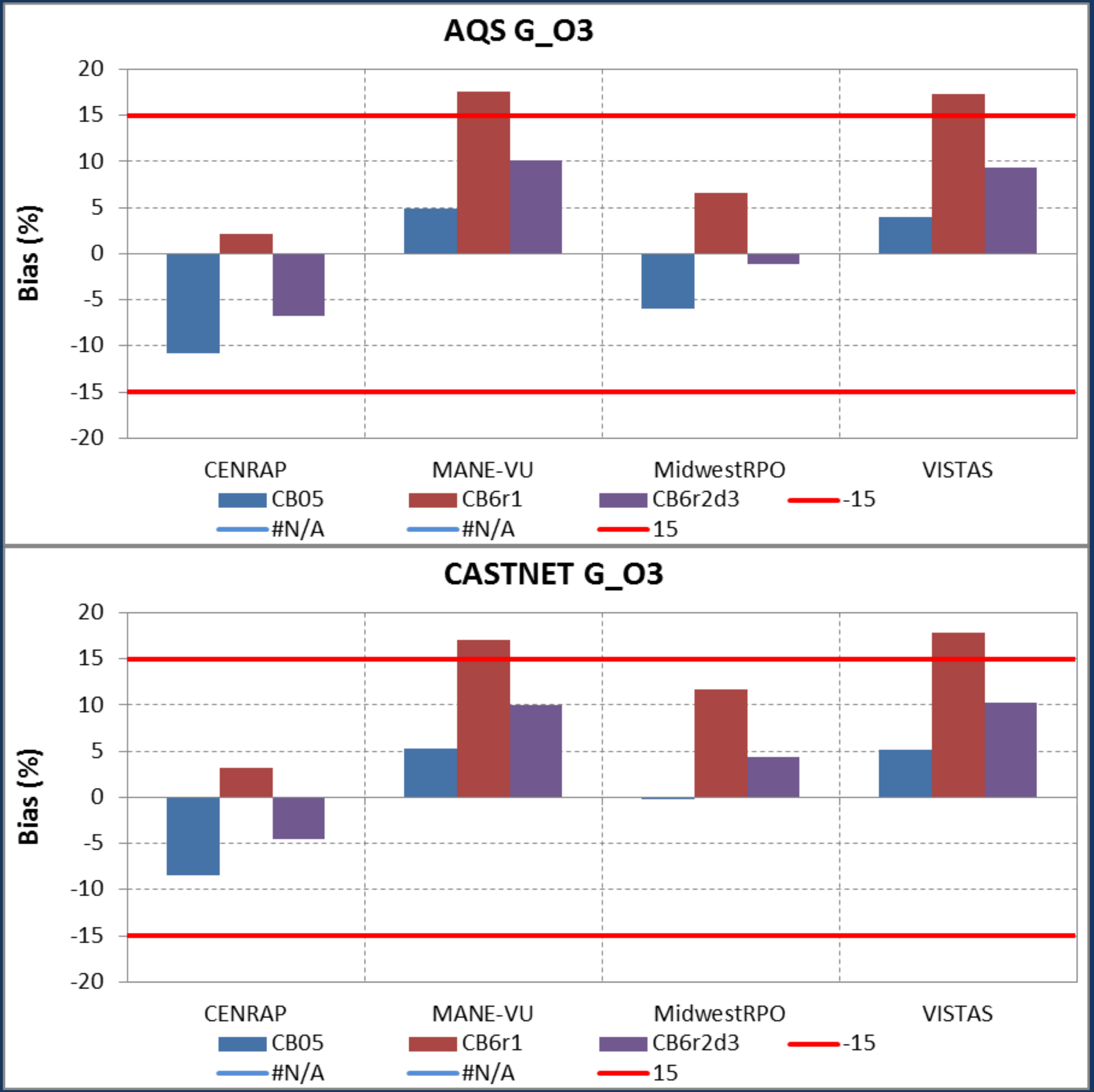

## Differences in June Average MDA8 O3

# June 2005 ozone model bias

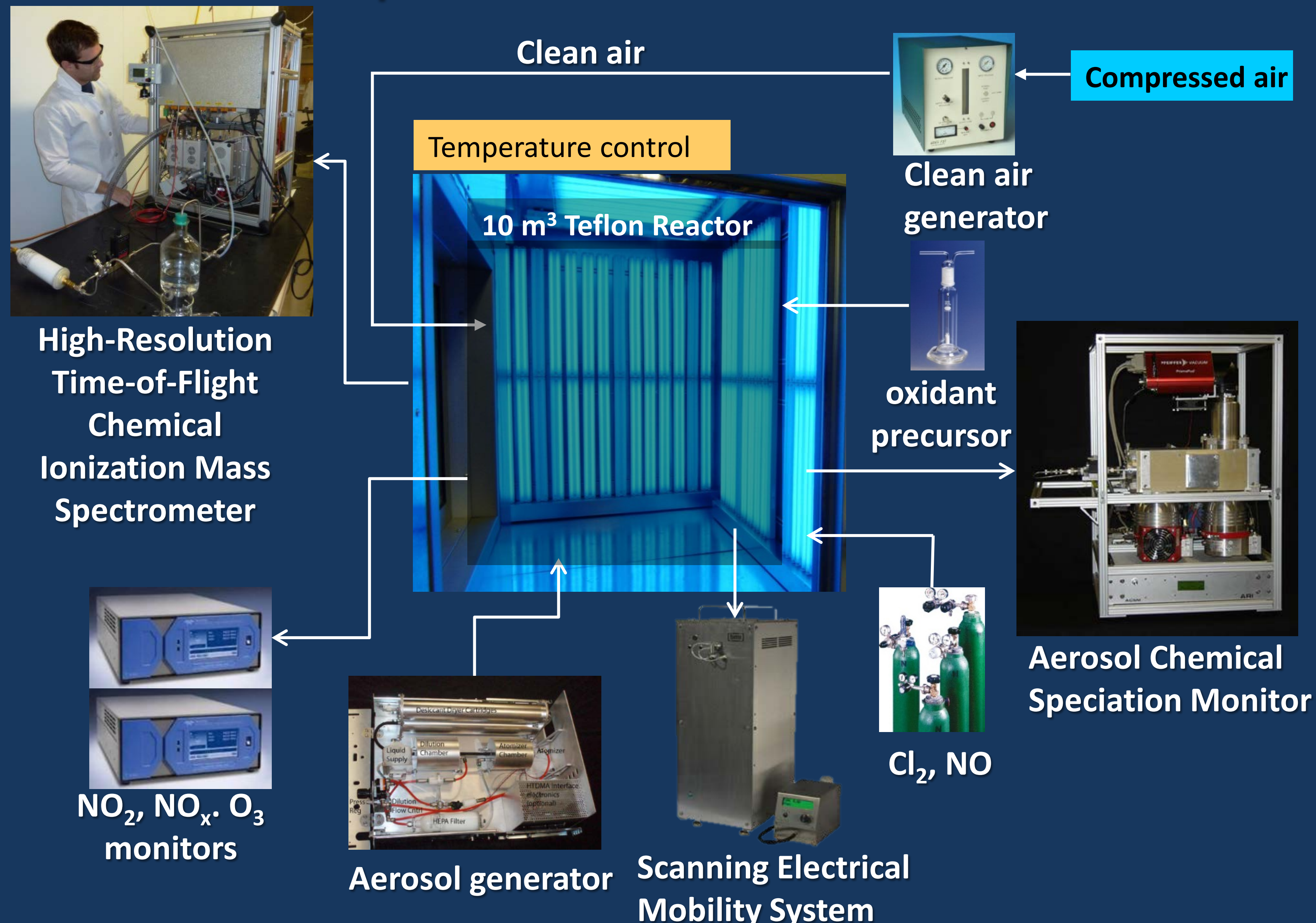
Fractional bias at EPA (AQS) and rural (CASTNET) monitors by RPO region

