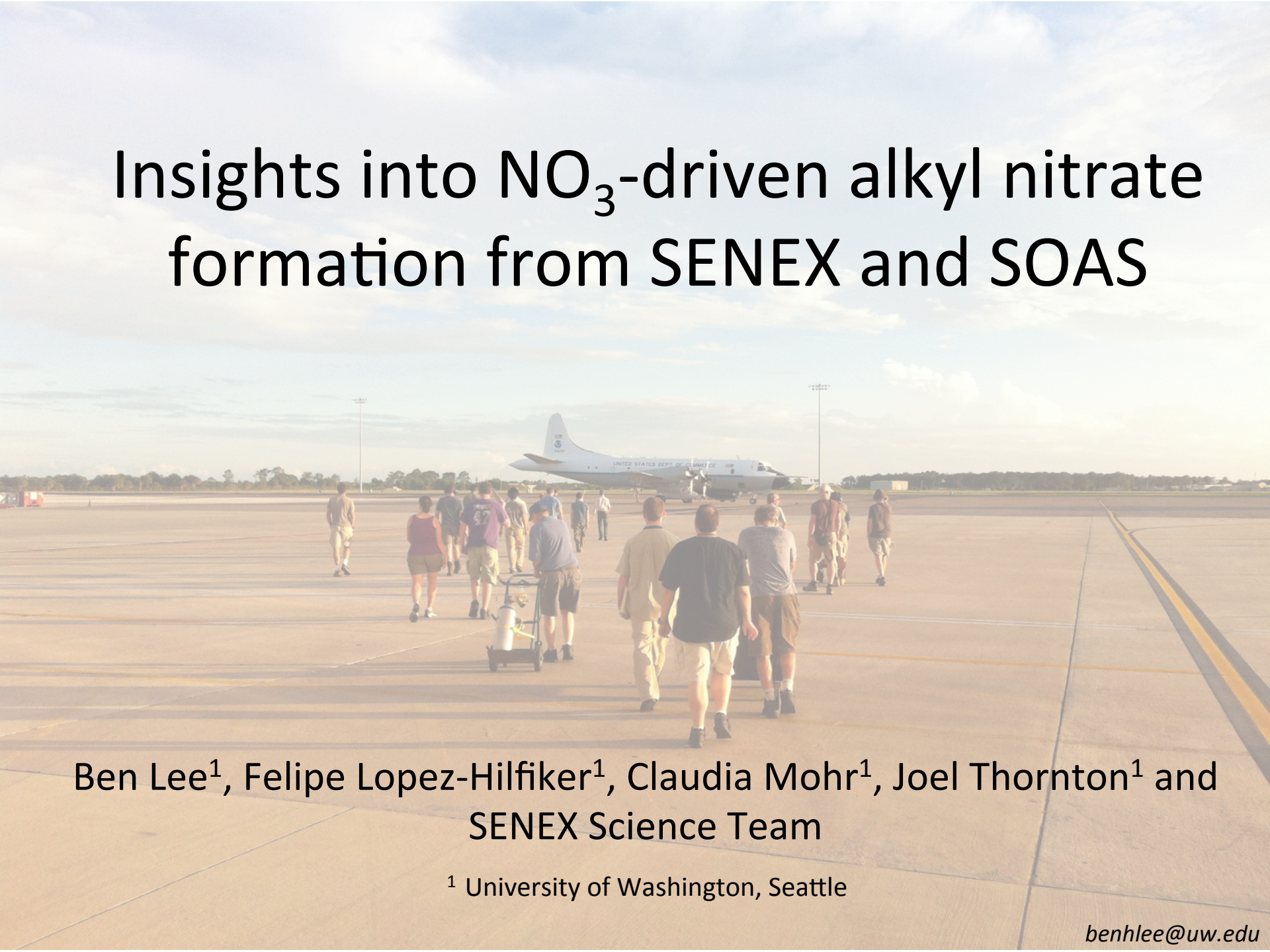
Insights into NO_3-driven alkyl nitrate formation from SENEX and SOAS



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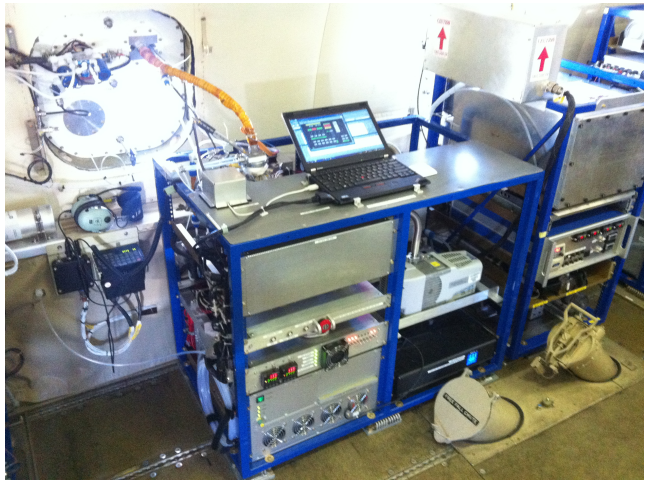
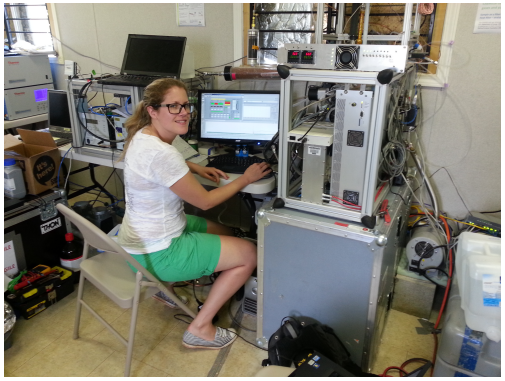
- High-Resolution Time-of-Flight Chemical-Ionization-Mass-Spectrometer using Iodide adducts



- Smyrna, TN (F. Lopez-Hilfiker, B. Lee)
- Centerville, AL (C. Mohr, A. Lutz)

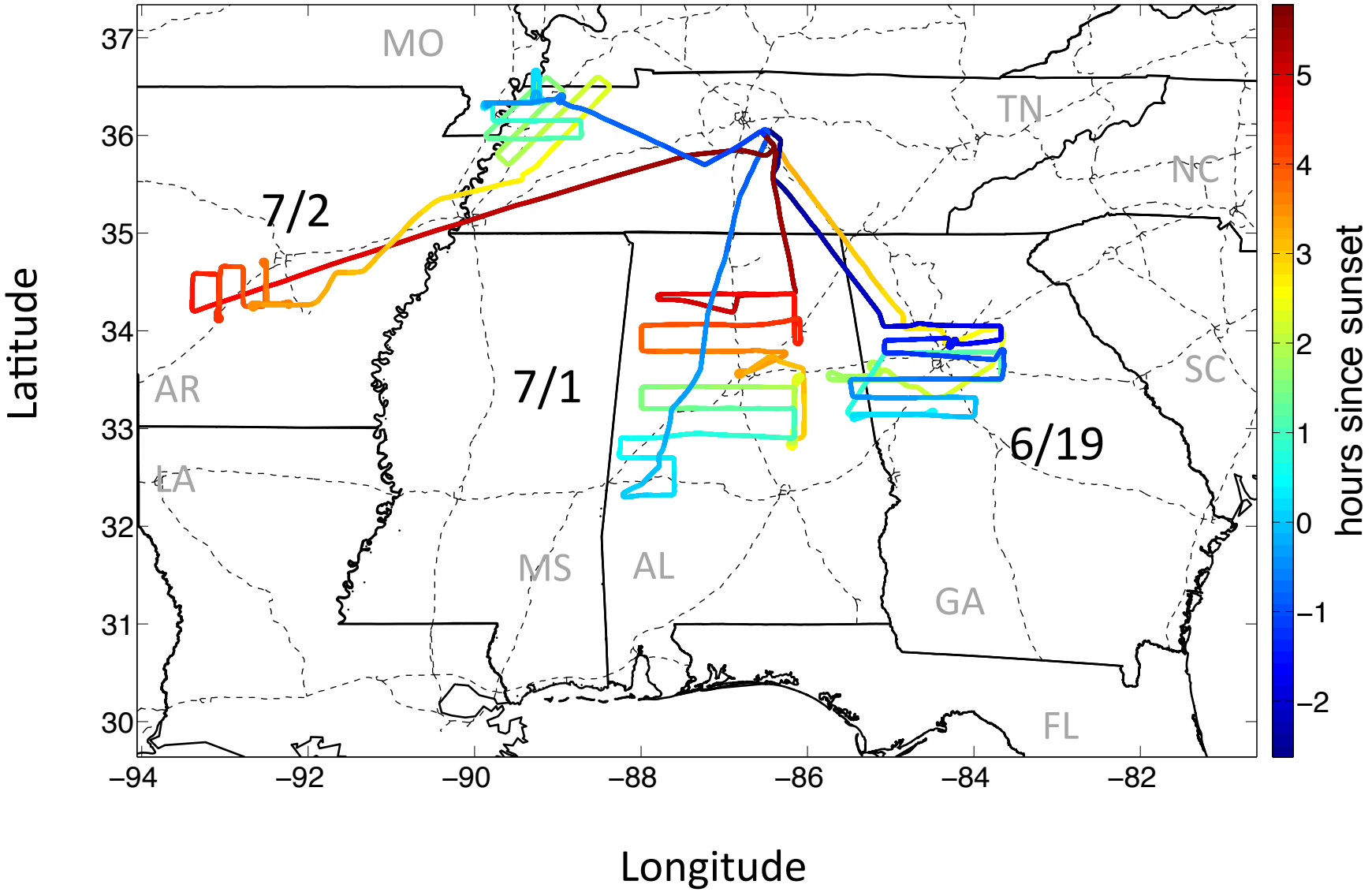
- SOAS data will be posted soon, still in the quality control phase. If you want to see a specific compound or set of compounds from SOAS or SENEX, please contact us.



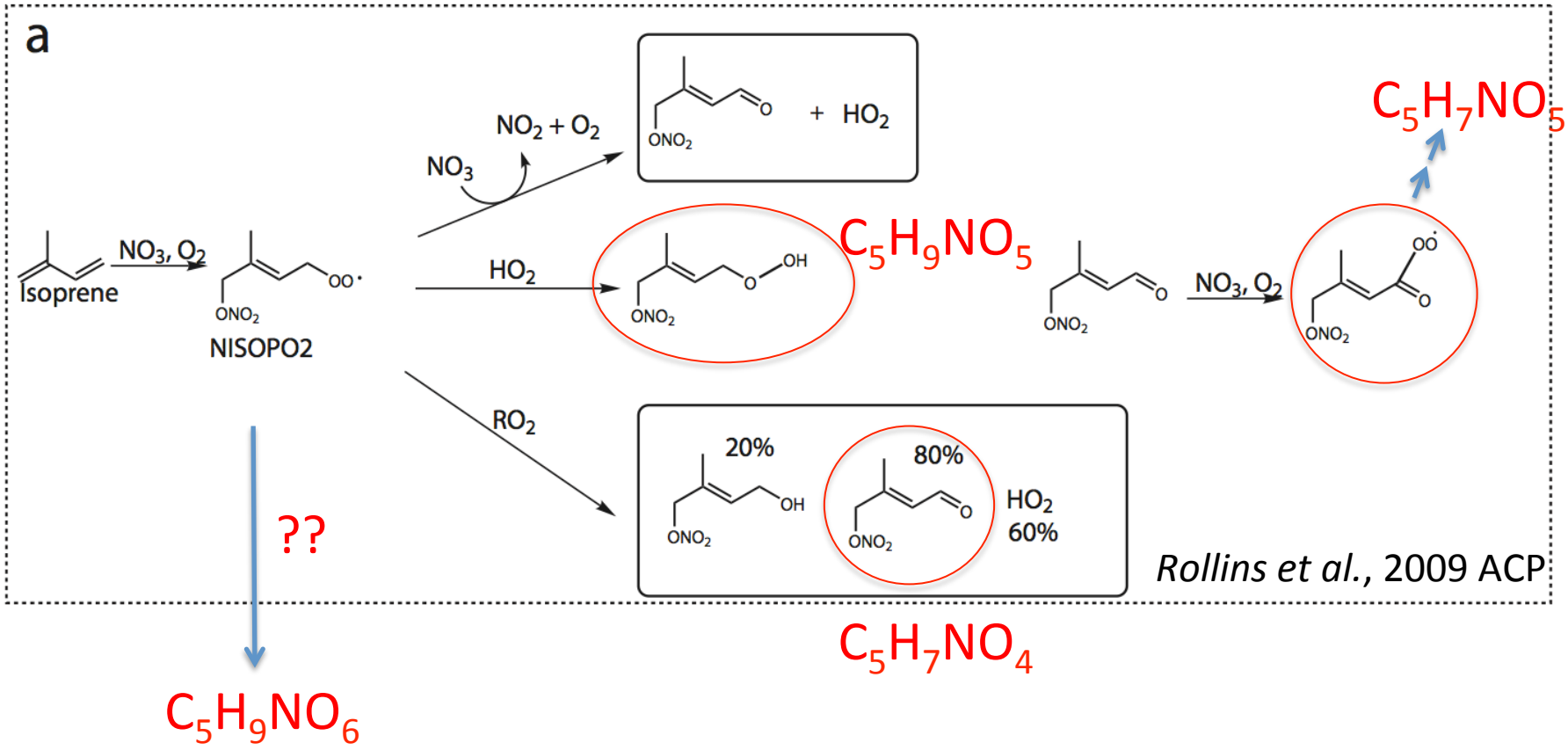
Do we see NO_3-driven alkyl nitrates?

