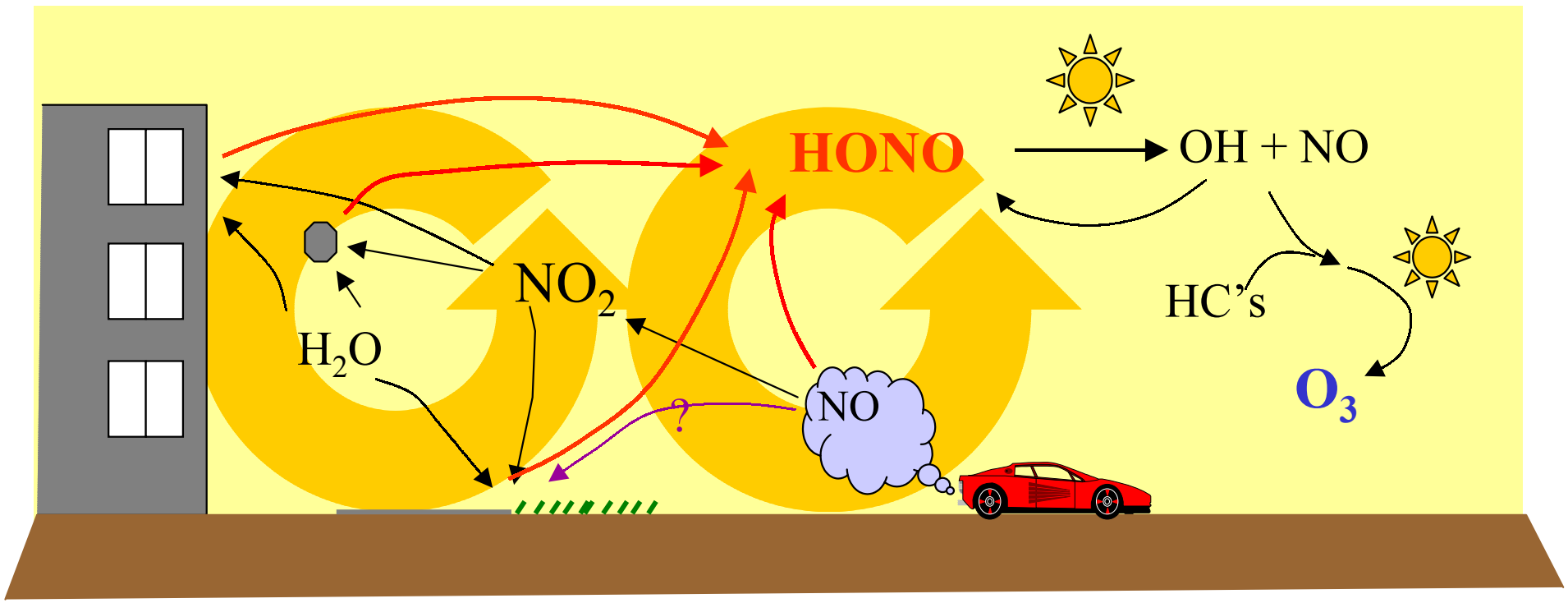
Nighttime Chemistry of Nitrogen Oxides: Measurements of Vertical Trace Gas Gradients during the Phoenix 2001 Study

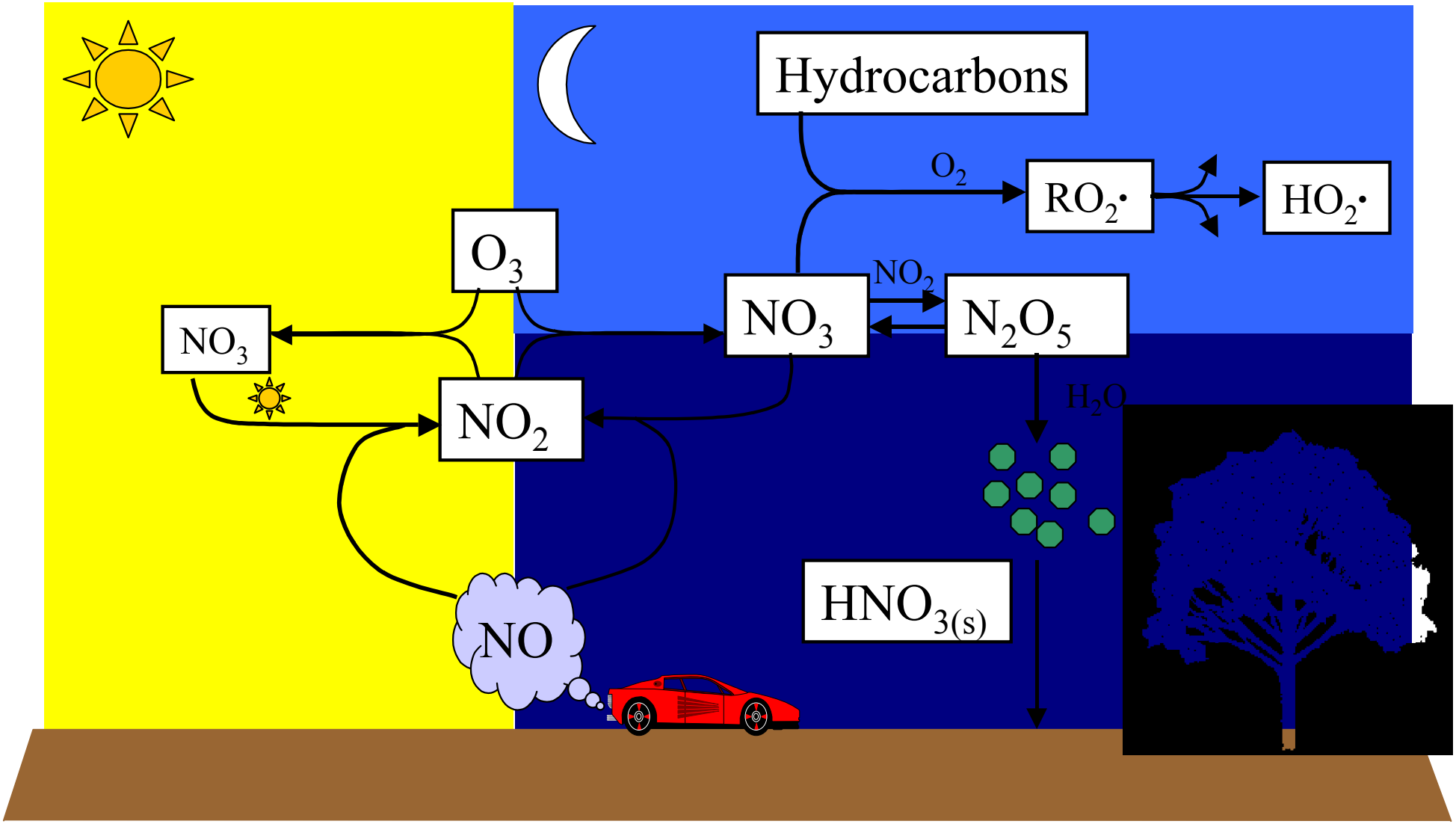
Jochen Stutz,
Ralf Ackermann, Shuhui Wang
Dept. Atmospheric Sciences, UCLA

