Nocturnal Vertical Gradients of O_3, NO_2, NO_3, HONO, HCHO, and SO_2 during CalNex 2010

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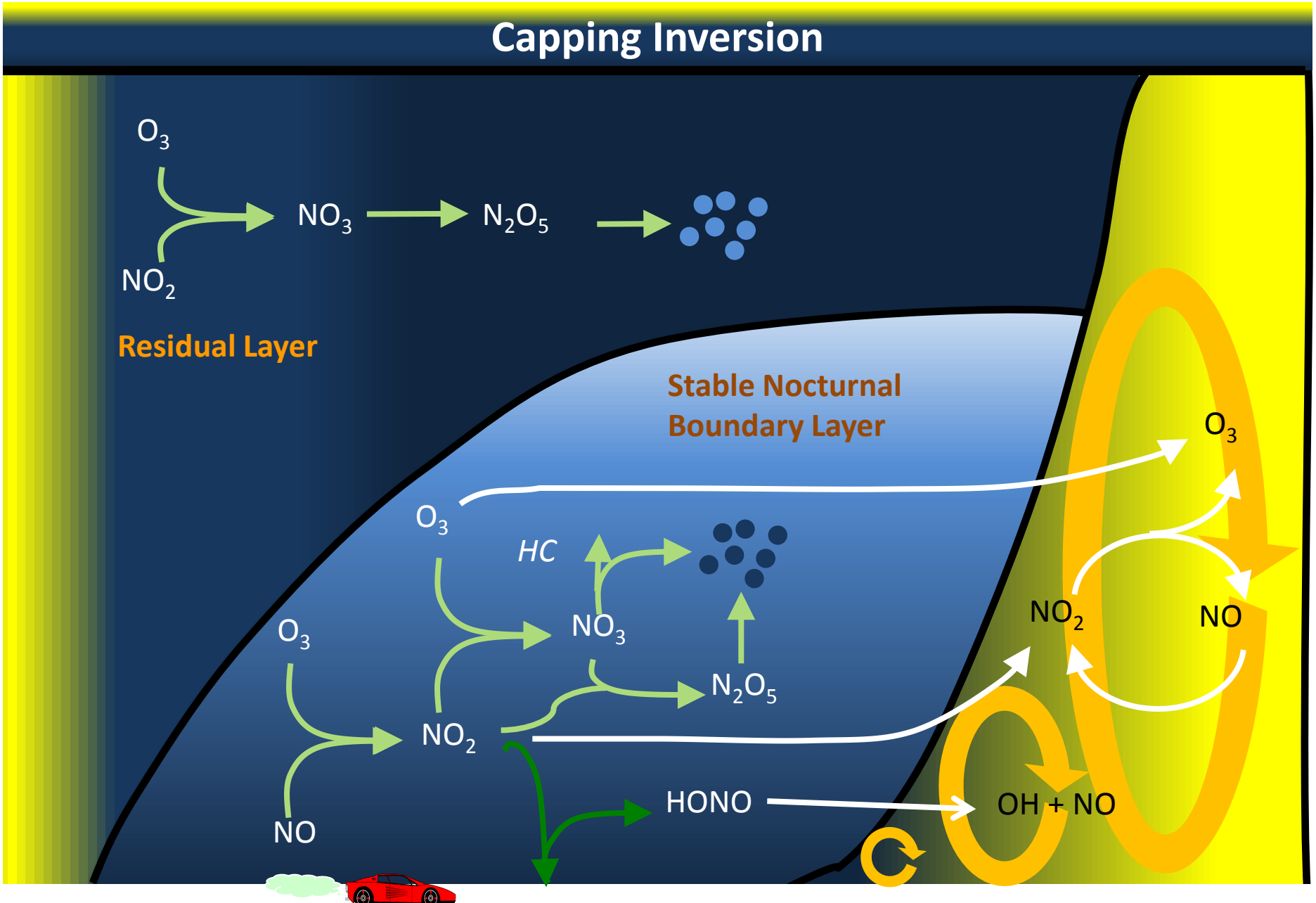
Motivation

- To better understand the **chemical** and **mixing processes** that influence atmospheric composition at night.
- To determine the **removal of NOx** from the nocturnal boundary layer by NO_3 chemistry.
- To study the formation of **HONO** and its impact on OH.
- To examine how nocturnal chemistry affects the initial condition for **ozone formation** during the day.