Unacceptable high bias with CB6r1 attributable to ON chemistry

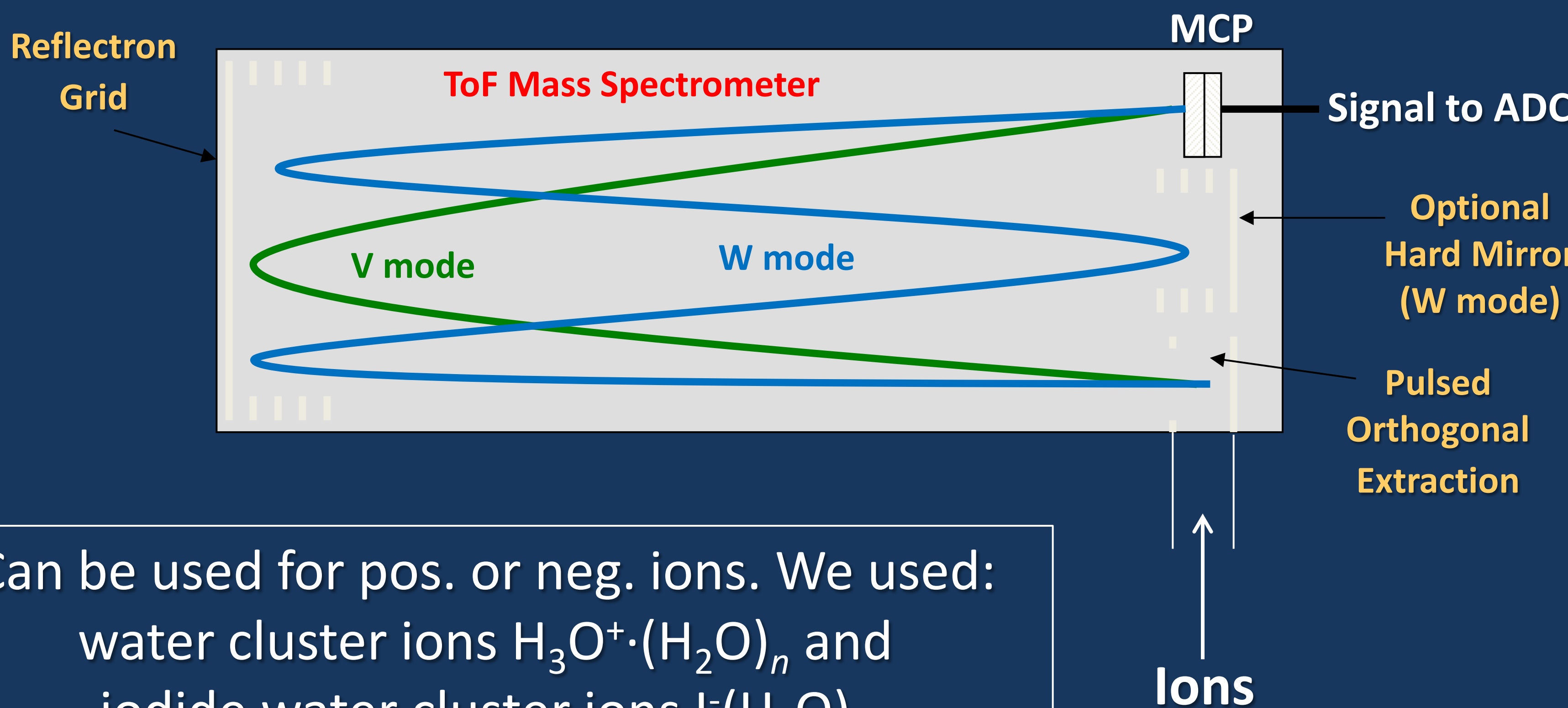
Acceptable performance with both CB6r2 and CB05



# Experimental Evidence



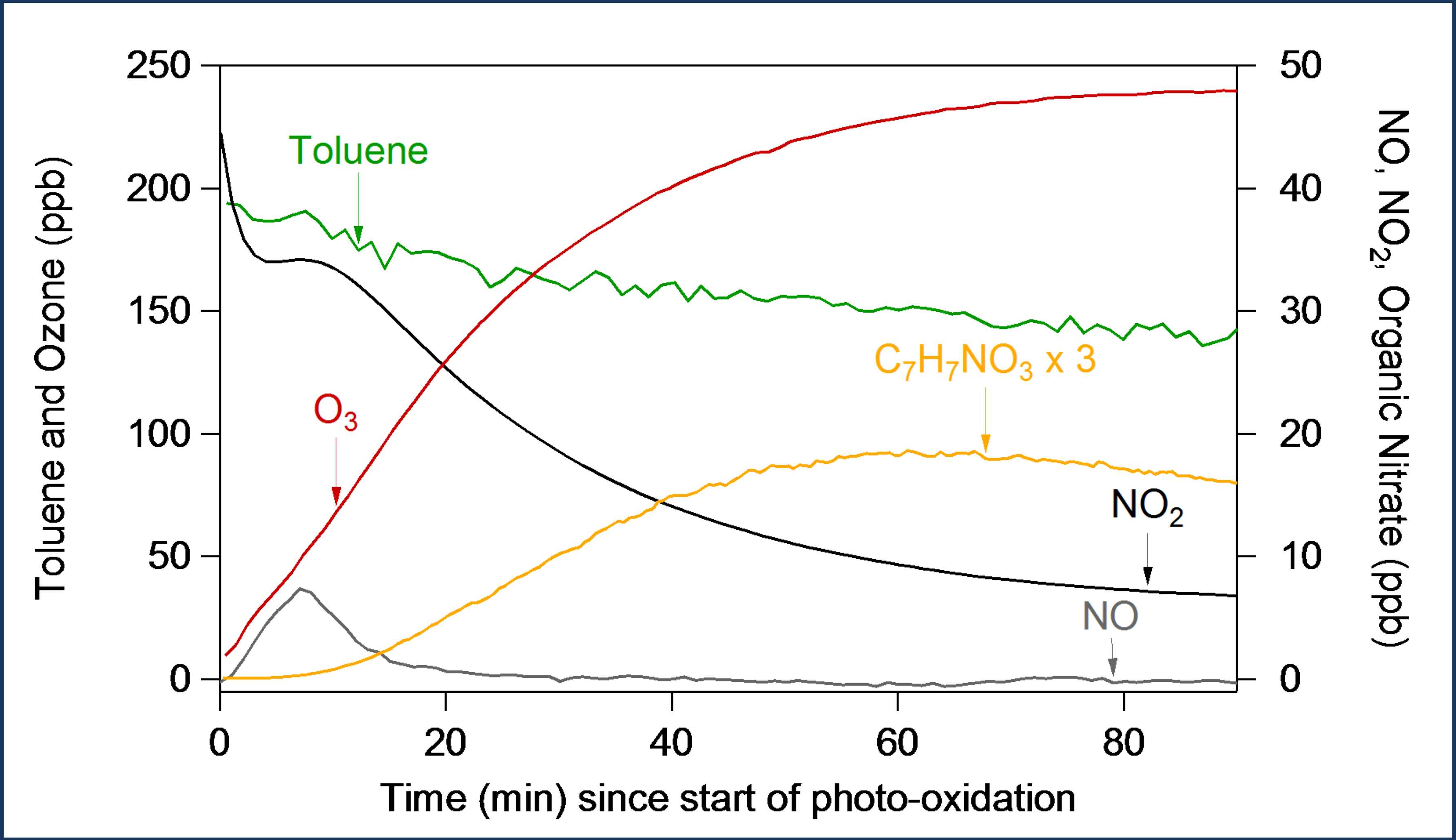
# High Resolution Time-of-Flight (HRToF) Chemical Ionization Mass Spectrometer