With data from:
C. Doran, C. Berkowitz, J. Fast, PNNL; C. Spicer, Battelle

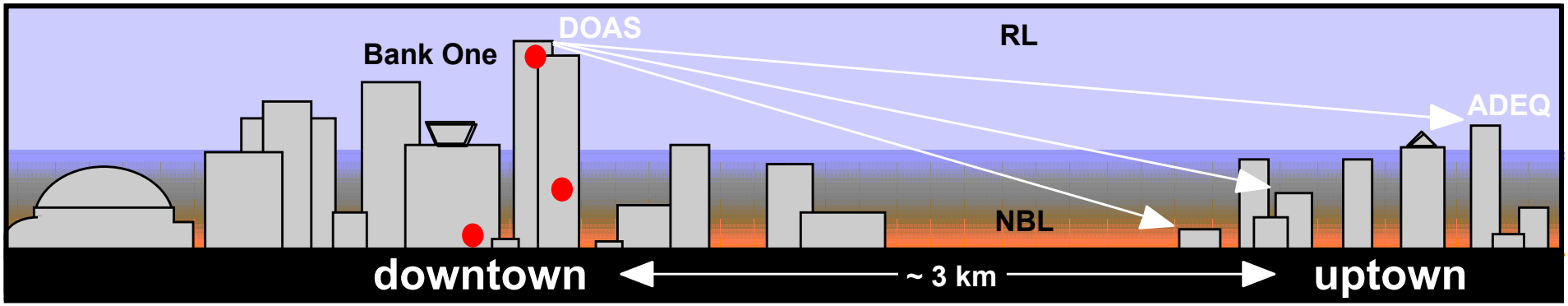
Chemistry of Nitrous Acid, HONO

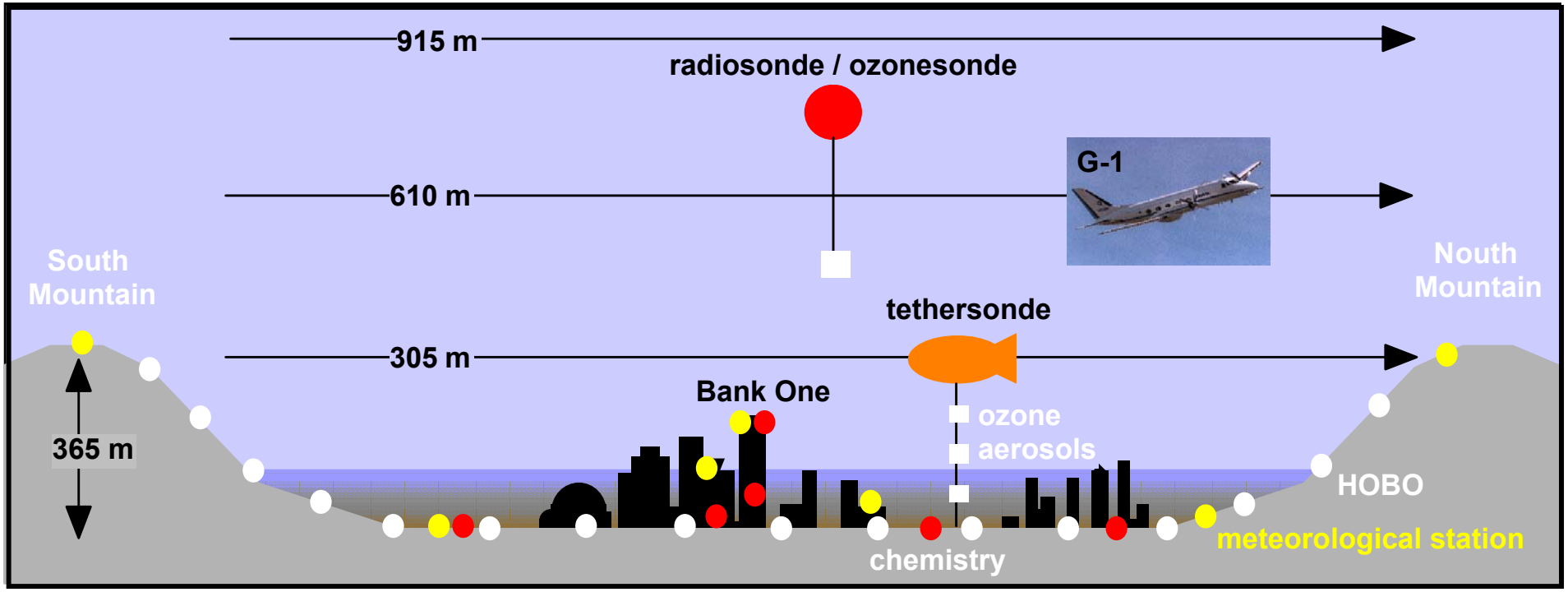


Chemistry of the nitrate radical, NO_3