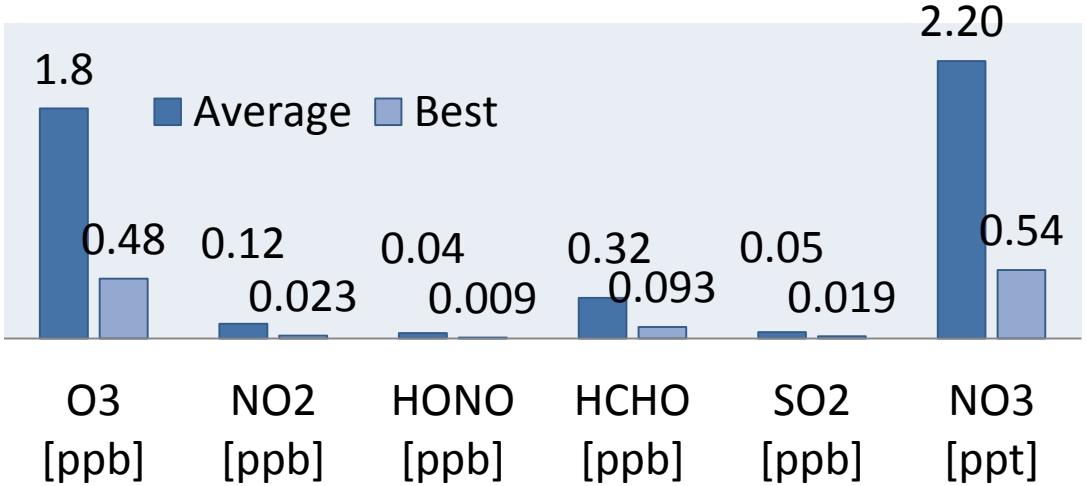
Nocturnal Chemistry in the Polluted BL

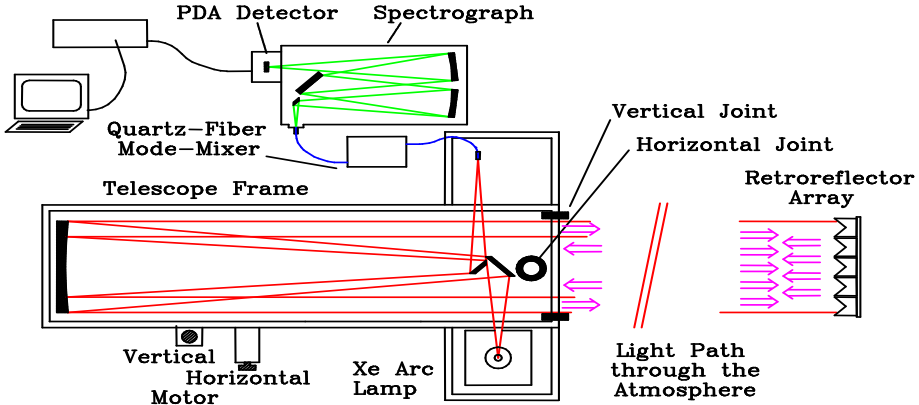


CalNex LP-DOAS Set Up

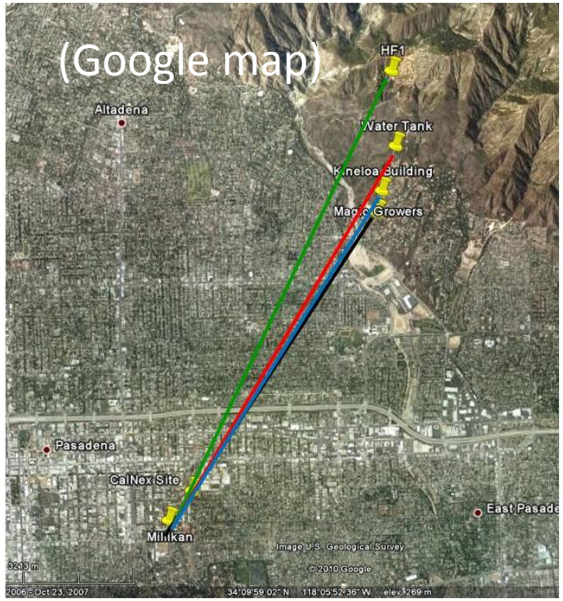
- **May 15 2010 – June 16 2010**
- **Los Angeles Supersite: Caltech**

Detection Limits





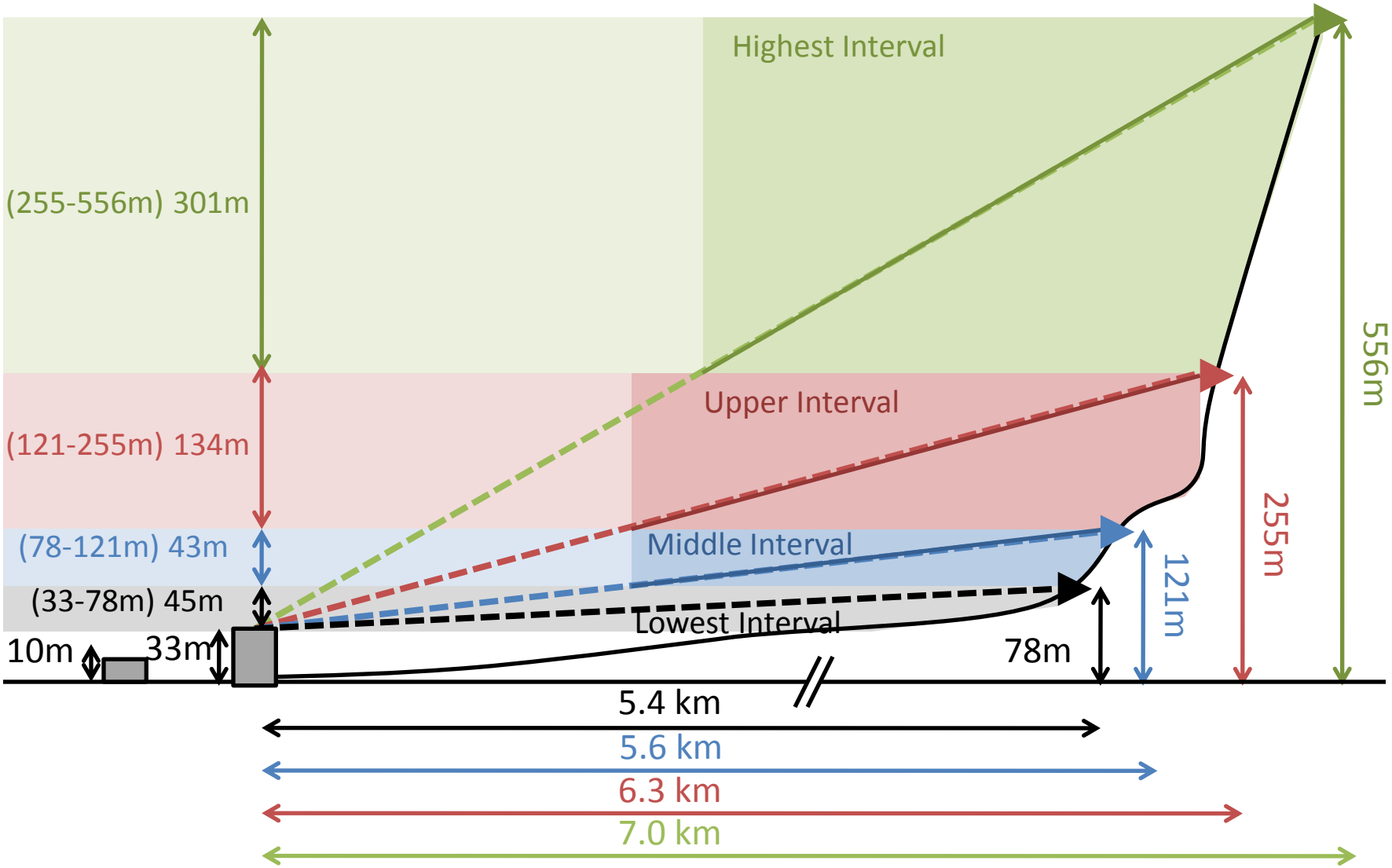
(LP-DOAS)