Can be used for pos. or neg. ions. We used: water cluster ions $H_3O^+ \cdot (H_2O)_n$ and iodide water cluster ions $I^-(H_2O)_n$

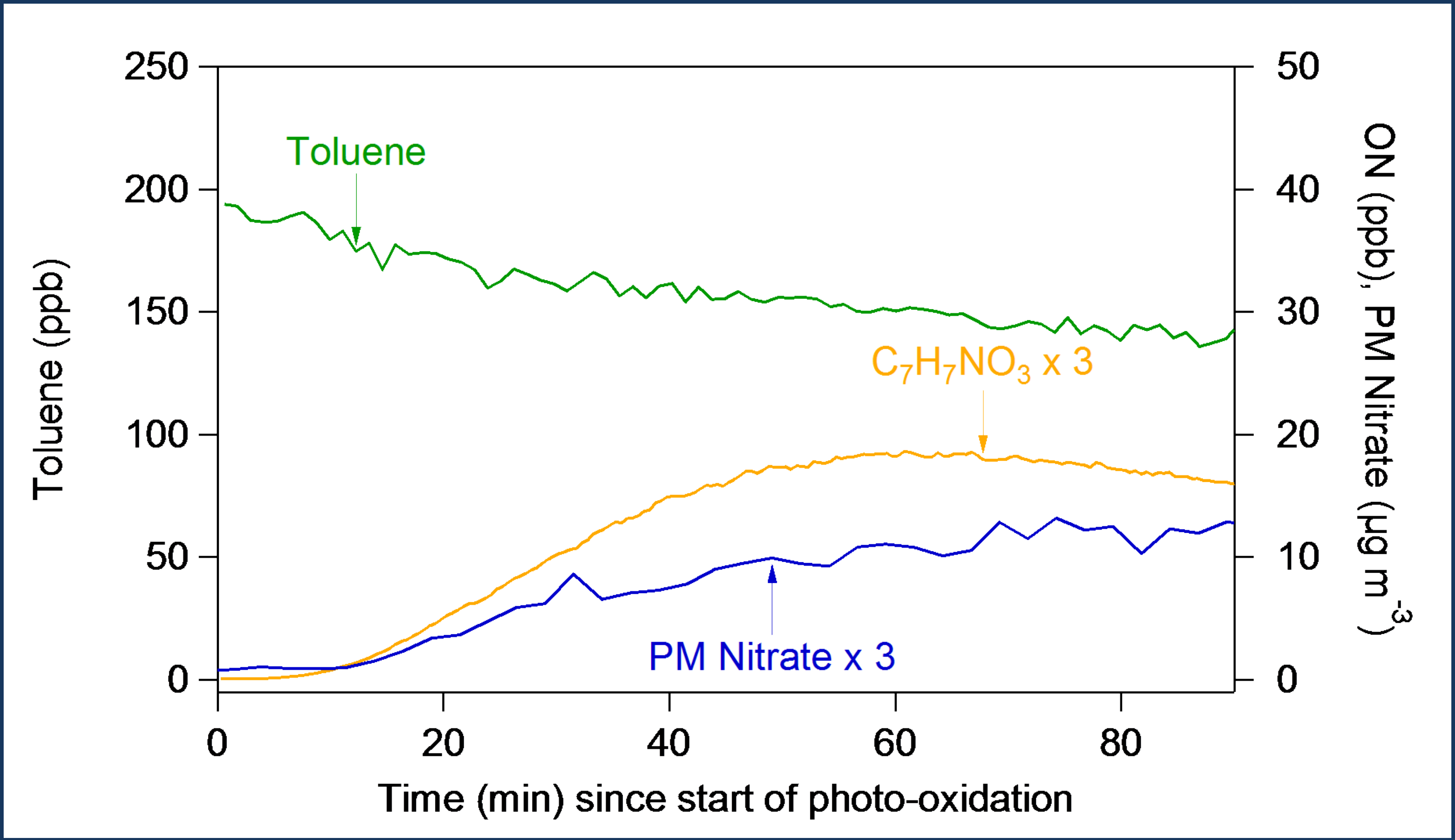
DeCarlo et al. *Anal. Chem.*, 2006.