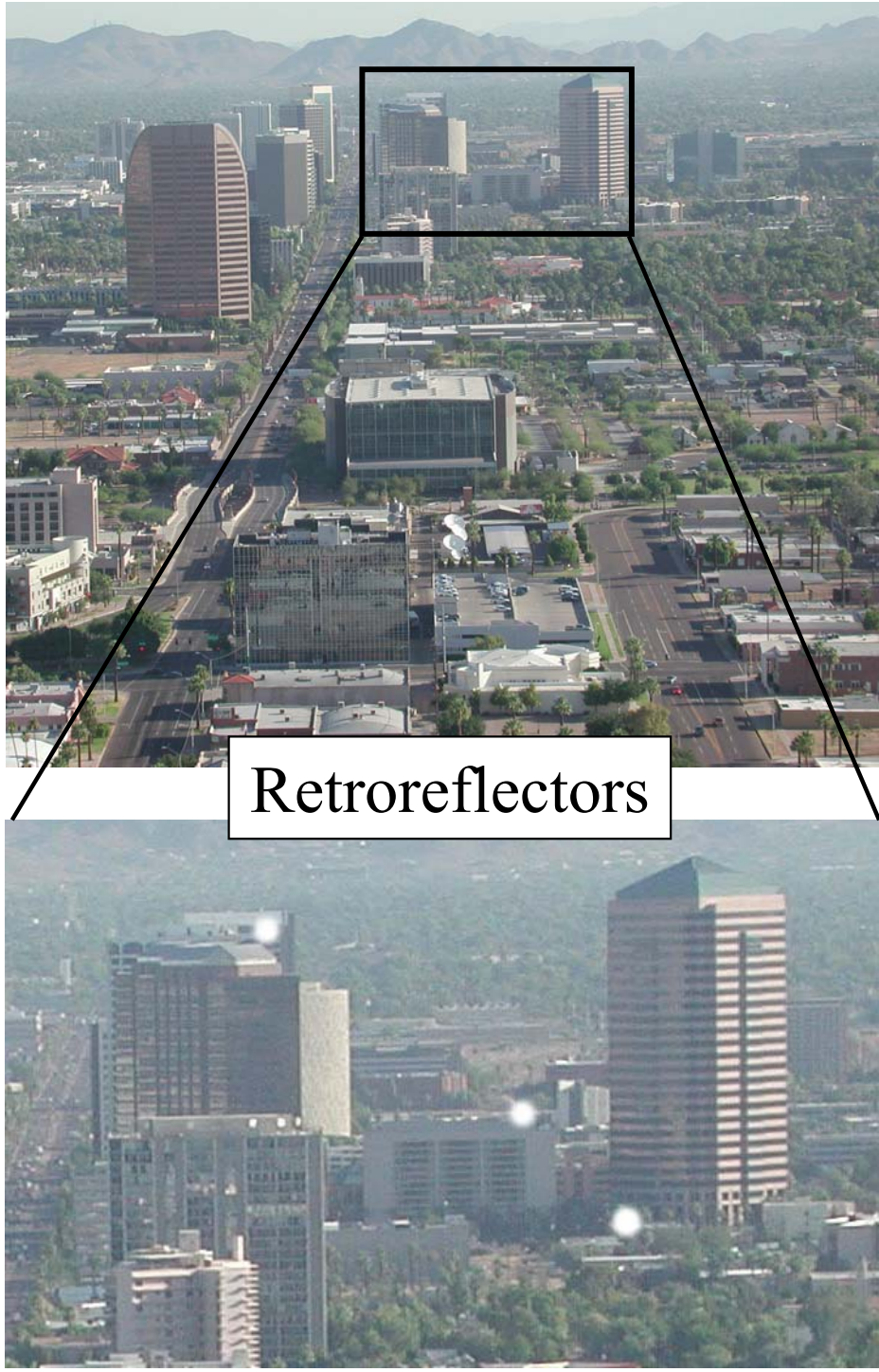


Field Campaign Design

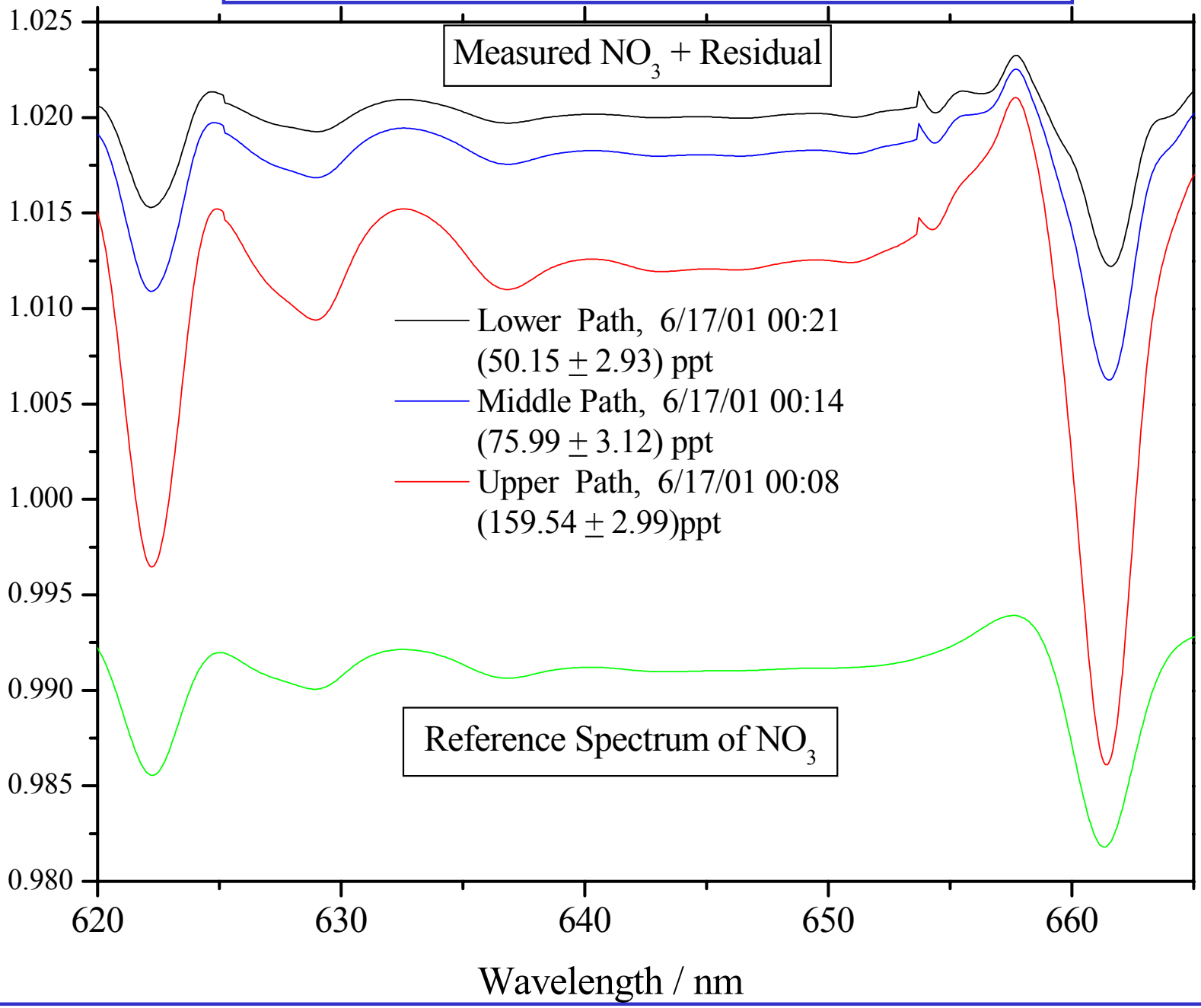




DOAS System


Retroreflectors

Example of NO_3 absorption spectra

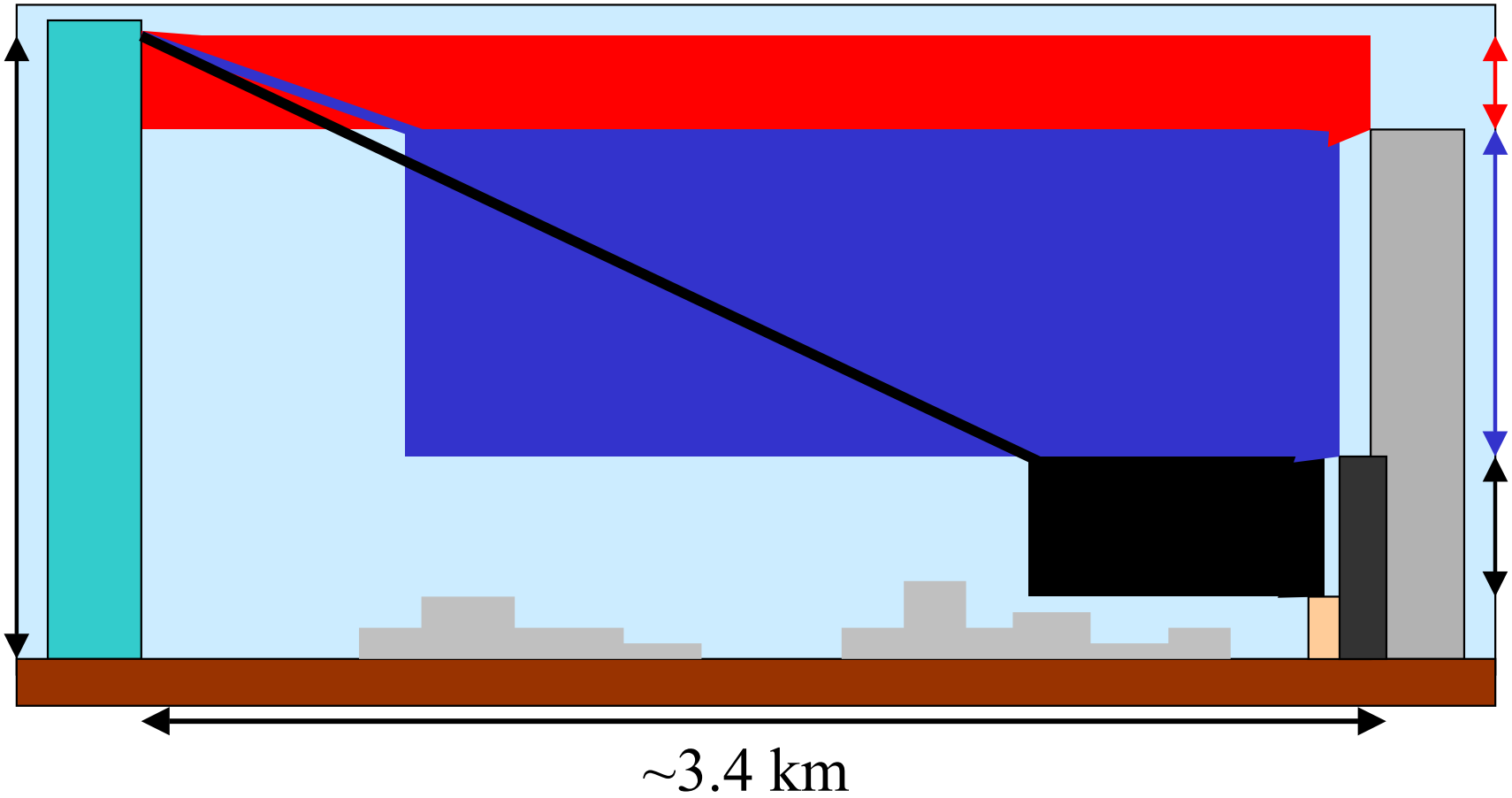


Box Concentrations

