

Wintertime reactive nitrogen chemistry:

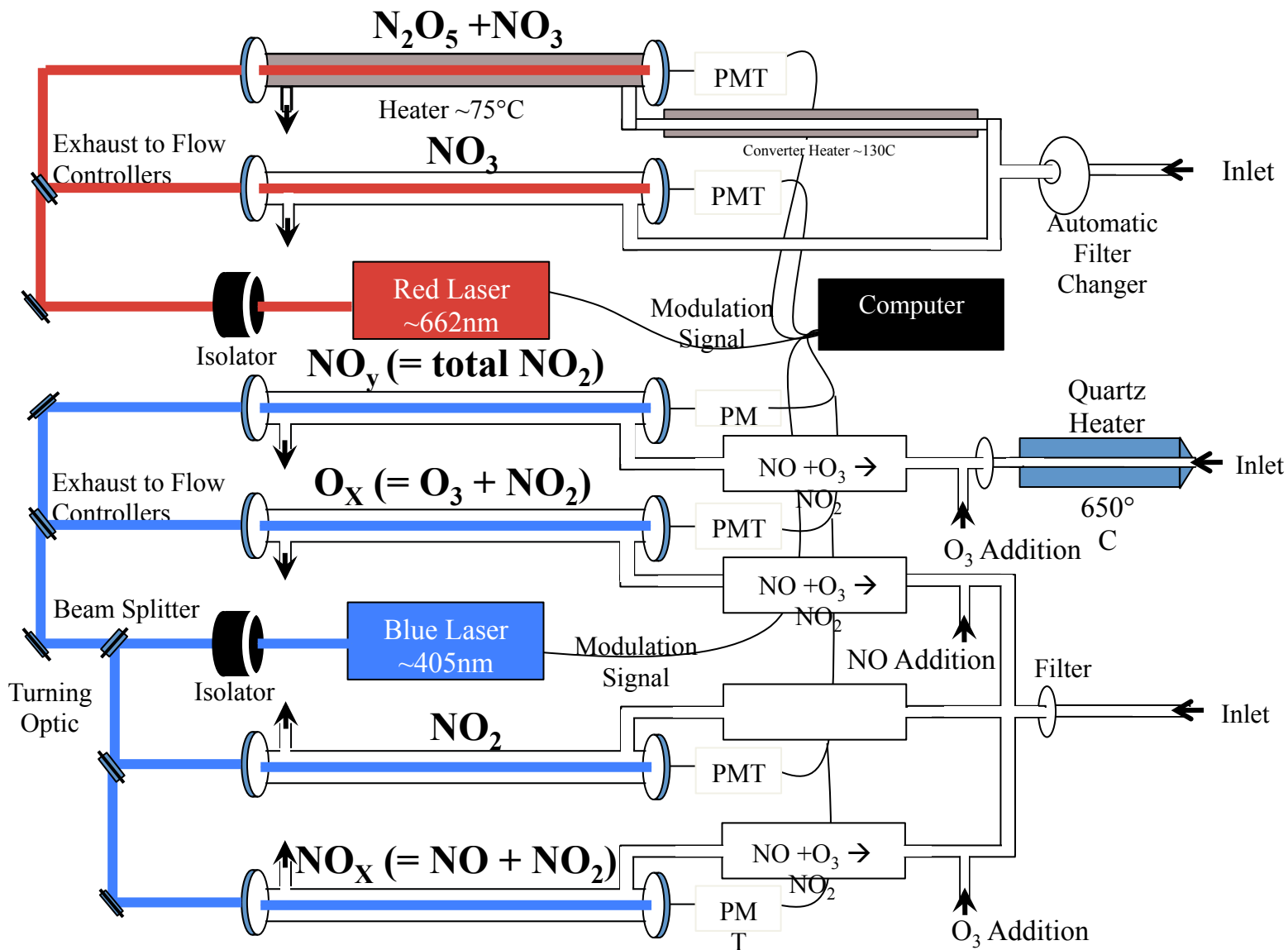
The state of the data, ClNO₂
production, and power plants

WINTER Data Meeting

September 2015

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William P. Dubé, Steven S. Brown

ARNOLD – 6 Channel cavity ring-down

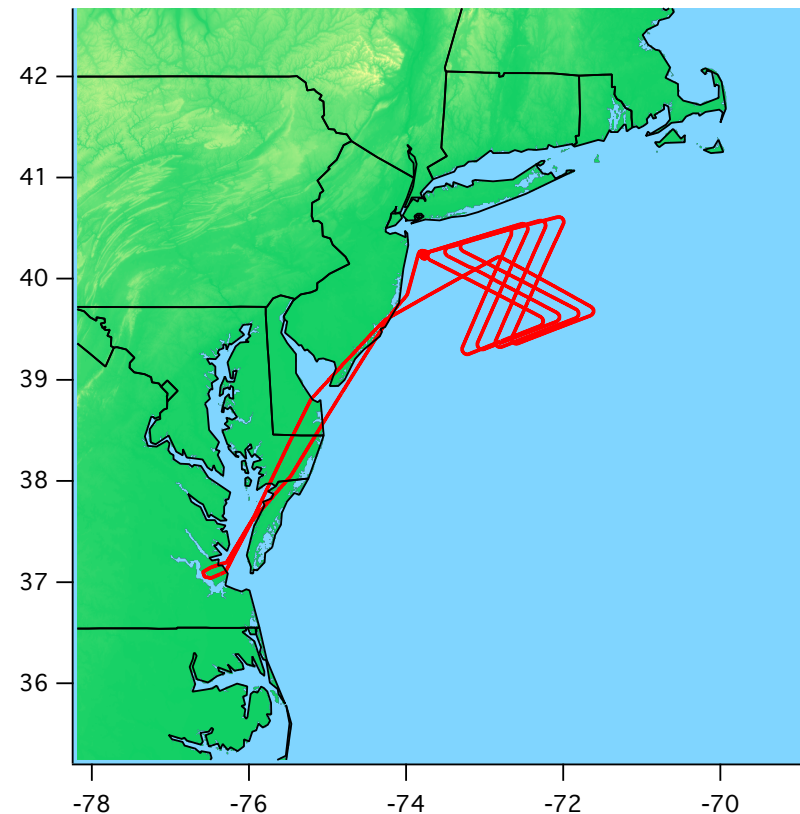


ARNOLD Data

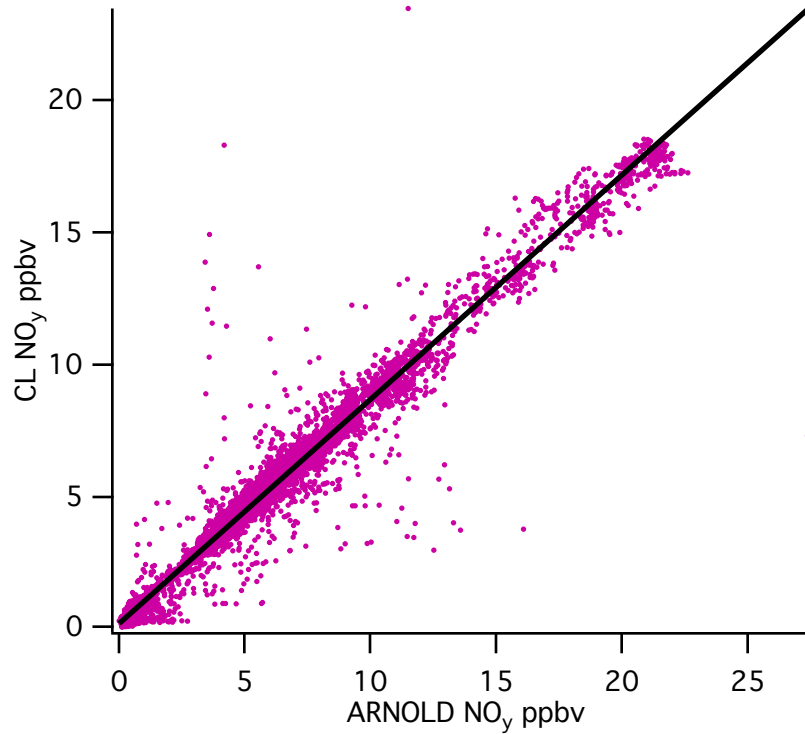
- NO_2 , NO , NO_y , O_3 , N_2O_5 , ~~NO_3~~
- No O_3 on flight 05
- All data nearly finalized- waiting on final RH data from RAF and final O_3 from CL
- Flights 5-13 will change very little from currently posted- waiting on final RAF data
- Flights 1-4, NO , NO_2 and O_3 will change significantly- will be scaled to CL O_3 , so those flights will not have independent data
- Unknown how much aerosol nitrate may be in NO_y

Research Flight 08 (“hourglass”)

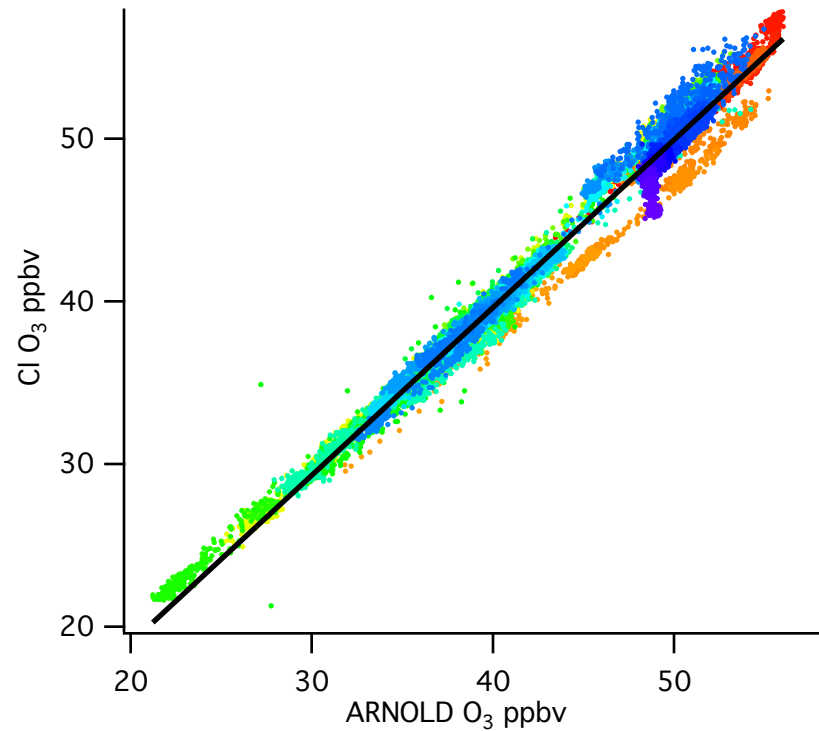
- Night into day
- Mostly in “soup” with some higher concentration plumes