- ANs are significant sink of NO_x
- Comprise ~10% of NO_y near the surface at day & night
- Nighttime chemistry may be as important as daytime chemistry to AN budget

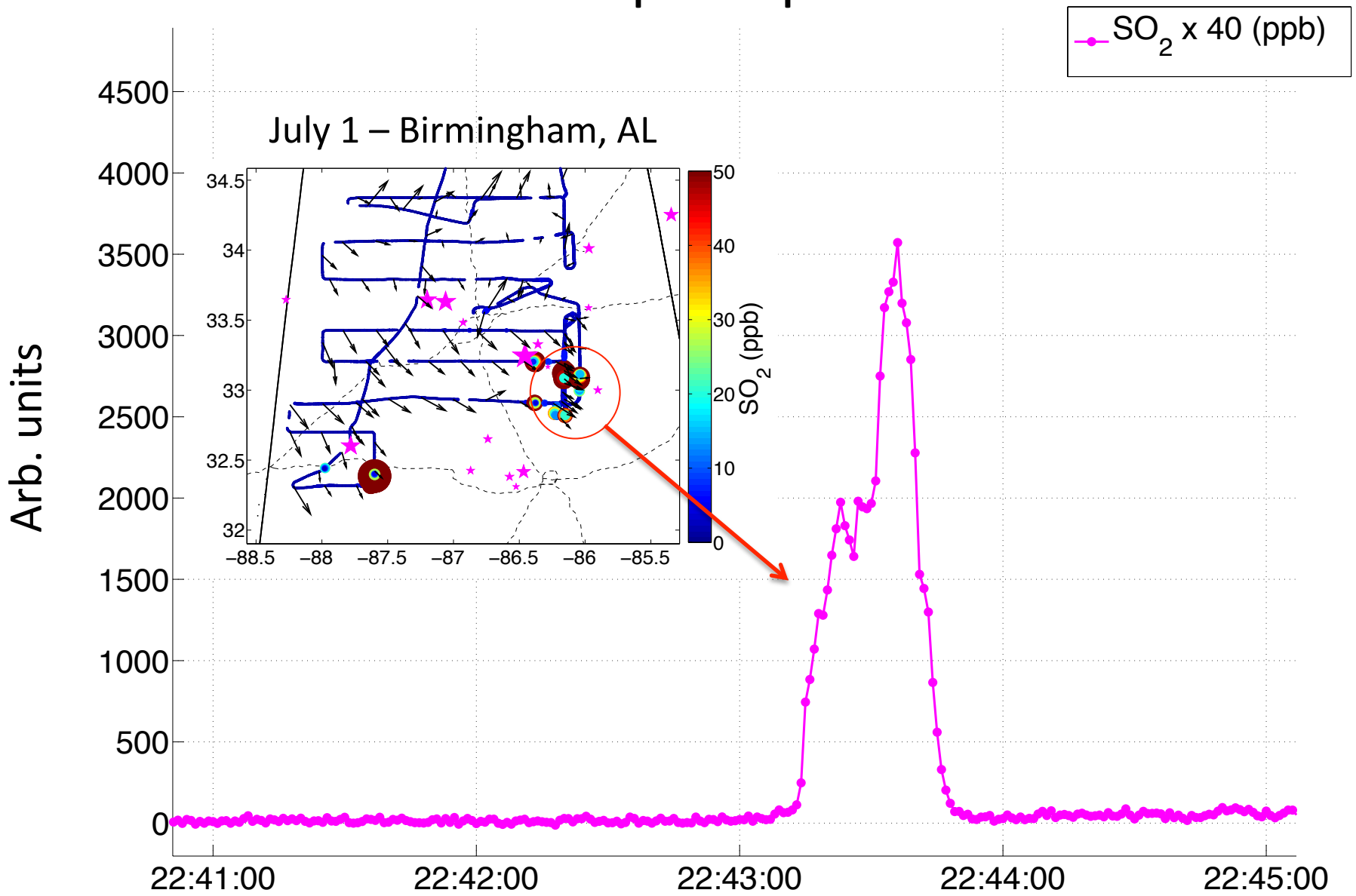
Day into night flights: 6/19, 7/1, 7/2



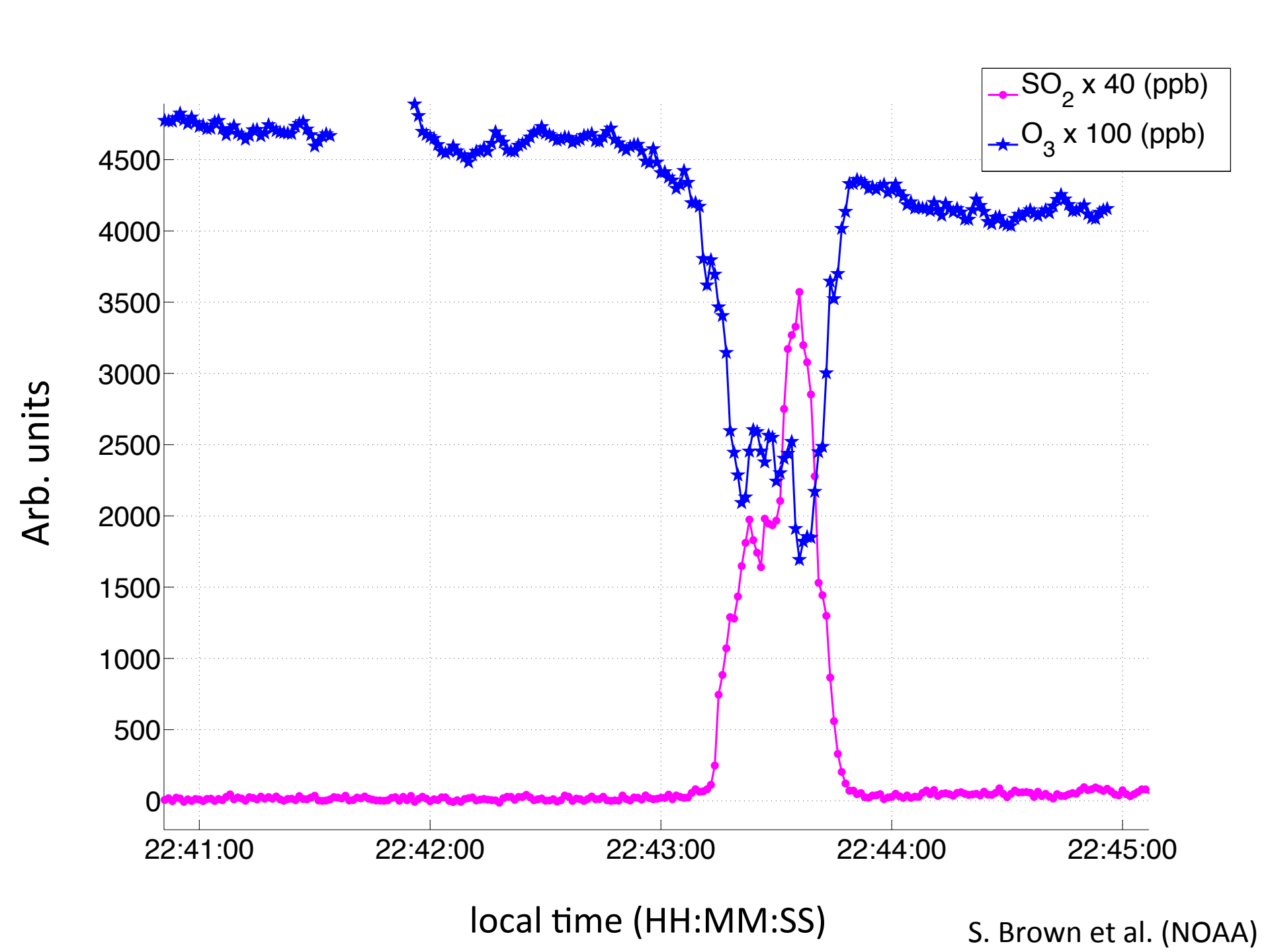
Alkyl nitrates produced from NO_3 + Isoprene

