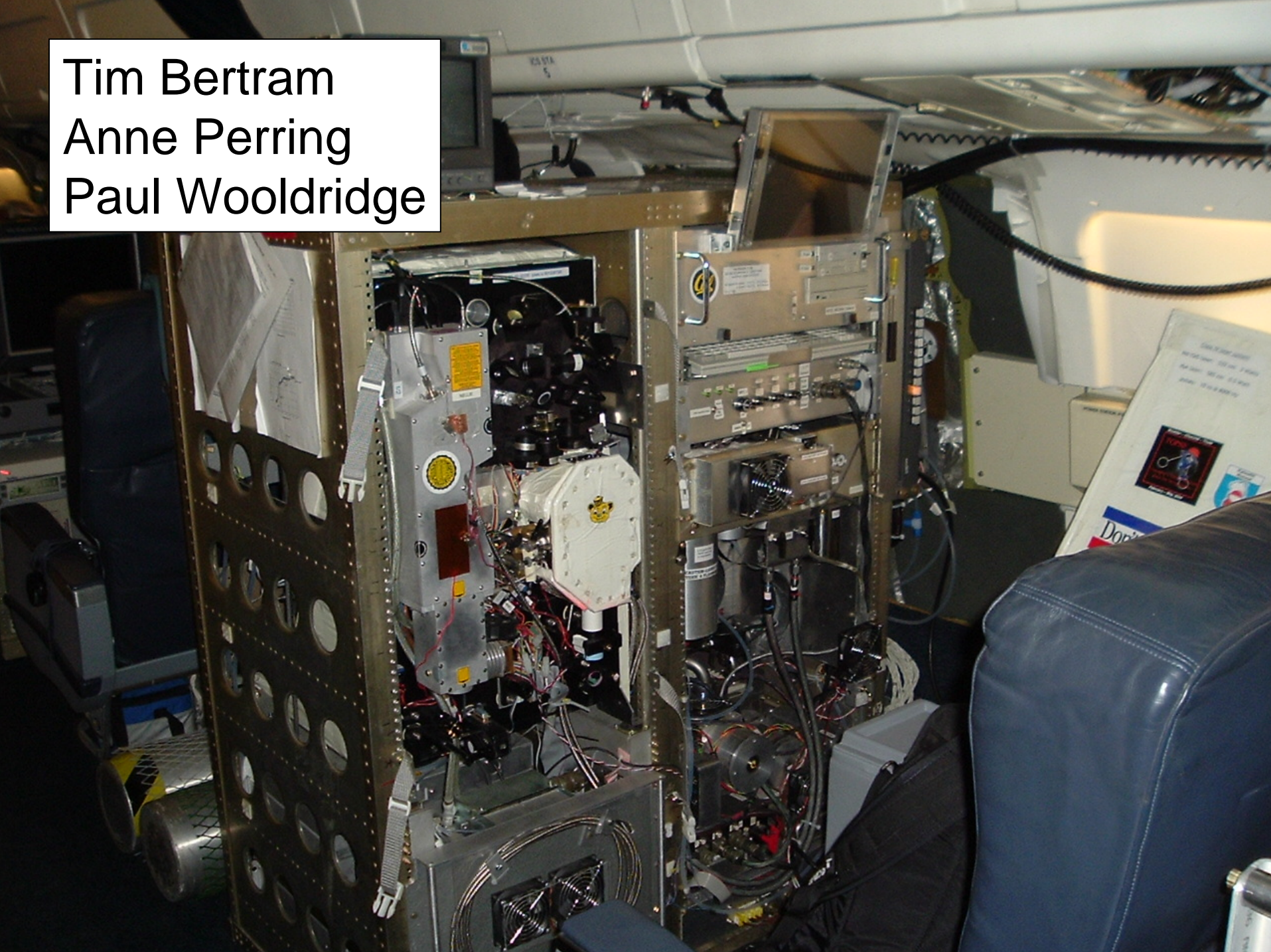


# Nitrogen Oxides

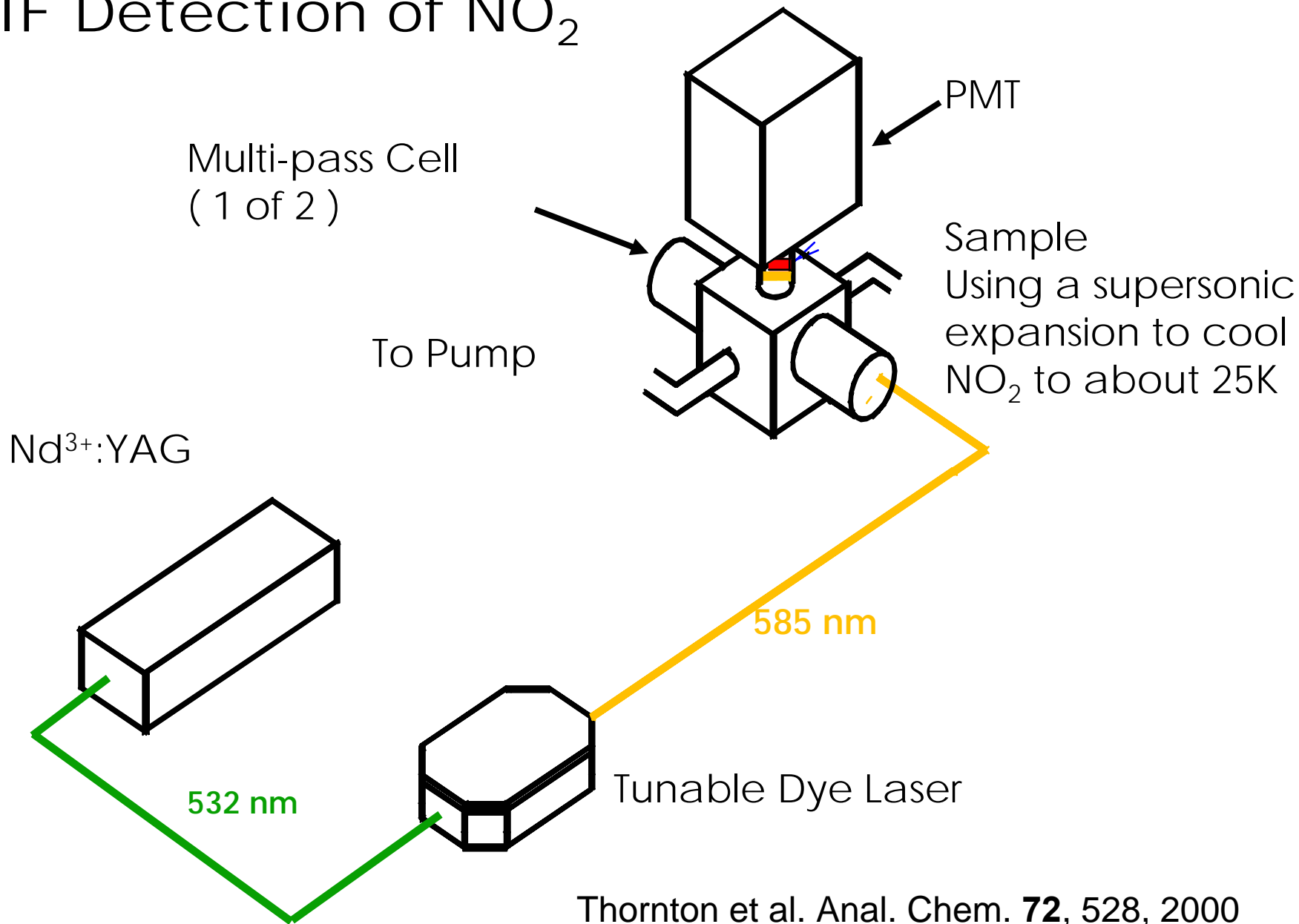


- The Berkeley TD-LIF Instrument/Comparisons
- Convection,  $\text{NO}_2$  peak at 10km, Age of air,
- $\text{HO}_x$  chain termination (by  $\text{NO}_x$ ) in the continental boundary layer

Tim Bertram  
Anne Perring  
Paul Wooldridge

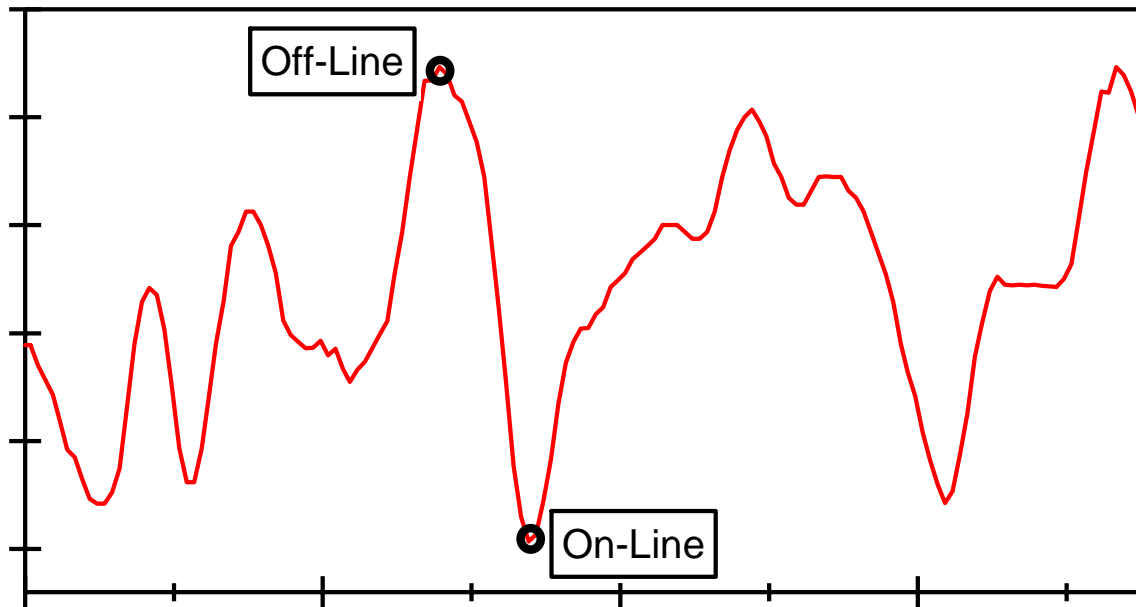


# LIF Detection of NO<sub>2</sub>

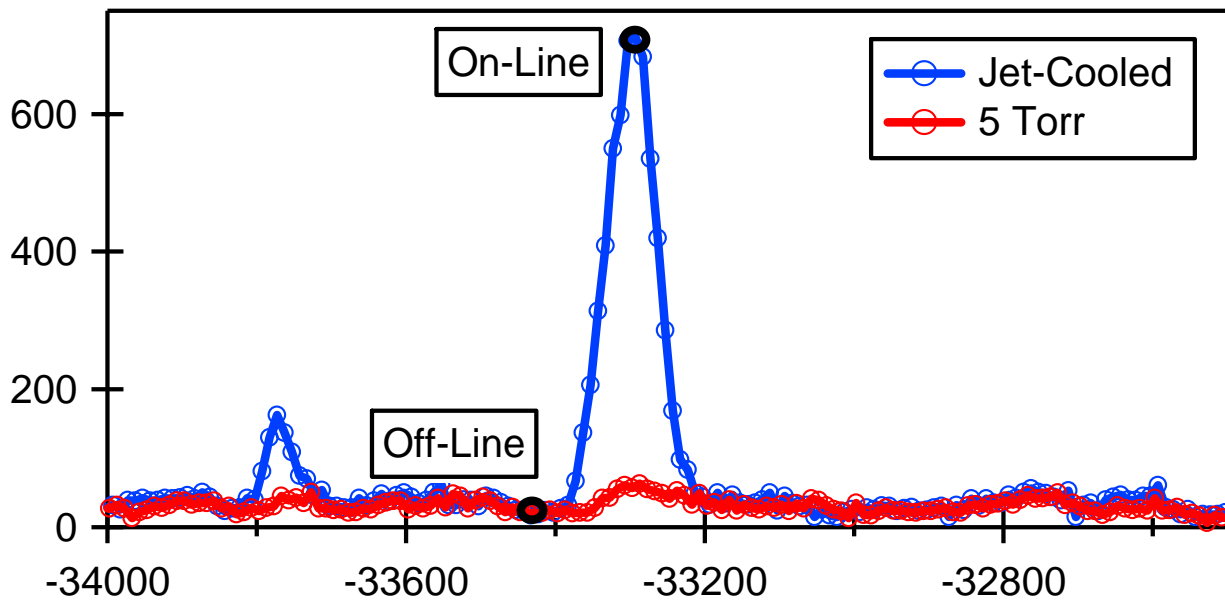


Thornton et al. Anal. Chem. **72**, 528, 2000  
Cleary et al. Appl. Opt. **41**(33), 6950, 2002