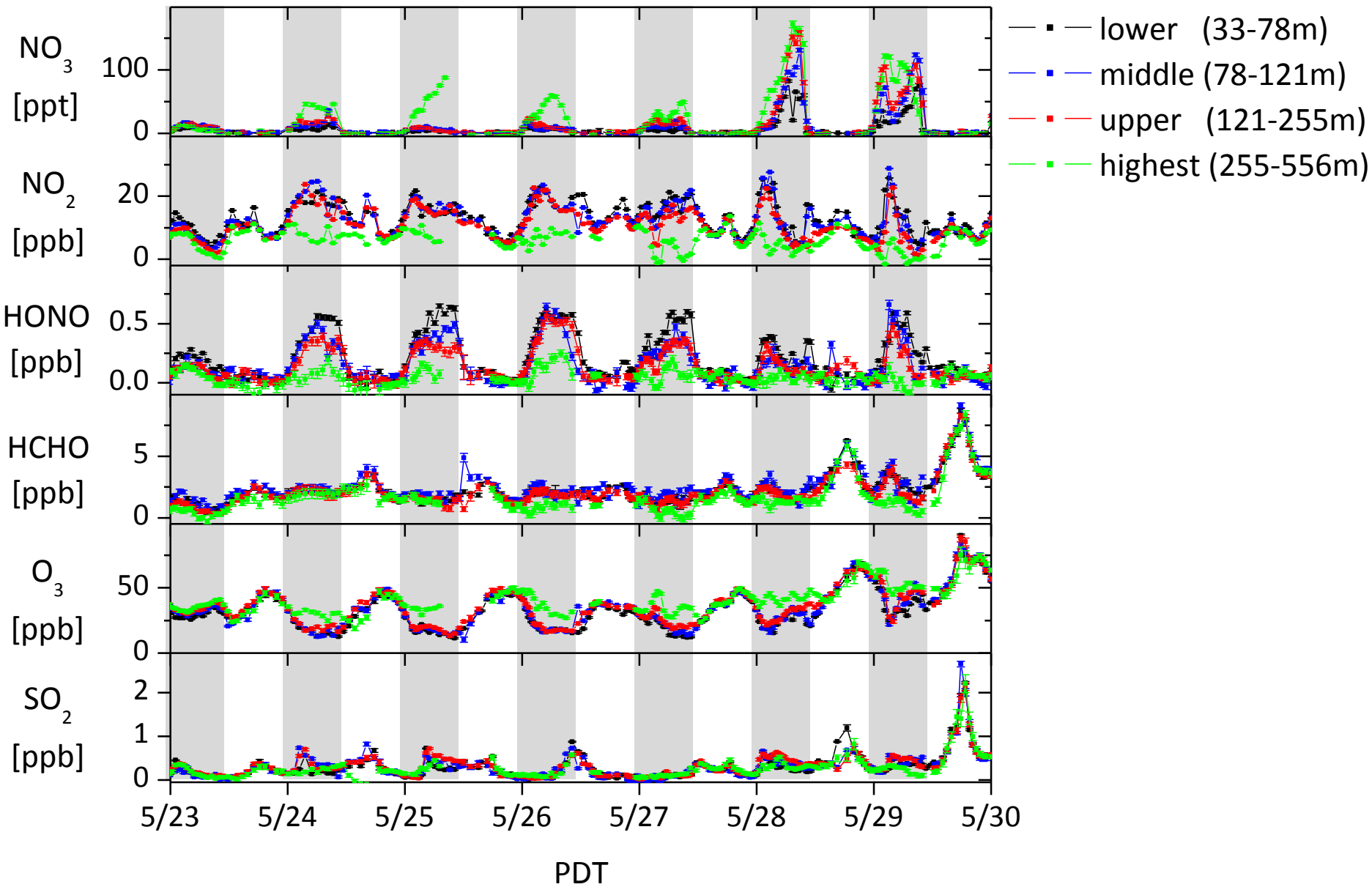
Trace Gas Profile Retrieval

---- *Measured Path Averaged Concentrations*

—— *Retrieved Height Interval Concentrations (subtracting scale from the ground upwards)*