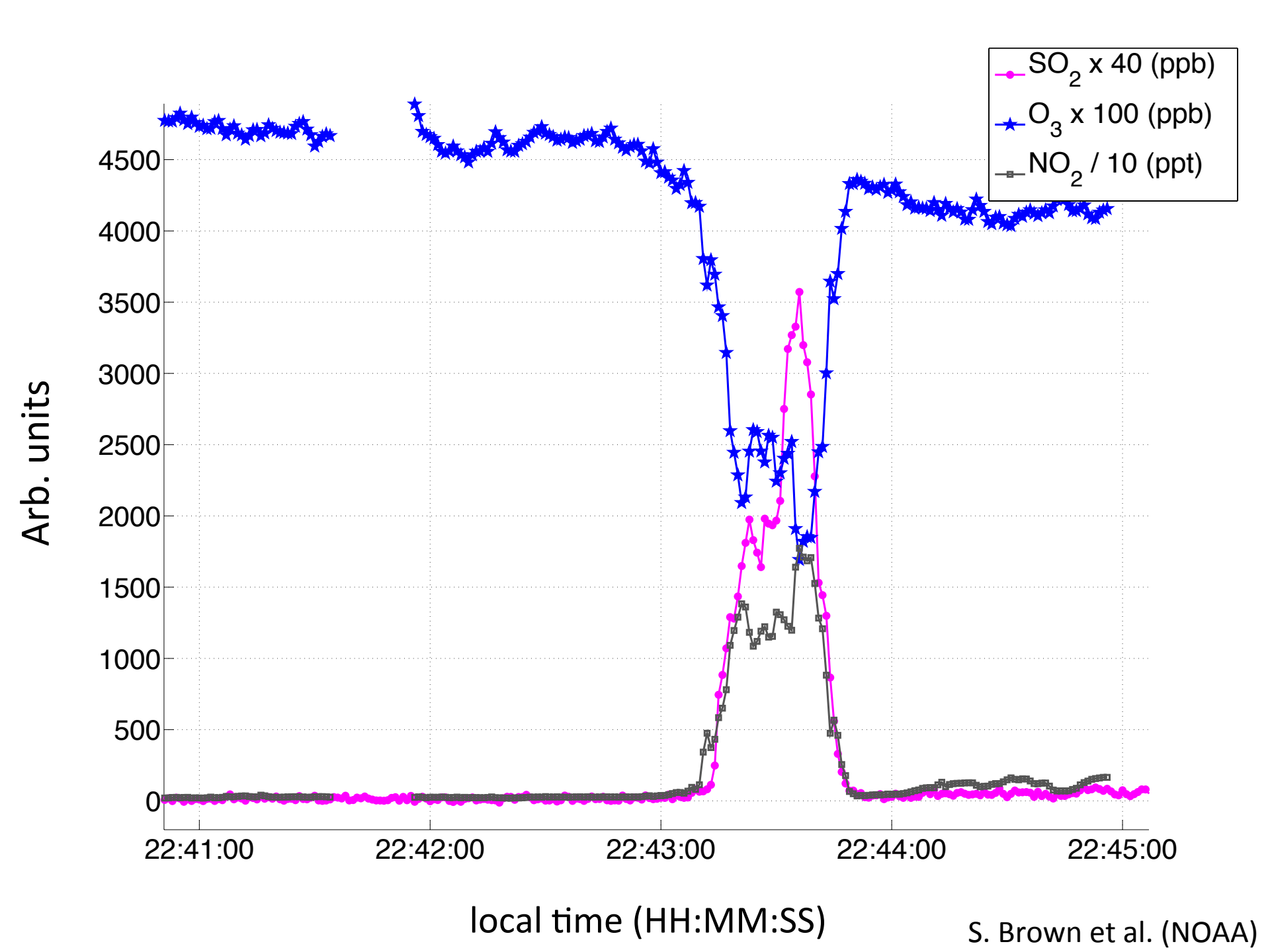


Power plant plumes

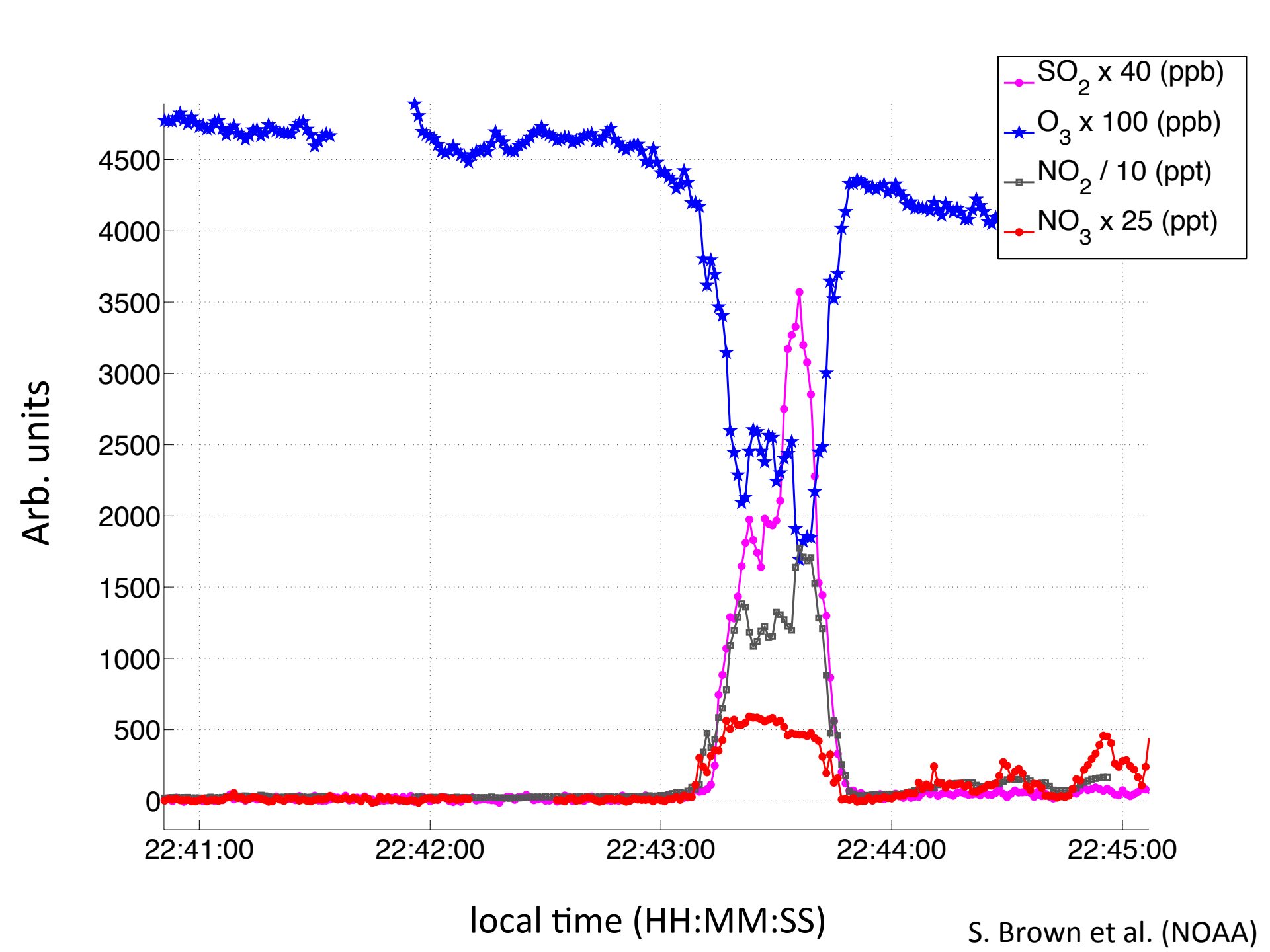


J. Holloway (NOAA)

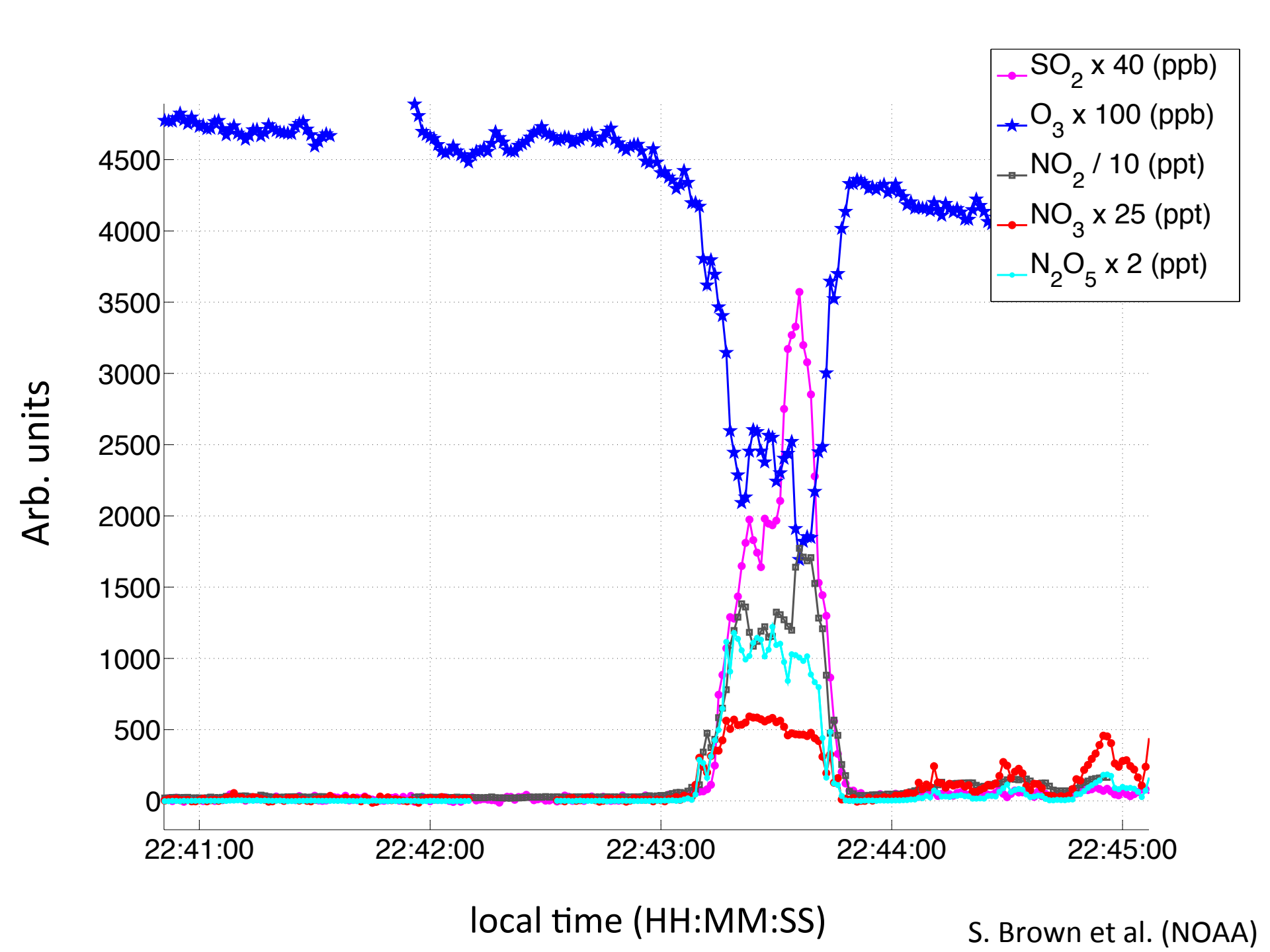

SO2 x 40 (ppb)
O3 x 100 (ppb)
Arb. units
4500
4000
3500
3000
2500
2000
1500
1000
500
0
22:41:00
22:42:00
22:43:00
22:44:00
22:45:00
local time (HH:MM:SS)
S. Brown et al. (NOAA)



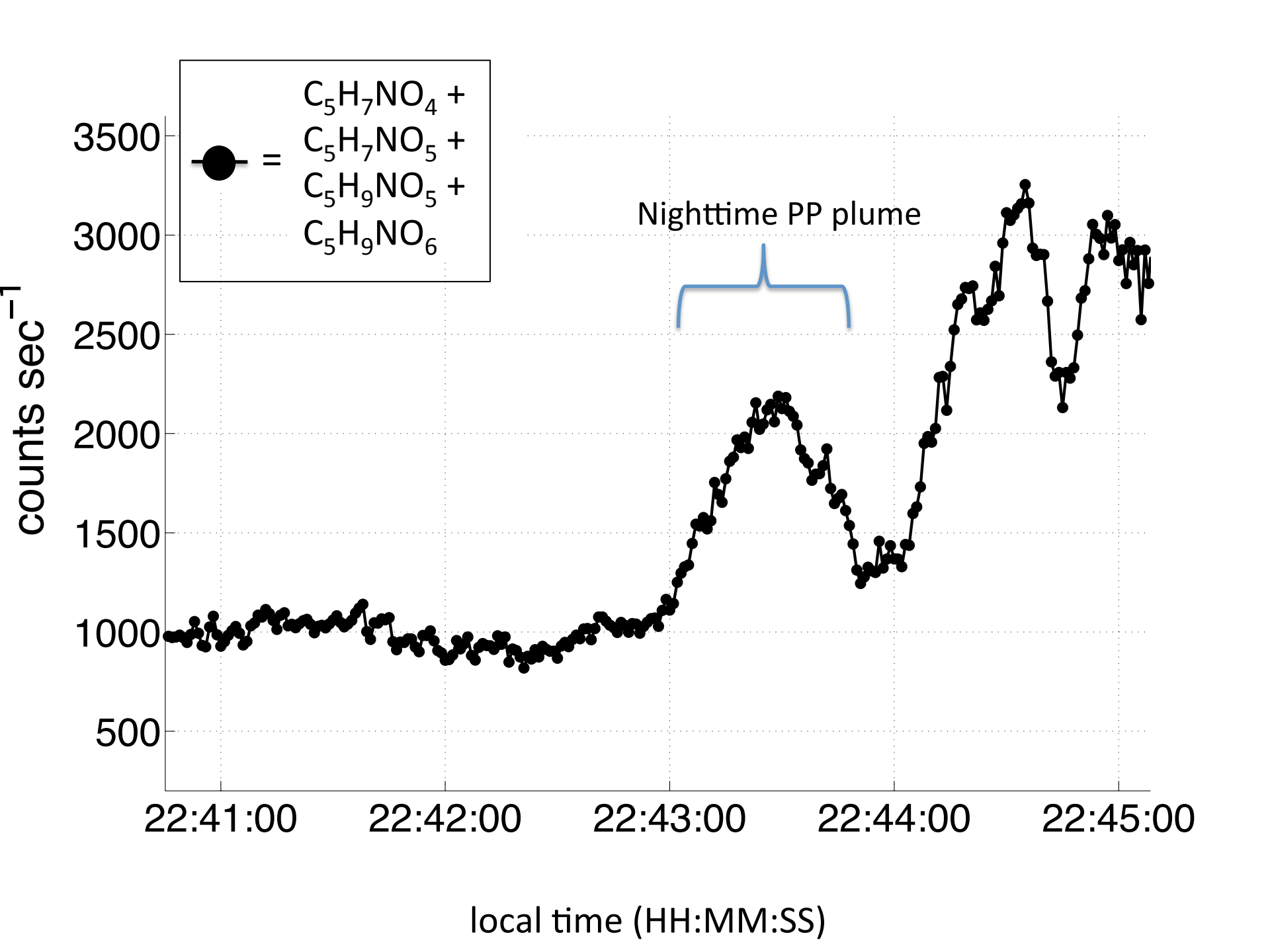
S. Brown et al. (NOAA)