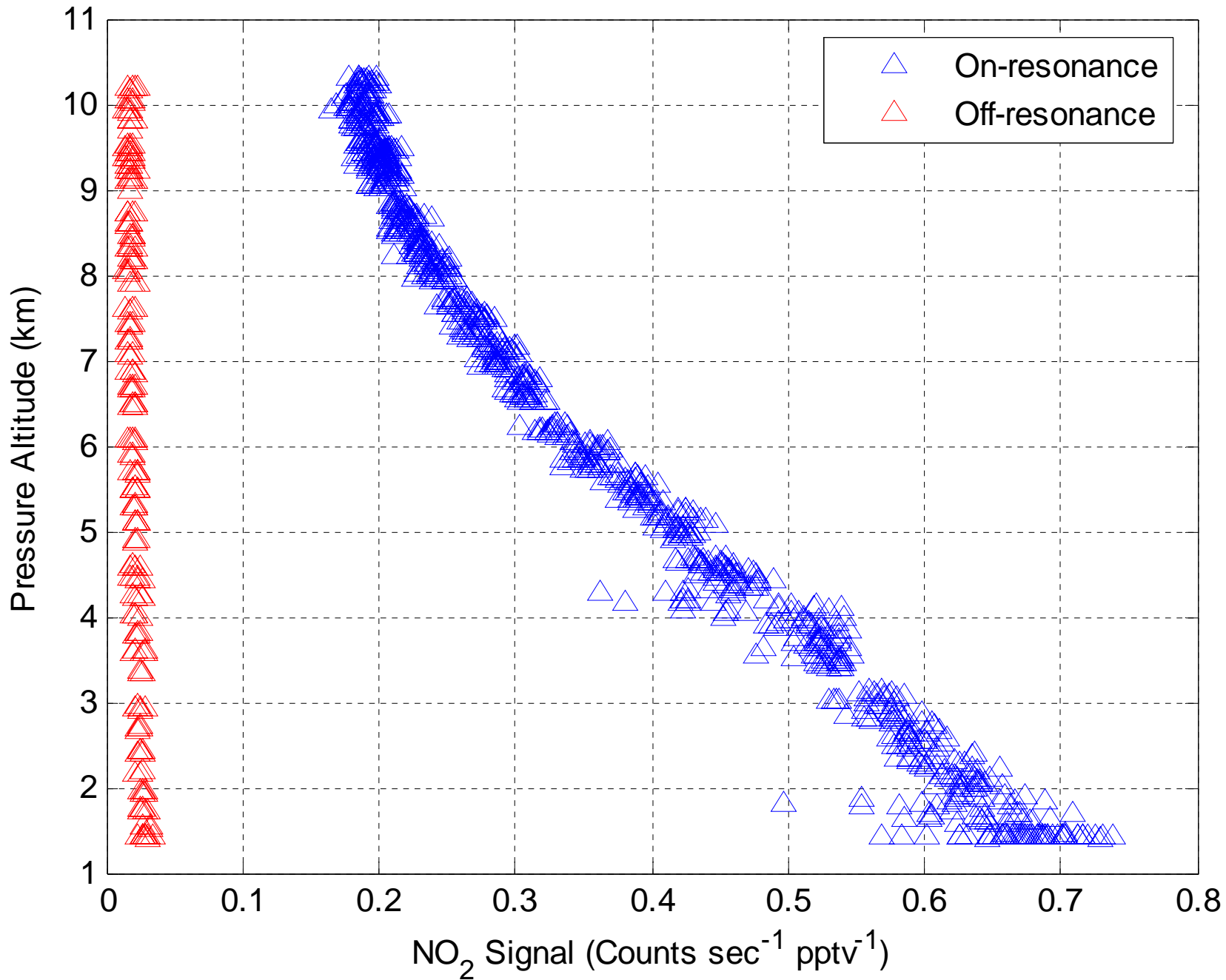
NO<sub>2</sub> Reference Cell Transmission

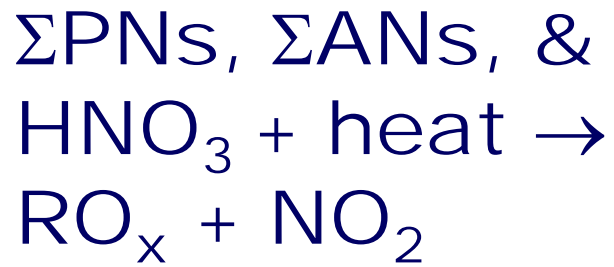


PMT Counts (NO<sub>2</sub> Fluorescence)