# VOC (toluene) + OH + $NO_x$ → $O_3$ + ONs



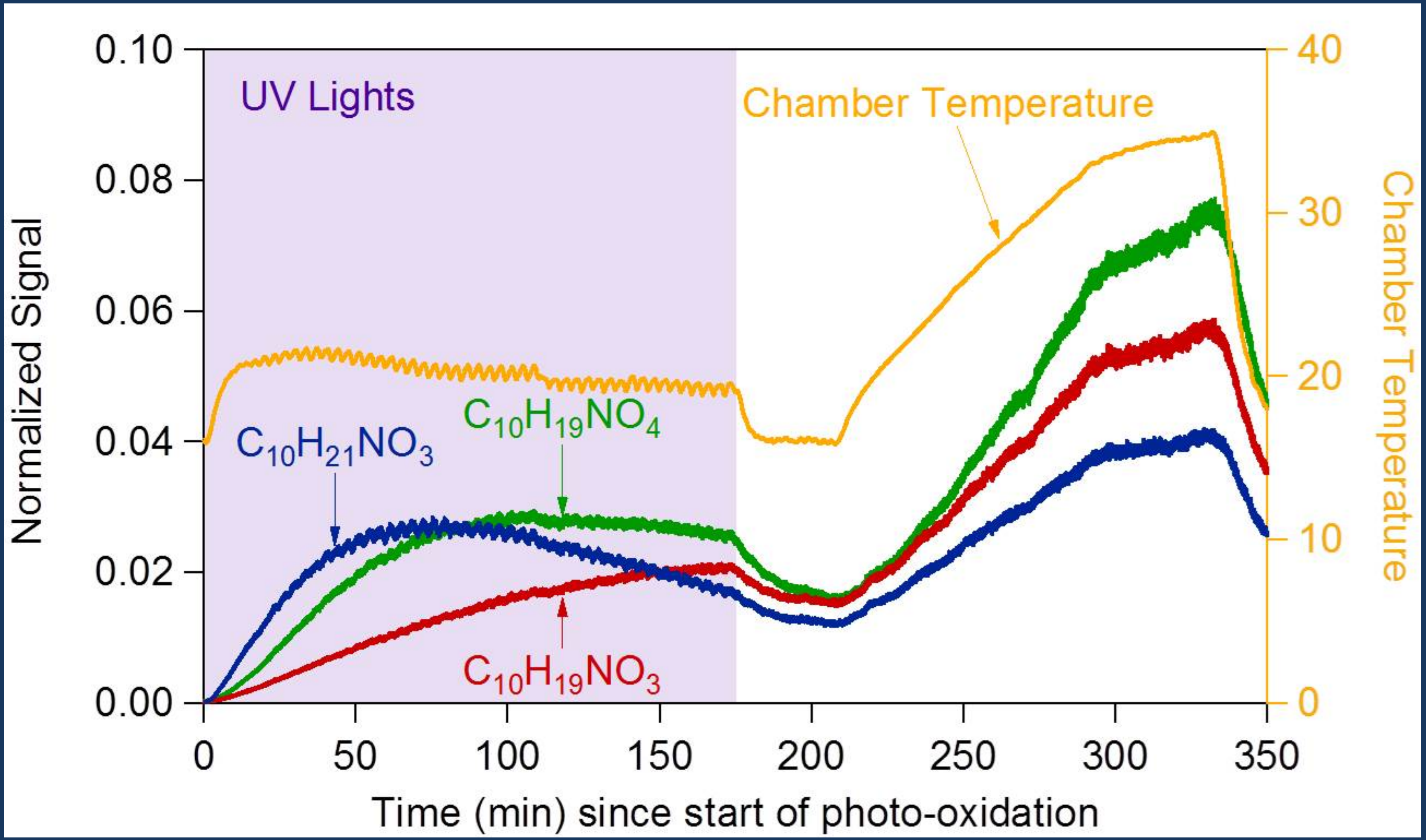

Toluene and $NO_x$ decrease, $O_3$ and ON increase
→ VOC is a $O_3$ source and $NO_x$ sink.

# ONs Partition to Particle Phase



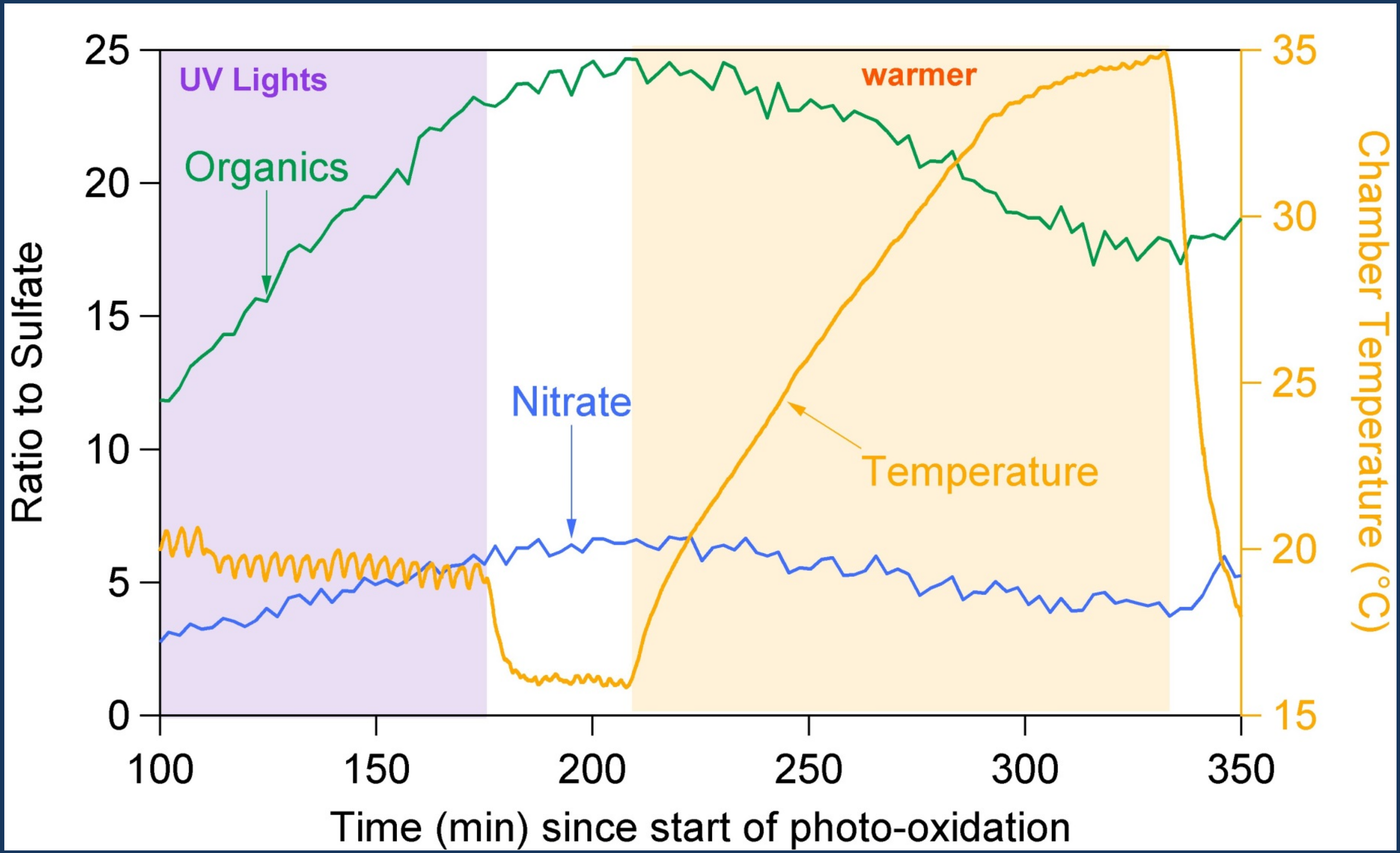

(PM Nitrate is just sum of NO and $NO_2$ fragments)

# ONs Partition Reversibly




Gas-phase data from an α-pinene + OH + NOx experiment

# ONs Partition Reversibly




Particle-phase data from an α-pinene + OH + NOx experiment

# Evidence from Environmental Chamber Experiments

Organic Nitrates

- Are formed in VOC + NOx reactions
- Partition to the particle
- Partitioning is reversible

Ongoing experiments

- VOC + NOx at varying relative humidity
- Vary temperature to observe partitioning