CL comparison with ARNOLD

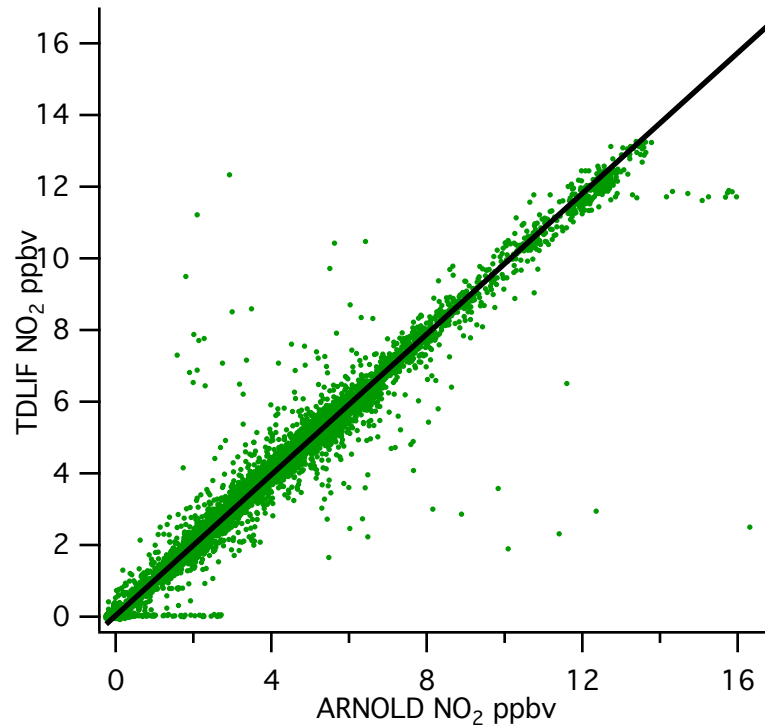


$$CL = 0.86 * ARNOLD + 0.18$$



$$CL = 1.03 * ARNOLD - 1.6$$

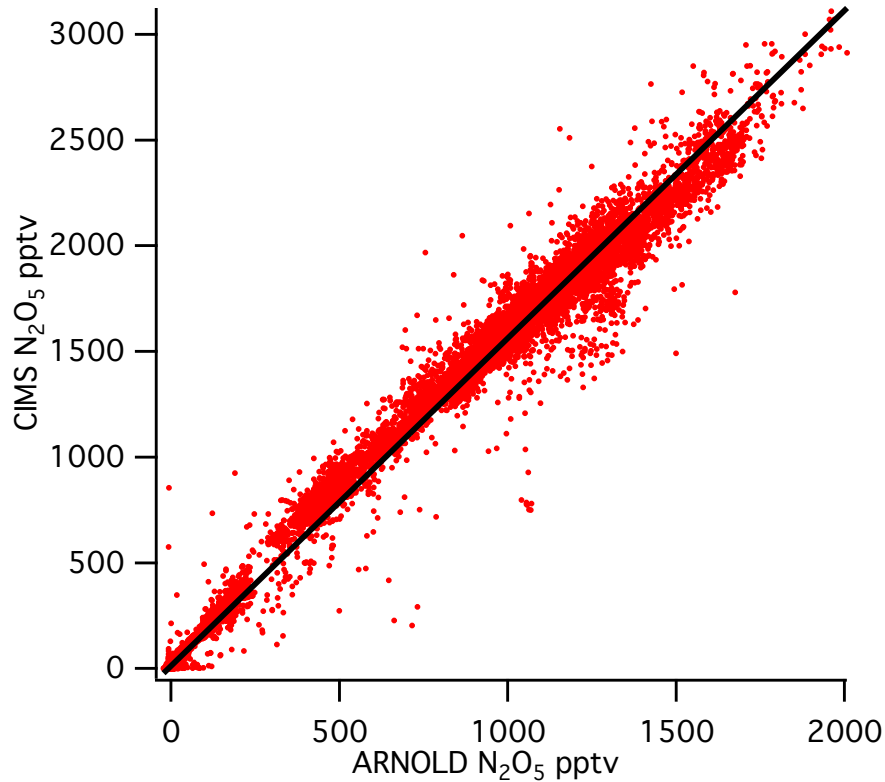
TDLIF comparison with ARNOLD



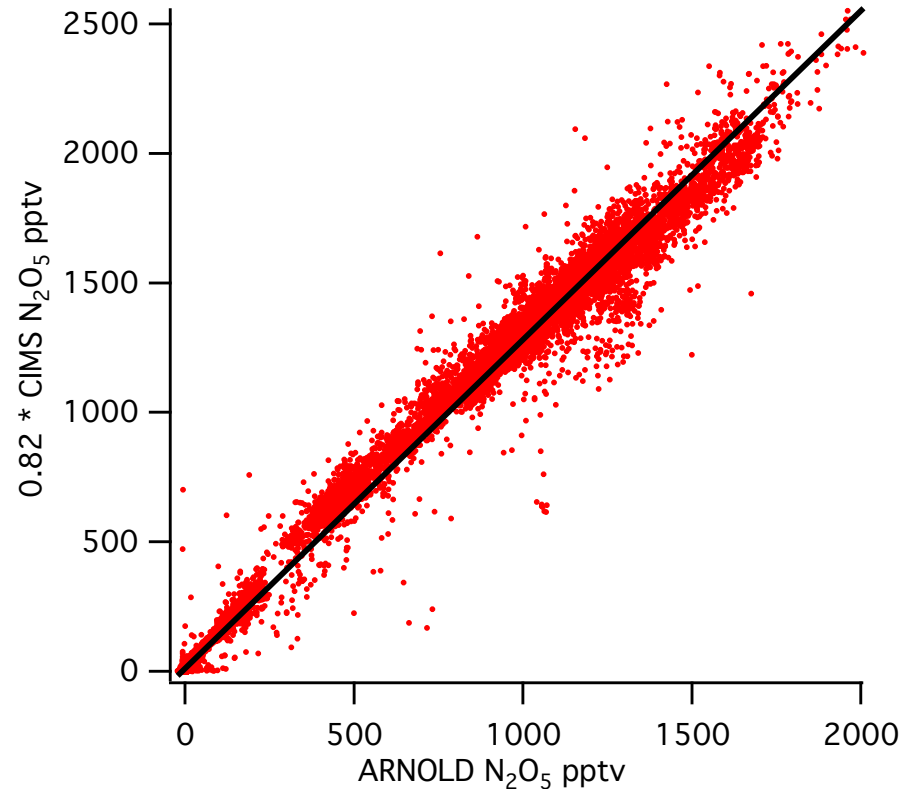
$$\text{TDLIF} = 0.98 * \text{ARNOLD} + 0.05$$

$$\text{TDLIF data} * 0.82$$

CIMS comparison with ARNOLD



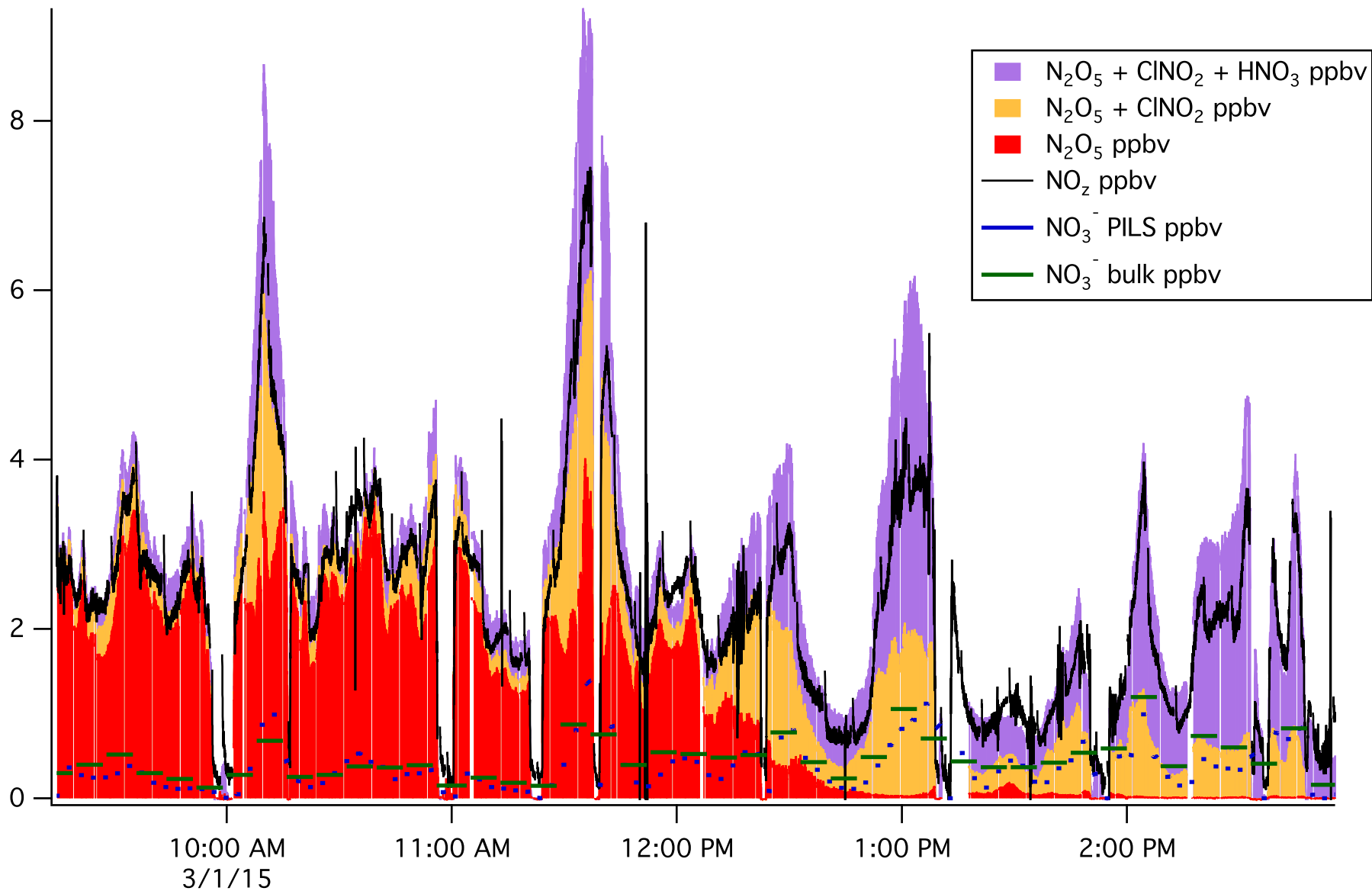
$$\text{CIMS} = 1.55 * \text{ARNOLD} + 14.2$$