Etalon Step Number

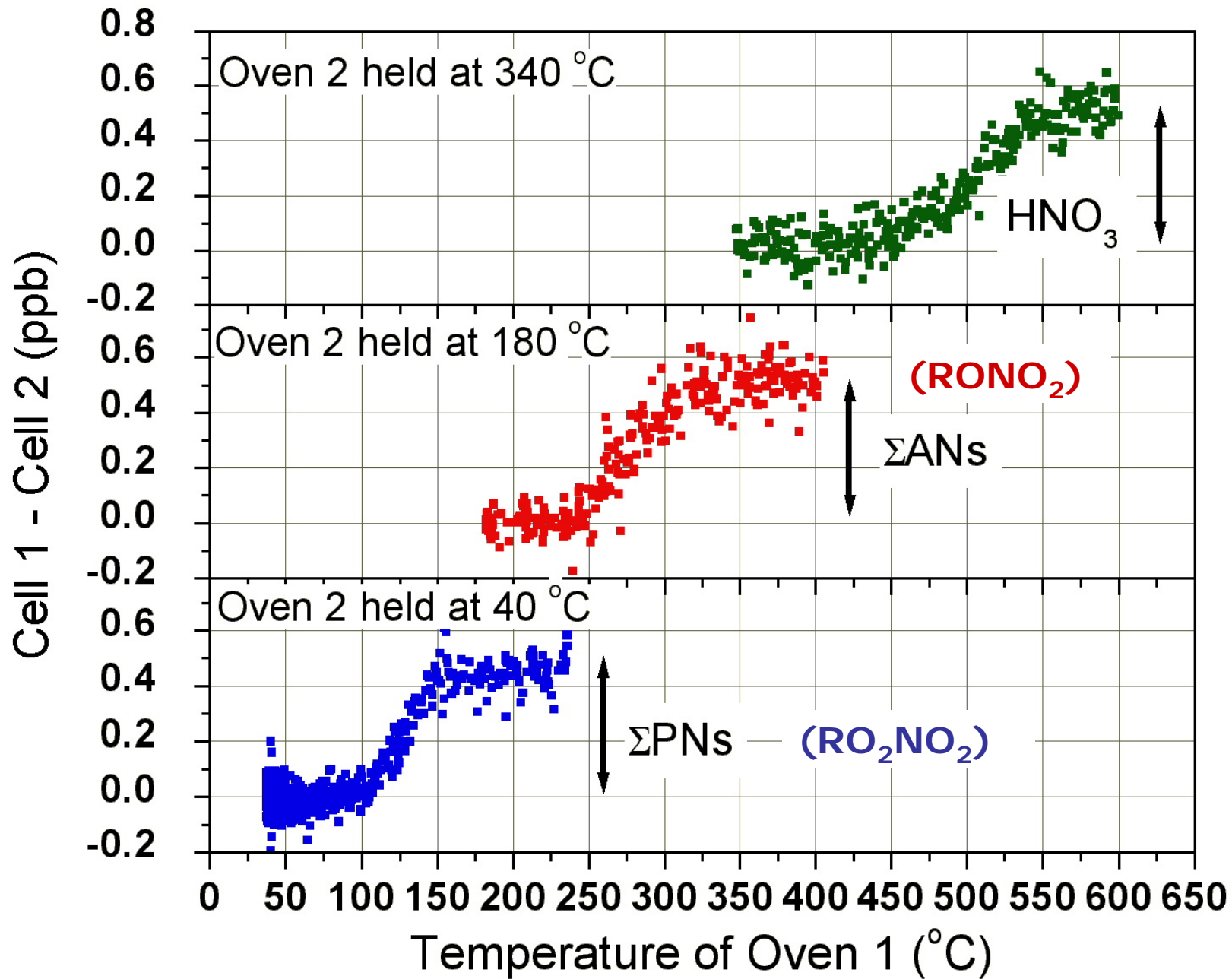


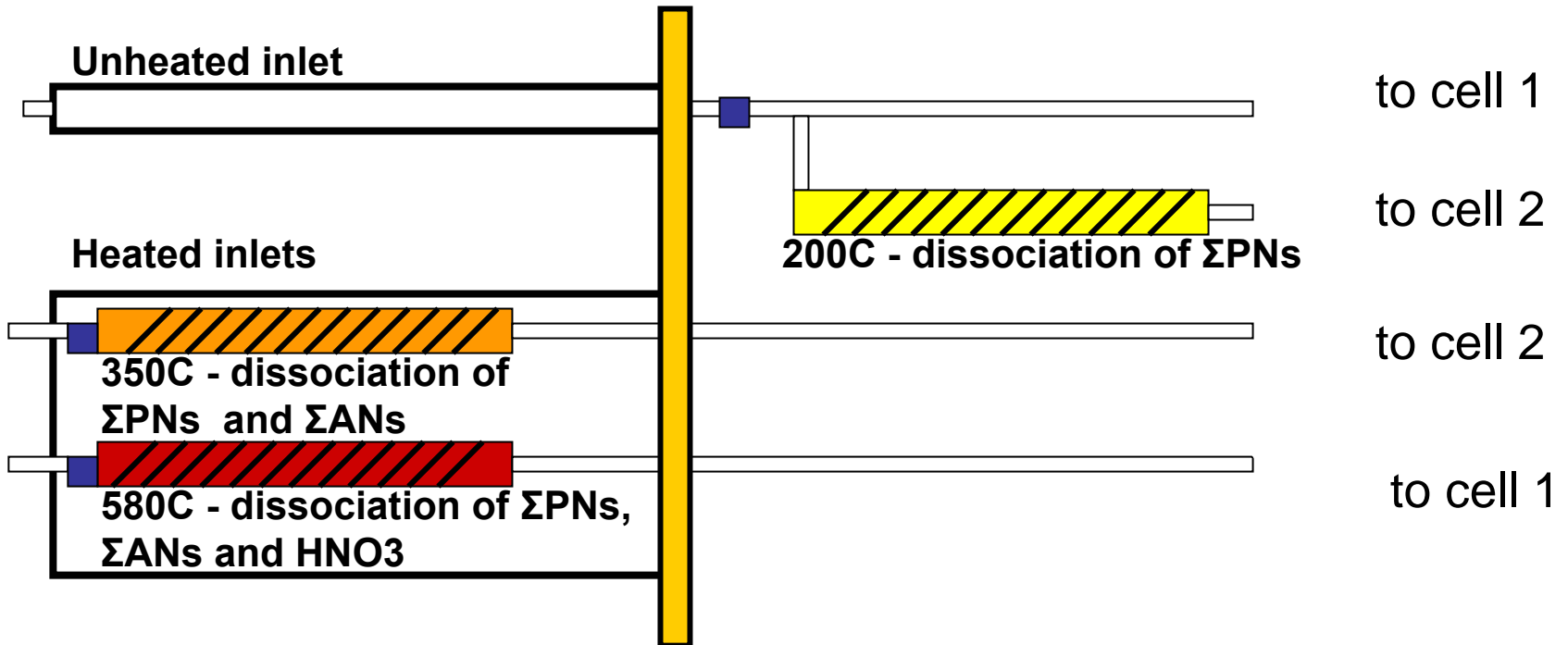
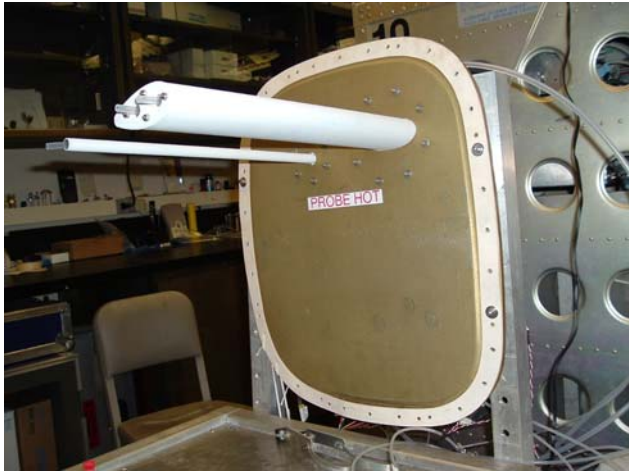


Thermal  
Dissociation-LIF

Doug A. Day, et al,  
JGR., **107(D6)**, '02.

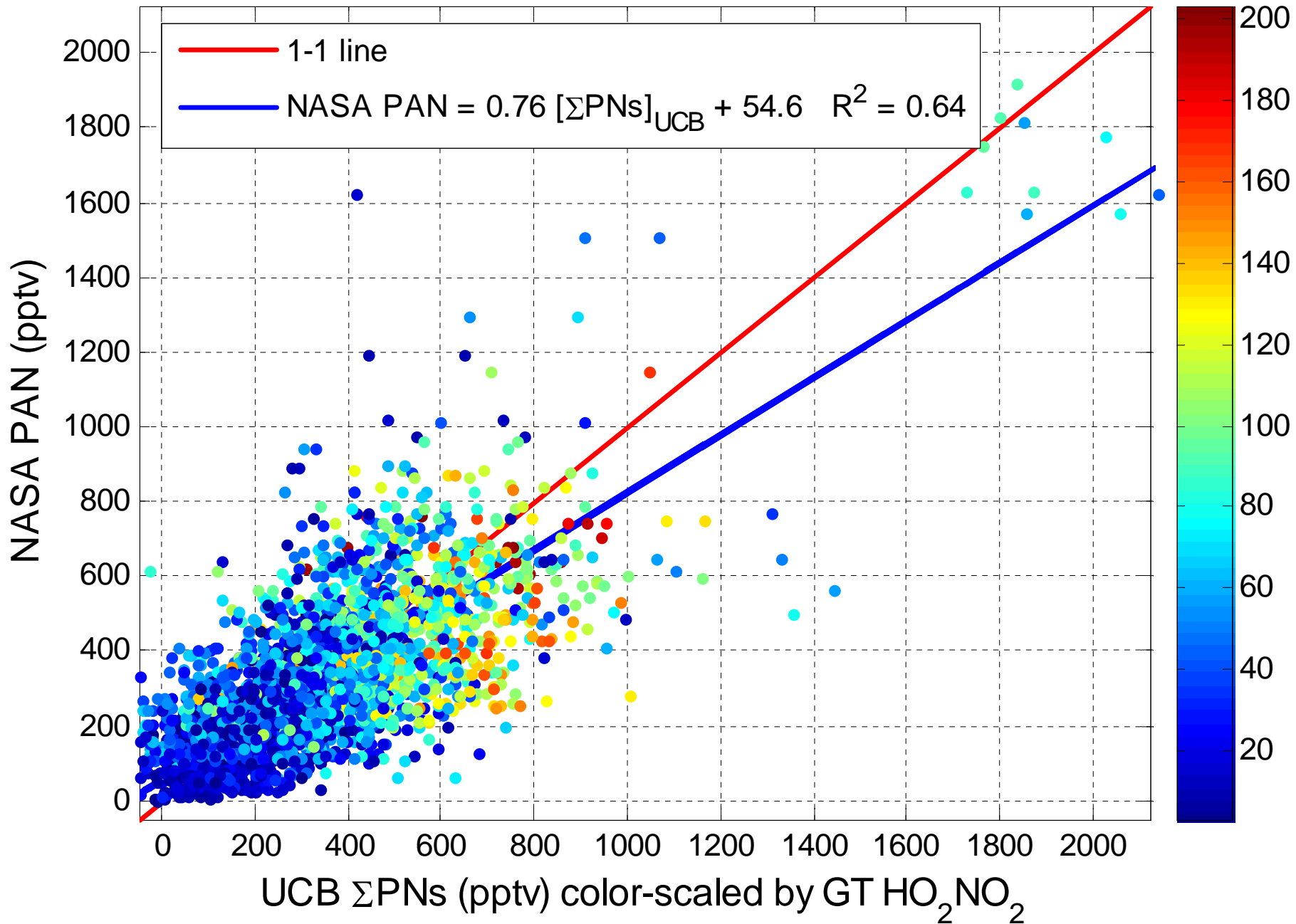


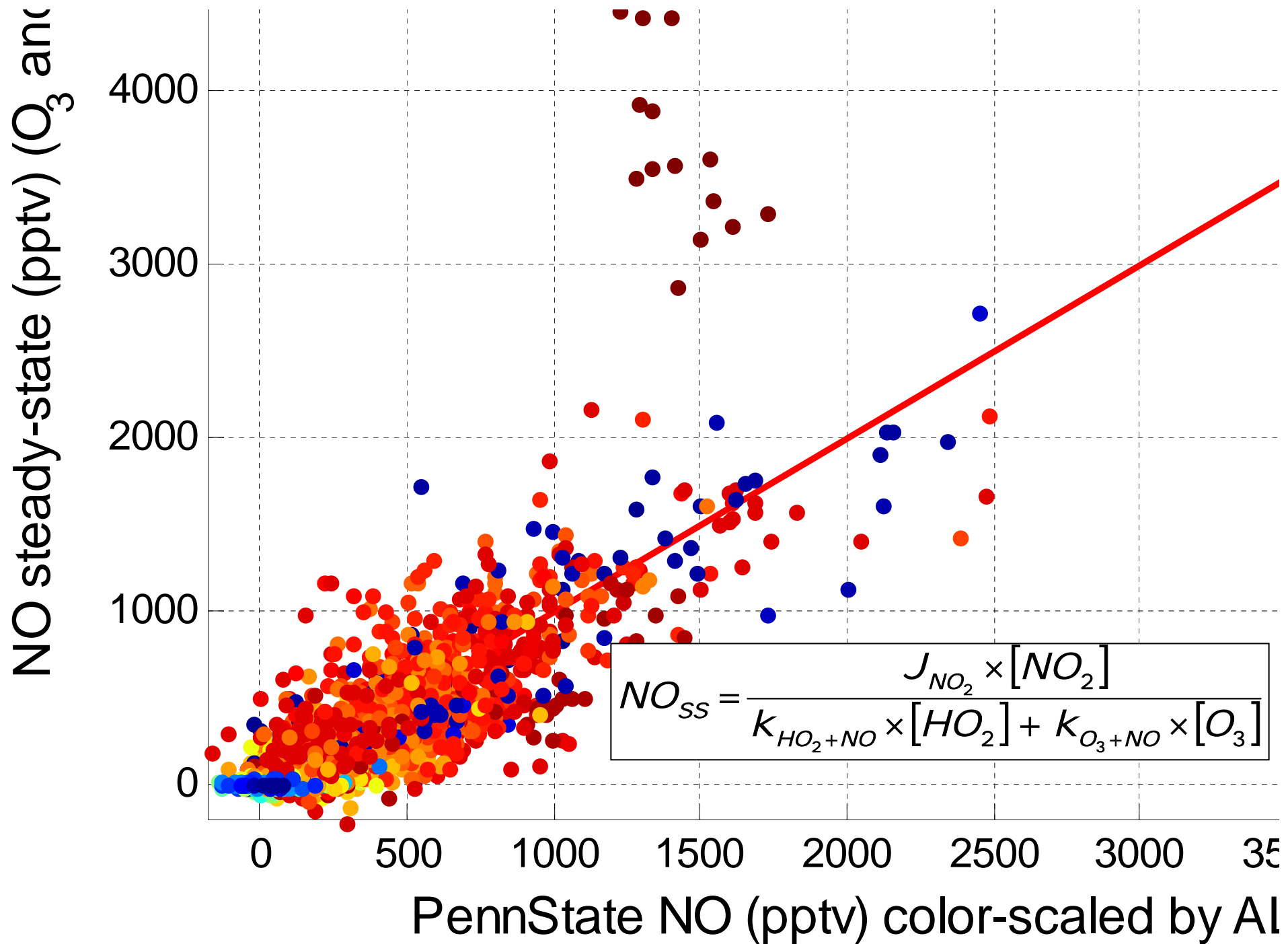






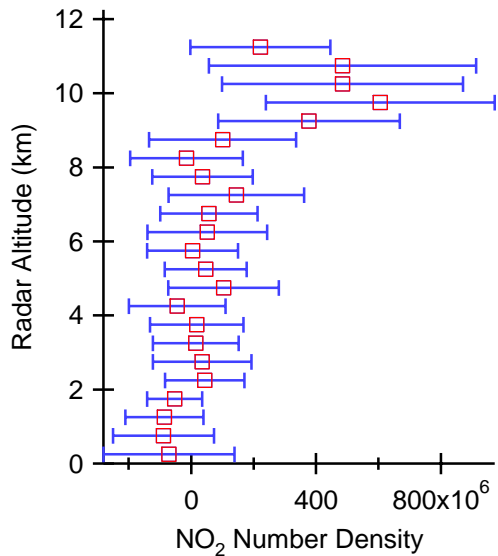
# DC-8 $\Sigma$ PNs PAN Comparison



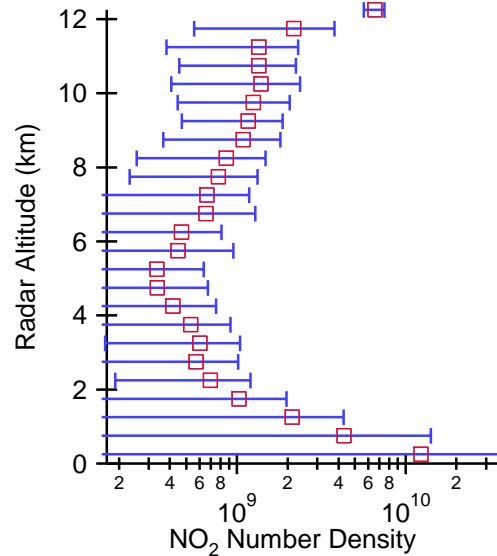


Convection/Age of Air

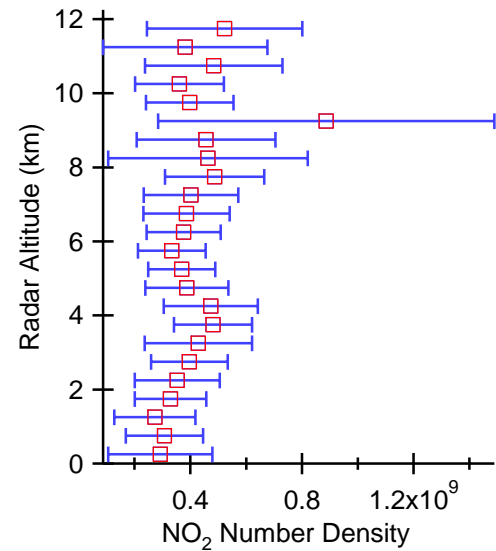
PACIFIC Profiles (500m bins 5 profiles)