upper box: h = 110 - 140 m

middle box: h = 40 - 110 m

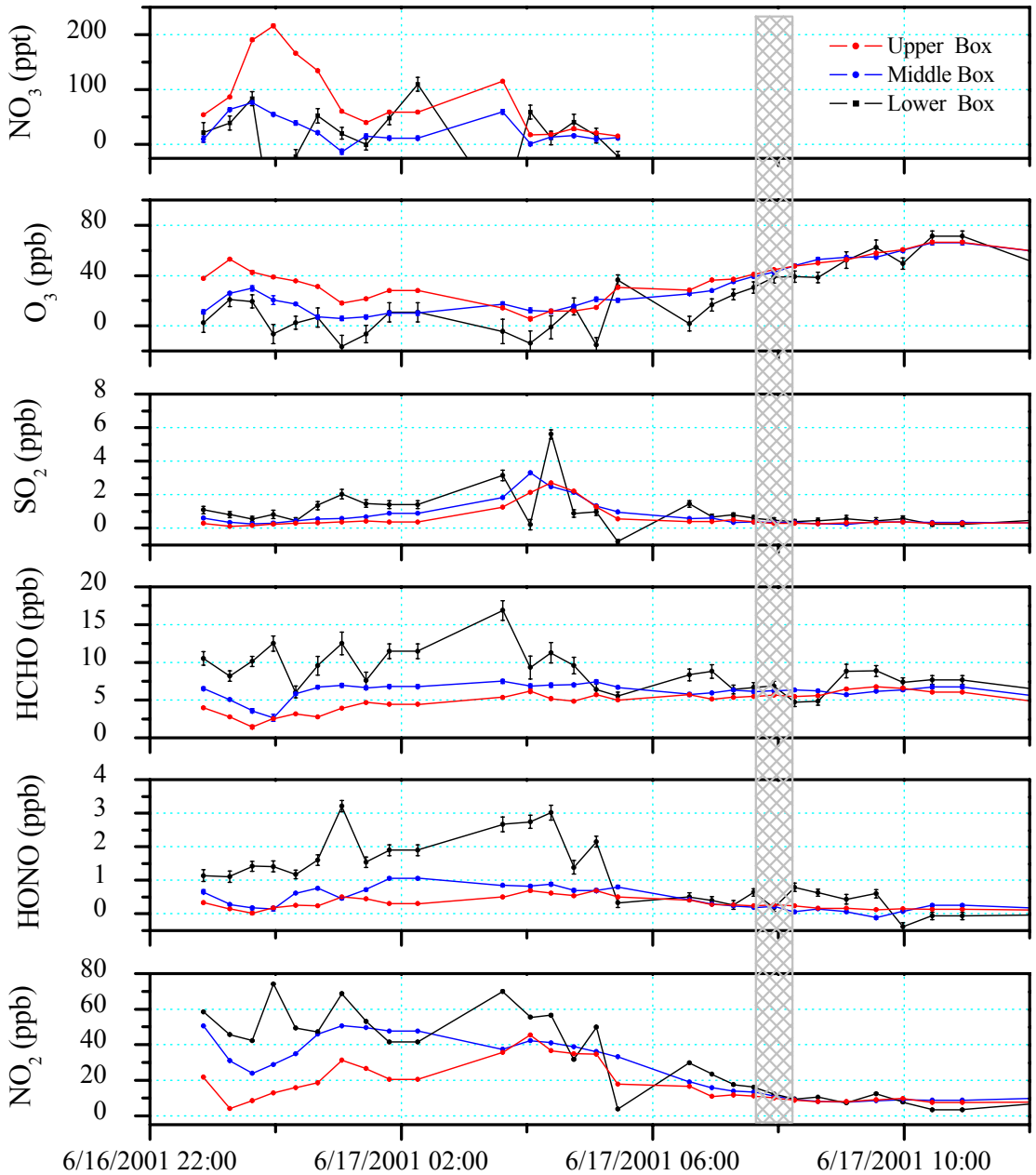
lower box: h = 10 - 40 m



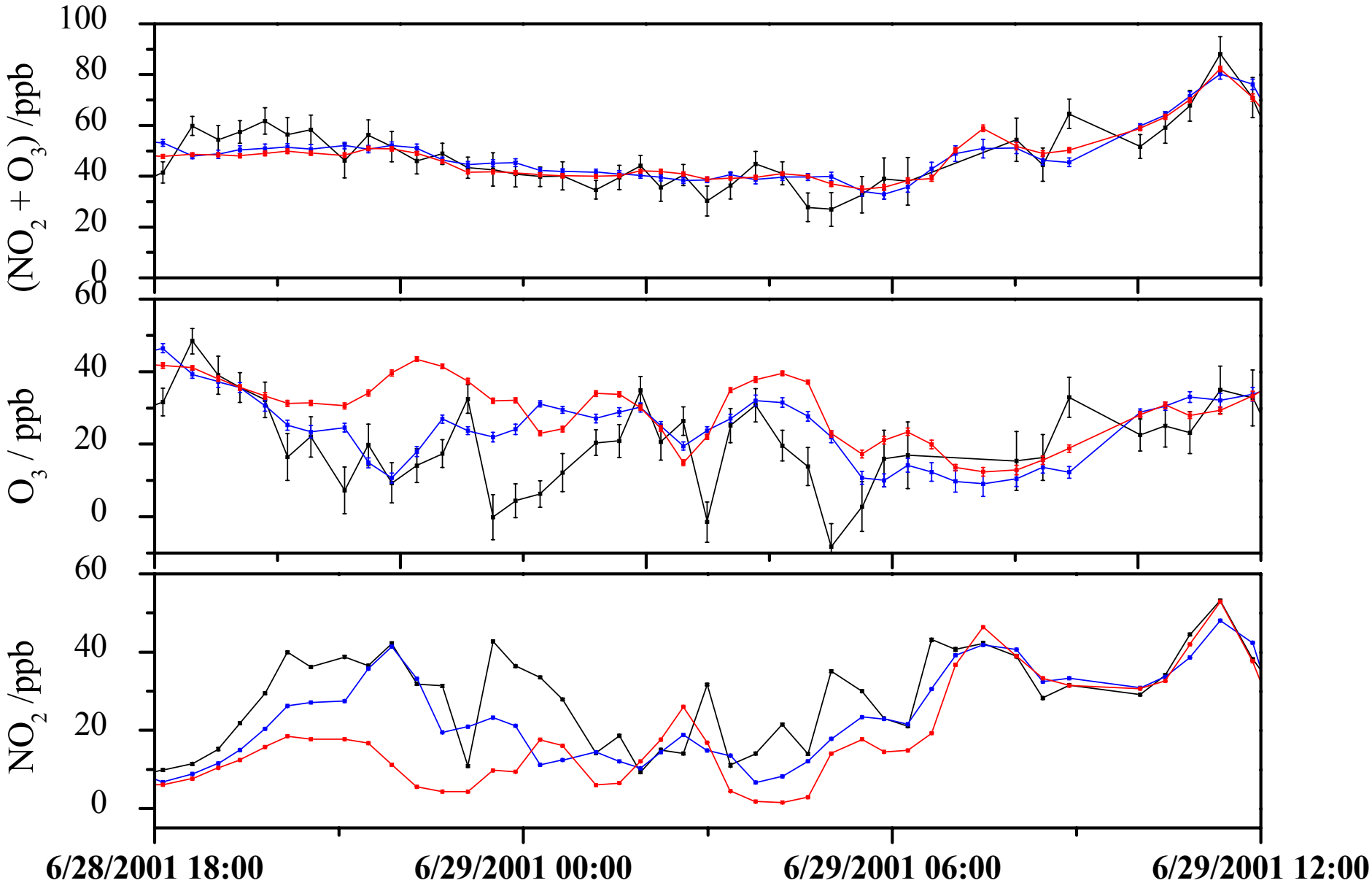
Detection Limits of Measured Species

Measured Species	Wavelength Region	Average "Box" Detection Limit (2σ)		