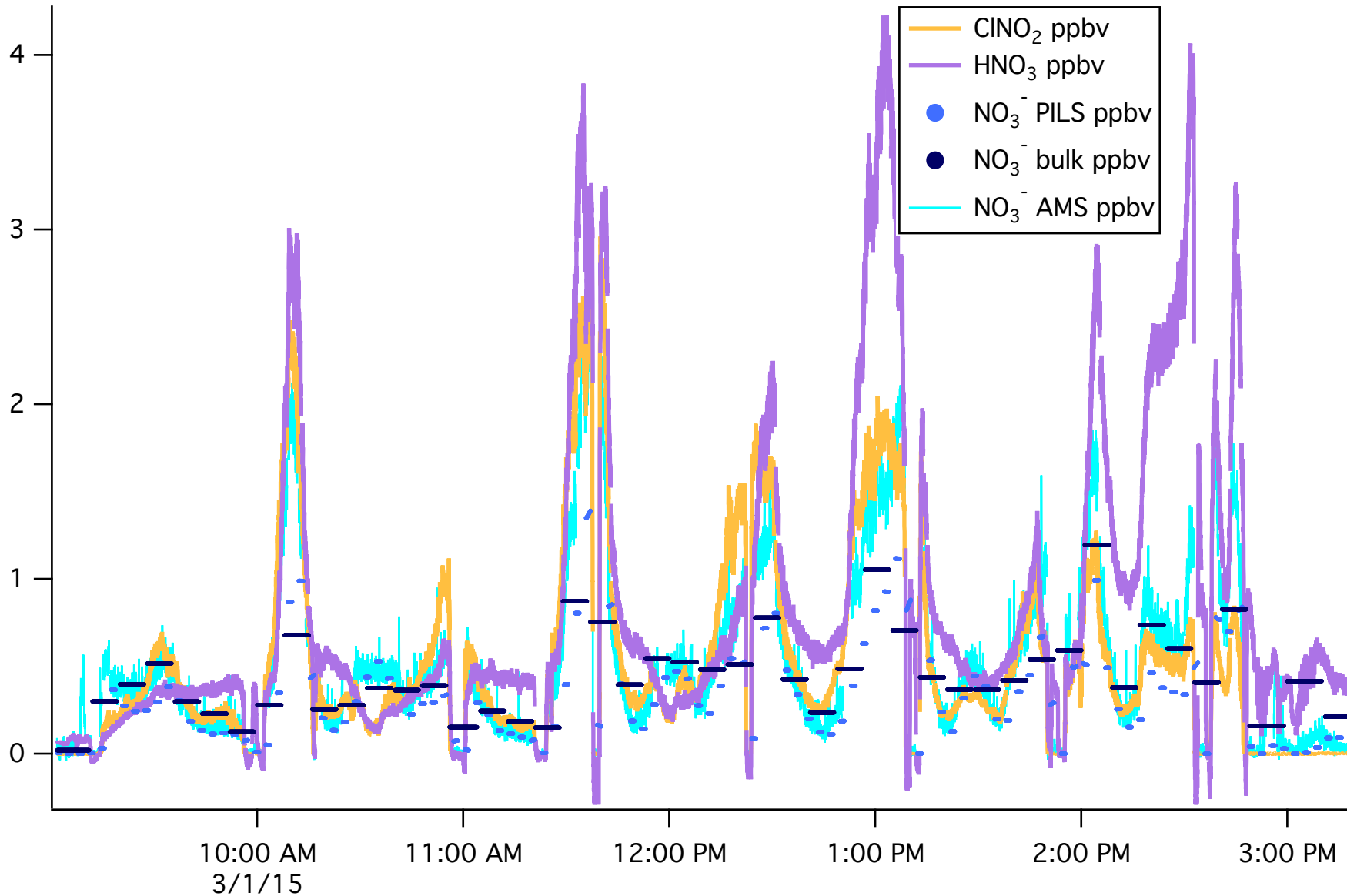
$$\text{CIMS} = 1.27 * \text{ARNOLD} + 12.0$$

$$\text{CIMS} * 0.82$$

N_2O_5 , ClNO_2 , various NO_3^- , flight 08

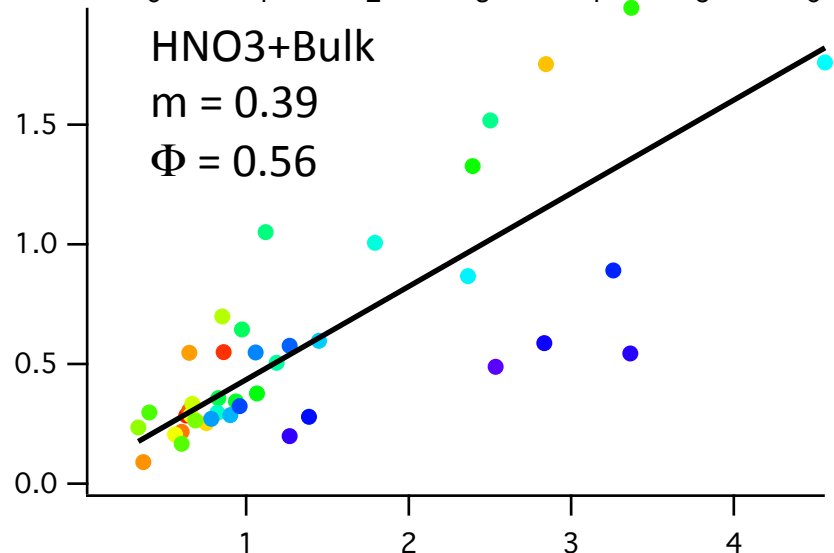
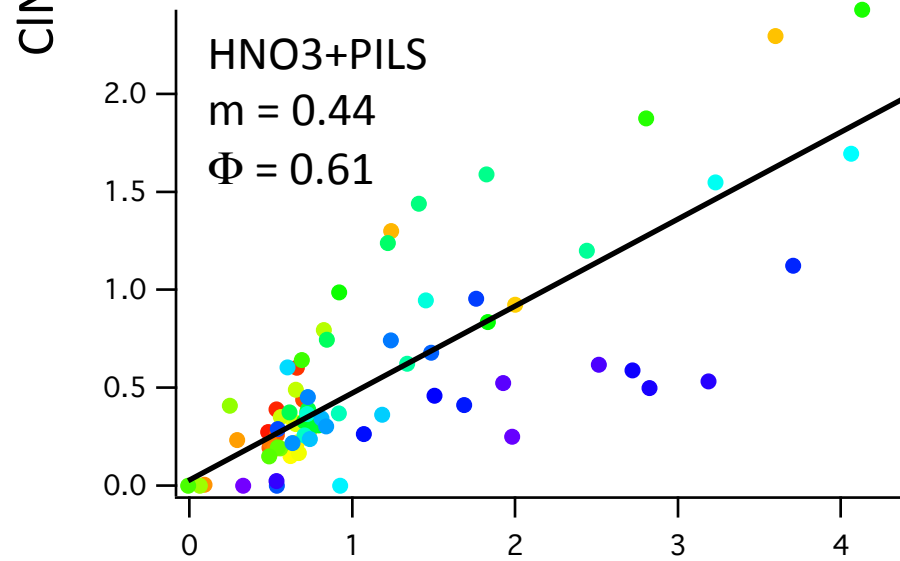
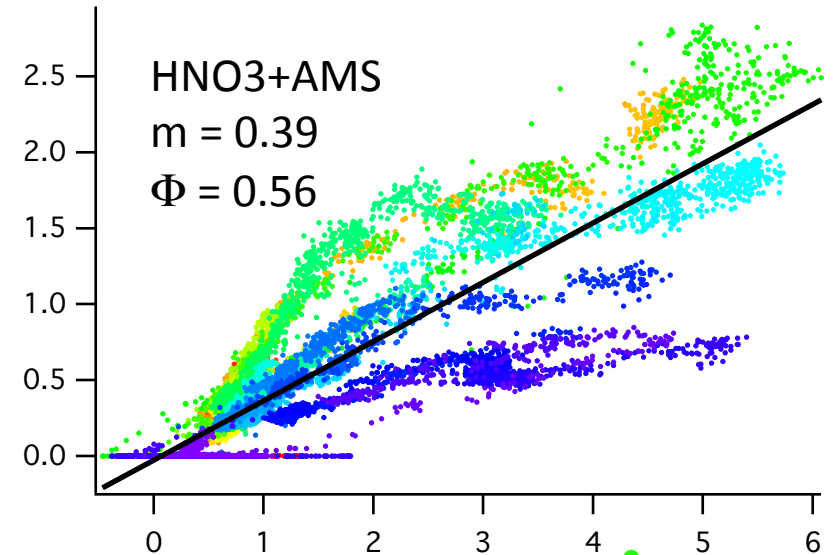
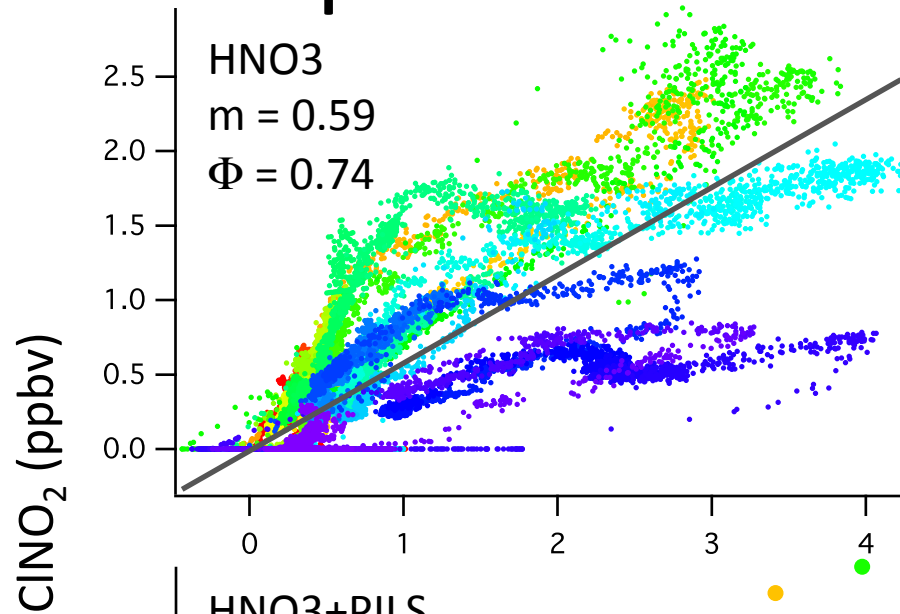


ClNO₂ and nitrate, flight 08



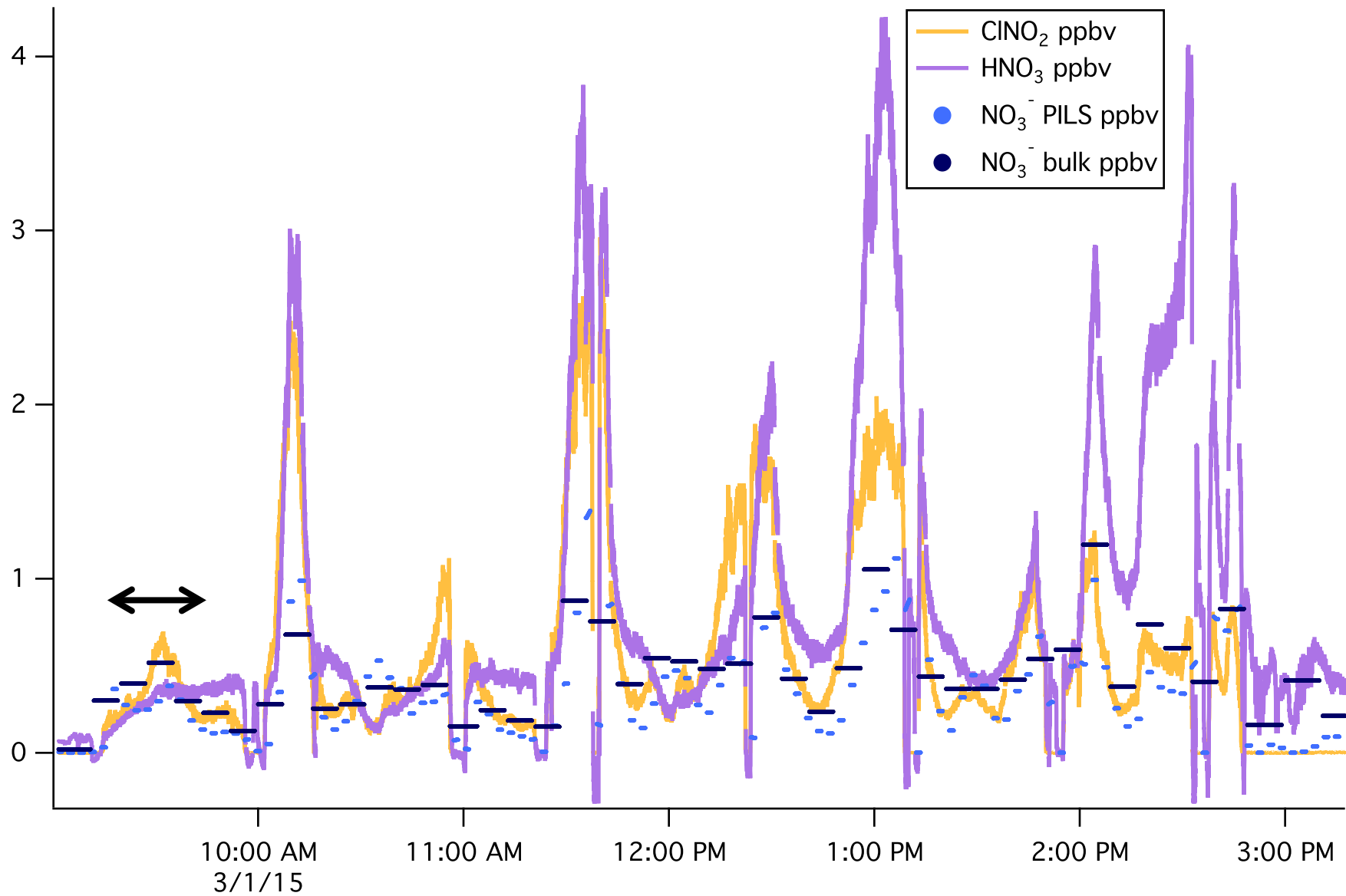
Average ClNO₂ production

- Graphs colored by time red → violet
- Φ is ClNO₂ production ($2m/(1+m)$)