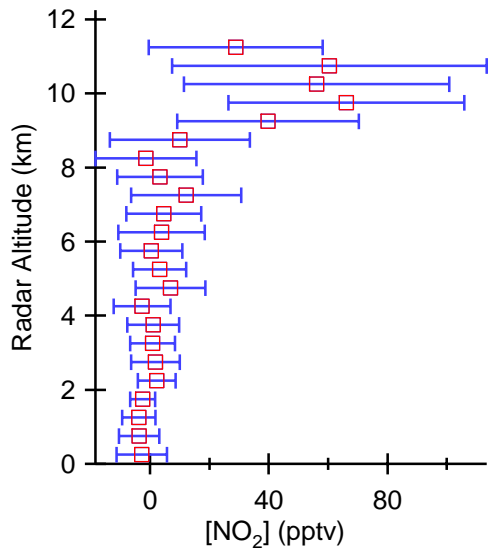
CONTINENTAL Profiles (500m bins 52 profiles)



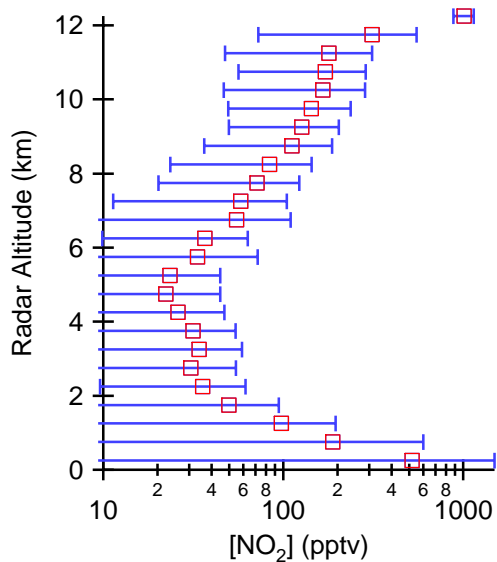
ATLANTIC Profiles (500m bins 6 profiles)



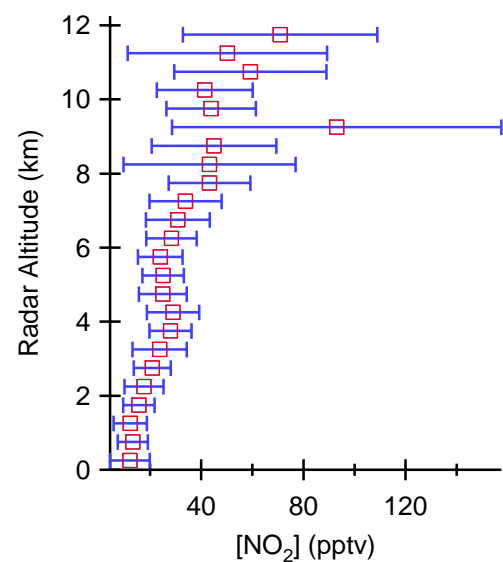
PACIFIC Profiles (500m bins 5 profiles)



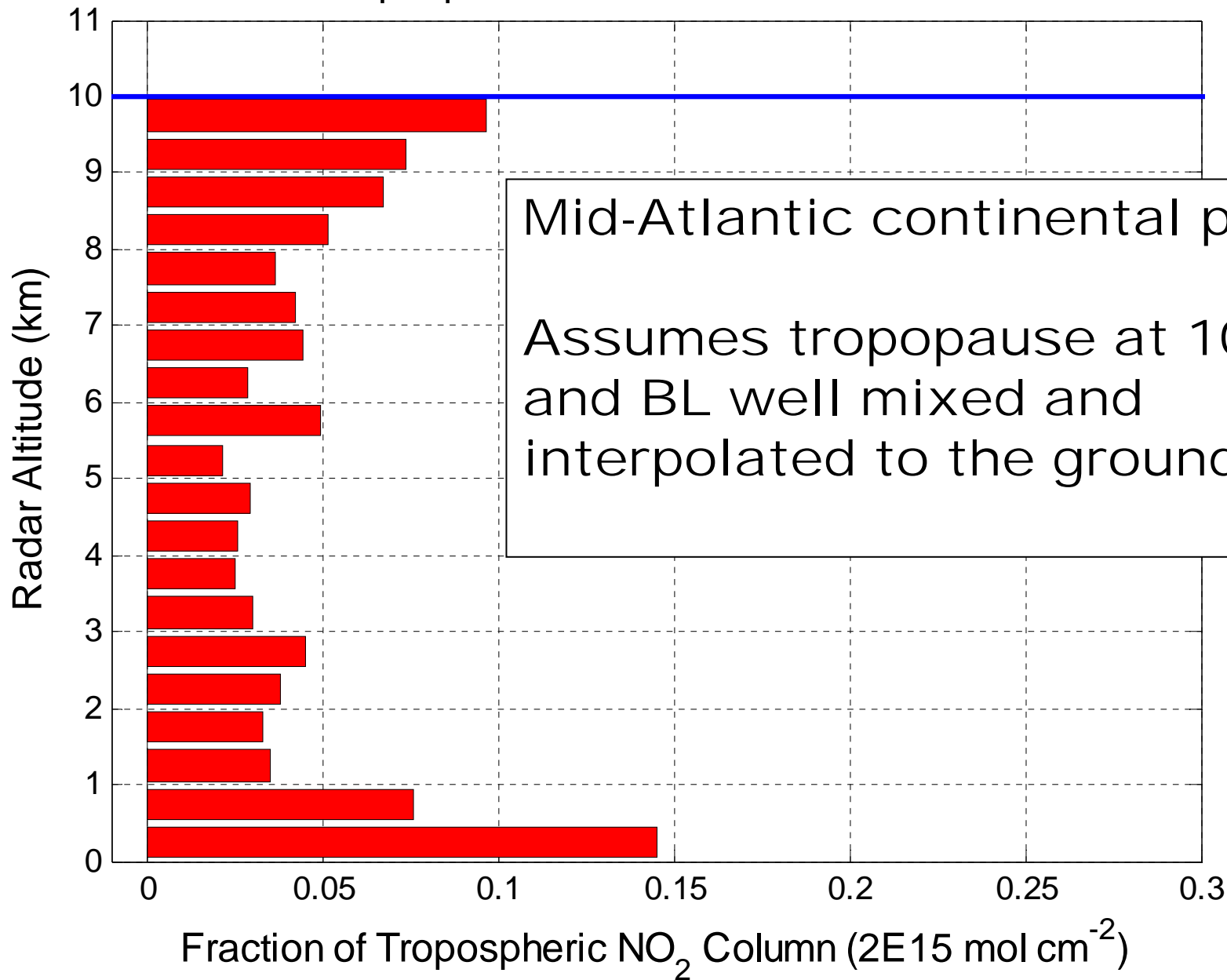
CONTINENTAL Profiles (500m bins 52 profiles)



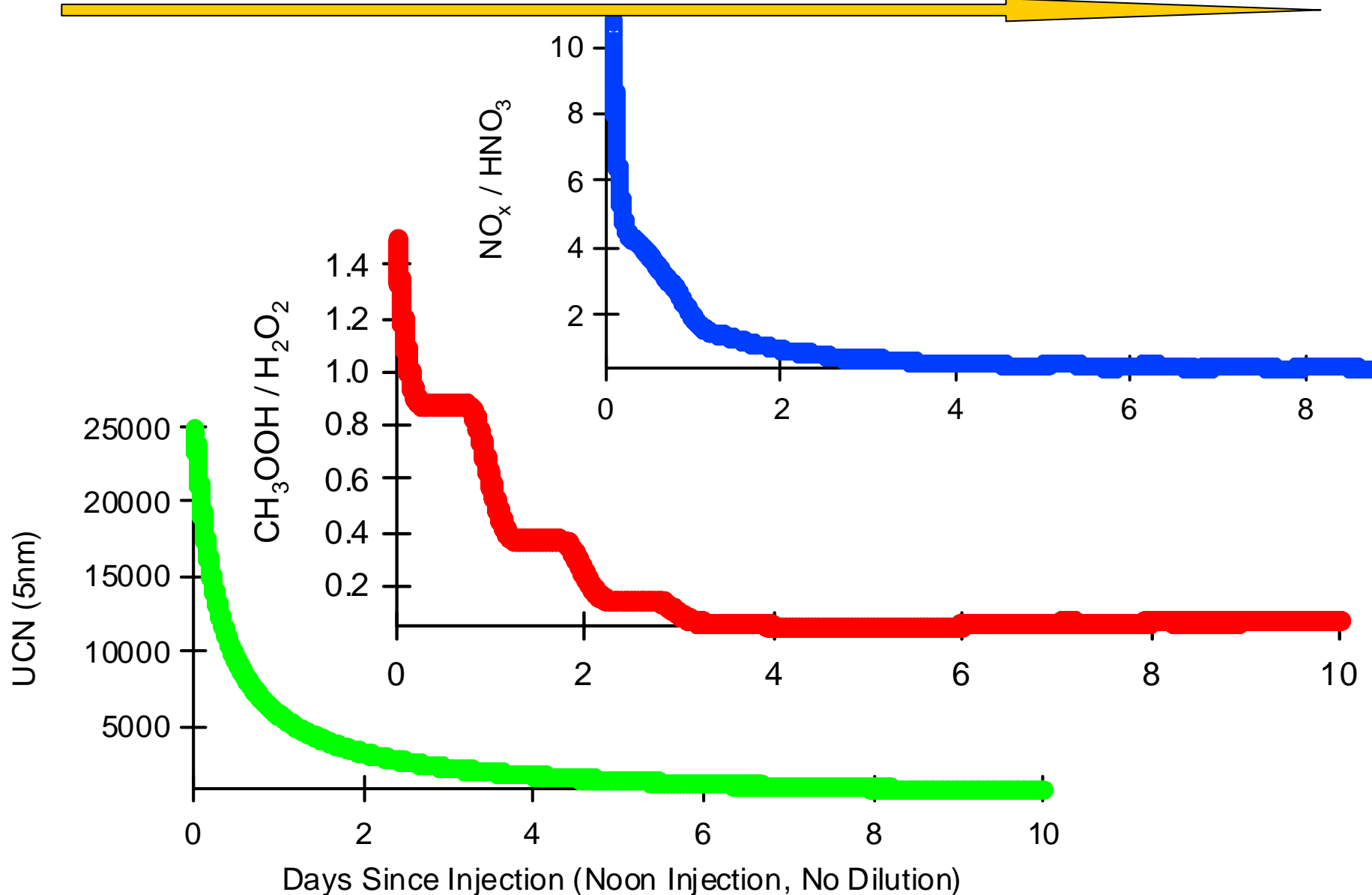
ATLANTIC Profiles (500m bins 6 profiles)