# DISCOVER-AQ measurements in Houston - Overview

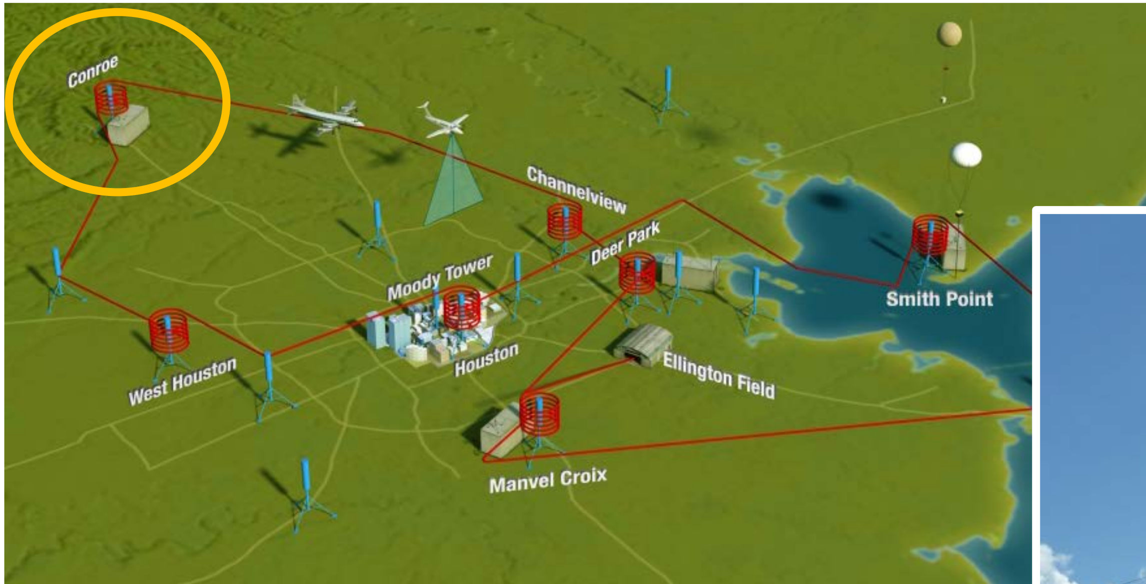
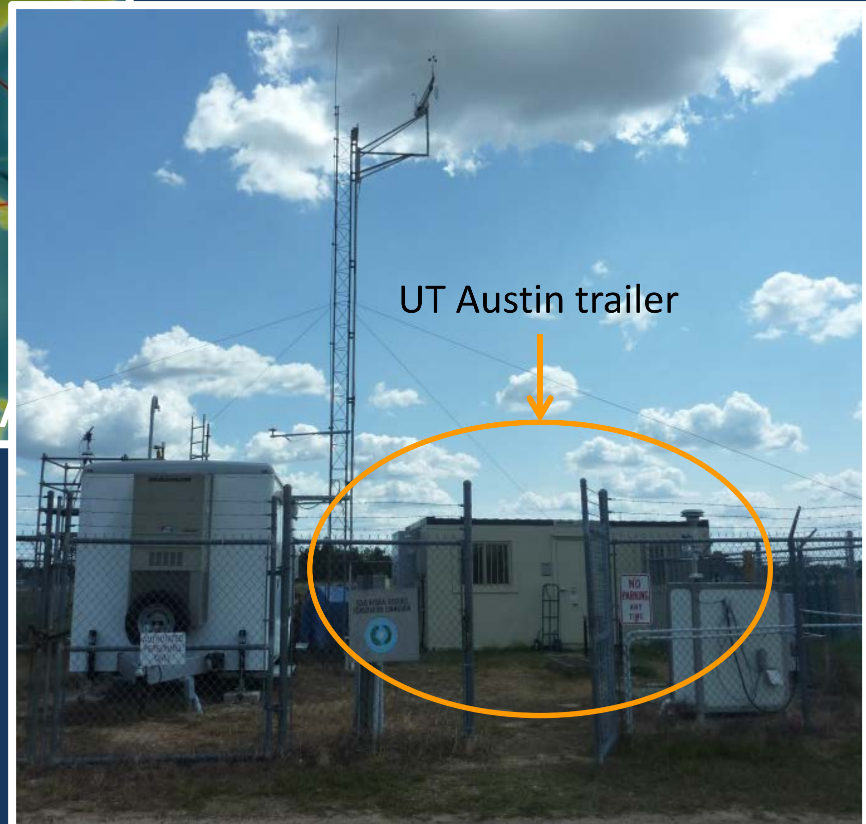
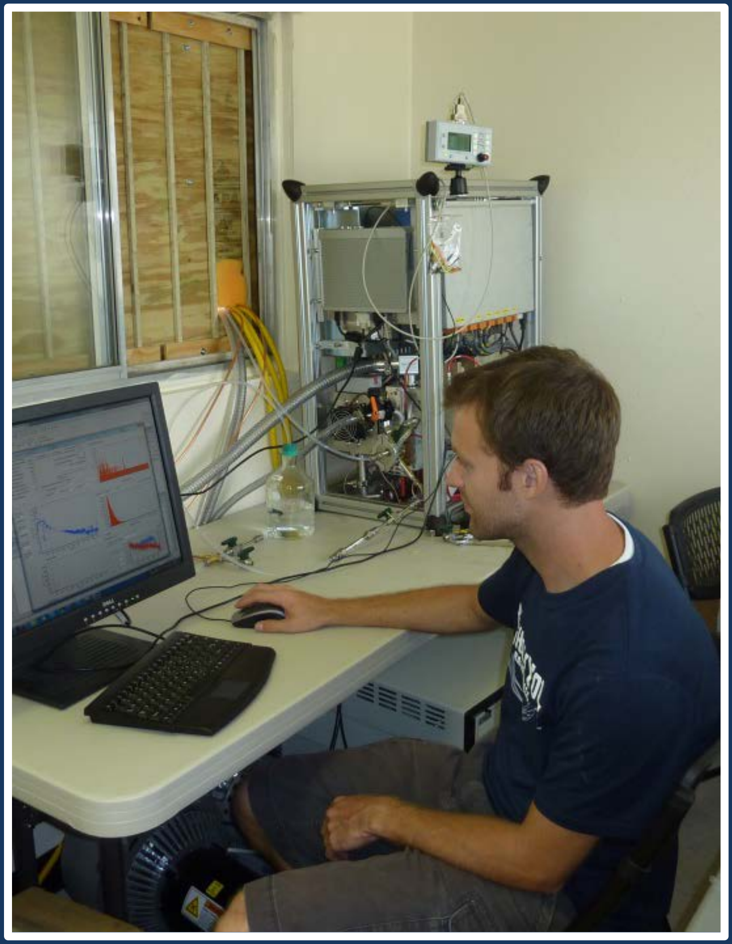