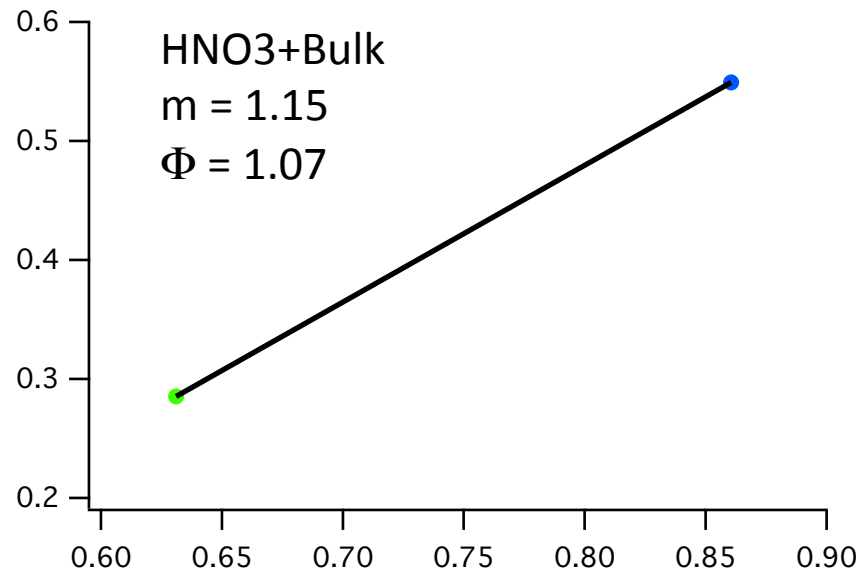
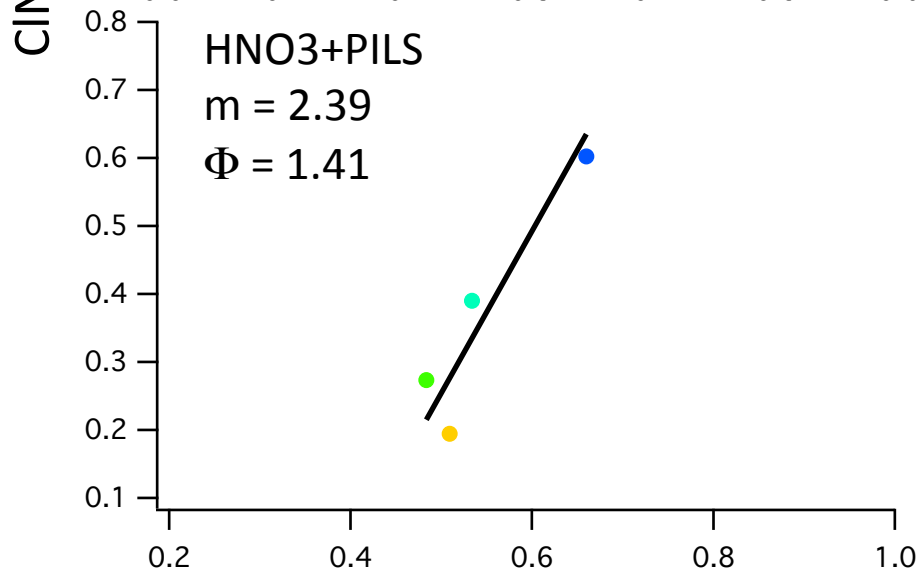
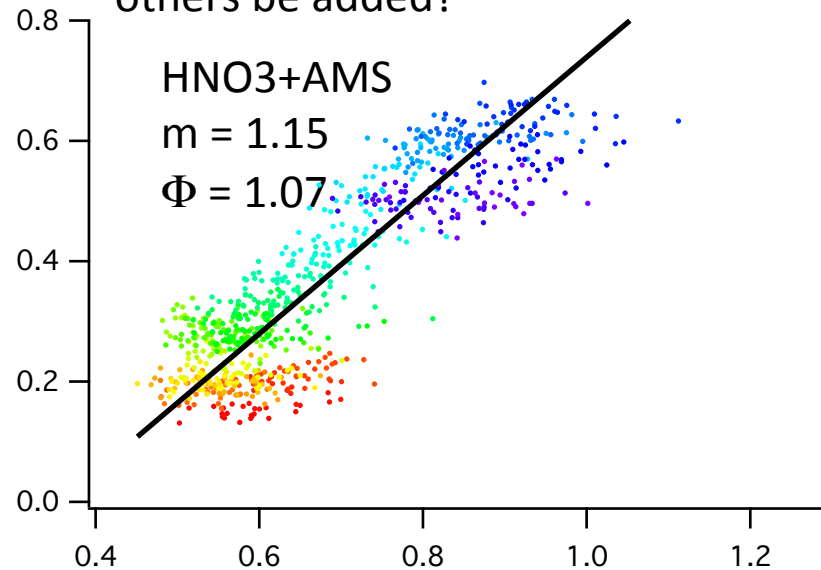
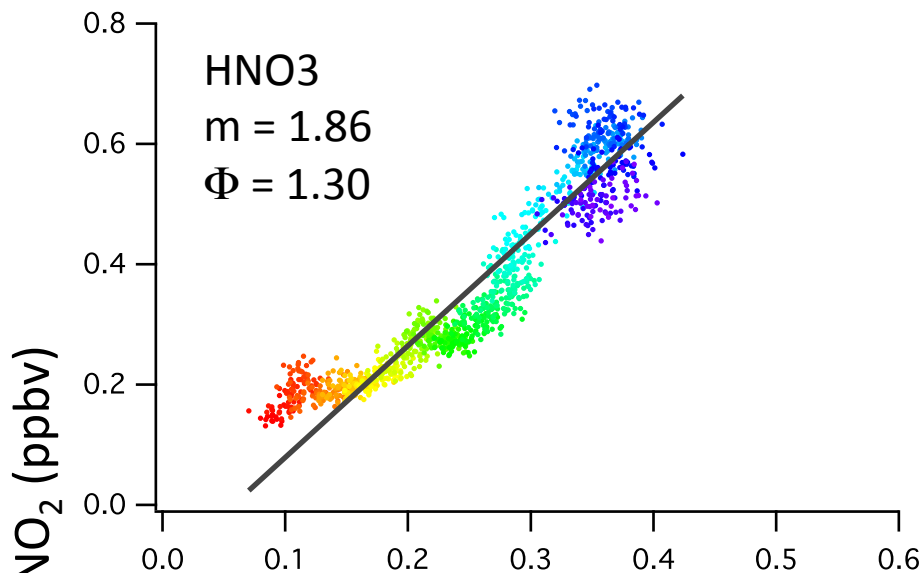
NO₃⁻ (ppbv)

Initial ClNO₂ yield



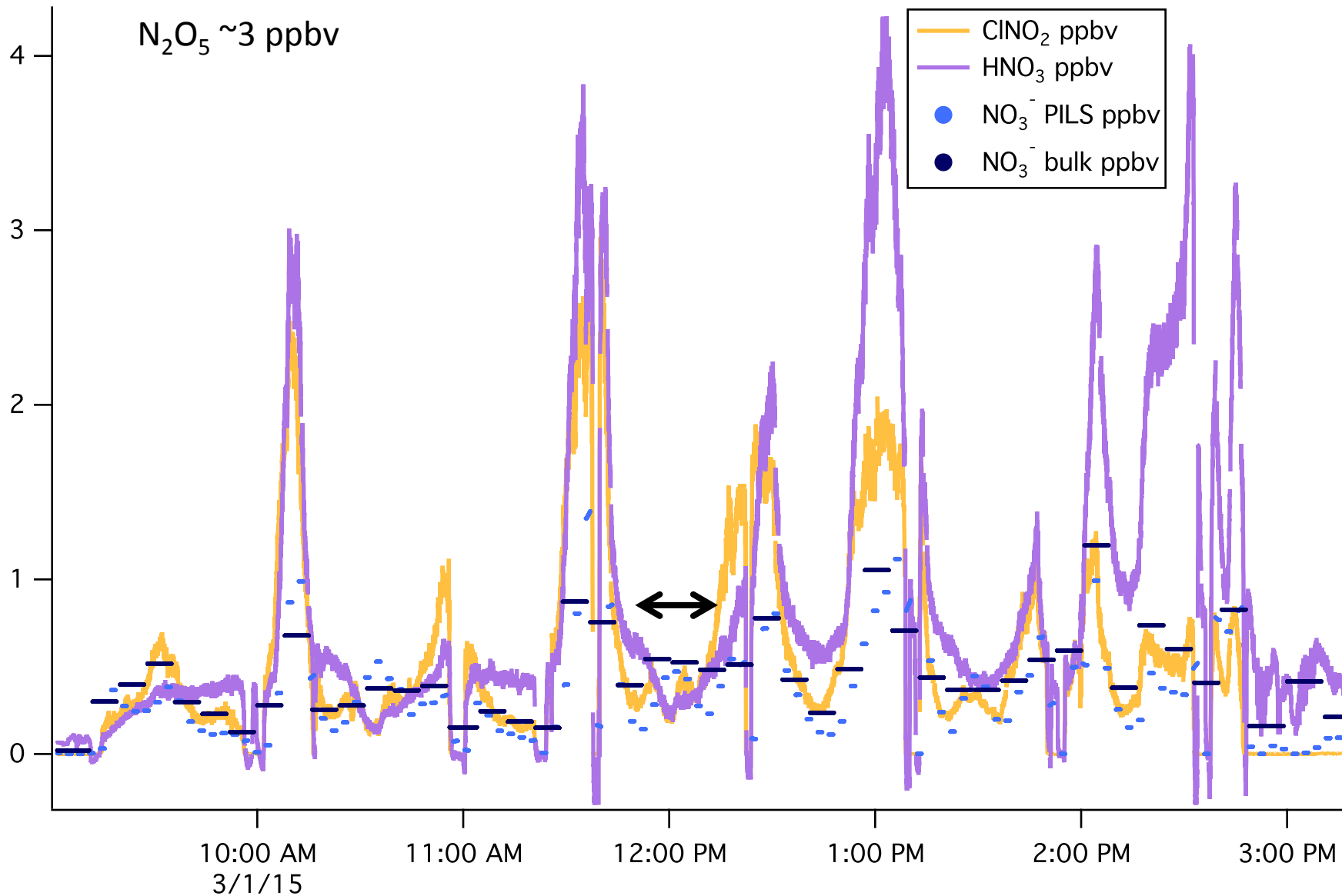
Initial ClNO₂ yield

- Graphs colored by time, red → violet
- Slope > 1 is unphysical
- Adding bulk gets slope < 1, but should others be added?