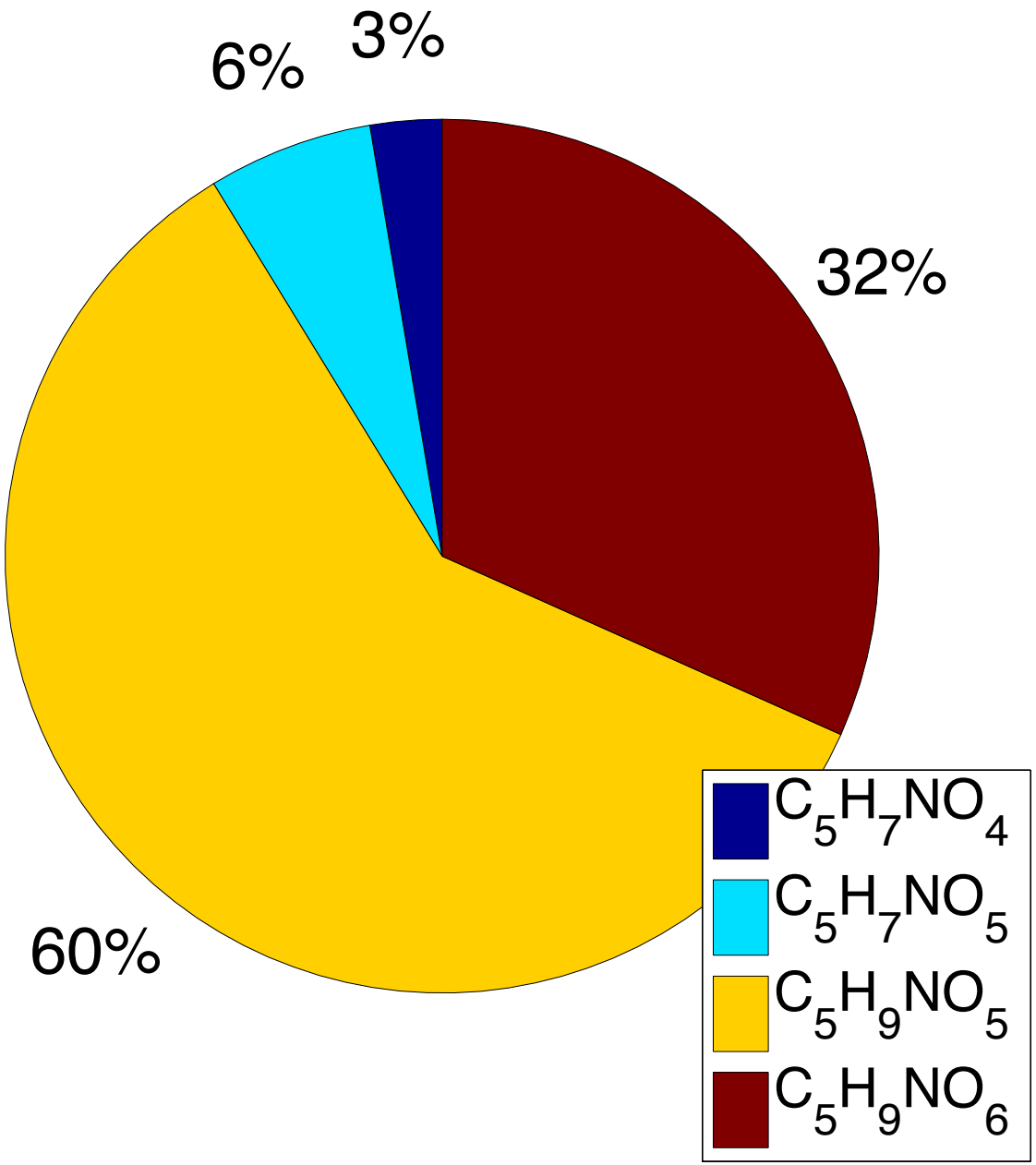
S. Brown et al. (NOAA)

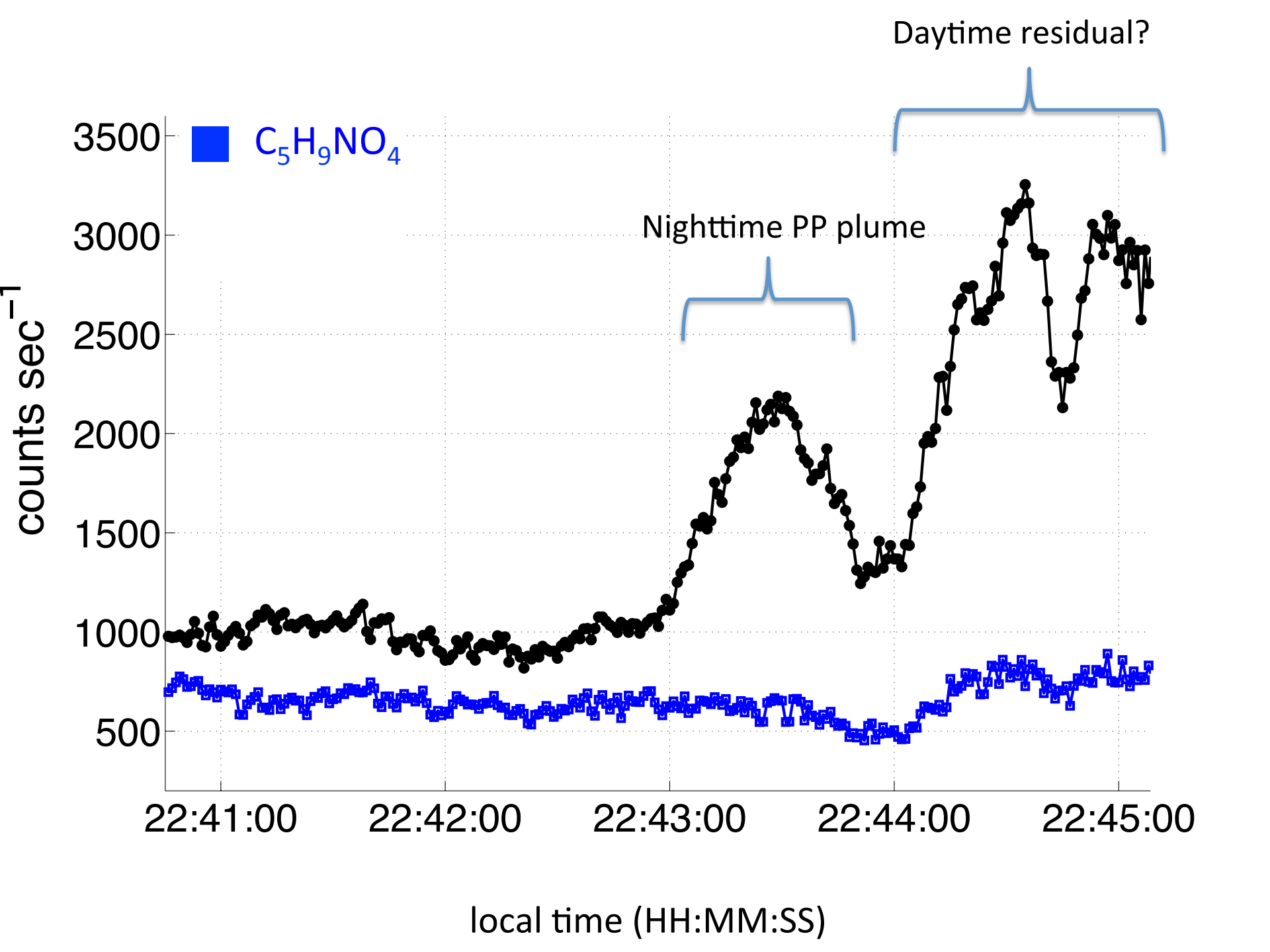


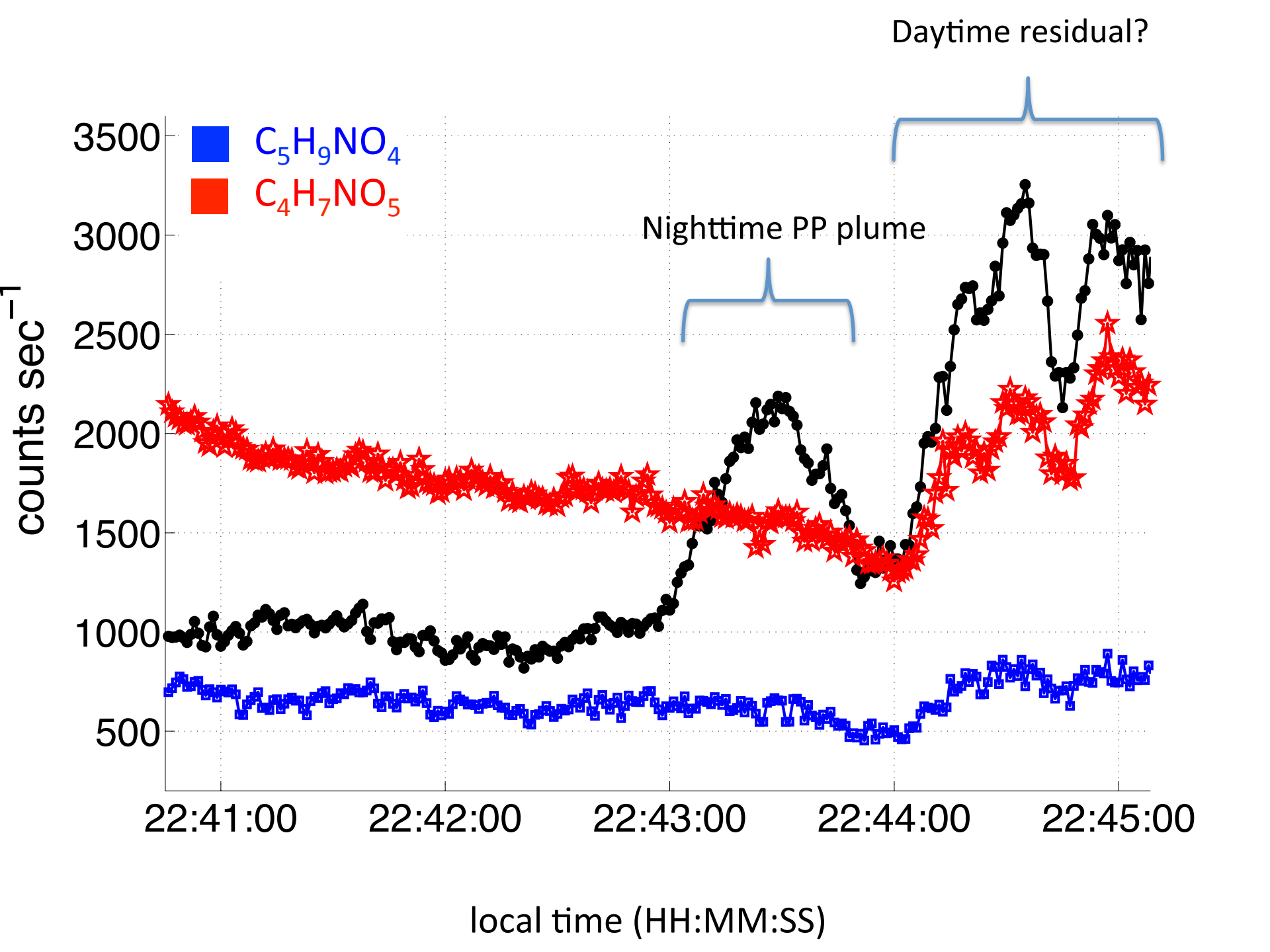
S. Brown et al. (NOAA)