		Upper	Middle	Lower
NO_2	336~371nm	0.11ppb	0.18 ppb	0.65 ppb
HONO	336~371nm	0.043 ppb	0.068 ppb	0.25 ppb
HCHO	303~326nm	0.23 ppb	0.38 ppb	1.43 ppb
SO_2	303~326nm	0.056 ppb	0.092 ppb	0.34 ppb
O_3	303~326nm	1.74 ppb	2.8 ppb	10 ppb
NO_3	617~668nm	3.82 ppt	6.45 ppt	20 ppt

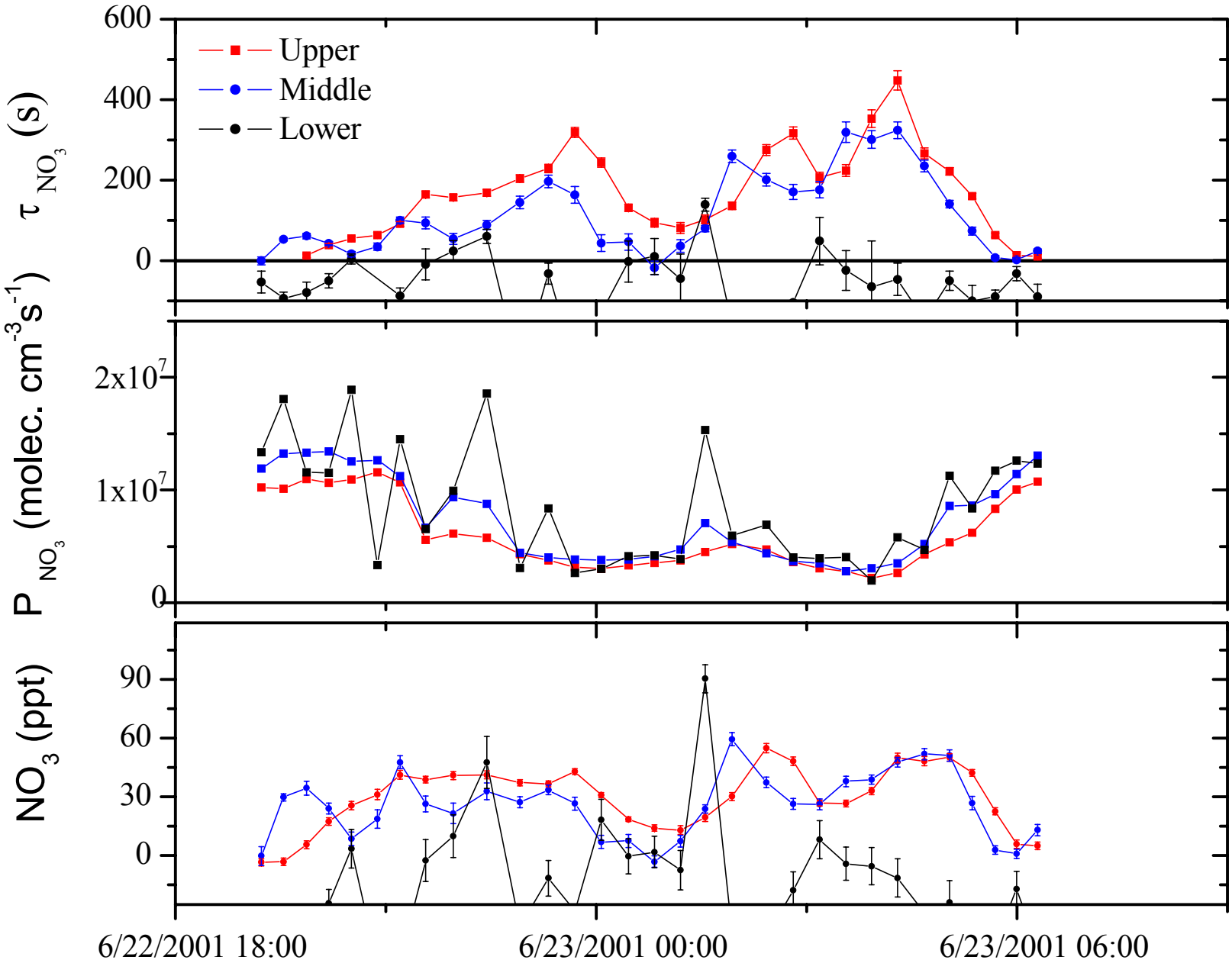
Trace Gas Gradients on June 17



Titration of Ozone by NO emitted at the Ground



Gradients of NO_3 Lifetime



HONO Dependence on R.H.