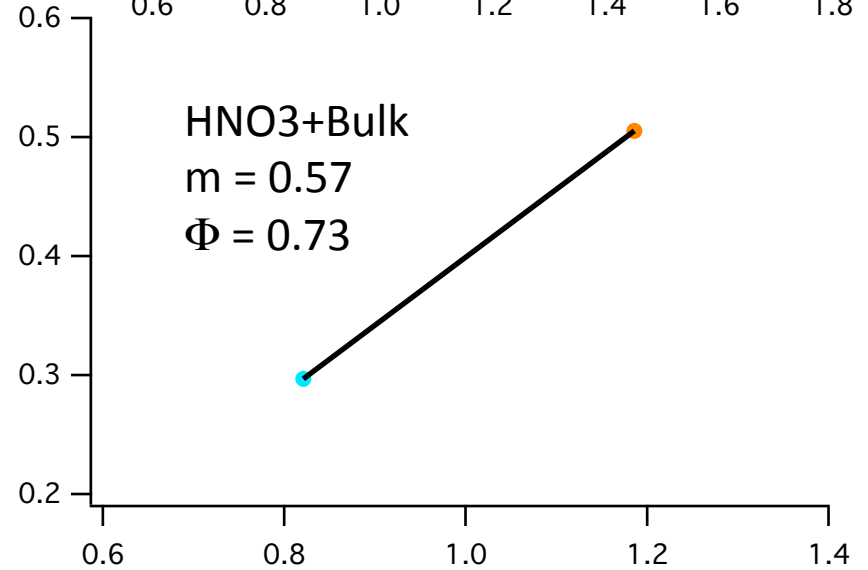
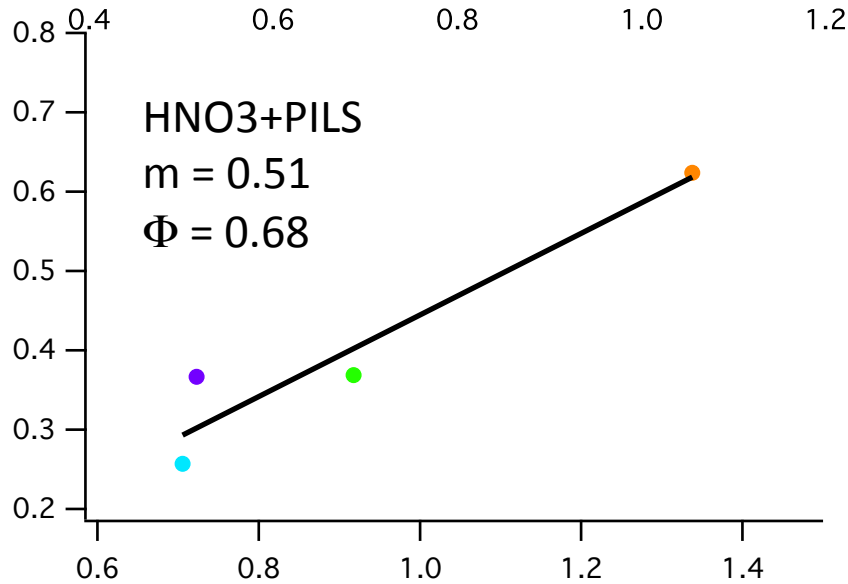
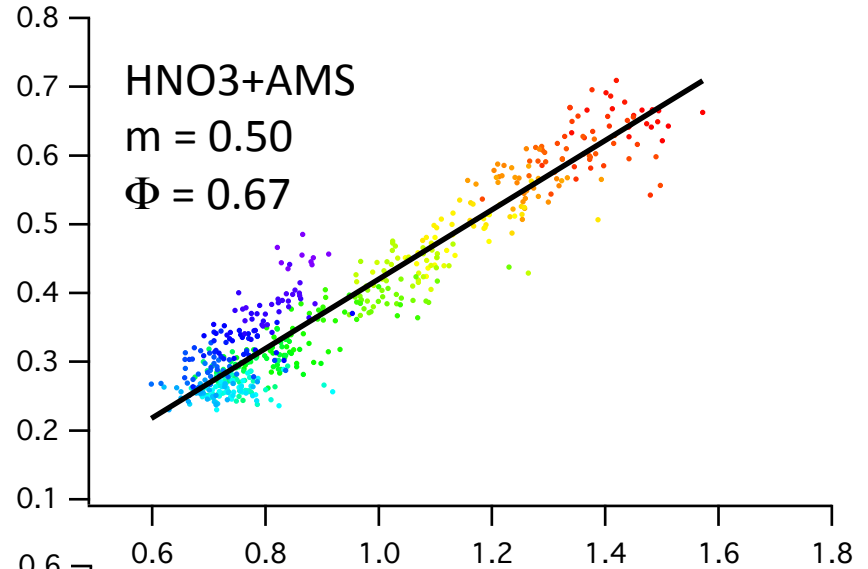
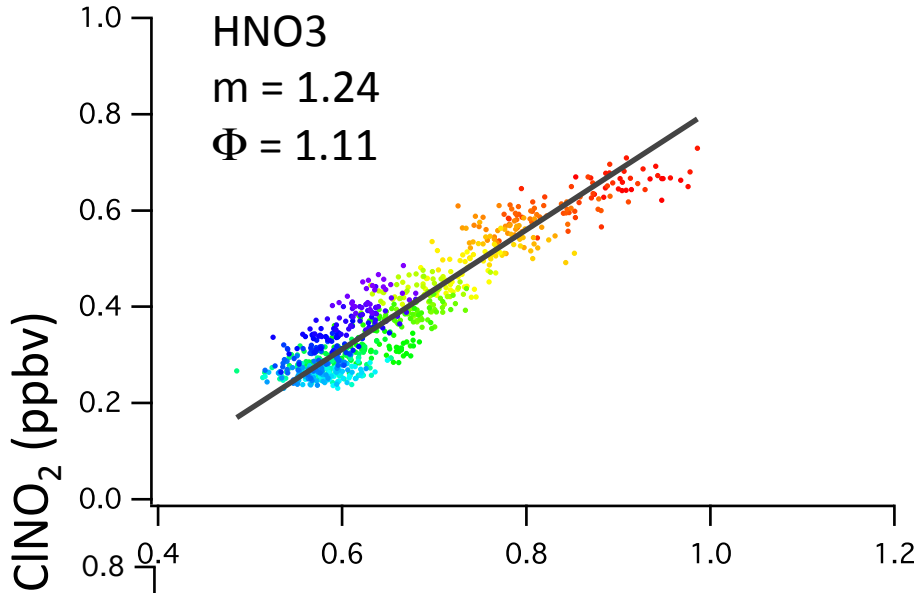
NO₃⁻ (ppbv)

Background ClNO₂ yield



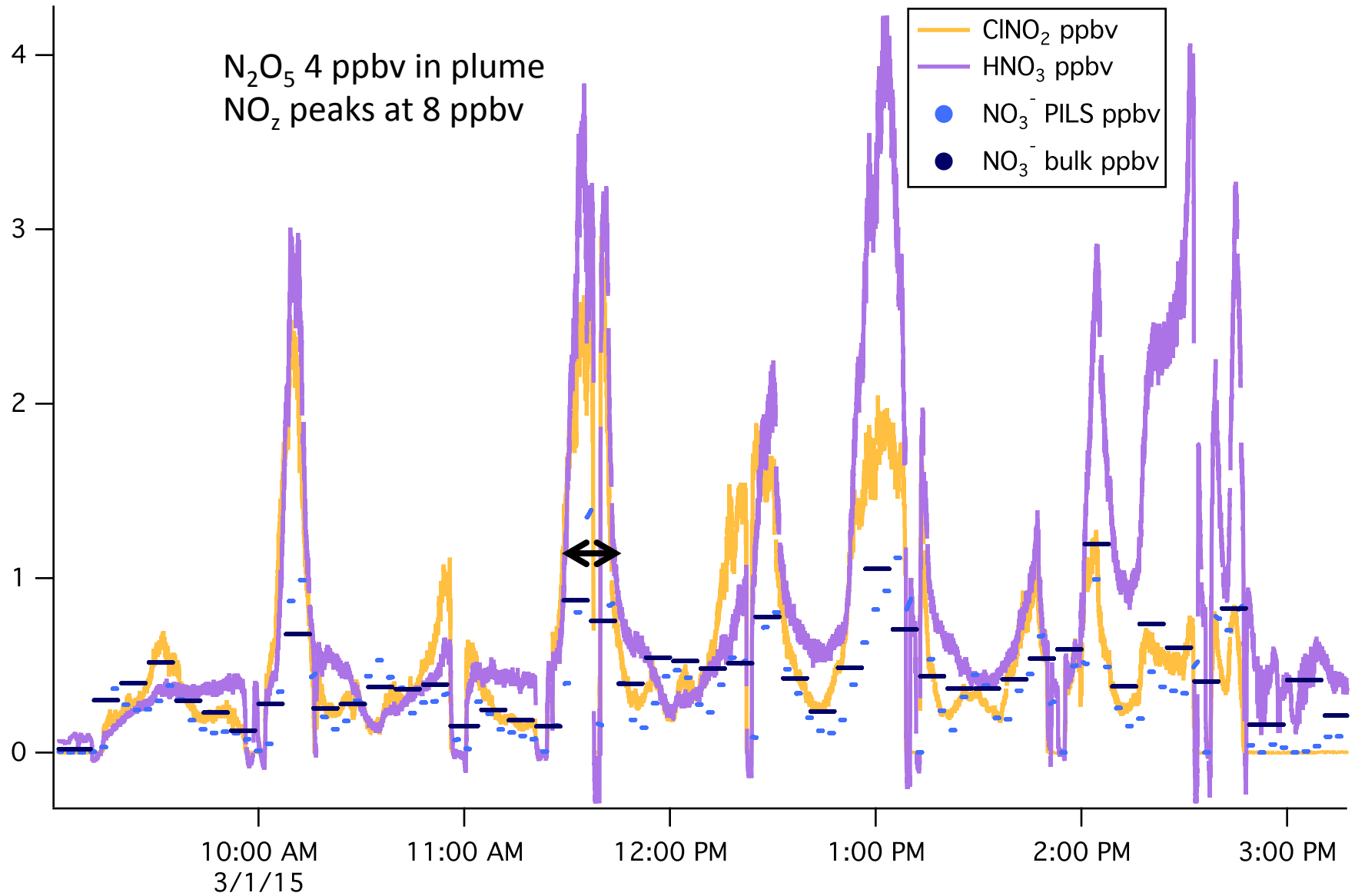
Background

- Background ClNO_2 yield much higher than in plume
- All aerosol NO_3^- give similar result- no supermicron NO_3^- ?