= $C_5H_7NO_4$ + $C_5H_7NO_5$ + $C_5H_9NO_5$ + $C_5H_9NO_6$
Nighttime PP plume
3500
3000
2500
2000
1500
1000
500
counts sec^{-1}
22:41:00
22:42:00
22:43:00
22:44:00
22:45:00
local time (HH:MM:SS)

AN signal distribution in nighttime PP plumes




Daytime residual?
Nighttime PP plume
$C_5H_9NO_4$
3500
3000
2500
2000
1500
1000
500
counts sec^{-1}
22:41:00
22:42:00
22:43:00
22:44:00
22:45:00
local time (HH:MM:SS)


Daytime residual?
Nighttime PP plume
$C_5H_9NO_4$
$C_4H_7NO_5$
3500
3000
2500
2000
1500
1000
500
counts sec^{-1}
22:41:00
22:42:00
22:43:00
22:44:00
22:45:00
local time (HH:MM:SS)

Objective

Calculate the "*effective yield*" of NO_3-derived AN within power plant plumes, to determine how well nighttime chemistry explains regional measurement

Box model of nighttime PP plumes

$NO + O_3 \rightarrow NO_2$

$NO_2 + O_3 \rightarrow NO_3$

$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$

$N_2O_5 \rightarrow ClNO_2 + HNO_3$

$N_2O_5 \rightarrow NO_2 + NO_3$

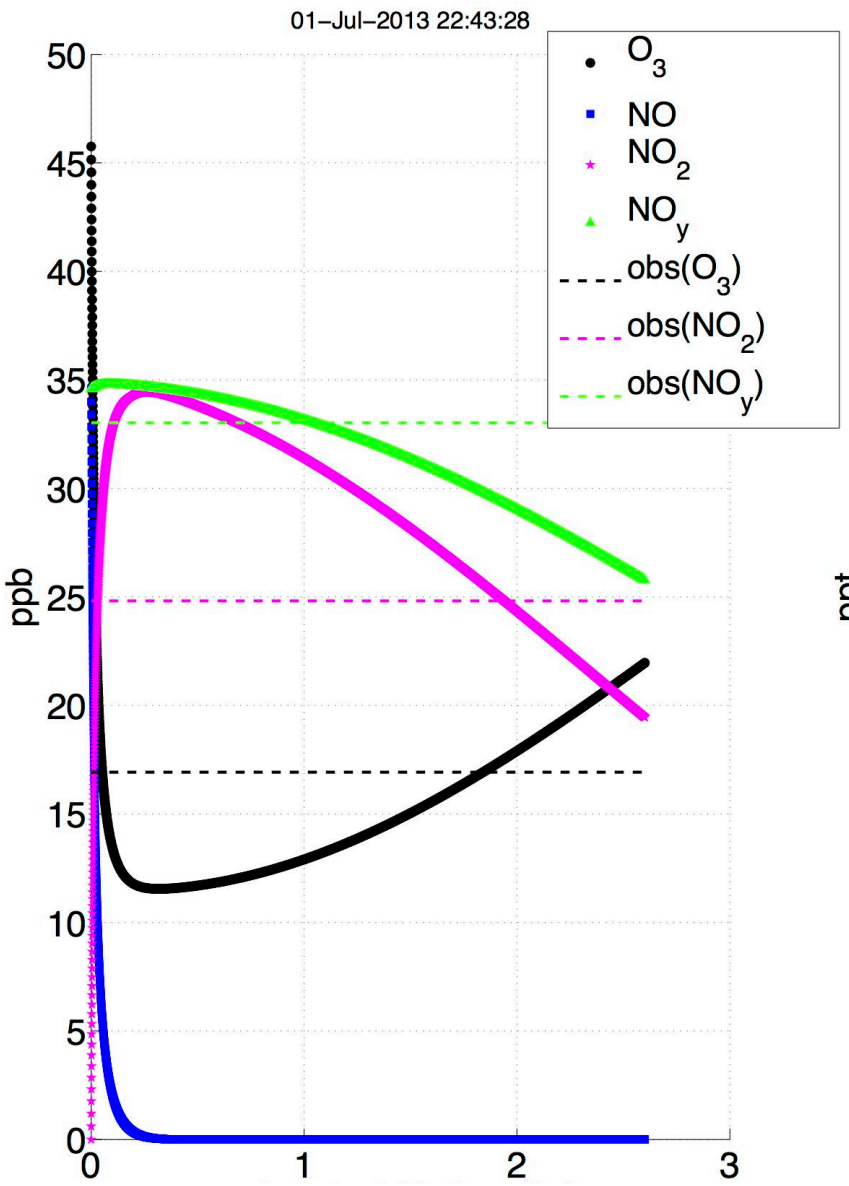
$NO_3 + ISOP \rightarrow ISOPN$

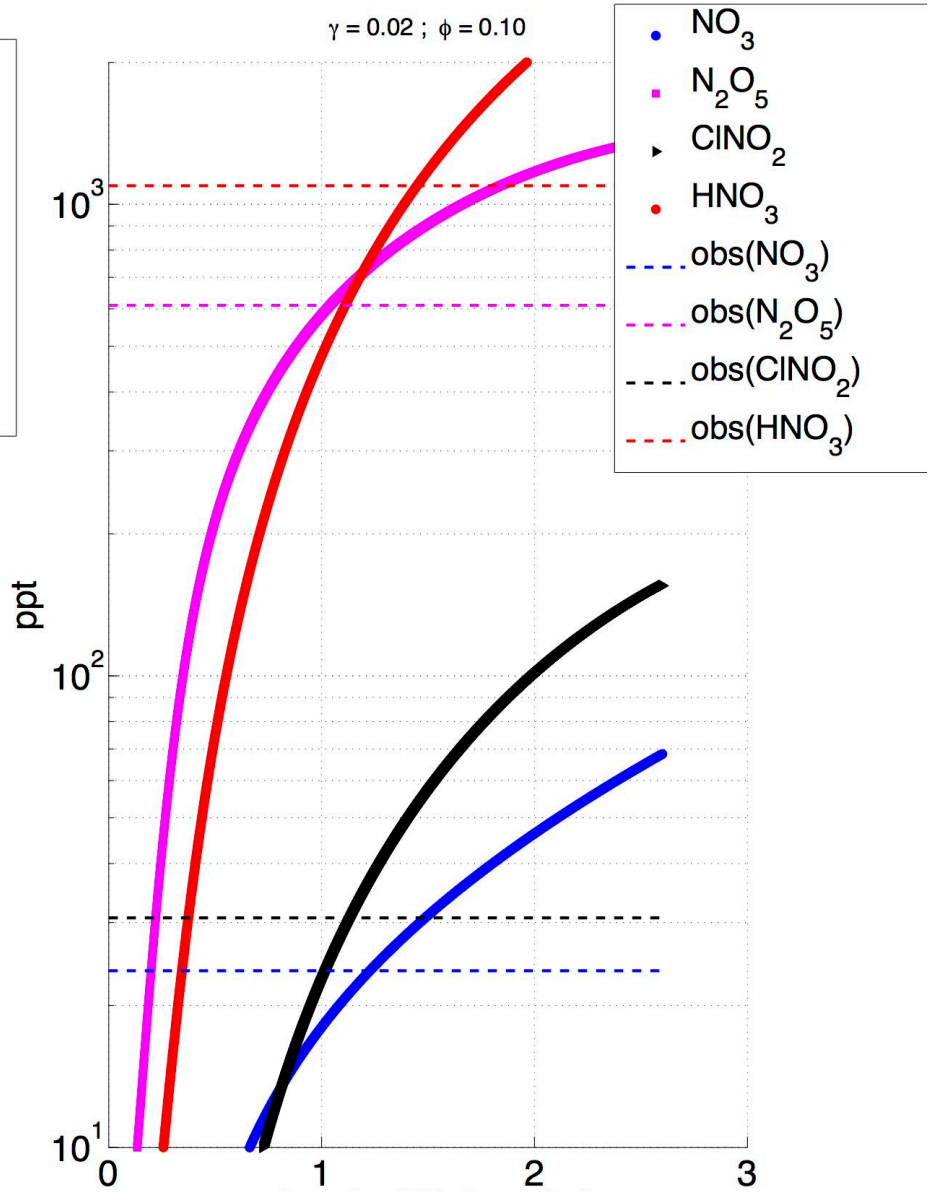
$NO_3 + MT \rightarrow MTN$

$$\frac{dC}{dt} = P - L + \left(C - C_{background}\right)k_{mix}$$

Optimize model-observation agreement of NO_2, NO_y, O_3, HNO_3, NO_3, $ClNO_2$ and N_2O_5 by varying **$[NO]_i$**, **entrainment rate**, **N_2O_5 loss parameters**