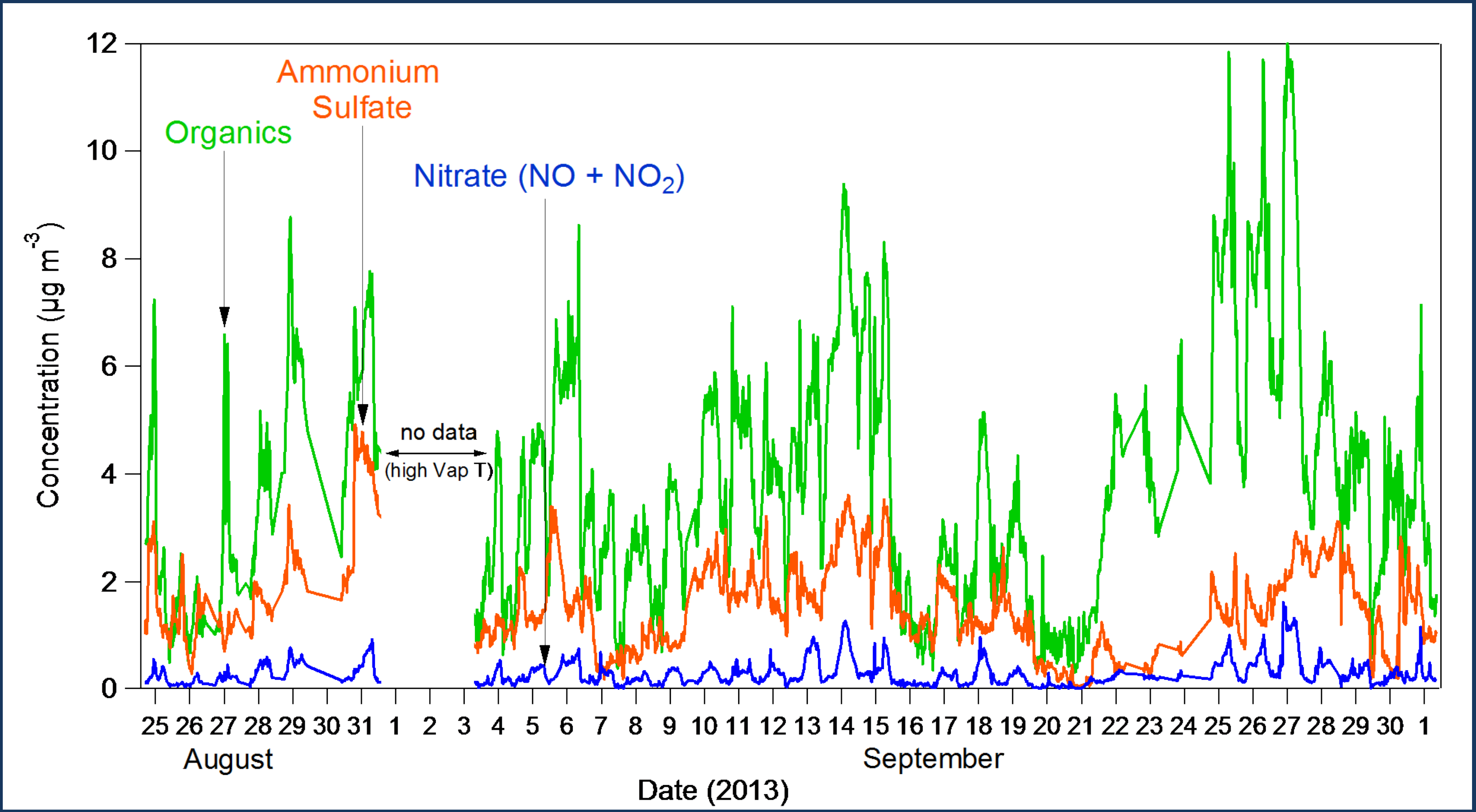

**Image from NASA http://discover-aq.larc.nasa.gov/**



# DISCOVER-AQ measurements in Houston – Instrument set-up

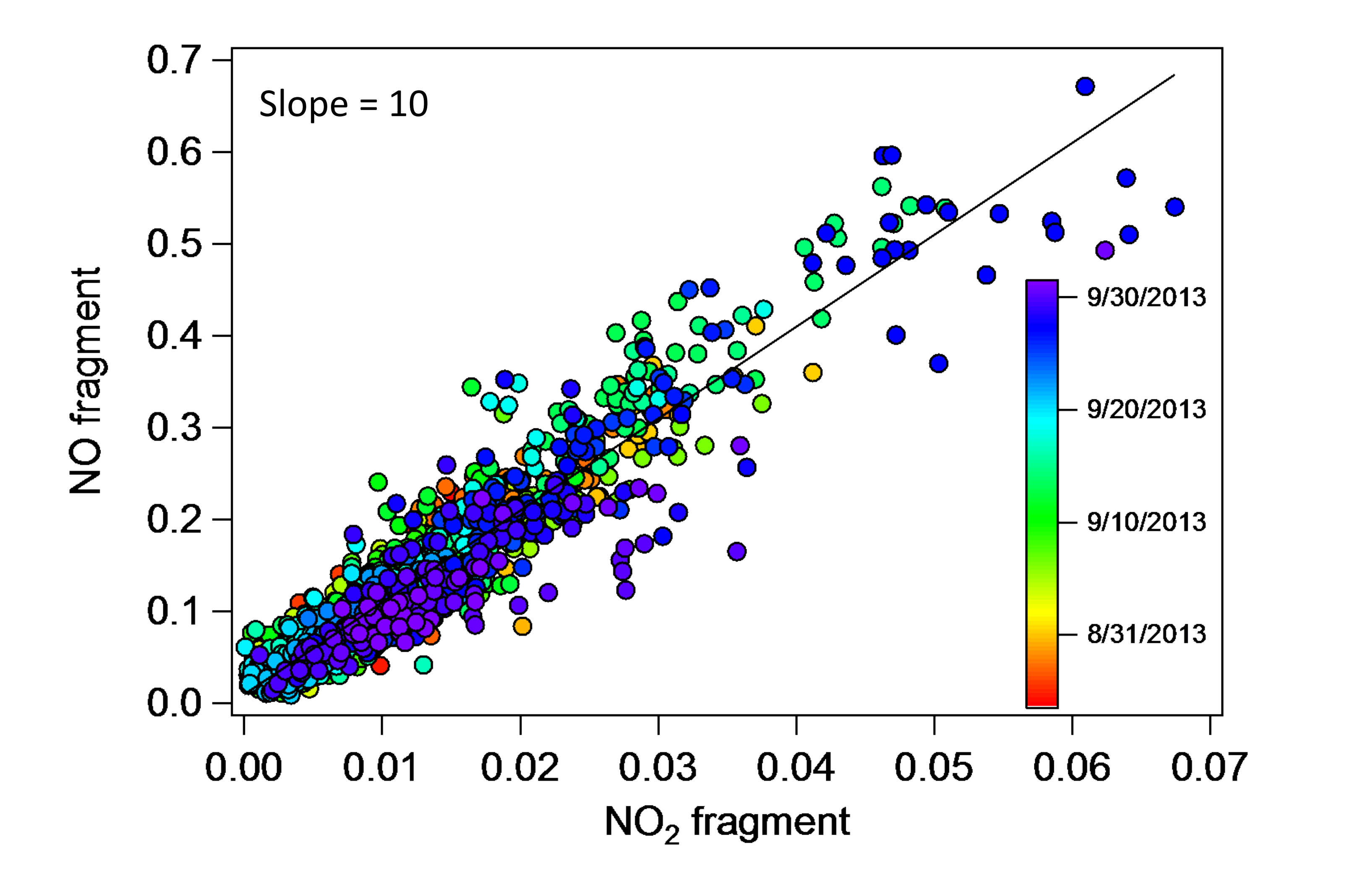



# $PM_1$ Composition - Overview



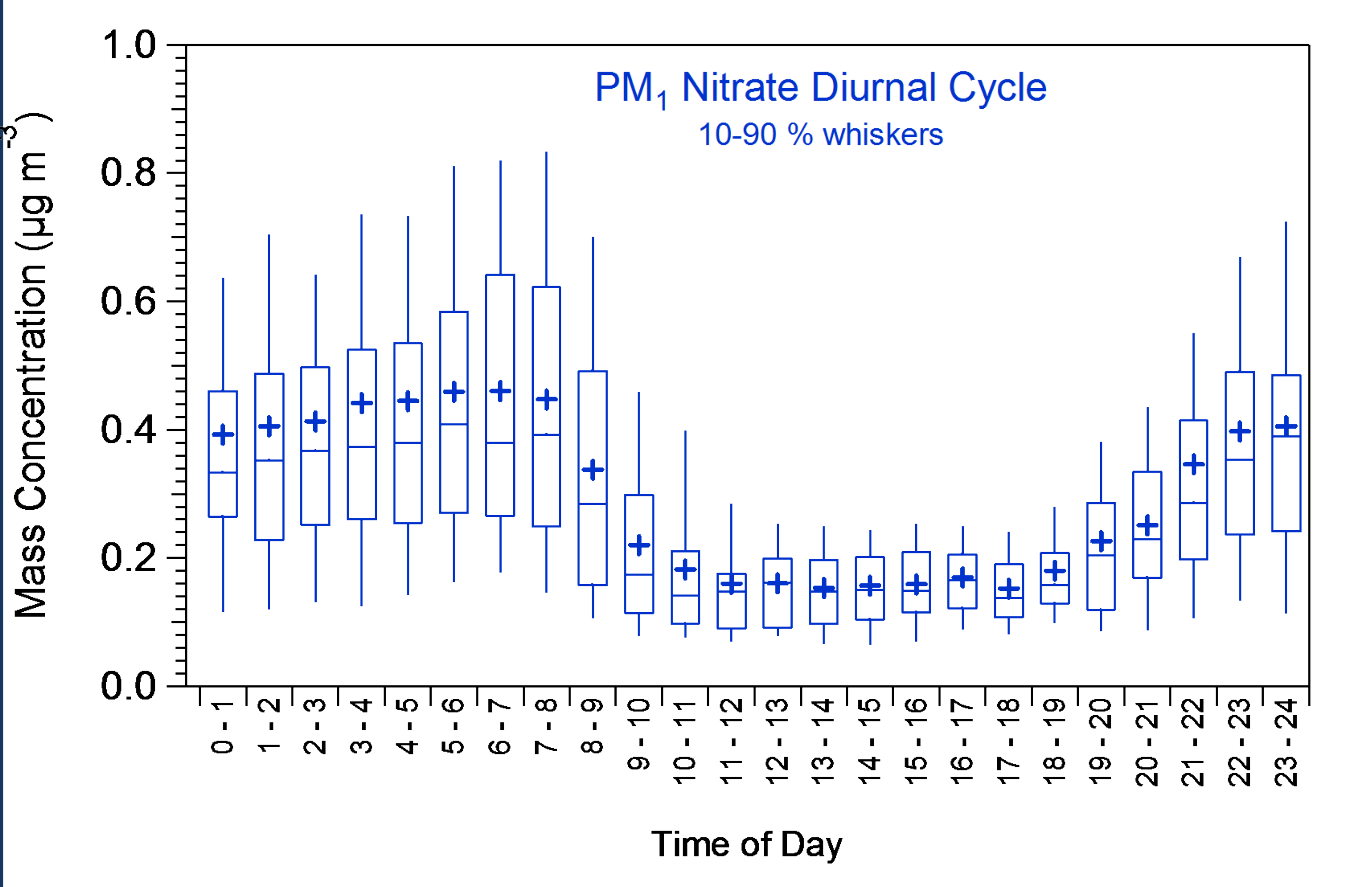

$PM_1$ composition was 70% organic on average; variable

# $PM_1$ Nitrate due to Organic Nitrate



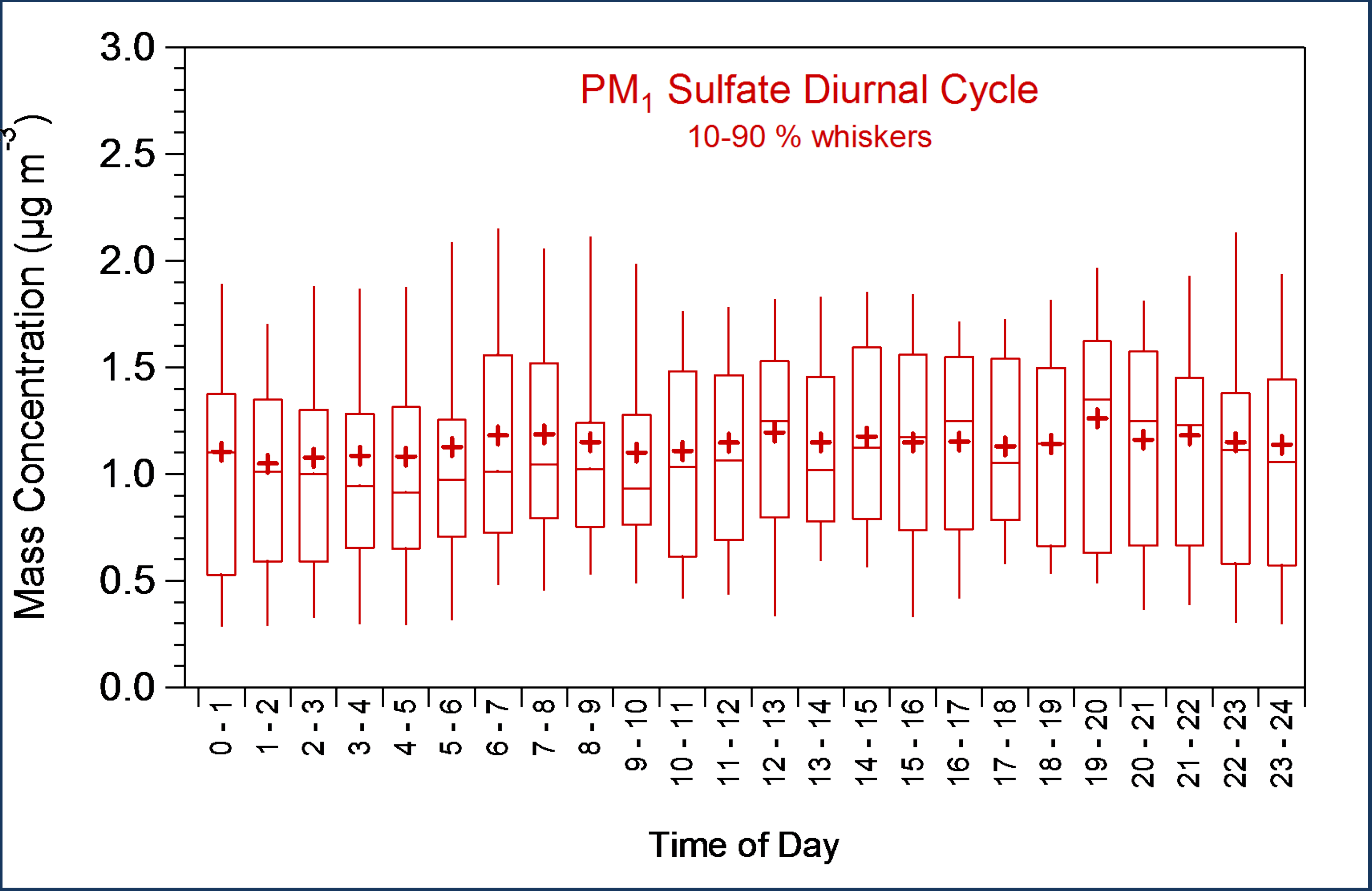

By comparison: $NO/NO_2$ of inorganic ammonium nitrate ~ 3

# $PM_1$ Nitrate Diurnal Cycle



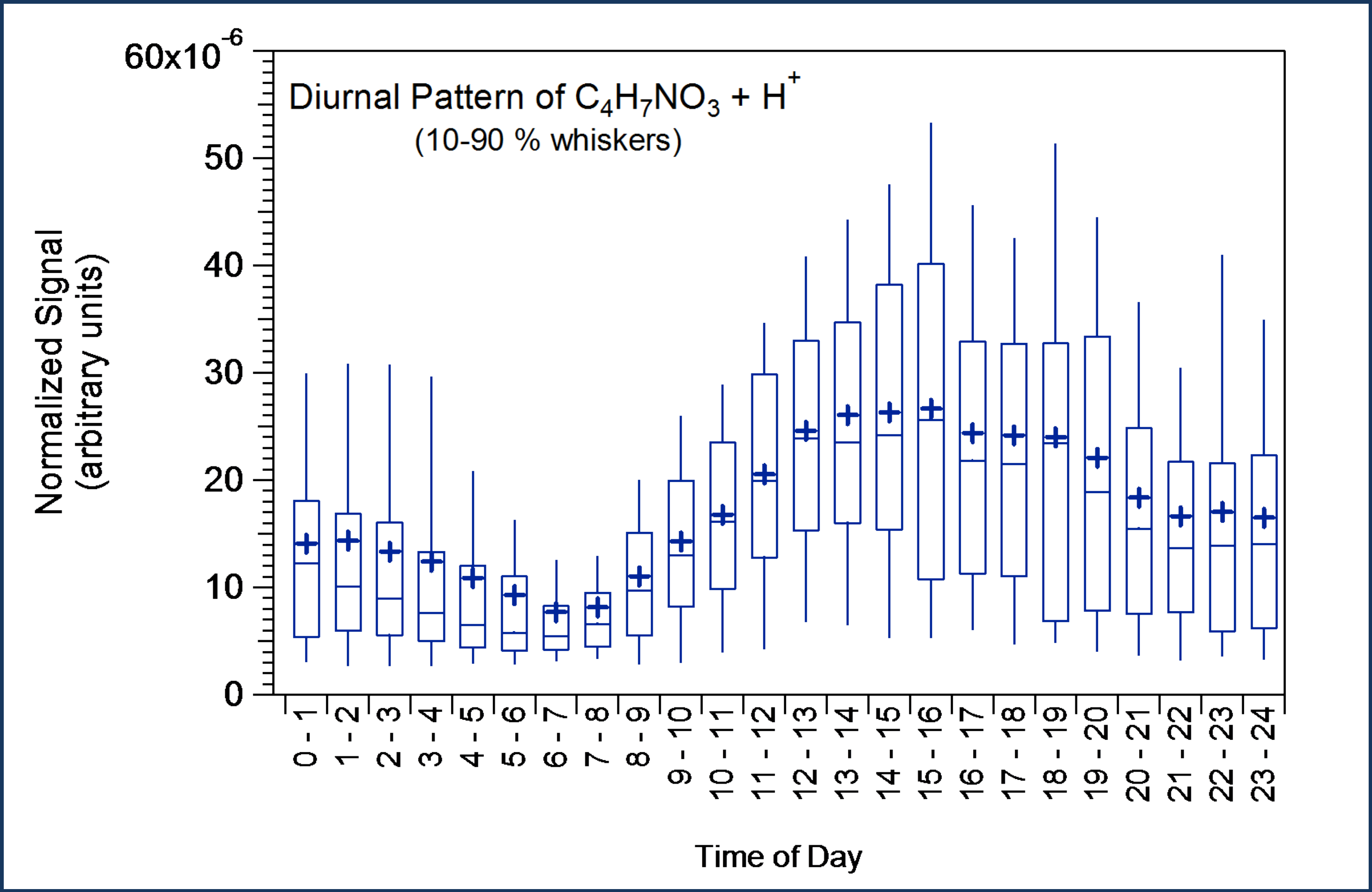

Likely not due to hydrolysis (RH lowest in the afternoon)

# $PM_1$ Sulfate Diurnal Cycle



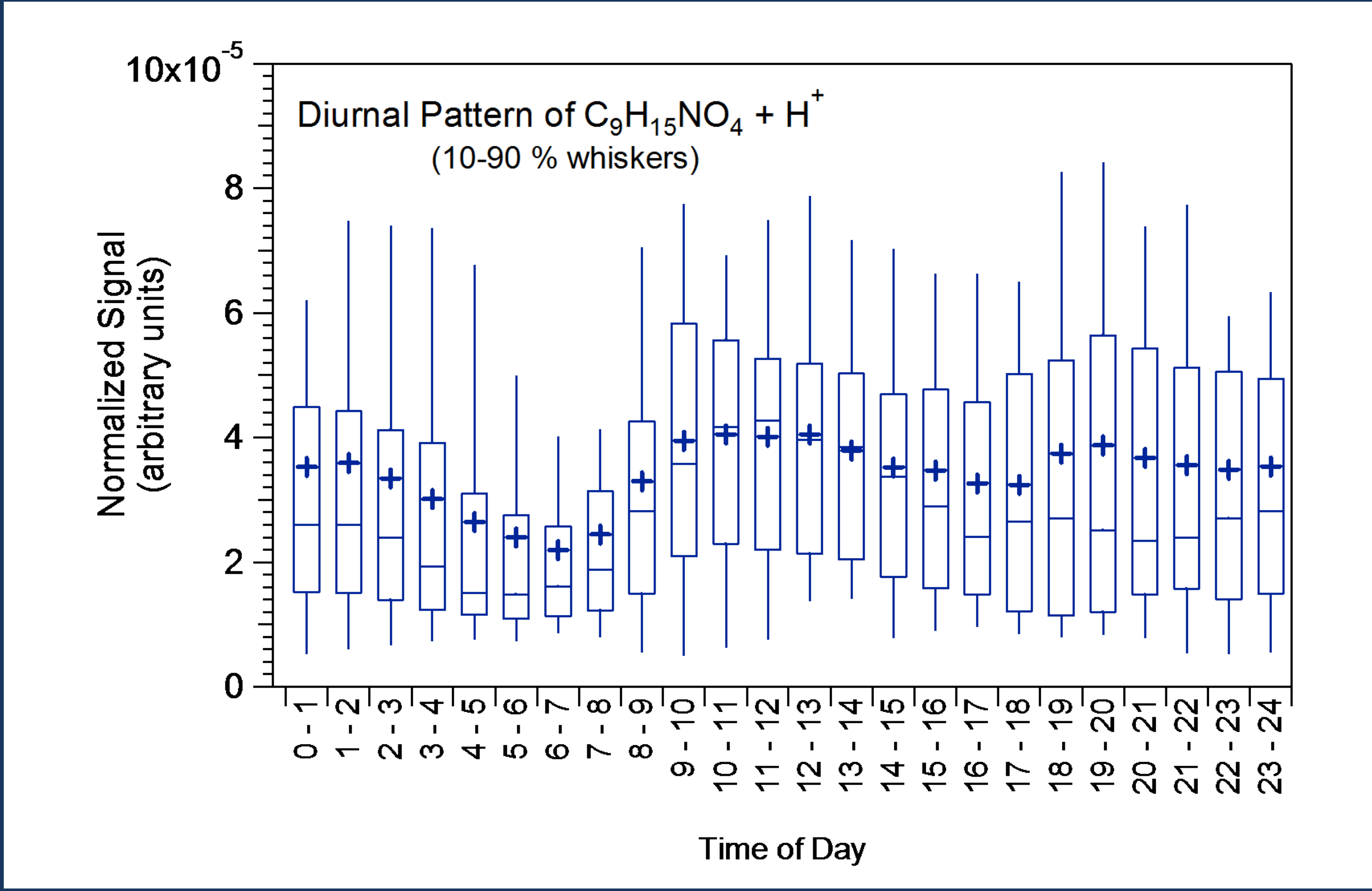