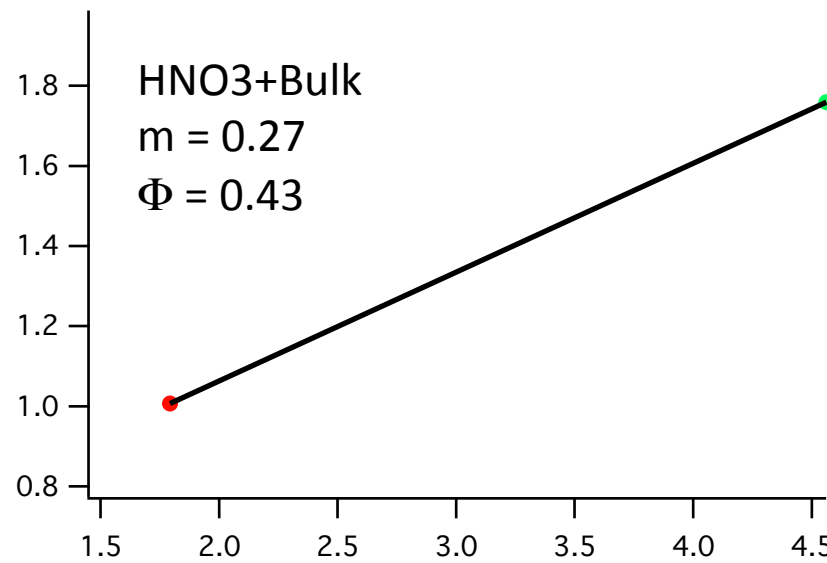
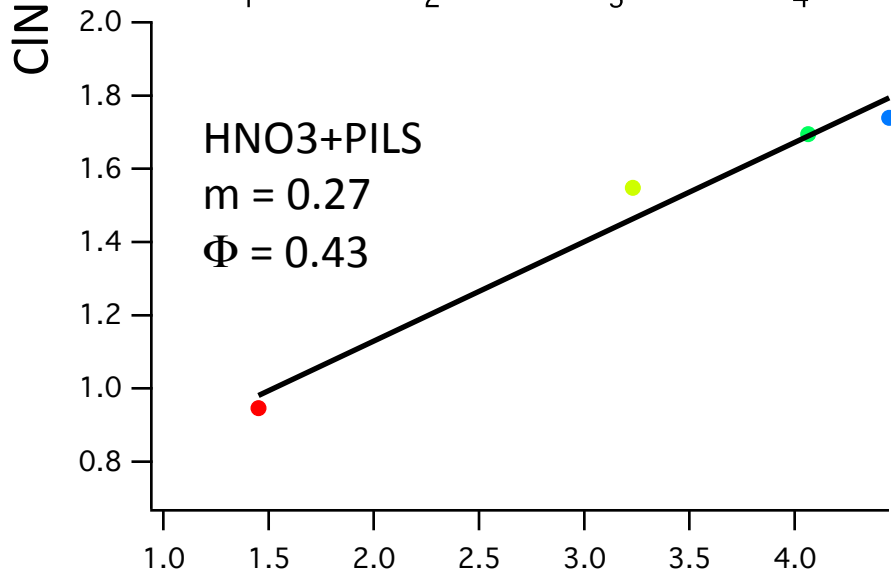
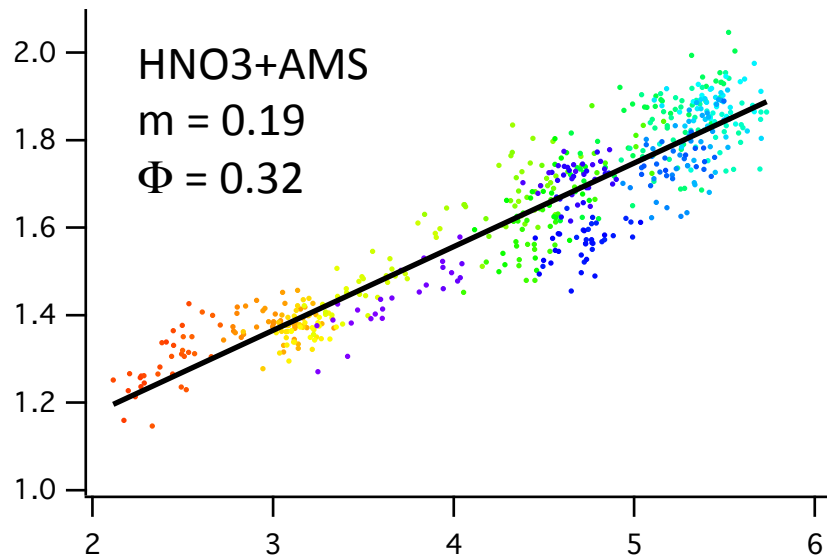
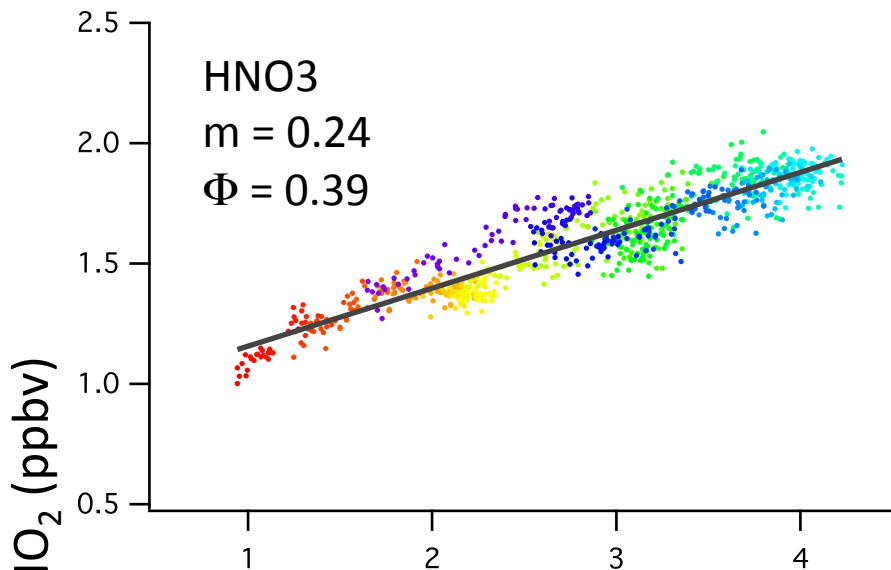
NO_3^- (ppbv)

In plume ClNO_2 yield



In plume

- Graphs colored by time, red \rightarrow violet
- In plume is much lower ClNO₂ yield
- Limited by Cl?



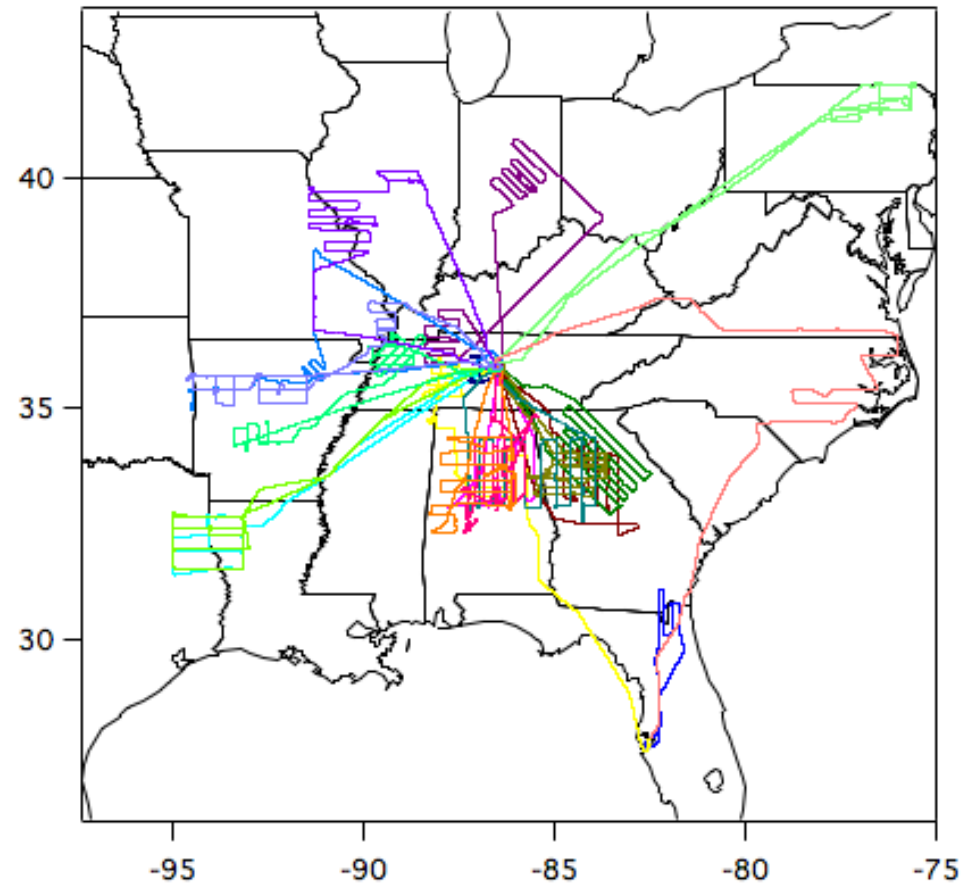
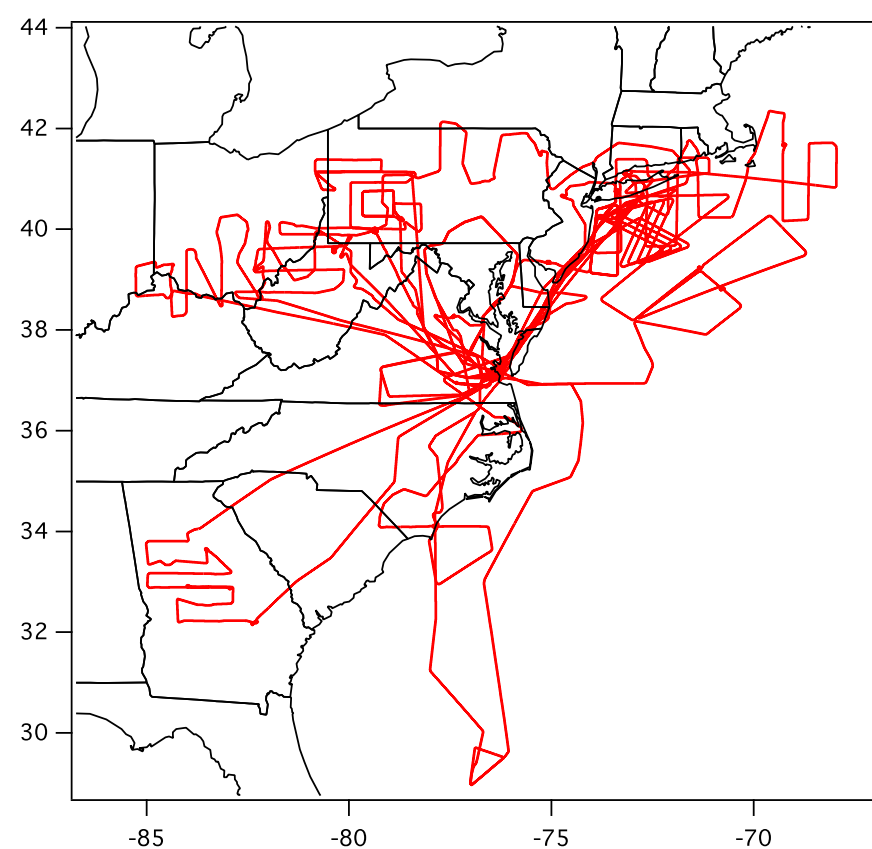
NO₃⁻ (ppbv)