Model output



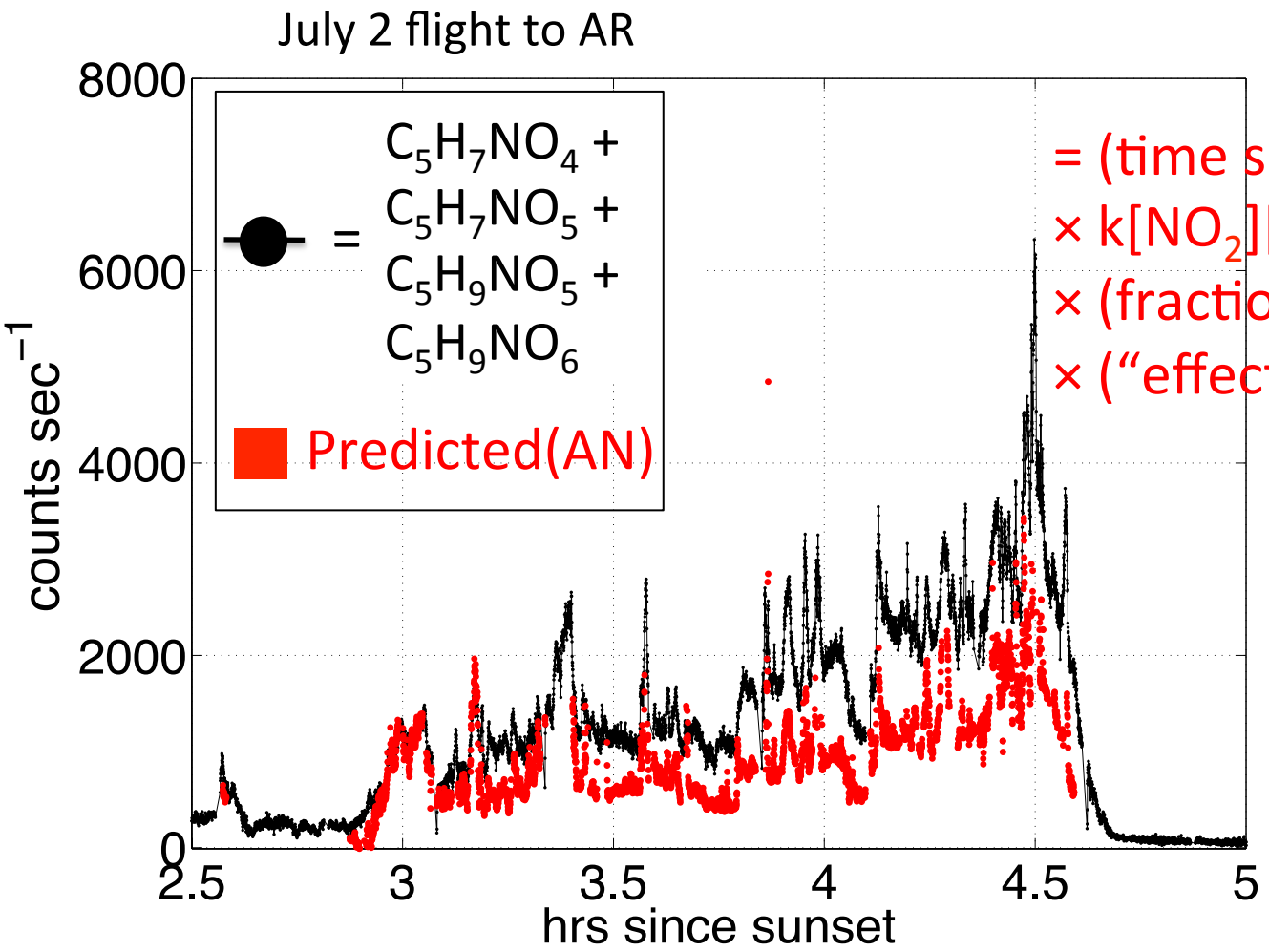


Result from 8 power plume plumes

$$\frac{\text{Observed AN enhancement (counts sec}^{-1}\text{)}}{\text{Modeled isoprene reacted (ppt)}}$$

= "*effective yield*" (counts sec^{-1} ppt^{-1})

Prediction from NO_3-chemistry only



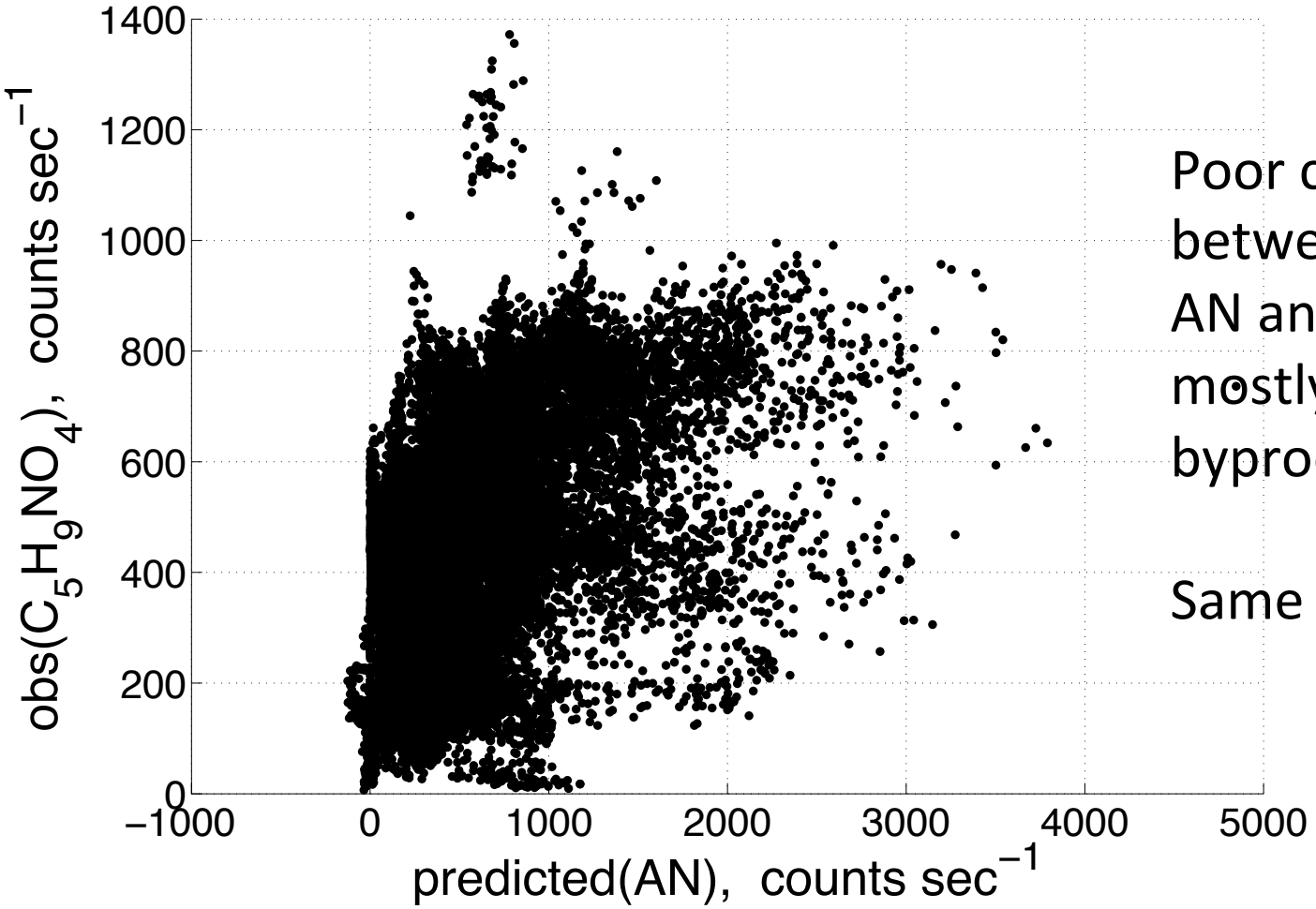
= (time since sunset)
× $k[NO_2][O_3]$
× (fraction NO_3 react with ISOP)
× ("effective yield")

S. Brown, J. Gilman, B. Lerner, J. de Gouw et al. (NOAA)

Prediction from NO_3-chemistry only

- ~70% of observed AN signal explained by invoking only NO_3 chemistry
- Good correlation suggests ANs driven by NO_3
- Observations that exceed prediction suggests higher yield and/or longer reaction times
- NO_3-driven chemistry important during daytime?

"Daytime" ISOPN ($C_5H_9NO_4$)



Poor correlation between NO_3-derived AN and $C_5H_9NO_4$, a mostly OH-derived byproduct

Same goes for $C_4H_7NO_5$

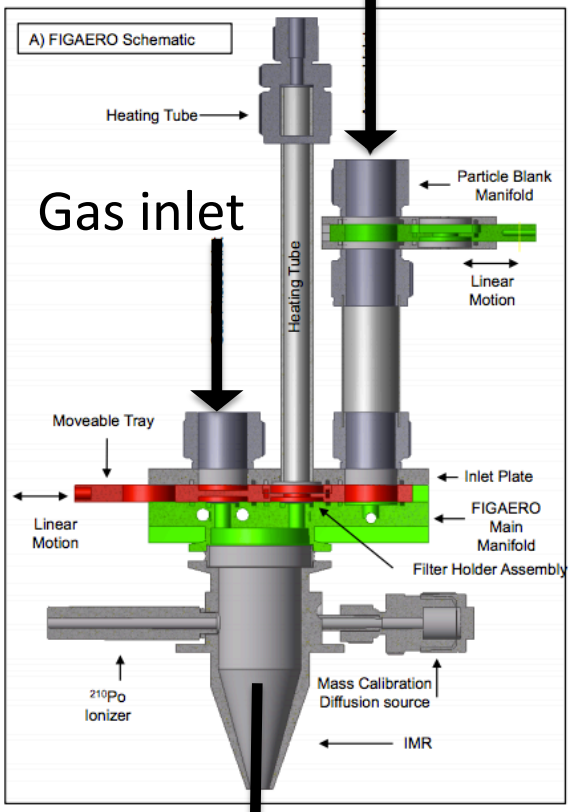
What about MT-derived nitrates?

No enhancements observed in nighttime power plant plumes

SOAS ground site

soas2013.rutgers.edu

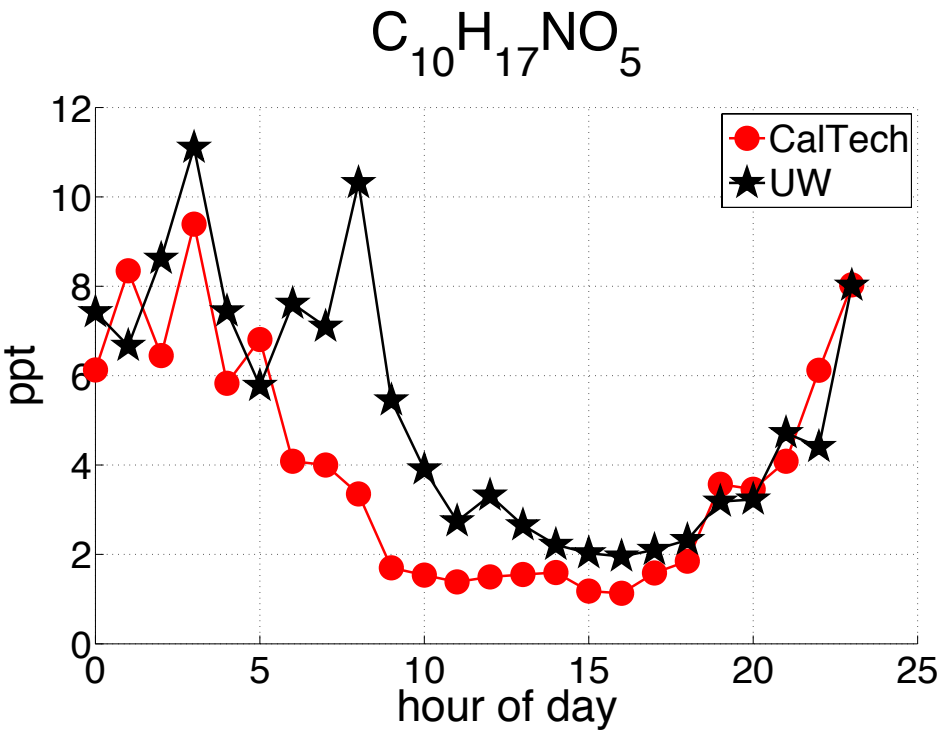
Aerosol inlet

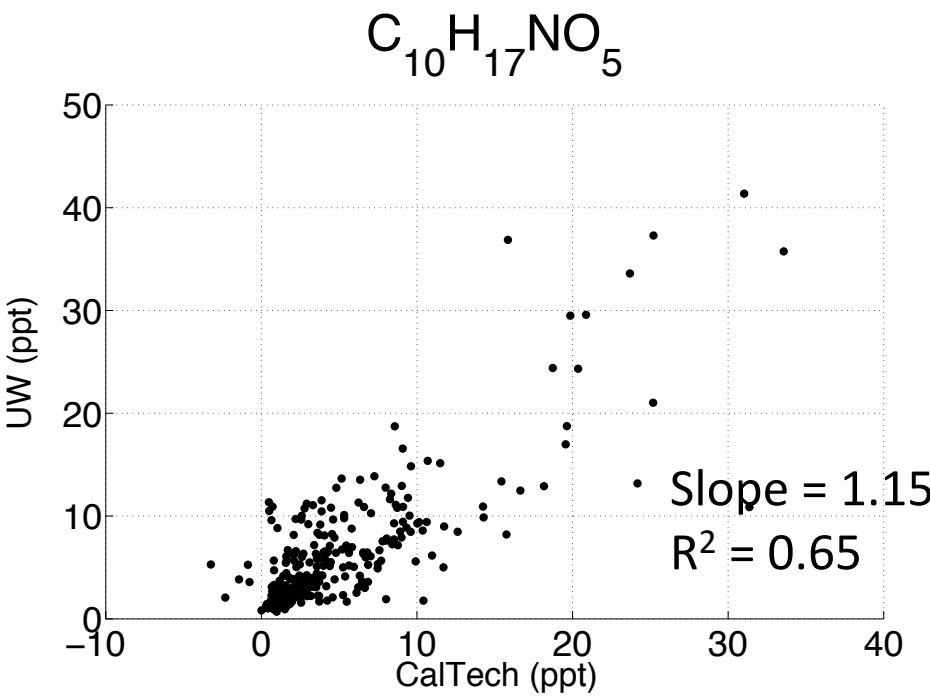


Flow to instrument

FIGAERO inlet allows alternating measurements in the gas and particle phases [*Lopez-Hilfiker et al.*, 2014, AMT]