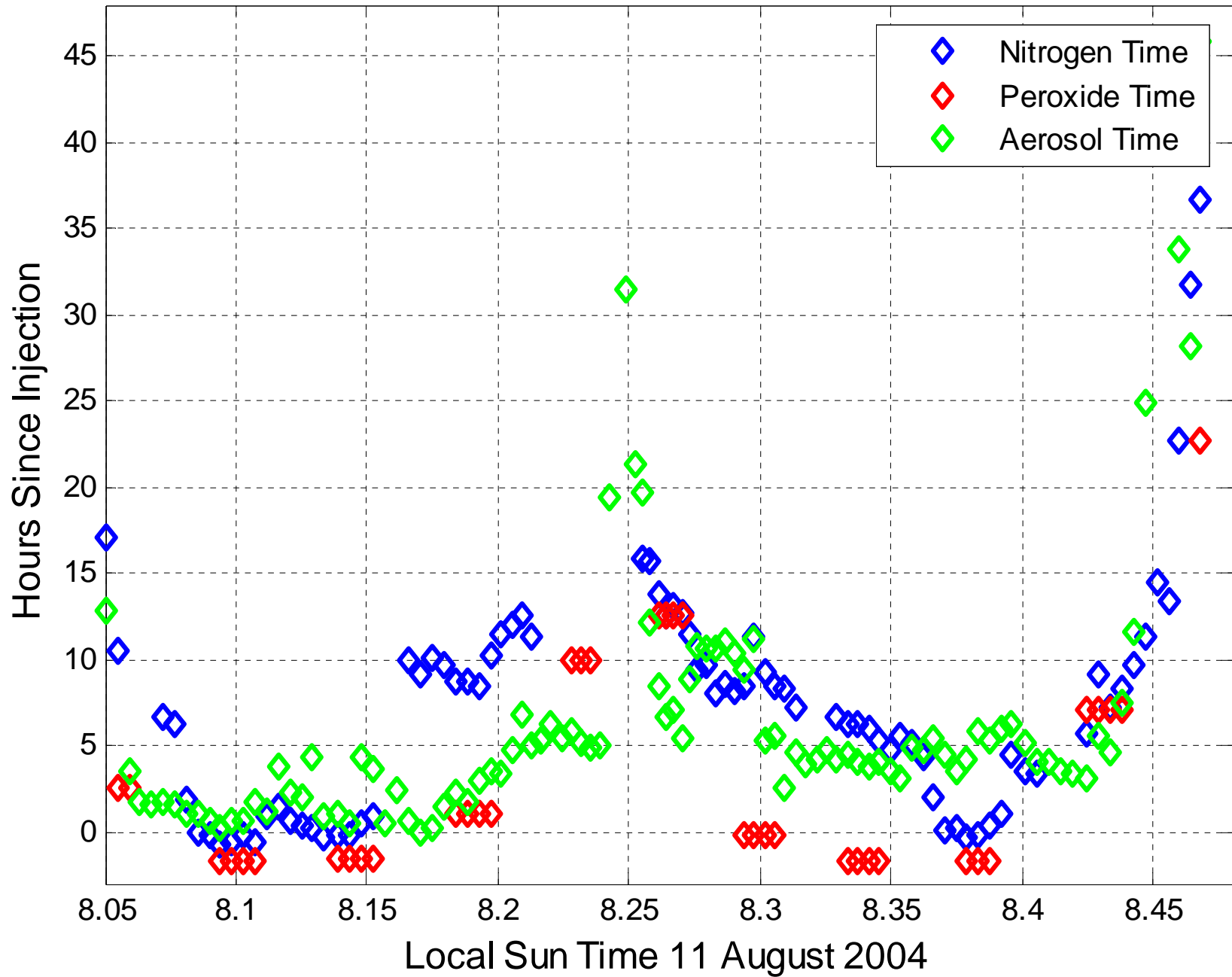


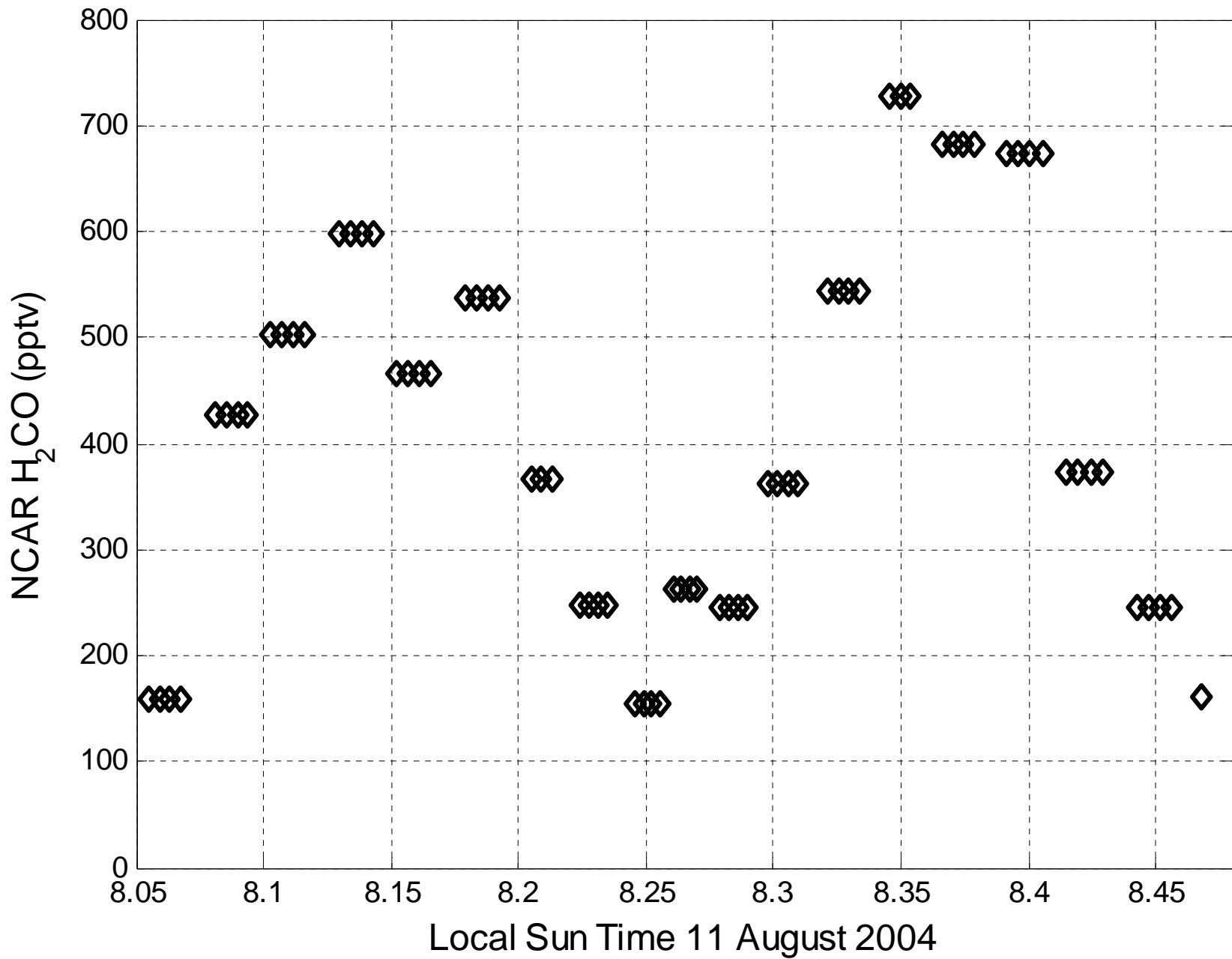
Fraction of Total Tropospheric Column at LAT = 33.66 LONG = 276.83