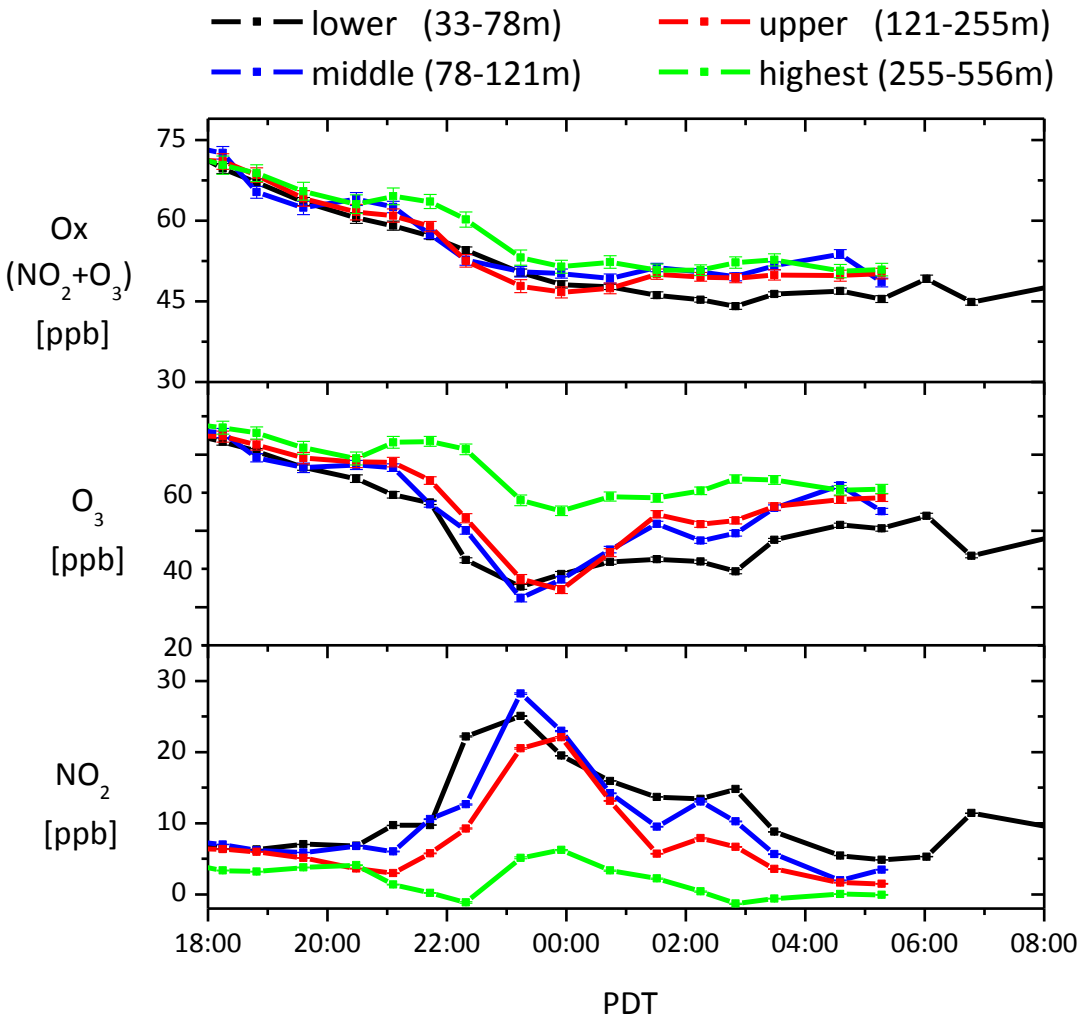


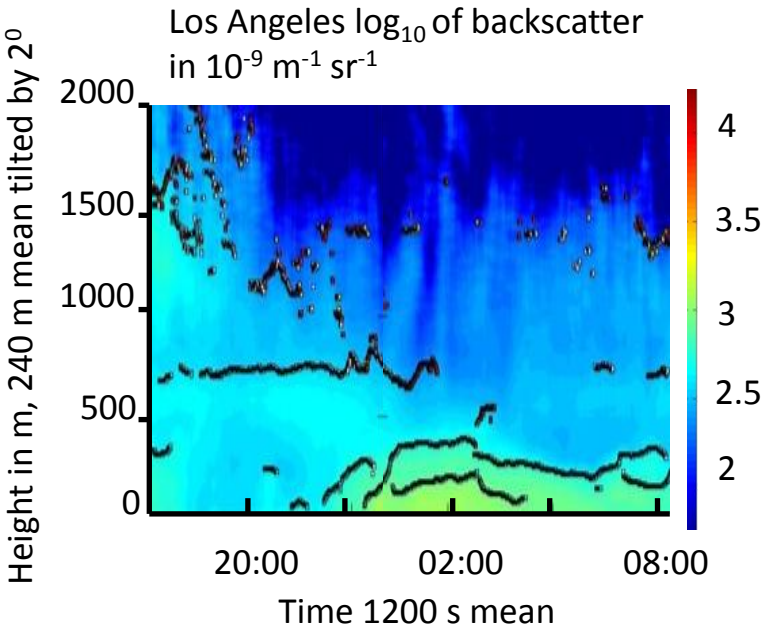
Trace Gases Vertical Profiles



Trace Gases Vertical Profiles

May 29– 30, 2010

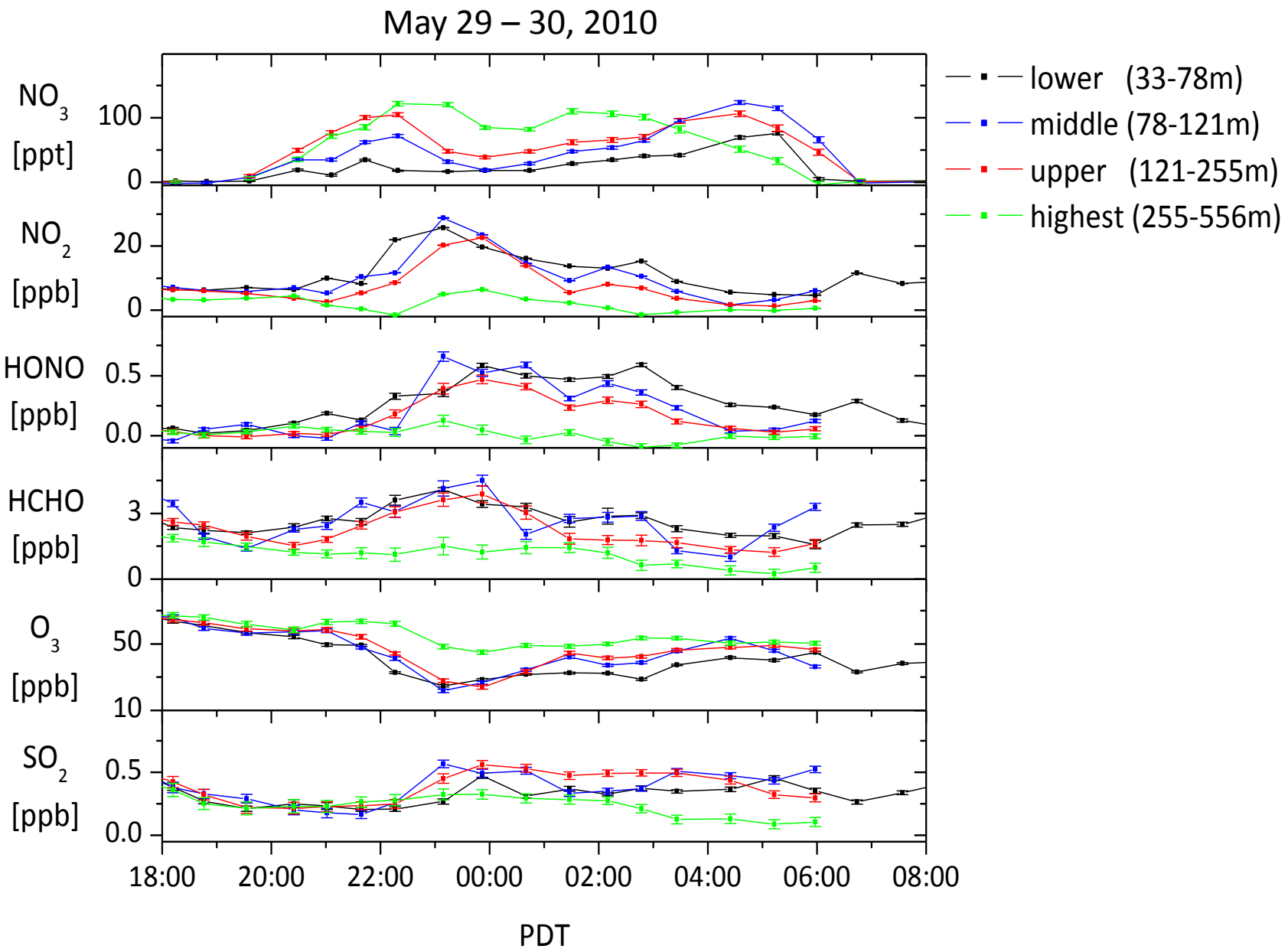




- Stable Nocturnal Boundary Layer.
- Profiles are driven by titration of O_3 by NO.