No diurnal cycle for sulfate

# Gas-phase nitrate diurnal cycle




Diurnal cycle suggests influence of photochemistry

# Gas-phase nitrate diurnal cycle




Significant organic nitrate concentrations in the gas phase

# Summary

- VOC + NOx forms organic nitrates
  → evidence from chamber experiments and from ambient measurements
- ONs can recycle NOx (experiments)
- When NOx recycling from ONs is included in CAMx, $O_3$ concentrations are over-predicted
- ONs are unavailable to NOx recycling. Why?
  1. They are irreversibly buried in particle phase → inconsistent with our experiments
  2. They are hydrolysed in the particle phase:

$$RONO_2 + H_2O \rightarrow ROH + HNO_3$$

# Recommendations

Organic nitrates (ON)

- Additional chamber experiments and analysis of field data to determine the gas/particle partitioning ratio of ON
- Chamber experiments at different RH to quantify effect of ON hydrolysis
- Update ON partitioning and life-time to hydrolysis in models

DISCOVER-AQ data analysis (beyond ON)

- Organic PM composition and sources (including analysis of filter data)
- QA, quantification of gas-phase species

# Acknowledgment


- Thanks to the DISCOVER-AQ research and organizational team

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  TCEQ has not yet reviewed the final project report and has not fully reviewed the findings presented here