# 0-D time dependent model: Noon injection, no dilution, 10km

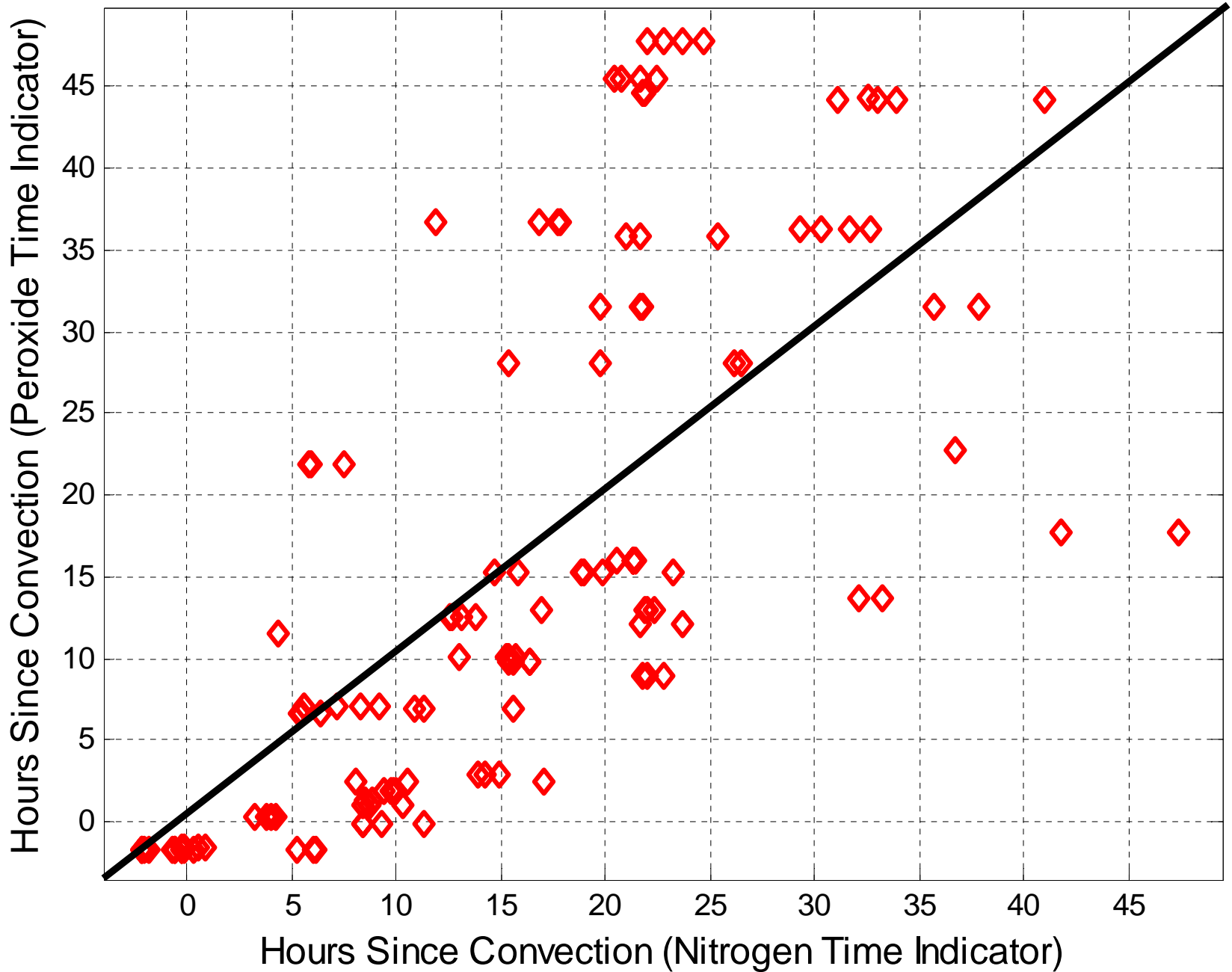






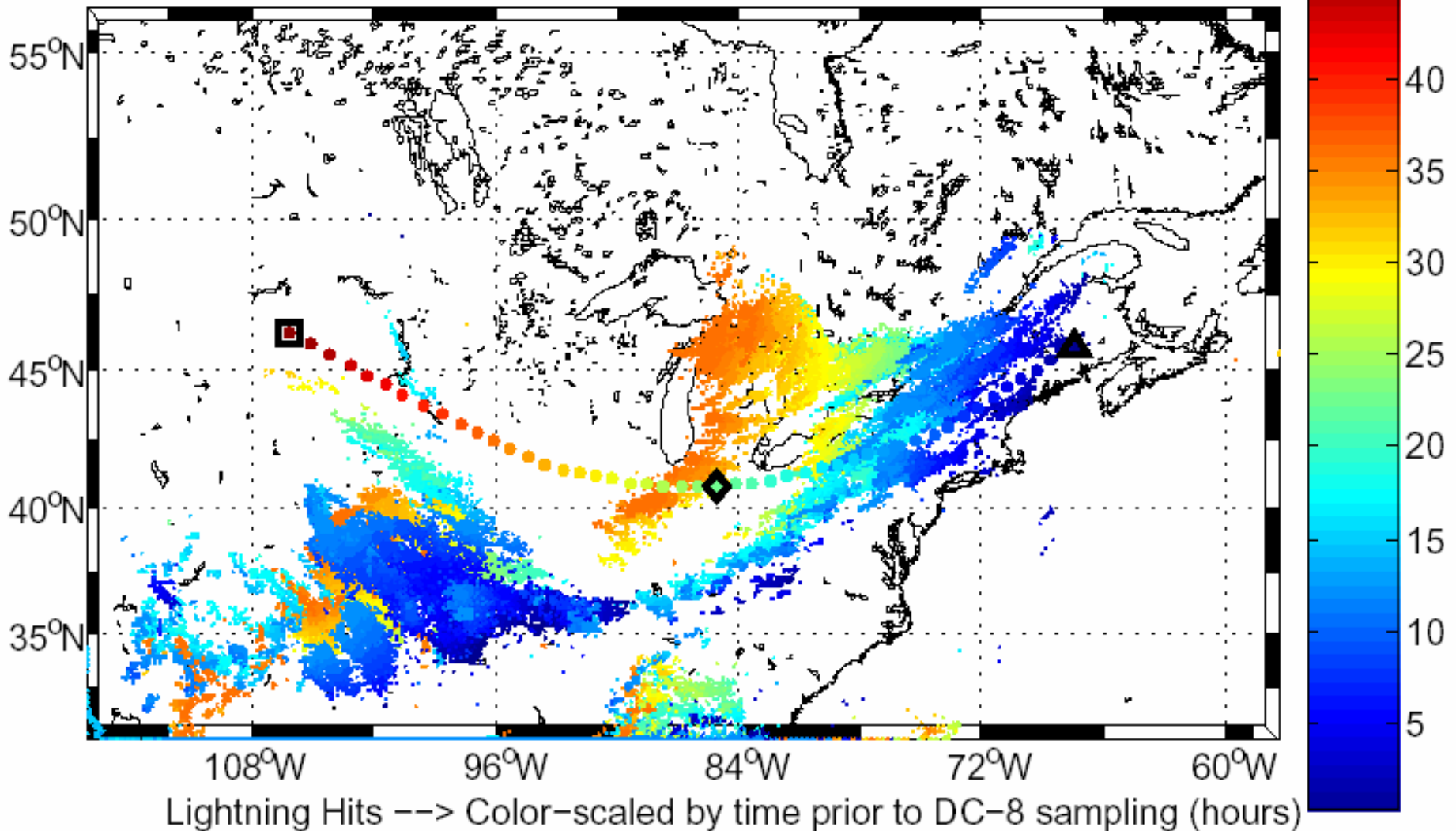


11 August 2004 ALT>8km

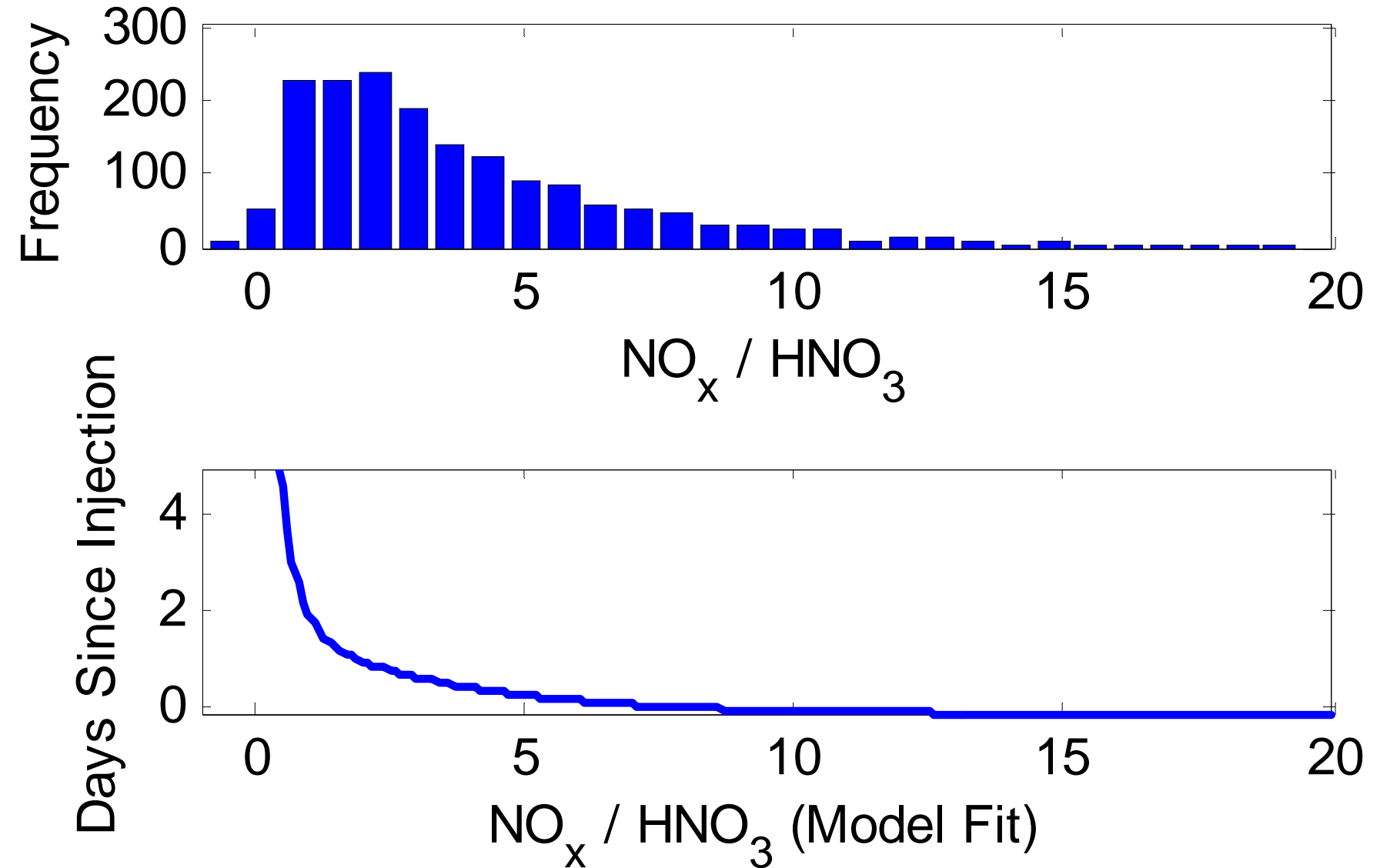


# Lightning hits 10/11 August 2004 2day back trajectory

NLDN Lightning 2 days prior to DC-8 Flight on 11 August 2004

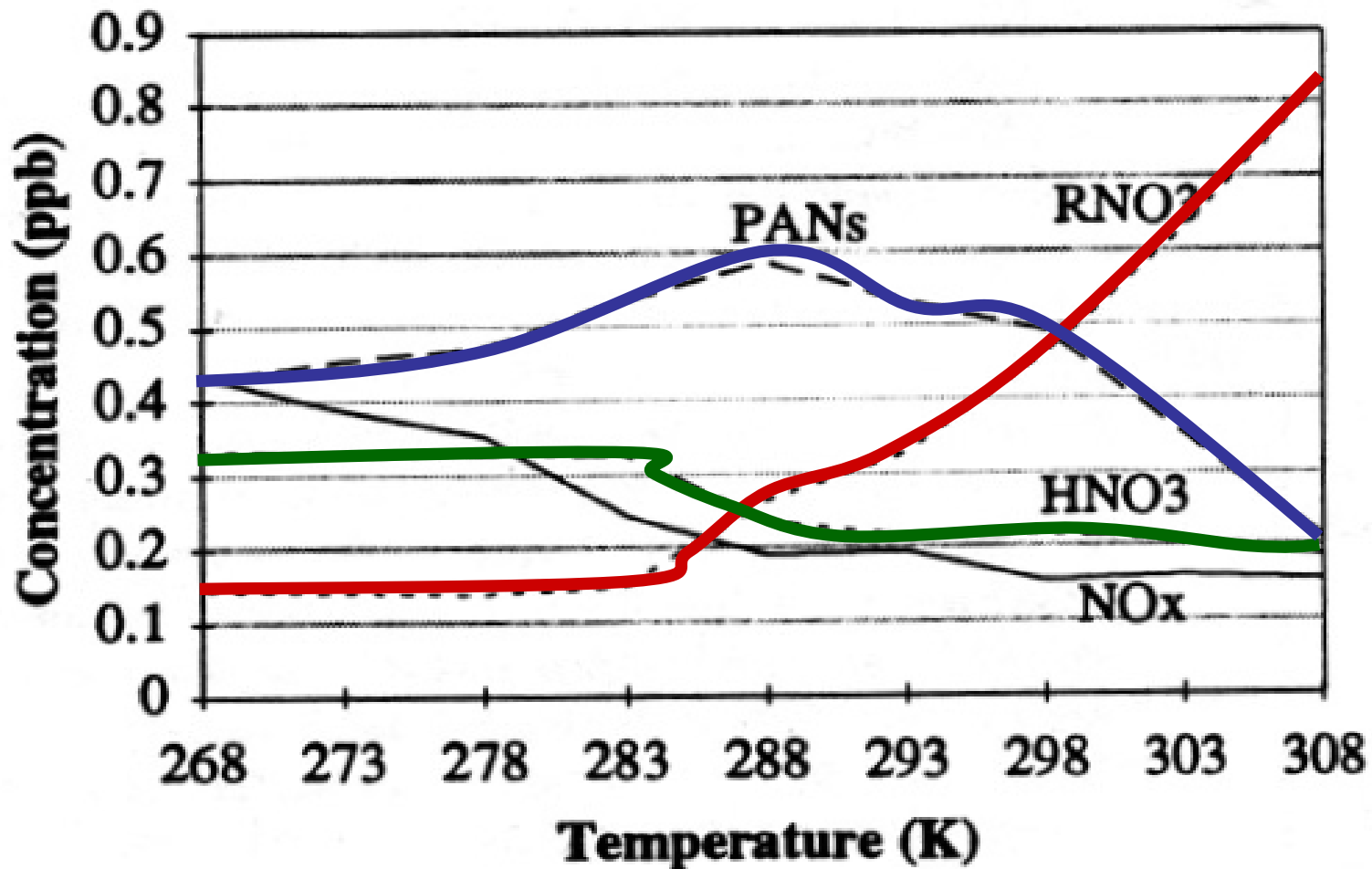


# 1-min merge data; Model fit to exponential



# Isoprene Nitrates

# Sillman and Sampson JGR 1995



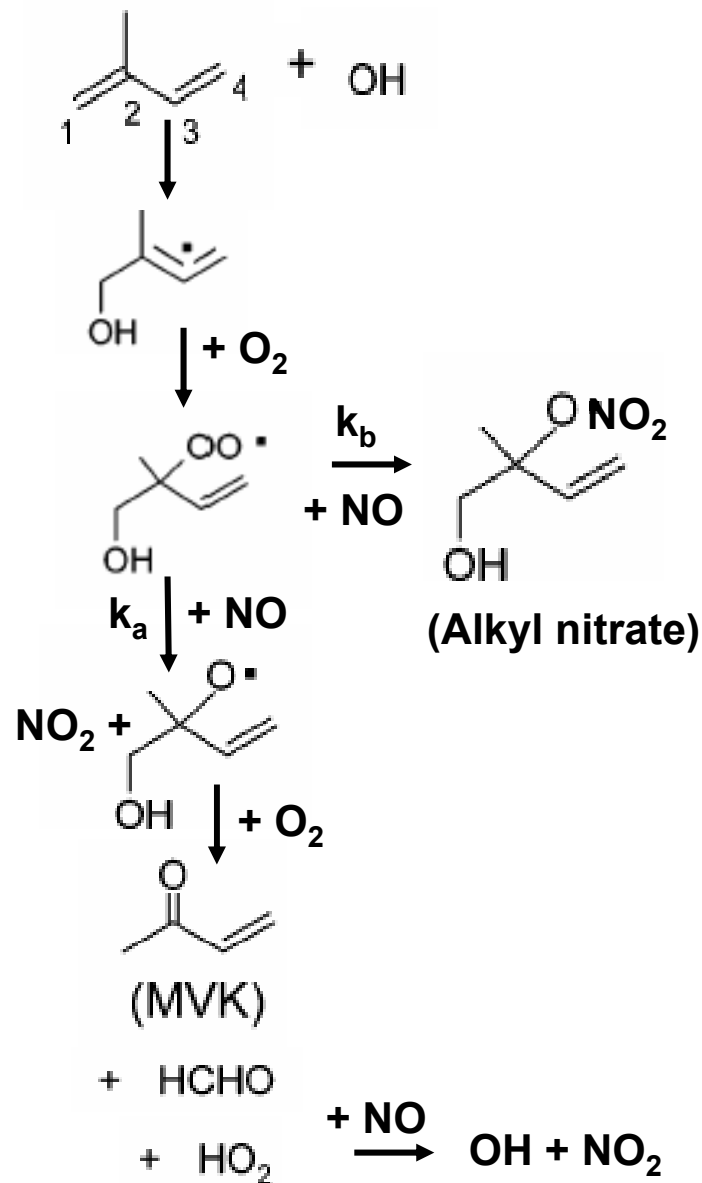
Hydrocarbons (RO<sub>2</sub>) →

← OH