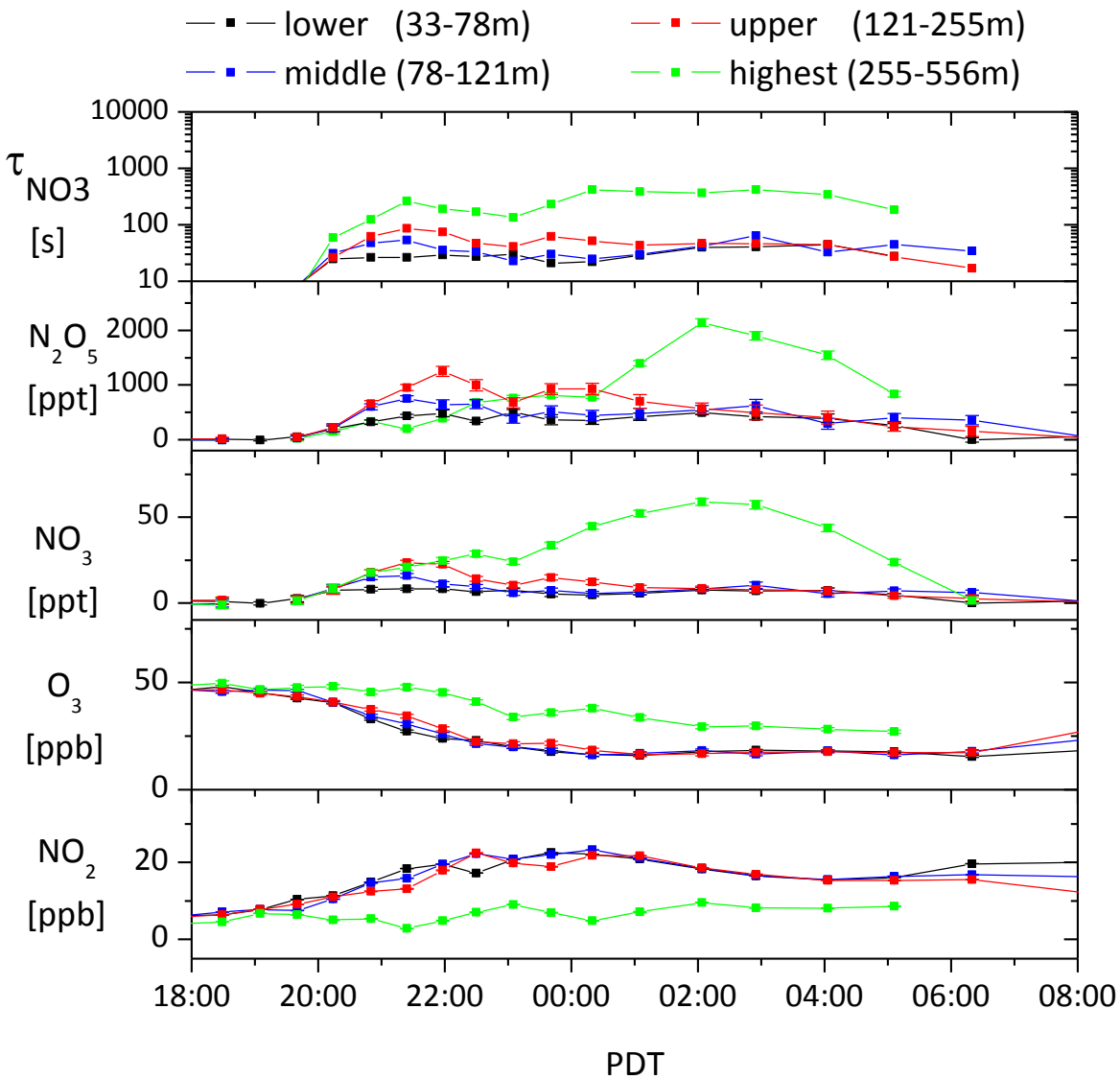
$$O_3 + NO \rightarrow NO_2 + O_2$$

Nocturnal Vertical Gradient



NO_3 Chemistry

May 26 – 27, 2010



NO_3 production rate:

$$\tau_{NO3}(PSS) = \frac{(K_1(T) \bullet [NO_2] \bullet [O_3])}{[NO_3]}$$

$$P(NO_3) = K_1(T) \bullet [NO_2] \bullet [O_3]$$

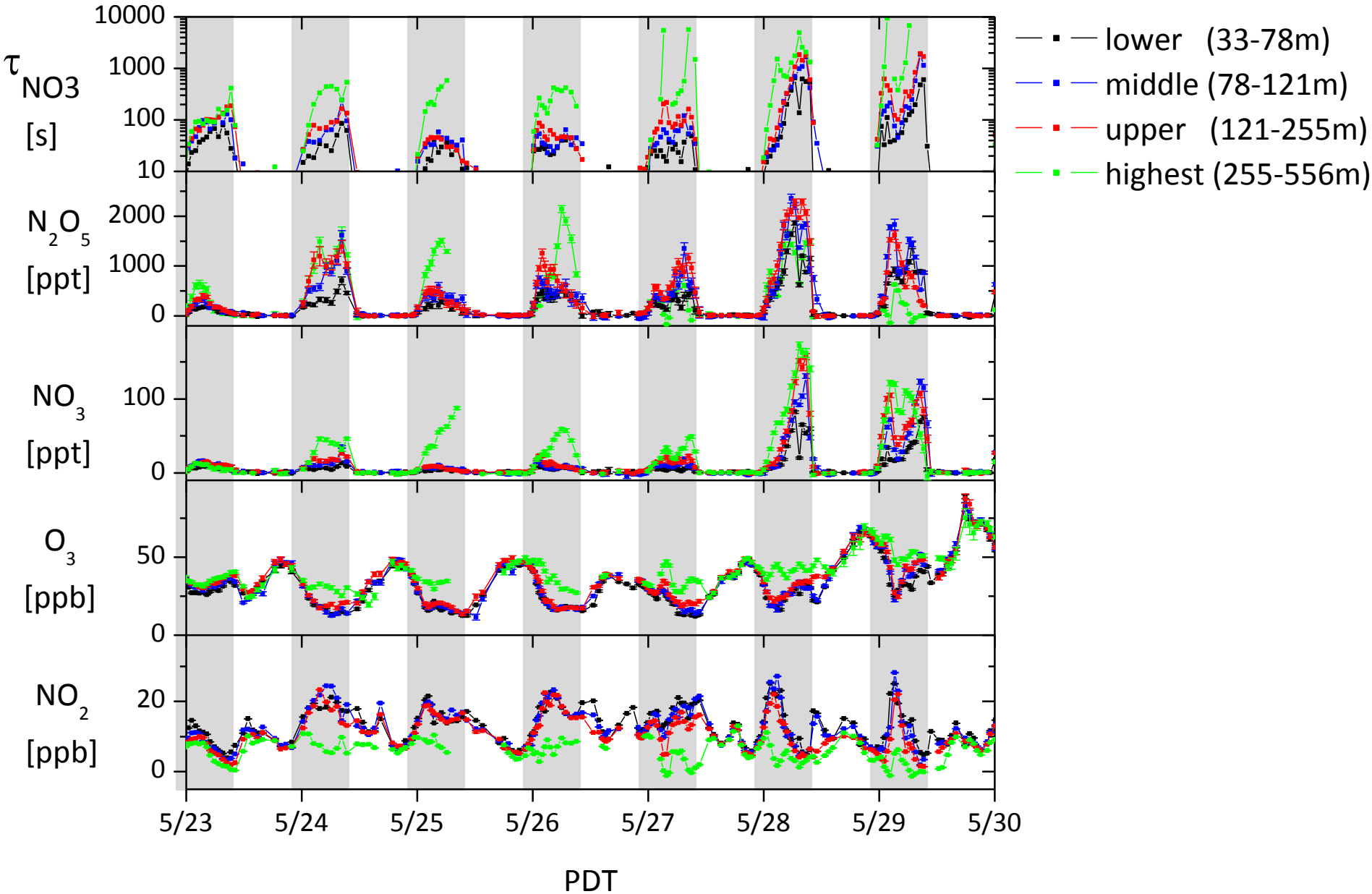
$$K_1 = 1.43 \times 10^{-13} * e^{-2470/T}$$