MT-derived nitrates



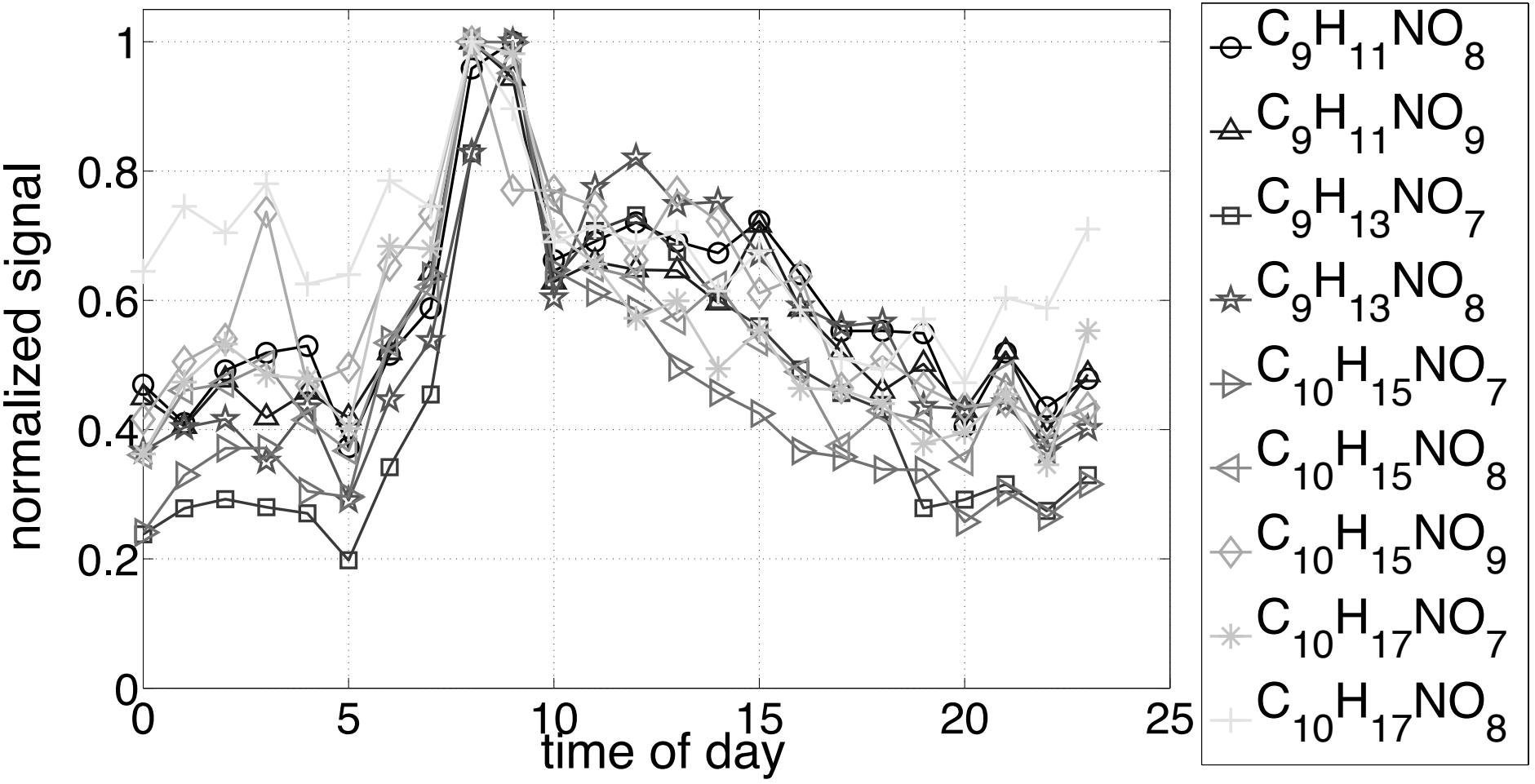


Good agreement with CalTech measurement (assuming same sensitivity as ISOPN) of gas-phase $C_{10}H_{17}NO_5$

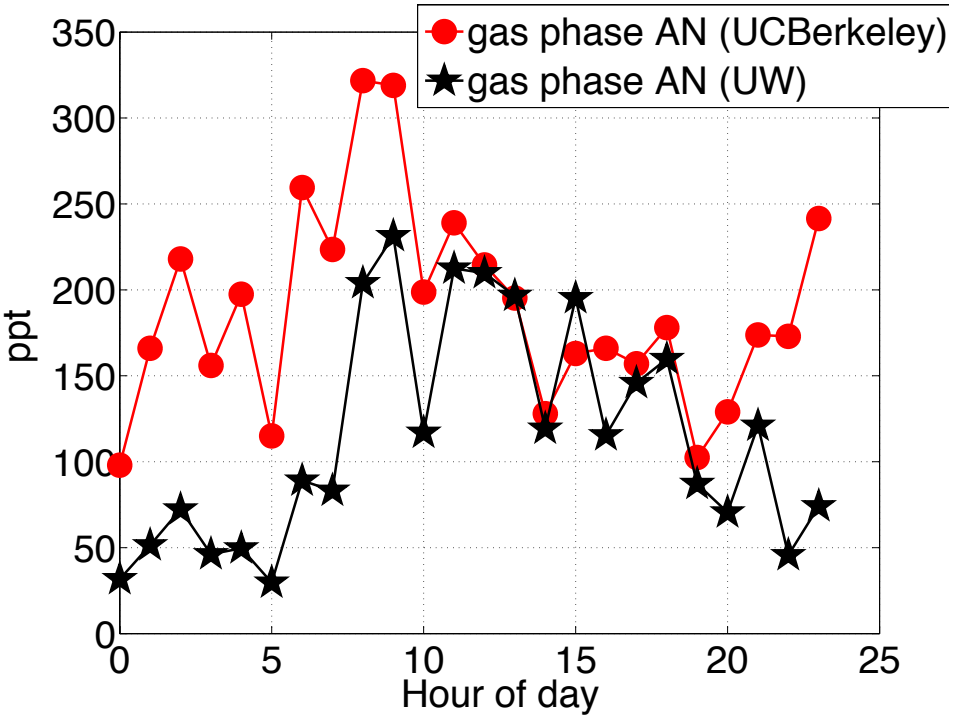
UW observe more pronounced enhancement in morning

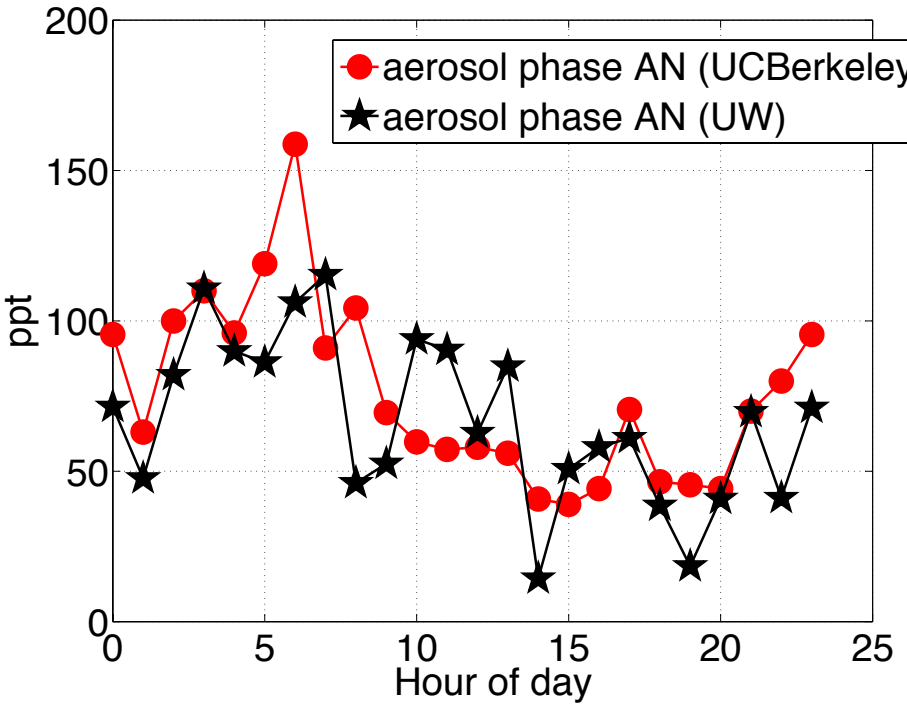
T. Nguyen, P. Wennberg et al. (CalTech)