Power plant plumes

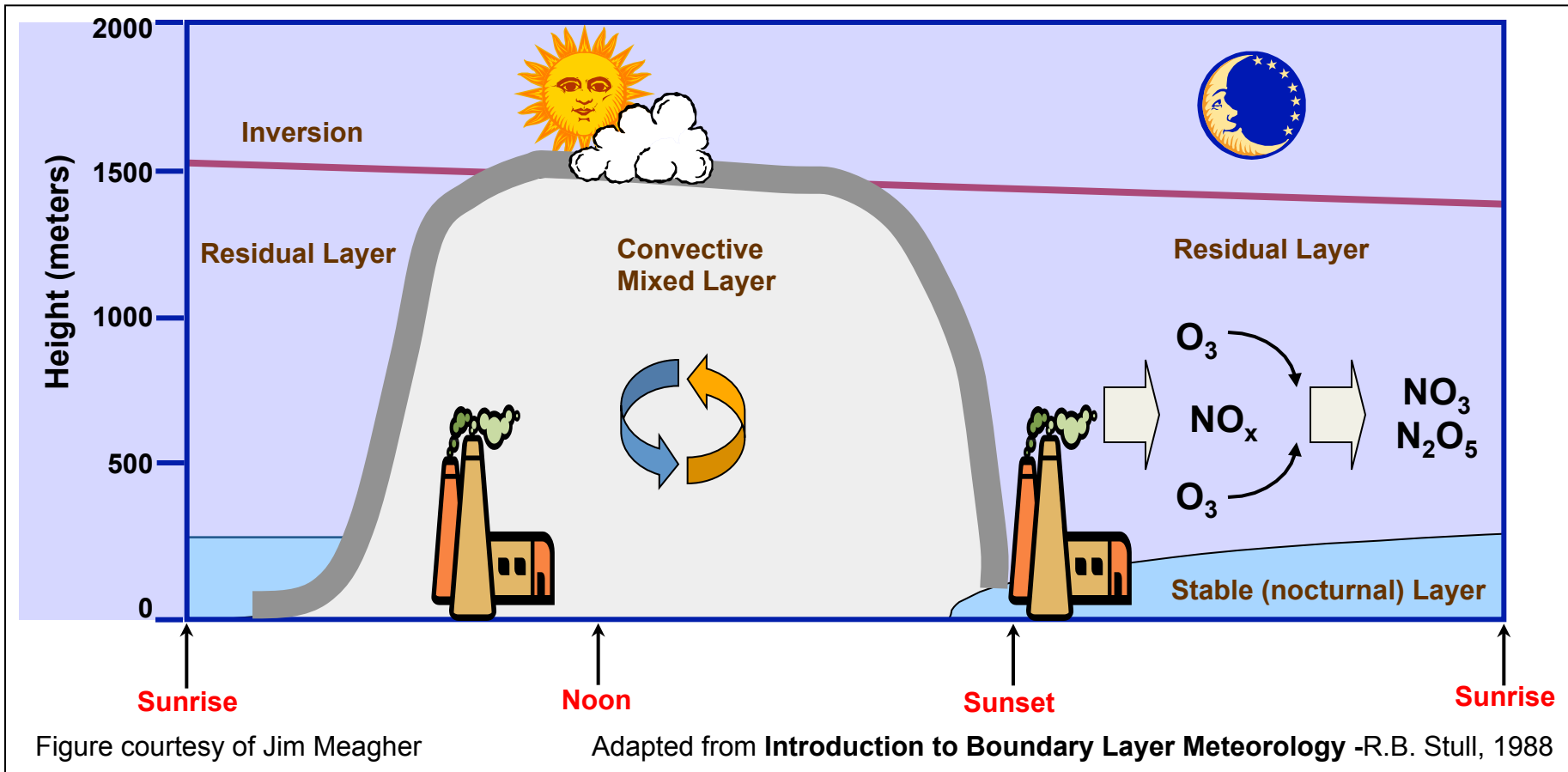
- Dispersion rates
- NO oxidation rates
- NO_x lifetime
- Formation of N₂O₅ and ClNO₂ (night)
- Plumes with and without complete ozone titration

Summer vs winter

- Comparing plumes from SENEX and WINTER
- Overlap in Atlanta night flights



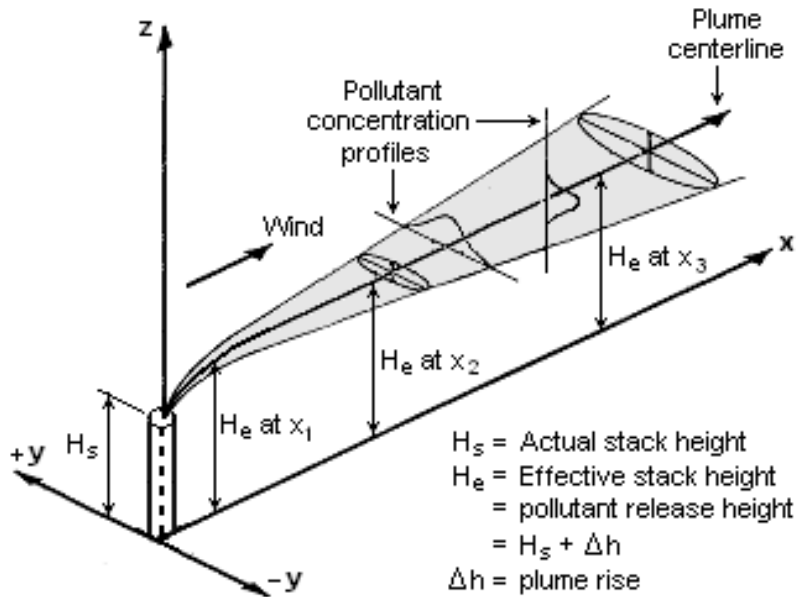
Nighttime Power Plant Plumes



- Coal-fired power plants are commonly used as base-load power – they have roughly constant output (and emissions) day to night
- Daytime emission into well mixed, convective boundary layer
- Nighttime emission into residual layer – not mixed to surface level

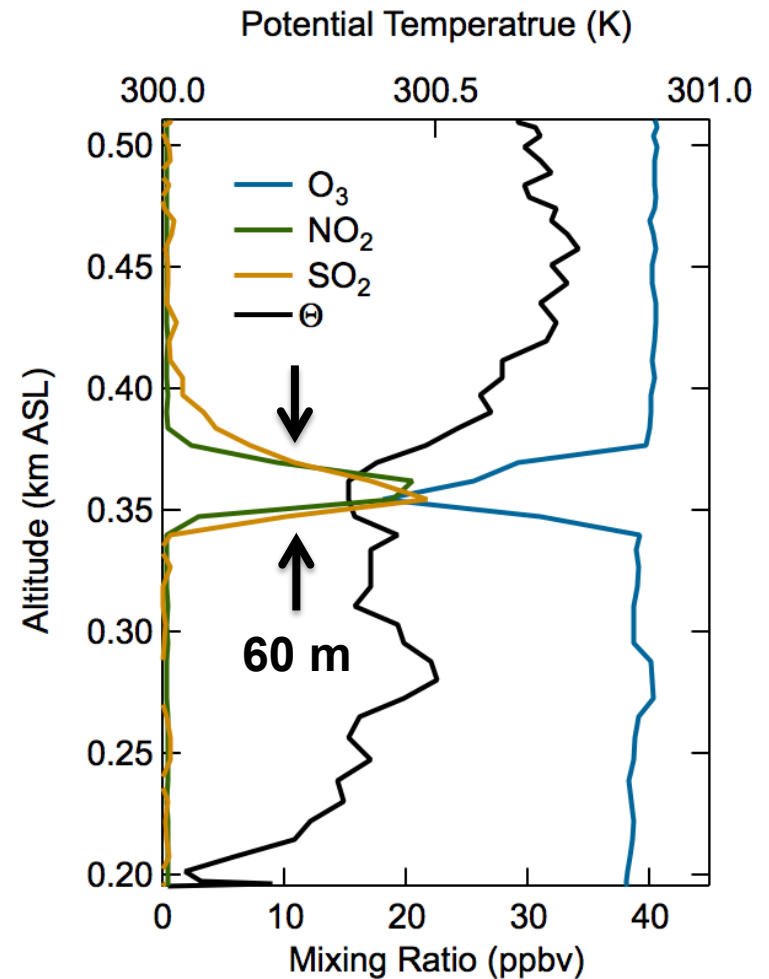
Nighttime power plant plumes can only be sampled with aircraft, tower or balloon

Plume Dispersion in Stable Boundary Layers “Fanning Plumes”



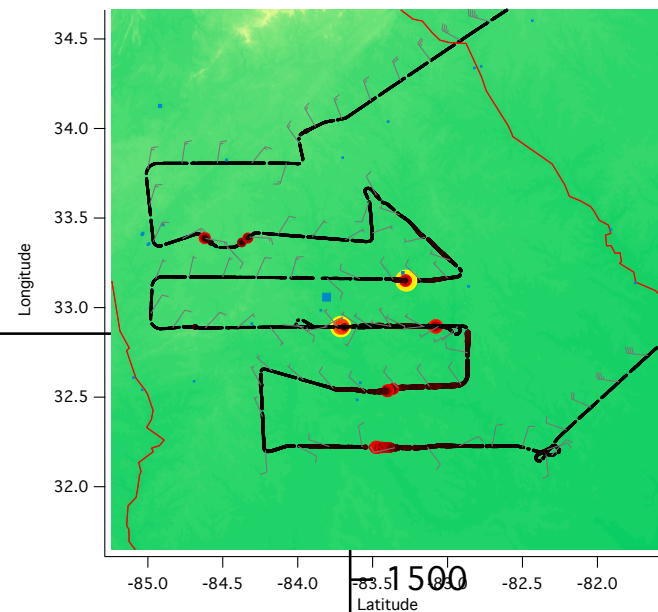
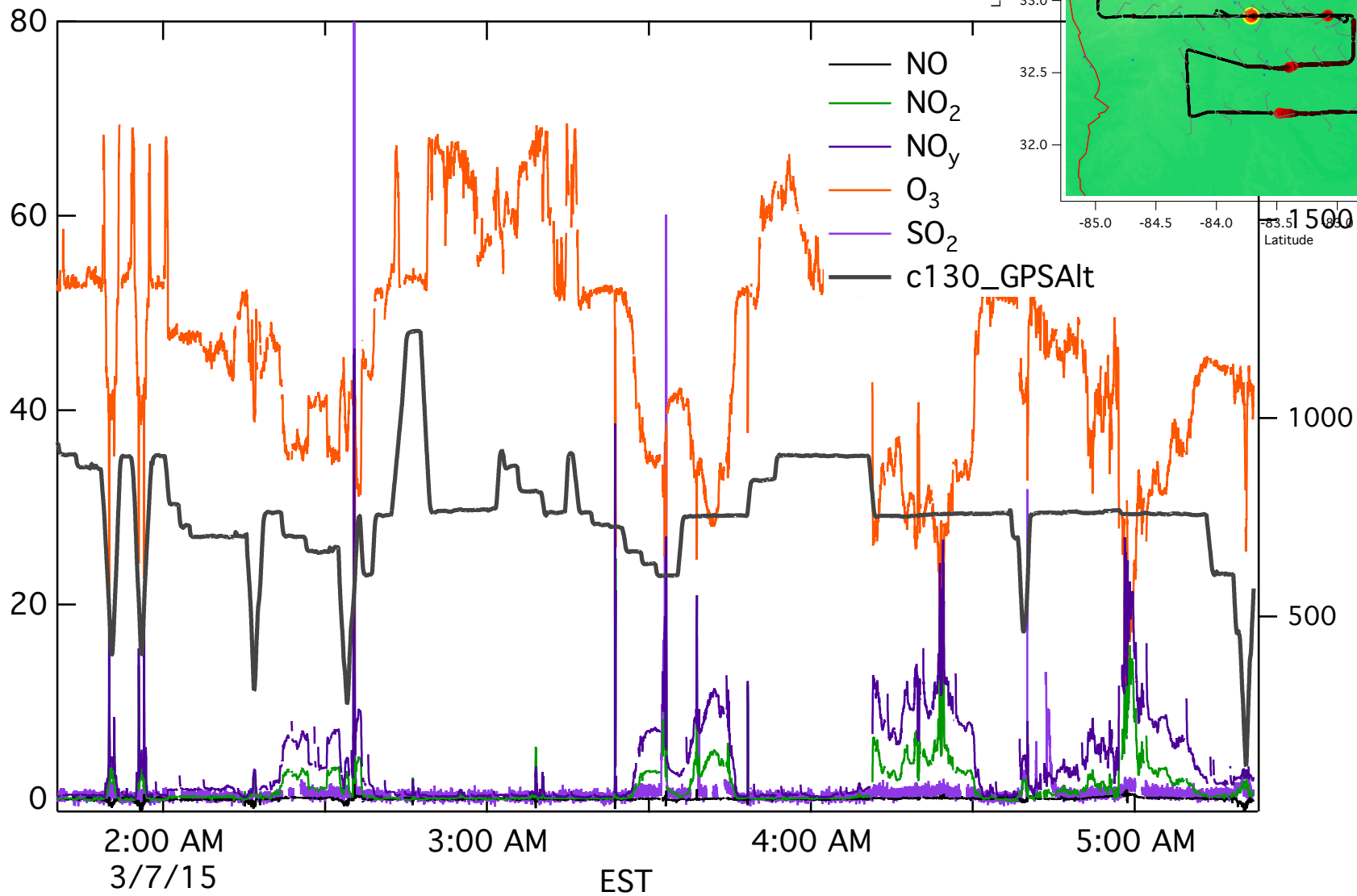
Source: Jeff Lew, UCLA