Mixing ratio of N_2O_5

$$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M$$

$$K = 5.58 \times 10^{-27} * e^{10724/T}$$

NO_3 Chemistry



NOx loss in the NBL

Reactions of NO_3 radical:

a) $NO_3 + NO \rightarrow 2\ NO_2$ **zero NOx loss**

b) NO_3 + HC → organic nitrates → → SOA **1 NOx loss**

c) NO_3 → → aerosol uptake **1 NOx loss**

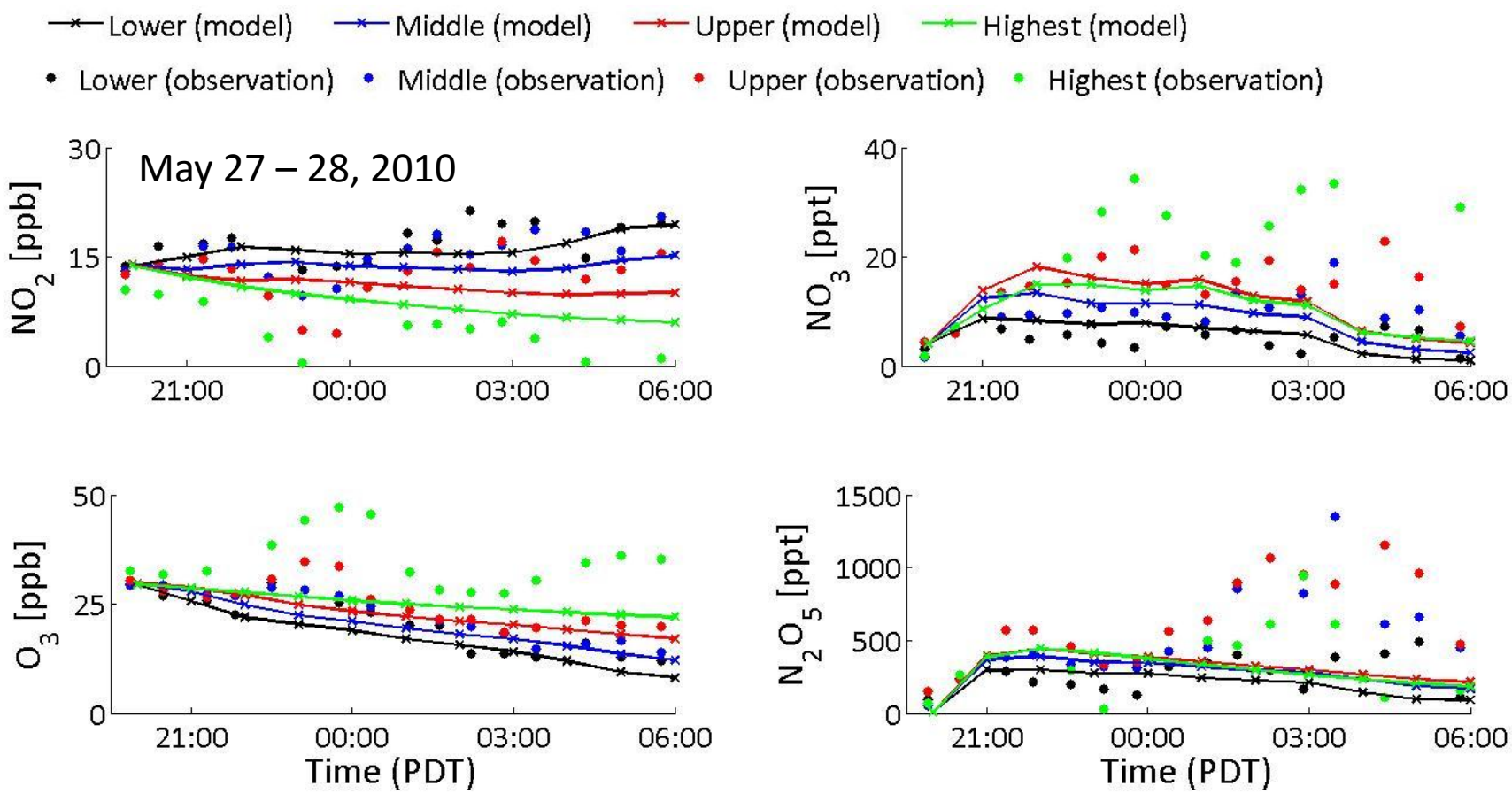
d) $NO_3 + NO_2 \leftrightarrow N_2O_5$ →aerosol uptake **2 NOx loss**

Overall loss frequency of NO_3 radical :

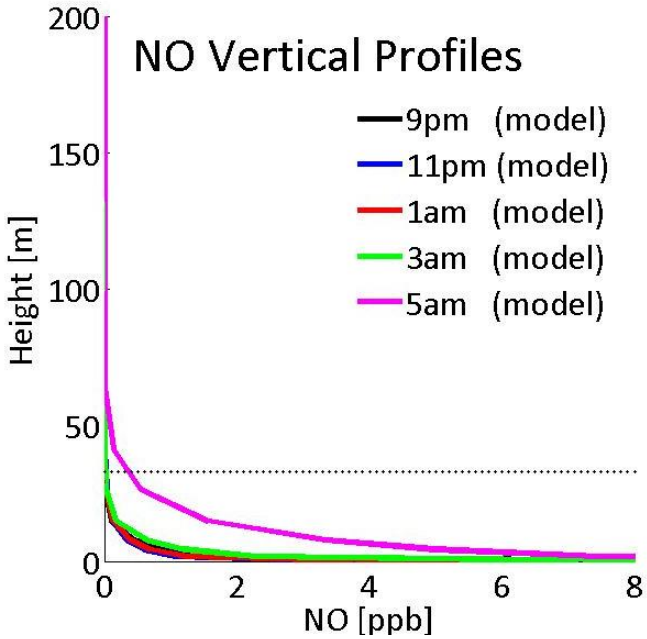
$$f_{NO3}(tot) = f_{NO3}(NO) + f_{NO3}(HC) + f_{NO3}(aer) + f_{NO3}(N_2O_5)$$

RCAT8.2 1-D radical chemistry and transport model

- Gas-phase Regional Atmospheric Chemistry Mechanism (RACM) :
  - 84 reactive species
  - 249 gas-phase chemical reactions
- 27 boxes from 0-3 km (log scale below 1 m).
- Biogenic and anthropogenic emissions .
- Deposition and chemistry on ground and aerosol.