Highly oxygenated N-containing C_9 and C_{10} compounds enhanced around sunrise



Sum of speciated ANs versus total AN



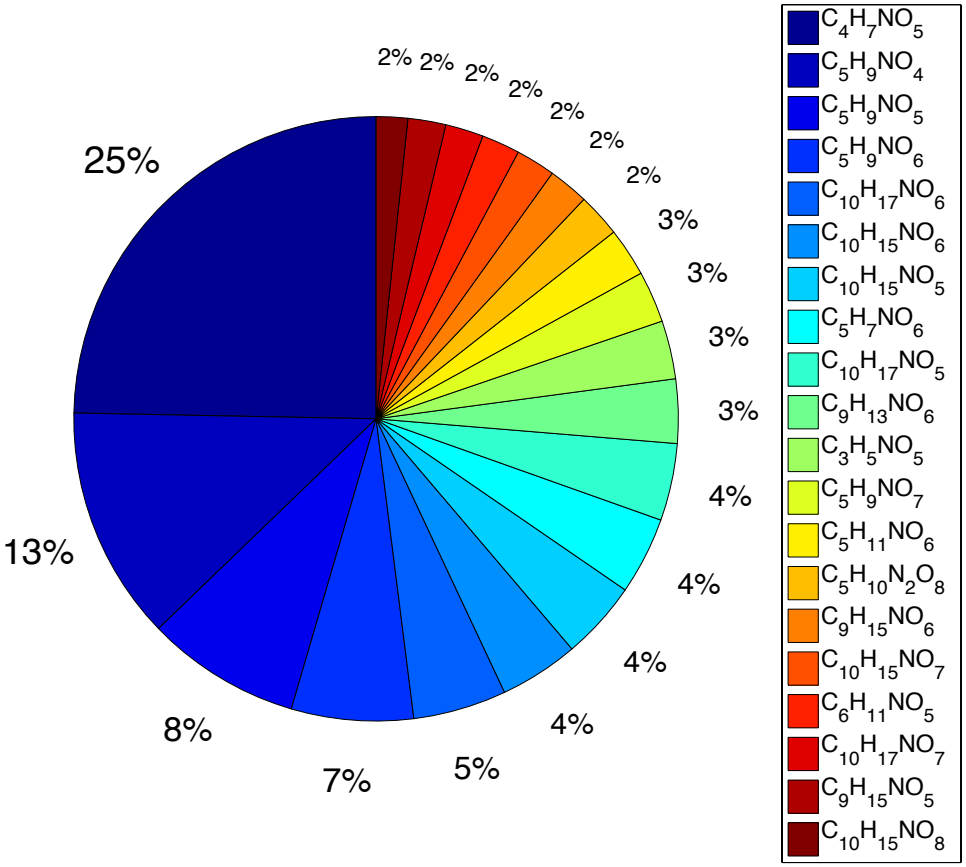


N = 402
Slope = 0.78
R^2 = 0.46

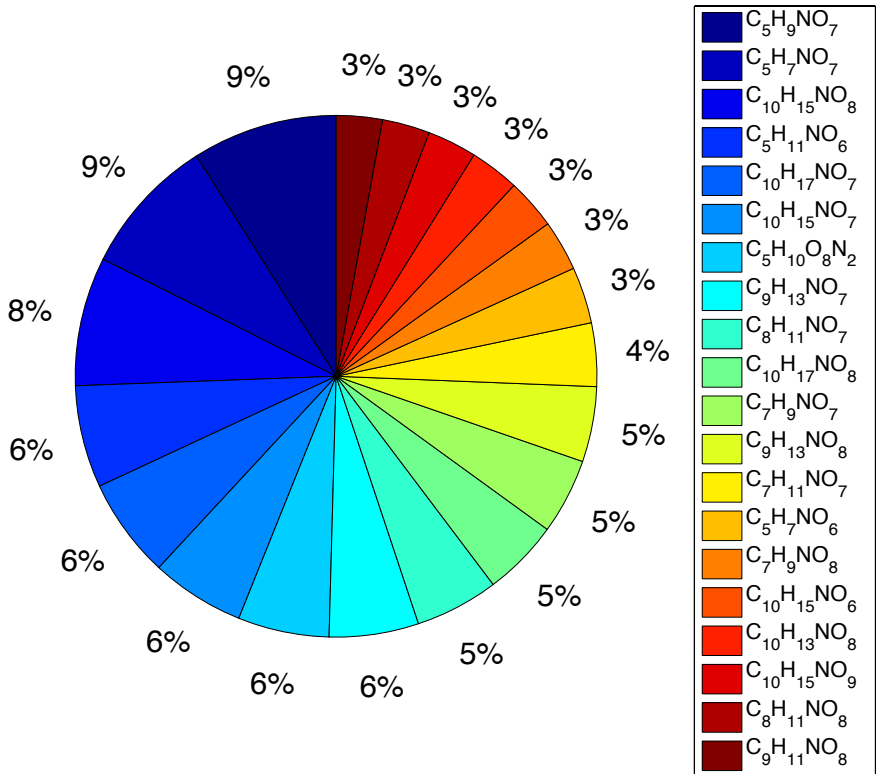
N = 139
Slope = 1.08
R^2 = 0.34

P. Wooldridge, R. Cohen et al. (UC Berkeley)

Gas-phase AN

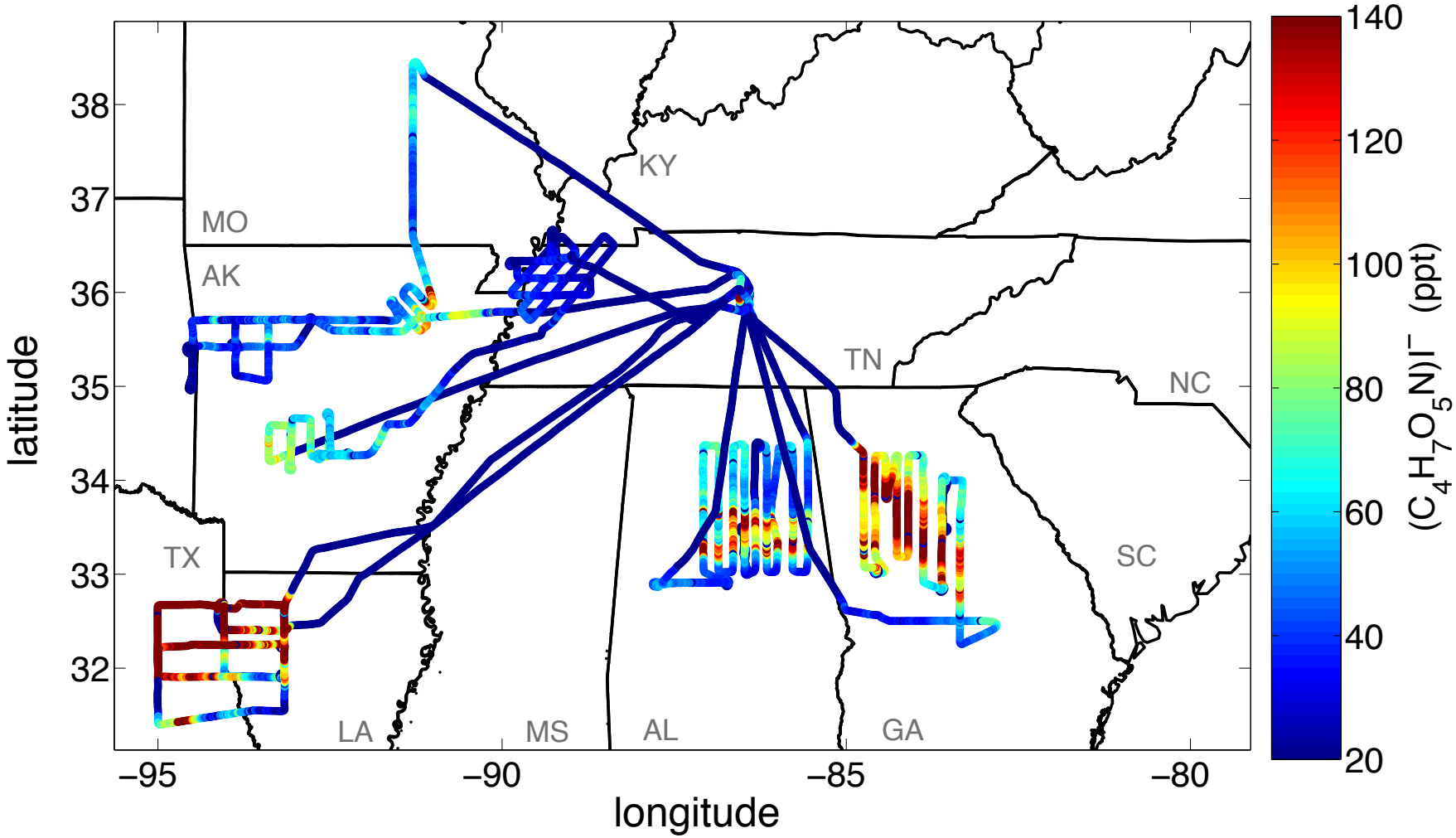


Particle-phase AN



Future work

Investigate *daytime* AN formation in emissions from urban centers and shale gas fields



SENEX & SOAS Teams

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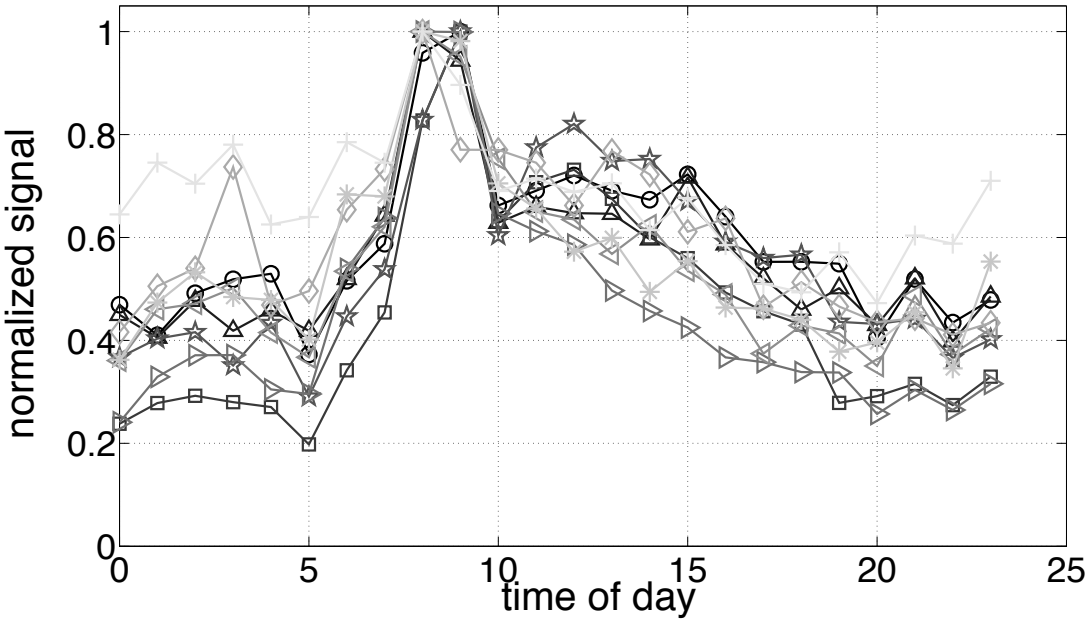

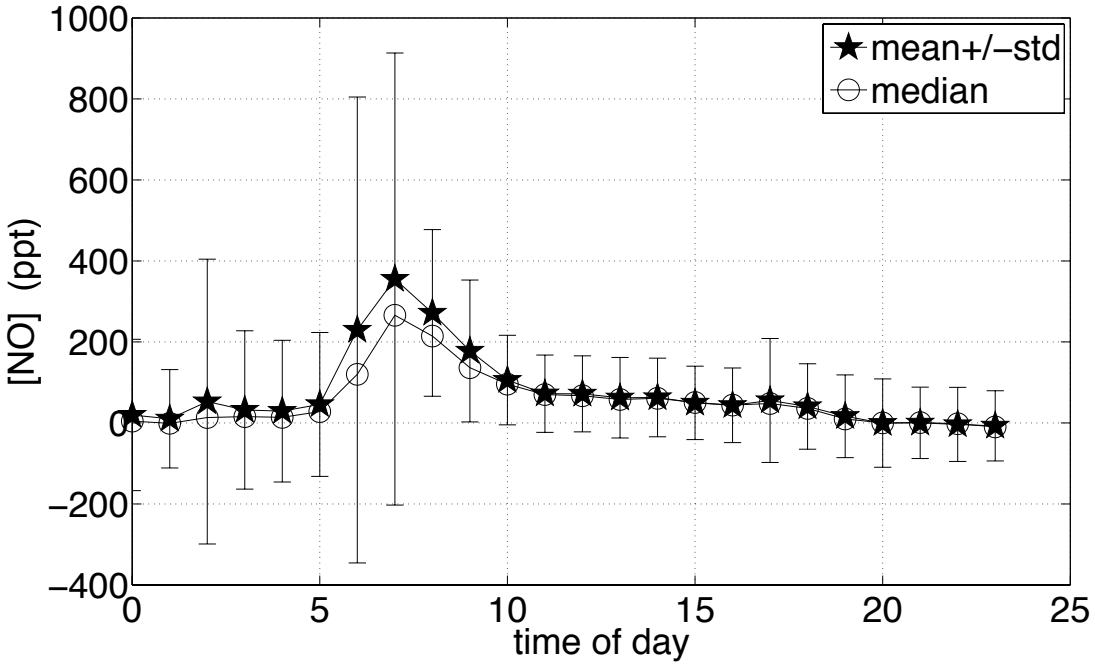

- Consistent with nitric oxide diurnal profile, indicates $RO_2 + NO \rightarrow RONO_2$ chemistry
- Suggests presence of MT-derived high-O:C RO_2 species in the gas-phase, consistent with work of *Ehn et al*. [2014, Nature]

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