- Prior NOAA aircraft observations (2004 Northeast, 2006 Texas) consistent with this picture of plume mixing
- Plume chemistry (e.g., N_2O_5 uptake) varied *widely*
- Recent power plant NO_x controls important

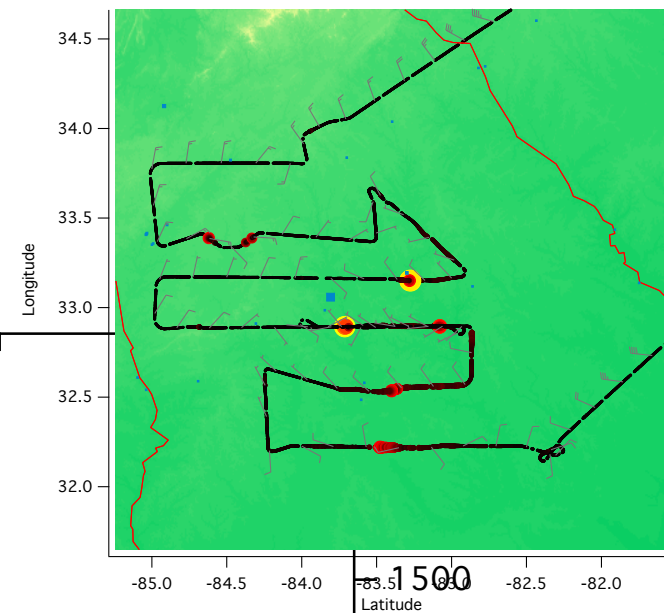
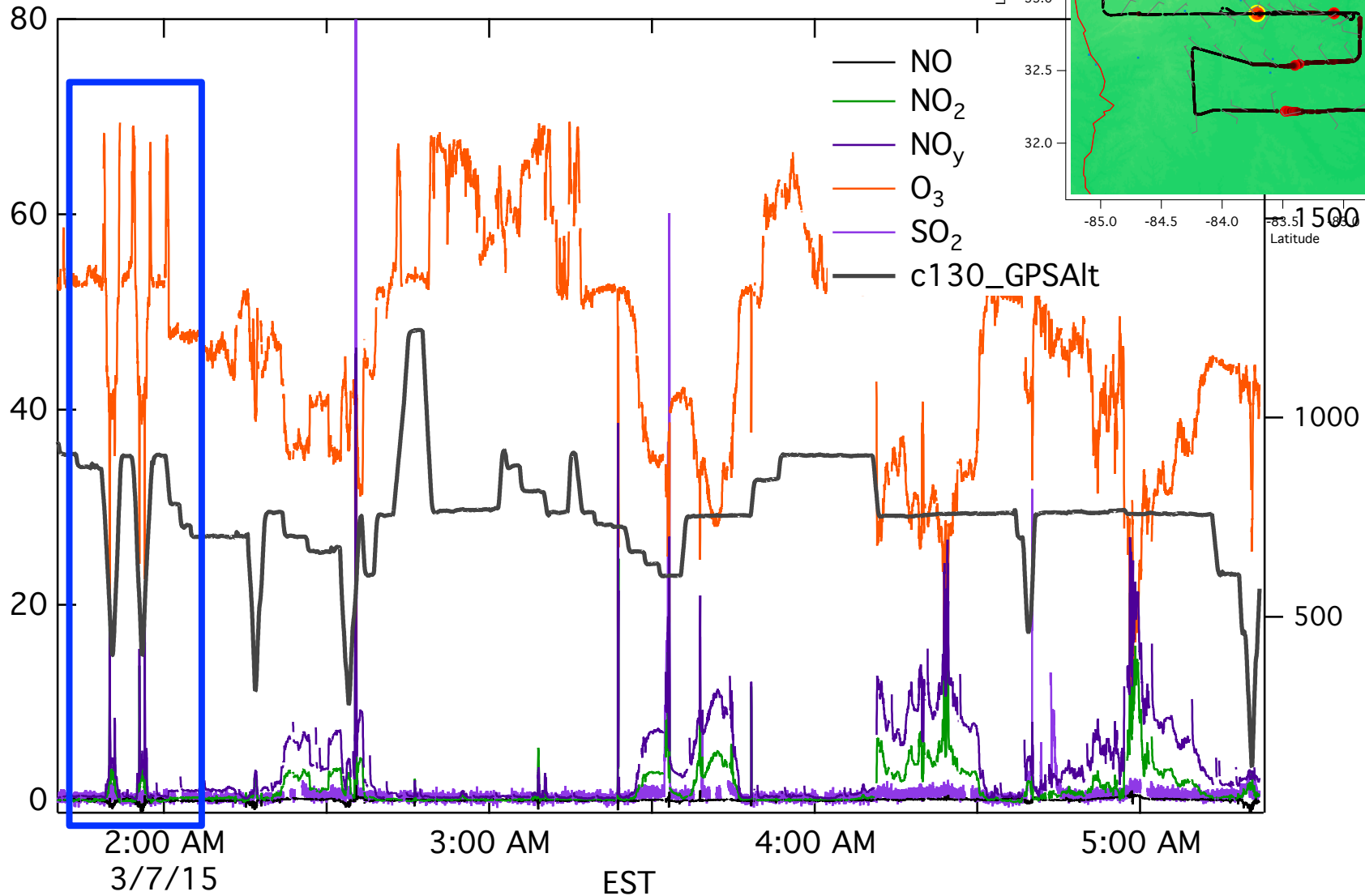


Vertical profile intercept of plume from Green County Power Plant, AL (SENEX)

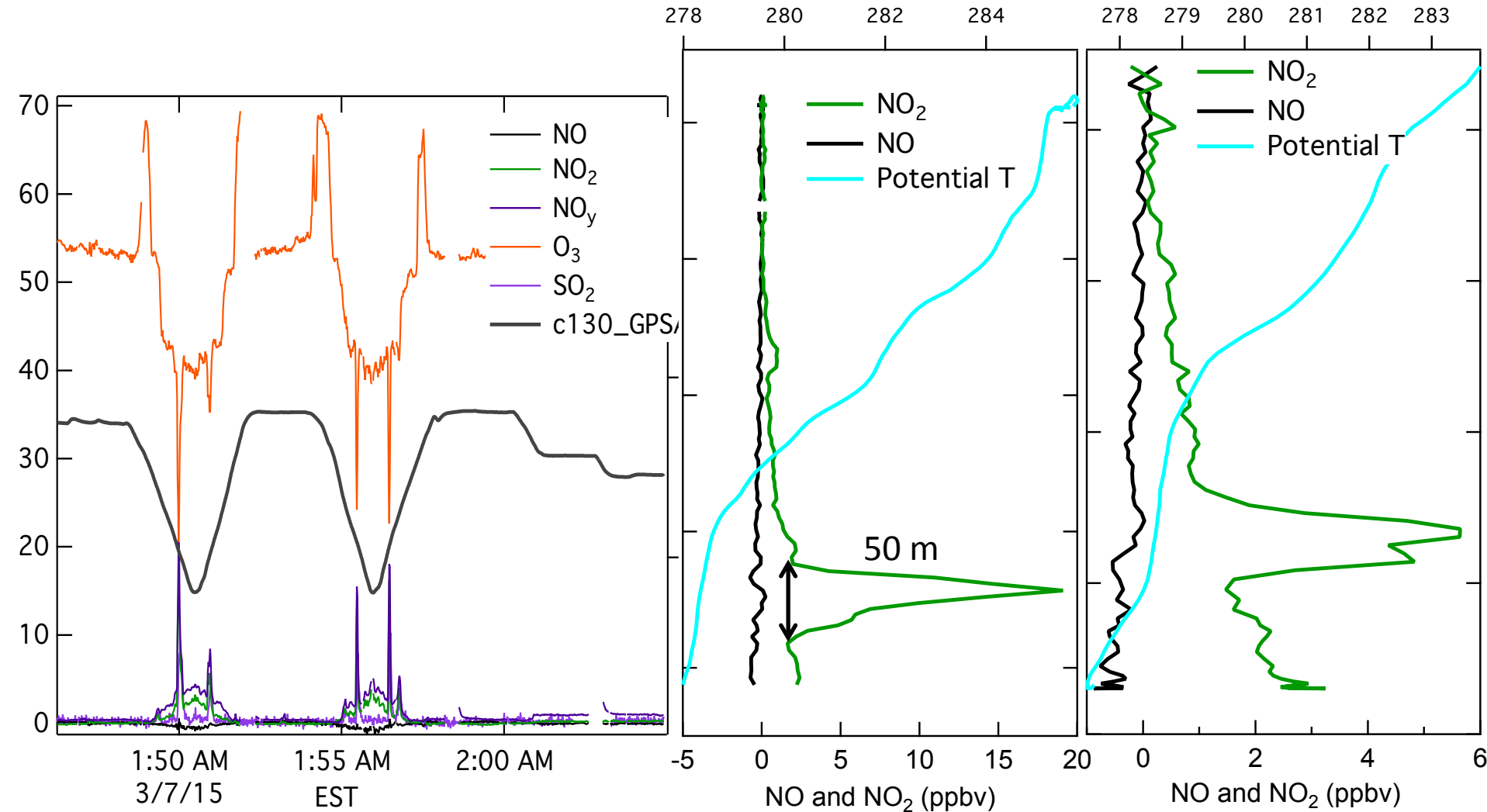
Flight 10- Atlanta, night



Flight 10- Atlanta, night



Vertical profiles of plume



Gaston Plume “Far” Field Intercept

- Plume width @ 55 km downwind from stack similar to near field
- Narrow Features retained even well downwind
- *IF* near field O_x budget is closed, plume can be aged from slope of NO_2 vs O_3 plot

$$t_{plume} \approx \frac{\ln[1 - S(m+1)]}{Sk\overline{O_3}}$$

$\overline{O_3}$ = average O_3

k = rate coefficient for $NO_2 + O_3$

m = slope of O_3 vs NO_2 plot

S = stoichiometric factor

= 1 for NO_3 loss, 2 for N_2O_5 loss

- Aged plume has relatively large N_2O_5 component of O_x