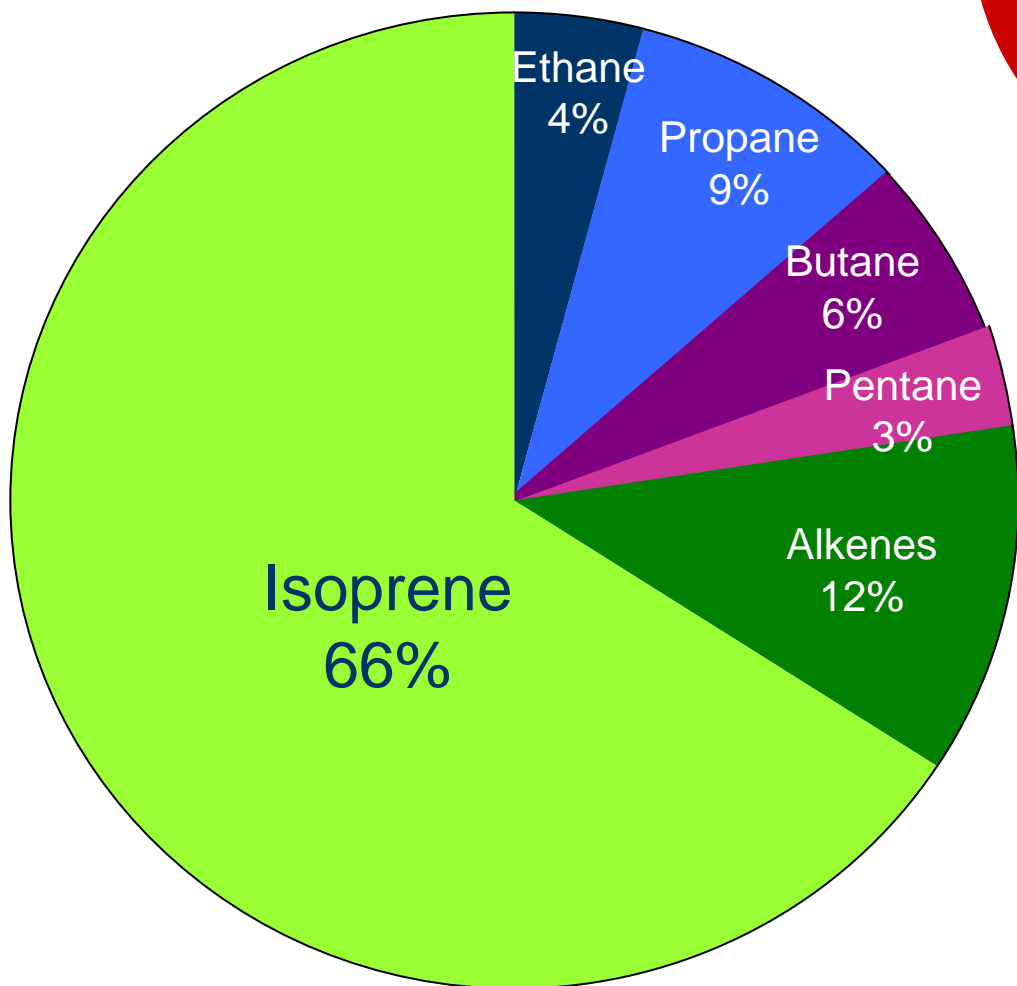
# Isoprene Oxidation

H<sub>2</sub>CO yield is 0.6

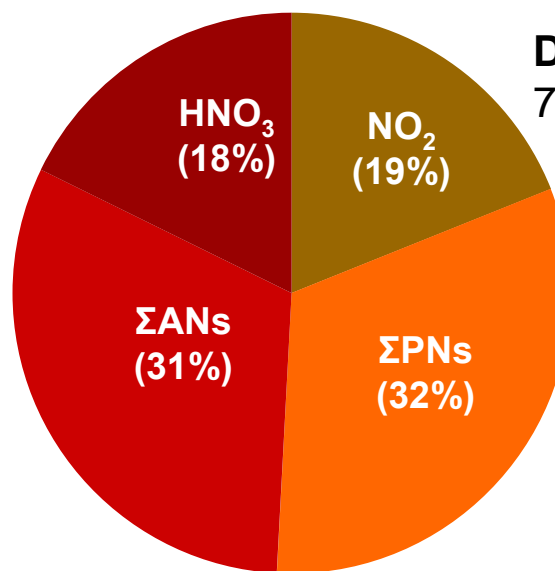
O<sub>3</sub> yield is  $2(1-\alpha)$  where  $\alpha$  is  $k_b/(k_a+k_b)$



# Observed contributions to $\text{RO}_2$ production



Hydrocarbon data provided by Blake et al, UC Irvine

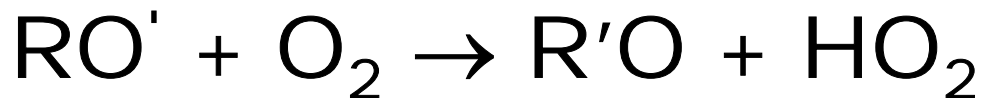


Distribution of  $\text{NO}_y$   
7/20/2004

\* $\text{HNO}_3$  data courtesy of  
Wennberg et al,  
CalTech

# $\Sigma$ ANs and $O_3$

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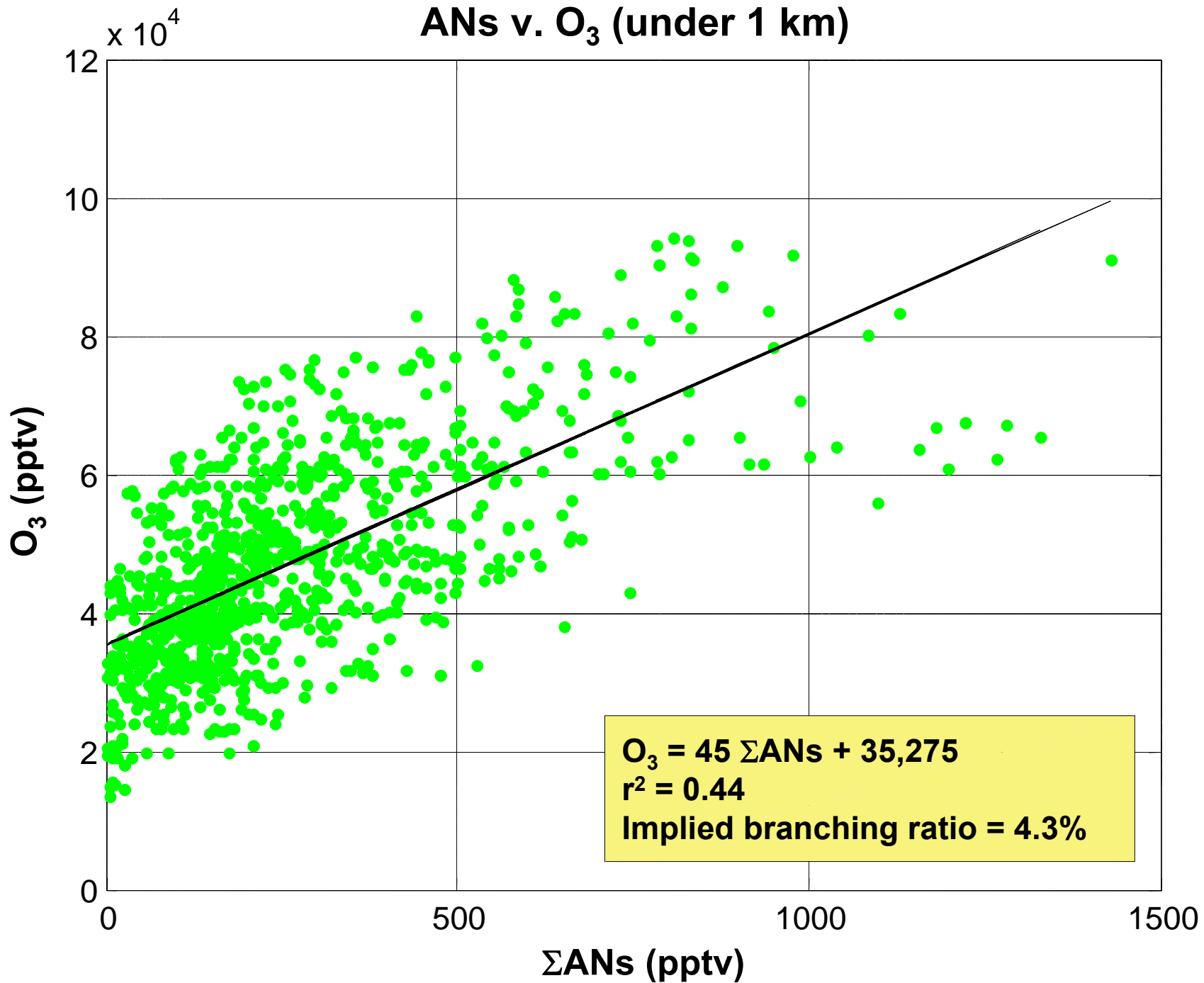