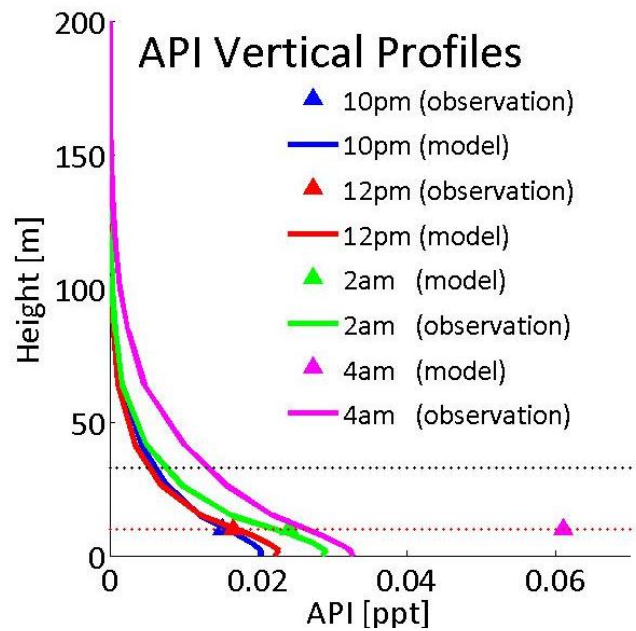


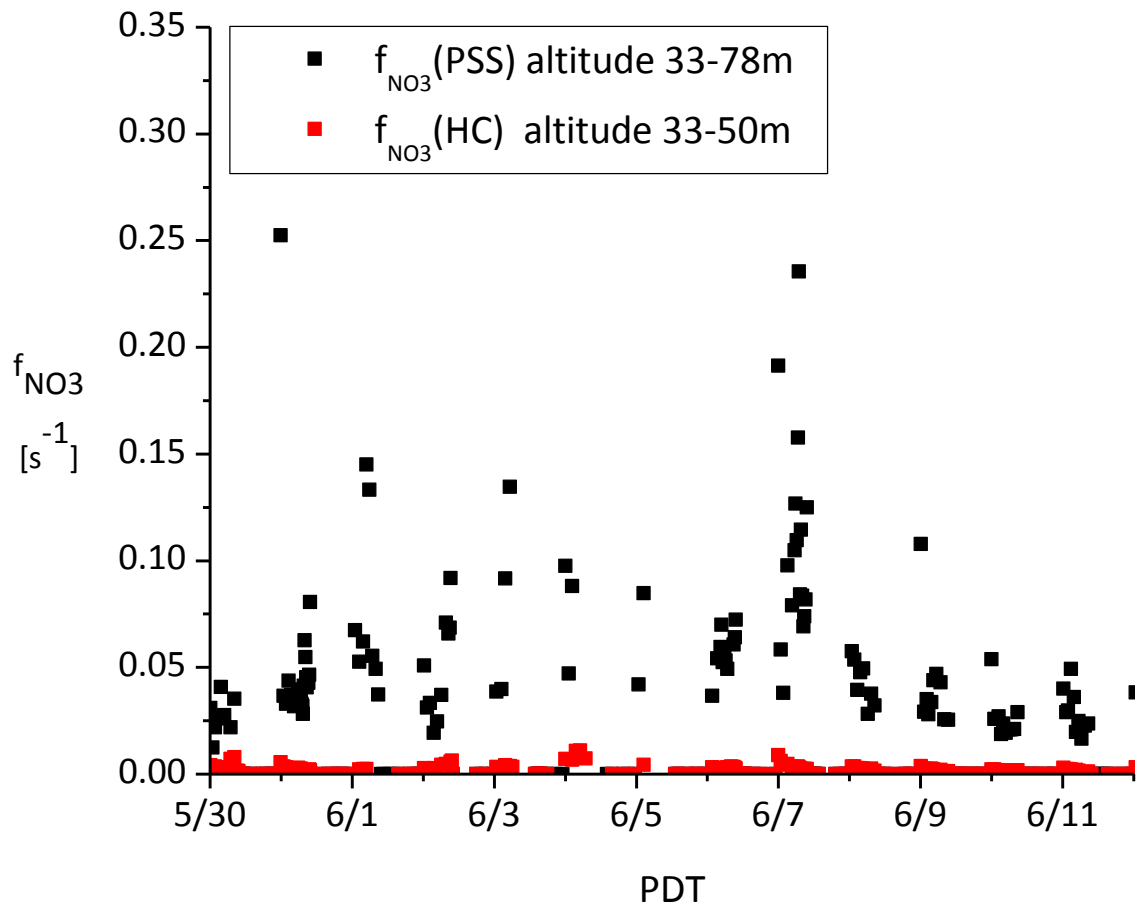
Preliminary NO_3 Loss Rate



$$f_{NO3}(tot) = \cancel{f_{NO3}(NO)} + \cancel{f_{NO3}(HC)} + f_{NO3}(aer) + \boxed{f_{NO3}(N_2O_5)}$$