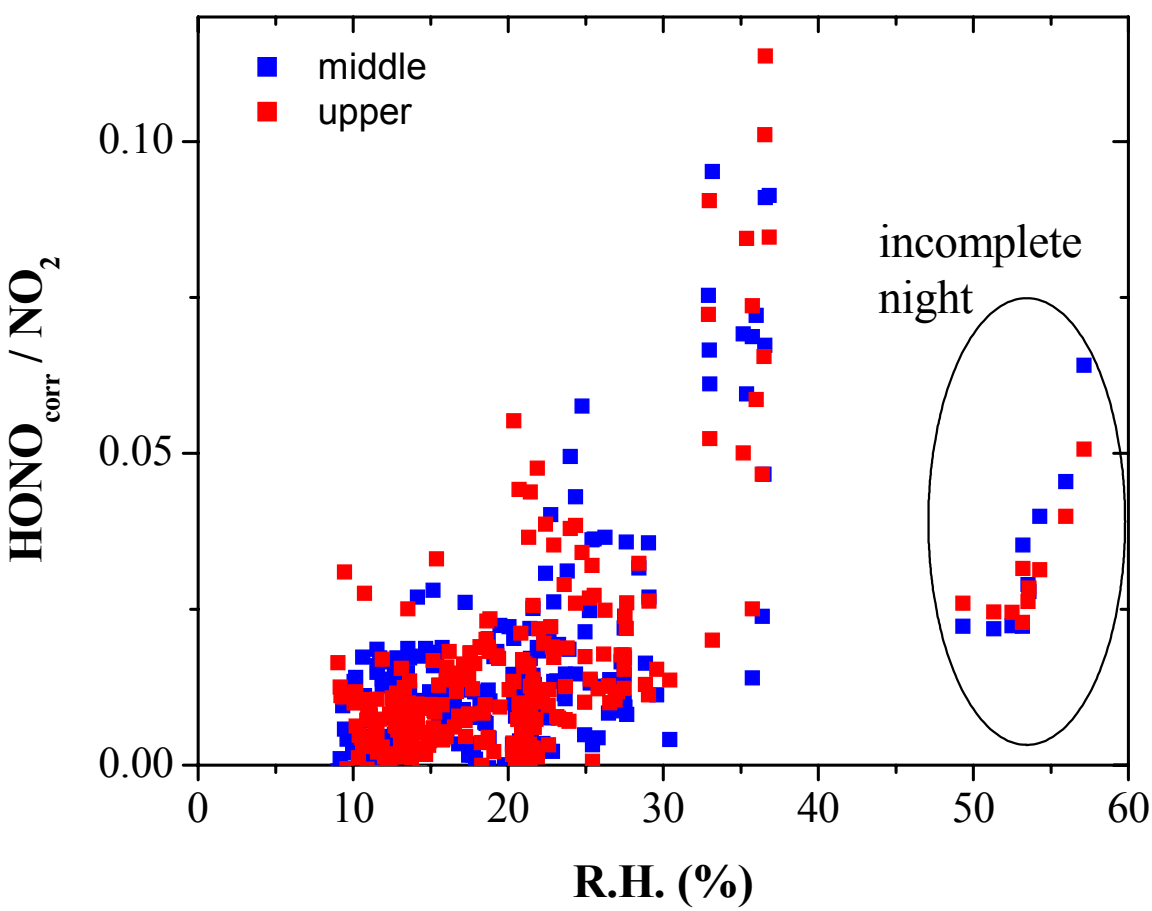
Heterogeneous HONO formation:

$$\frac{d[HONO]}{dt} \propto [NO_2]^{\alpha} \times [H_2O]_{surface} \propto [NO_2]^{\alpha} \times R.H.$$

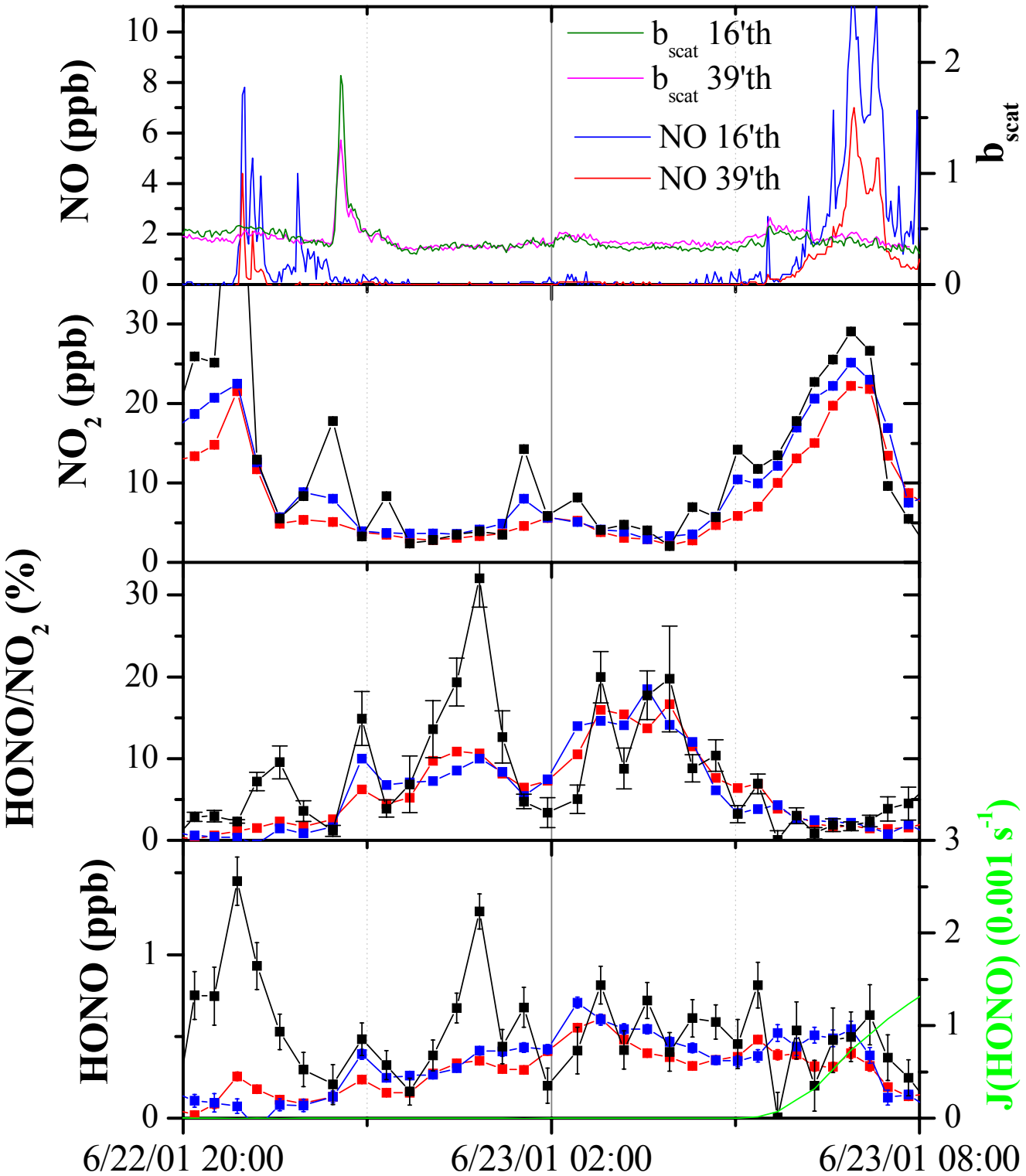
Correction for direct emission (Kirchstetter, 1993)