$2 \times 97 O_3 : 3 \Sigma ANs$

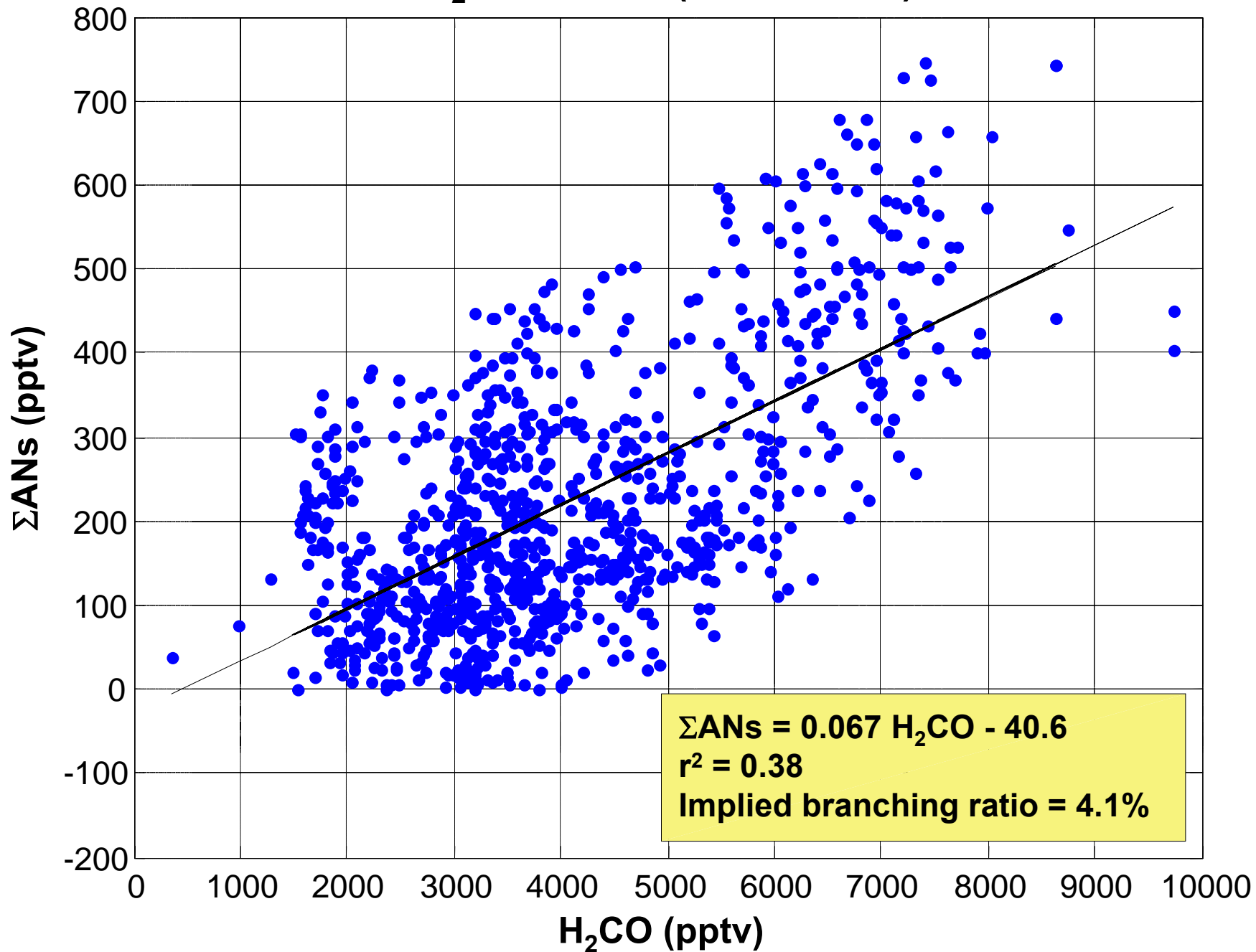
$65 O_3 : \Sigma AN$



# ANs v. O<sub>3</sub> (under 1 km)



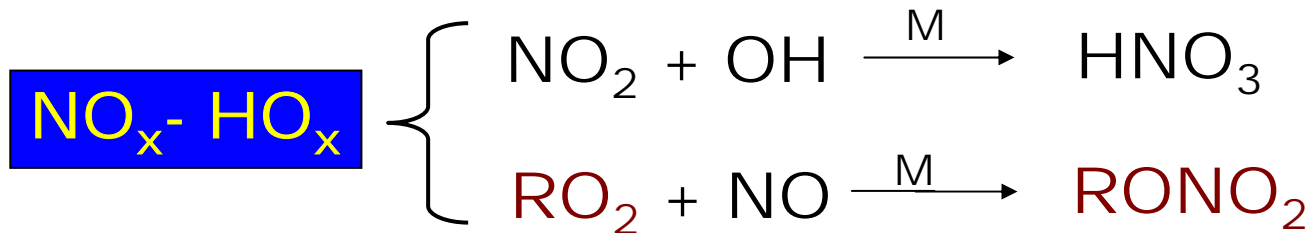
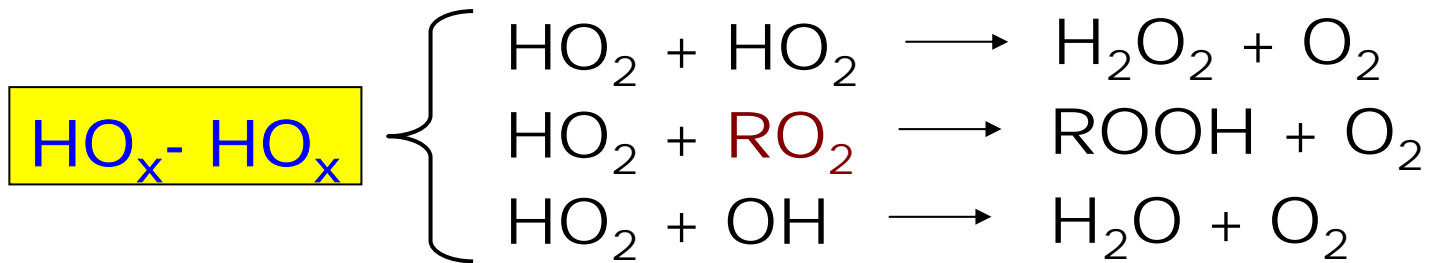
# H<sub>2</sub>CO v. ANs (under 1 km)



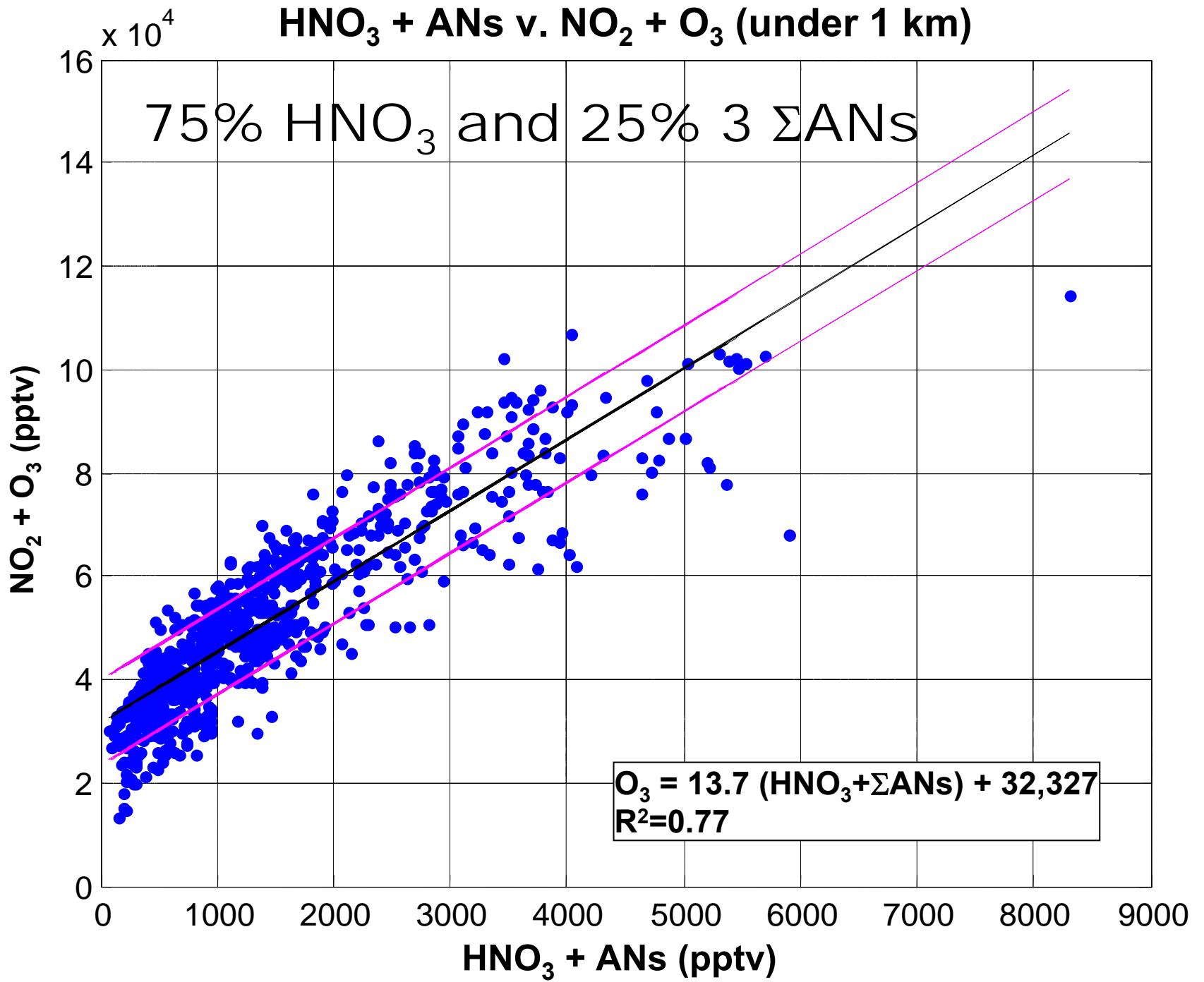
# HO<sub>x</sub> Chain Termination

# Chain Termination

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# HNO<sub>3</sub> + ANs v. NO<sub>2</sub> + O<sub>3</sub> (under 1 km)



# Plans & Questions



Describe distribution of age of air between 8 and 12 km. Understand how age affects other photochemical processes. What other short lived species (e.g.  $\text{H}_2\text{CO}$ ) are lofted by convection)? How well can we connect observations of atmospheric composition in the PBL to the observations at 8-12km? Will that provide a way to measure lightning  $\text{NO}_x$ ?



Assess whether data does cleanly constrain isoprene nitrate yield. Characterize  $\Sigma\text{AN}/\text{HNO}_3$  roles in  $\text{HO}_x$  chain termination. Where do the  $\Sigma\text{ANs}$  go?