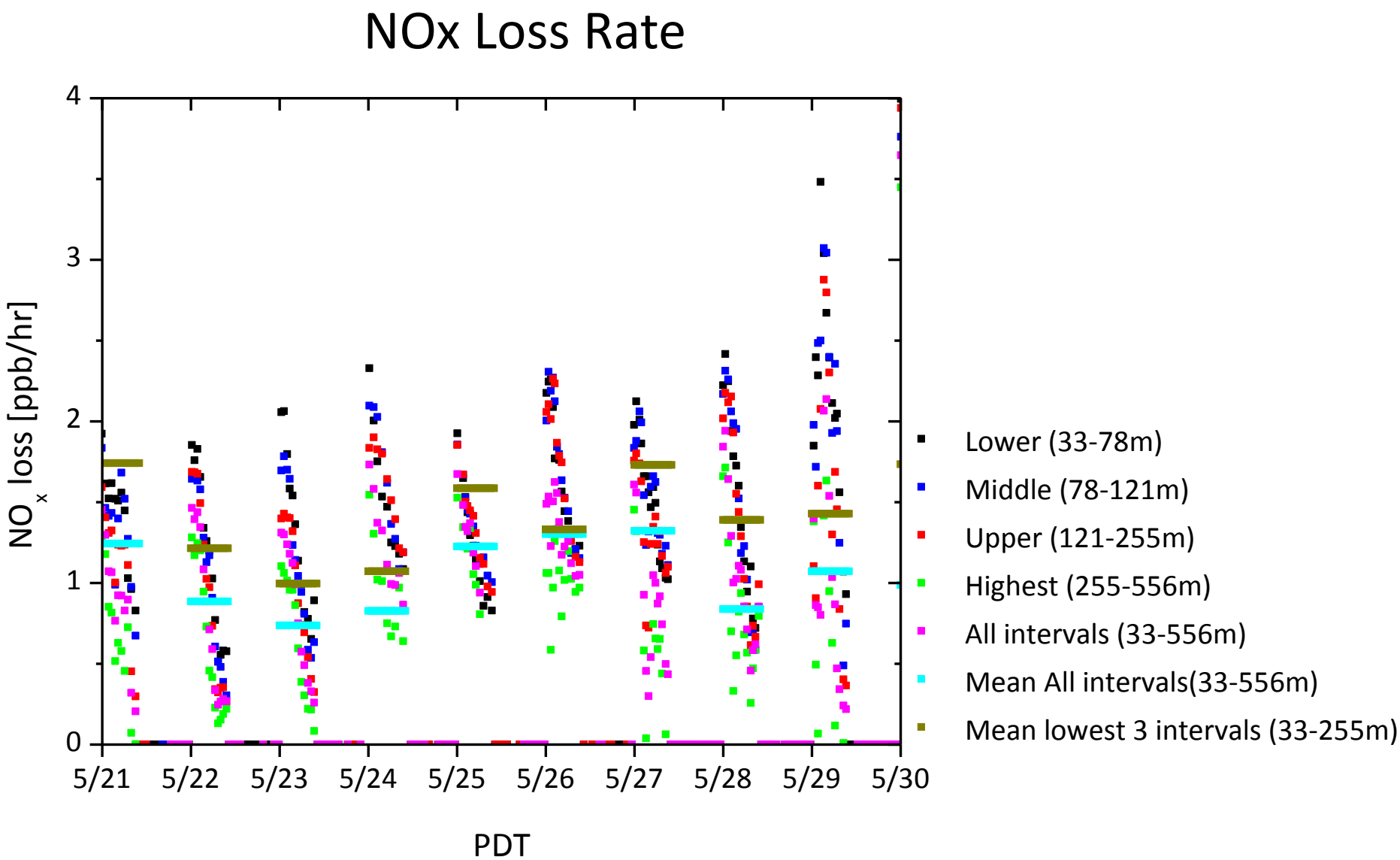
(Observations scaled with vertical profiles)





(HC data provided by NOAA)

Preliminary NOx Loss



Conclusion

- **Nocturnal vertical gradients** of trace gases were observed during CalNex.

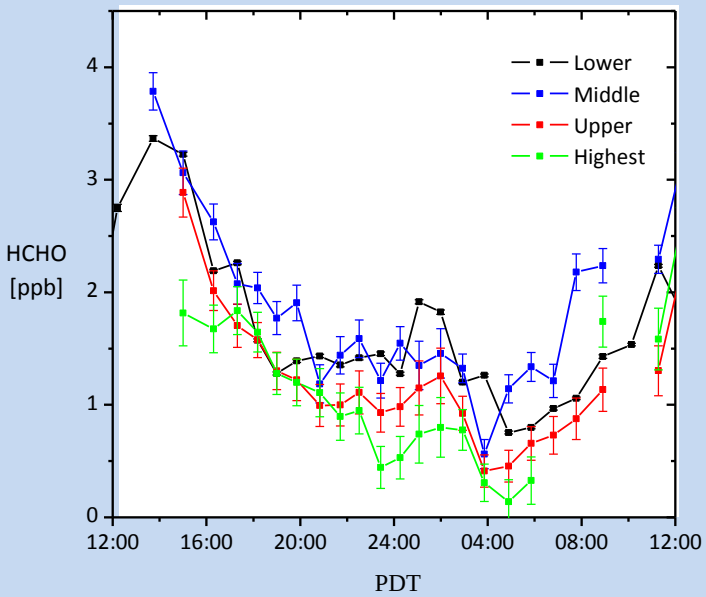
- **Ozone and NO_2** showed typical **diurnal variation** found in polluted areas: small ozone and large NO_2 mixing ratios at night and the opposite during the day.

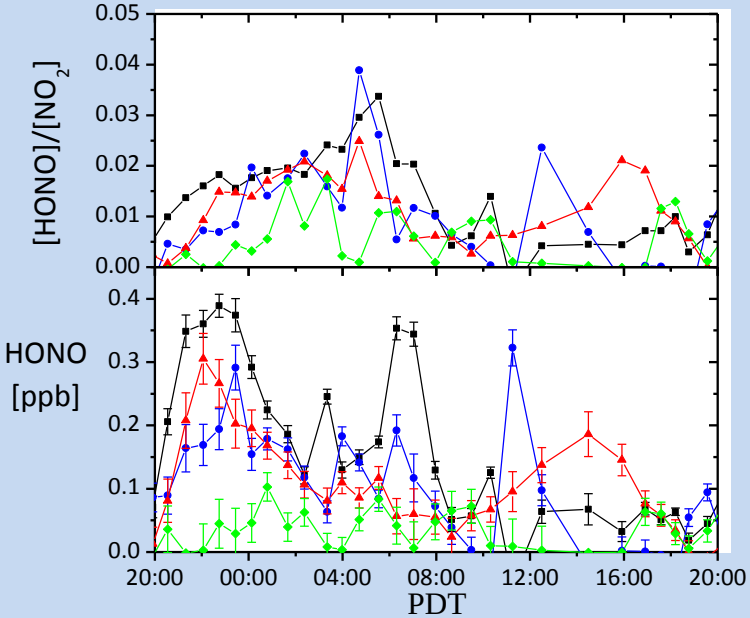
- **Nocturnal NO_3 and N_2O_5** mixing ratios were elevated during the experiment, indicating an **active radical chemistry** in the nocturnal boundary layer during CalNex -Los Angeles

- Assuming that NO_3 is predominantly lost through N_2O_5 uptake we found **~ 1ppb/hr nocturnal NOx loss** averaged over the lowest 500 m of the atmosphere (Houston ~1ppb/hr).

OUTLOOK

- Vertical profiles of HCHO and HONO will be investigated.





- Further analysis using the 1D model will be performed to analyze NO_3 ,HCHO, HONO and $ClNO_2$.

Acknowledgement

California Air Resources Board

Caltech

CALNEX
LOS ANGELES