$$[HONO_{corr}] = [HONO] - 0.003 \times [NO_x]$$

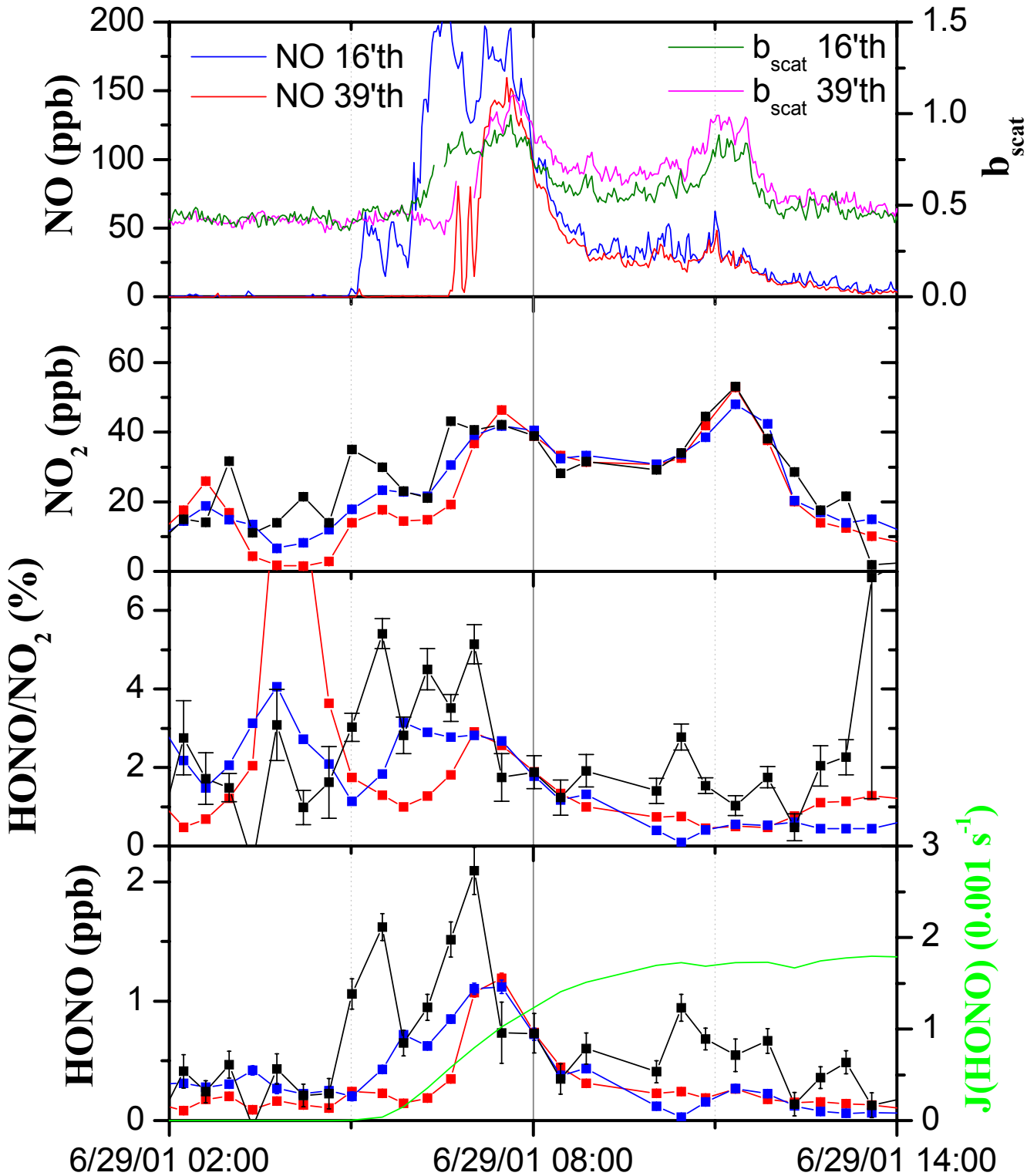
assume $\alpha = 1$; nights with sandstorms excluded



Influence of a Sandstorm on HONO



Daytime HONO



Conclusions

- At night strong vertical trace gas gradients were observed. Most likely reasons are:
  - NO titration
  - direct HCHO emissions
  - HONO emissions / formation
- Disappearing gradients show the onset of vertical mixing at sunrise.
- Dependence of NO_2 - HONO conversion on R.H. was observed.
- Daytime HONO at the ground points to daytime formation / emission and HONO as an important OH source.
- $HONO/NO_2$ ratios up to 0.35 after sandstorms suggest efficent NO_2 to HONO conversion on mineral particles.
- NO_3 levels at 120m height reach up to 250ppt.
- NO_3 levels are strongly influenced by NO / HC emissions at the ground. NO_3 radical chemistry strongly depends on altitude.

Outlook

- Include additional data (meteorology, HC, particles, aircraft) into analysis
- Set up NO_3 budget to determine heterogeneous N_2O_5 loss rate.
- Develop 1-dimensional chemical box model using NO titration to fix mixing parameters.
- Compare HONO / R.H. observation with data from TEXAQS 2000