

Continuous year-long measurements of atmospheric HOONO and NO₂ above a New England forest

Ben Lee¹, Bill Munger¹, Ezra Wood^{2,3}, Mark Zahniser³ and Steve Wofsy¹

¹ Harvard University

² Umass Amherst

³ Aerodyne Research, Inc.

AMS Conference on Atmospheric Biogeosciences

May 29, 2012

Daytime chemistry



Daytime chemistry



$$\frac{d[\text{HONO}]}{dt} = k_1[\text{OH}][\text{NO}] - k_2[\text{HONO}][\text{OH}] - J_{\text{HONO}}[\text{HONO}]$$

Daytime chemistry

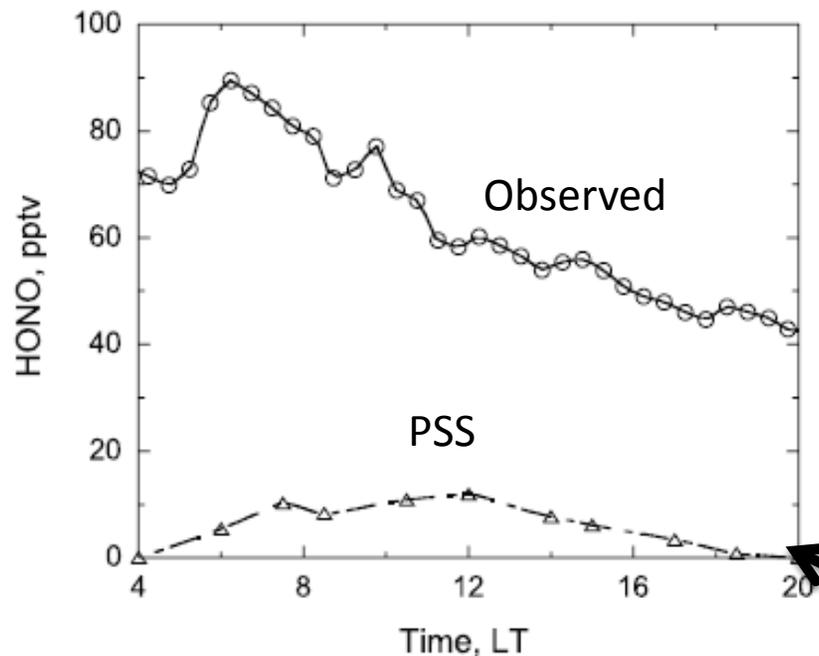


$$\frac{d[\text{HONO}]}{dt} = k_1[\text{OH}][\text{NO}] - k_2[\text{HONO}][\text{OH}] - J_{\text{HONO}}[\text{HONO}]$$

$$[\text{HONO}]_{\text{PSS}} = \frac{k_1[\text{OH}][\text{NO}]}{J_{\text{HONO}} + k_2[\text{OH}]}$$

Daytime chemistry

Pinnacle State Park, NY (Jul 1998)



$$\frac{d[\text{HONO}]}{dt} = k_1[\text{OH}][\text{NO}] - k_2[\text{HONO}][\text{OH}] - J_{\text{HONO}}[\text{HONO}]$$

$$[\text{HONO}]_{\text{PSS}} = \frac{k_1[\text{OH}][\text{NO}]}{J_{\text{HONO}} + k_2[\text{OH}]}$$

Implications

- “Missing” HONO source accounts for 20-40% of $P(\text{HO}_x)$
- Pathway to recycle deposited NO_x back into atmosphere in reactive form

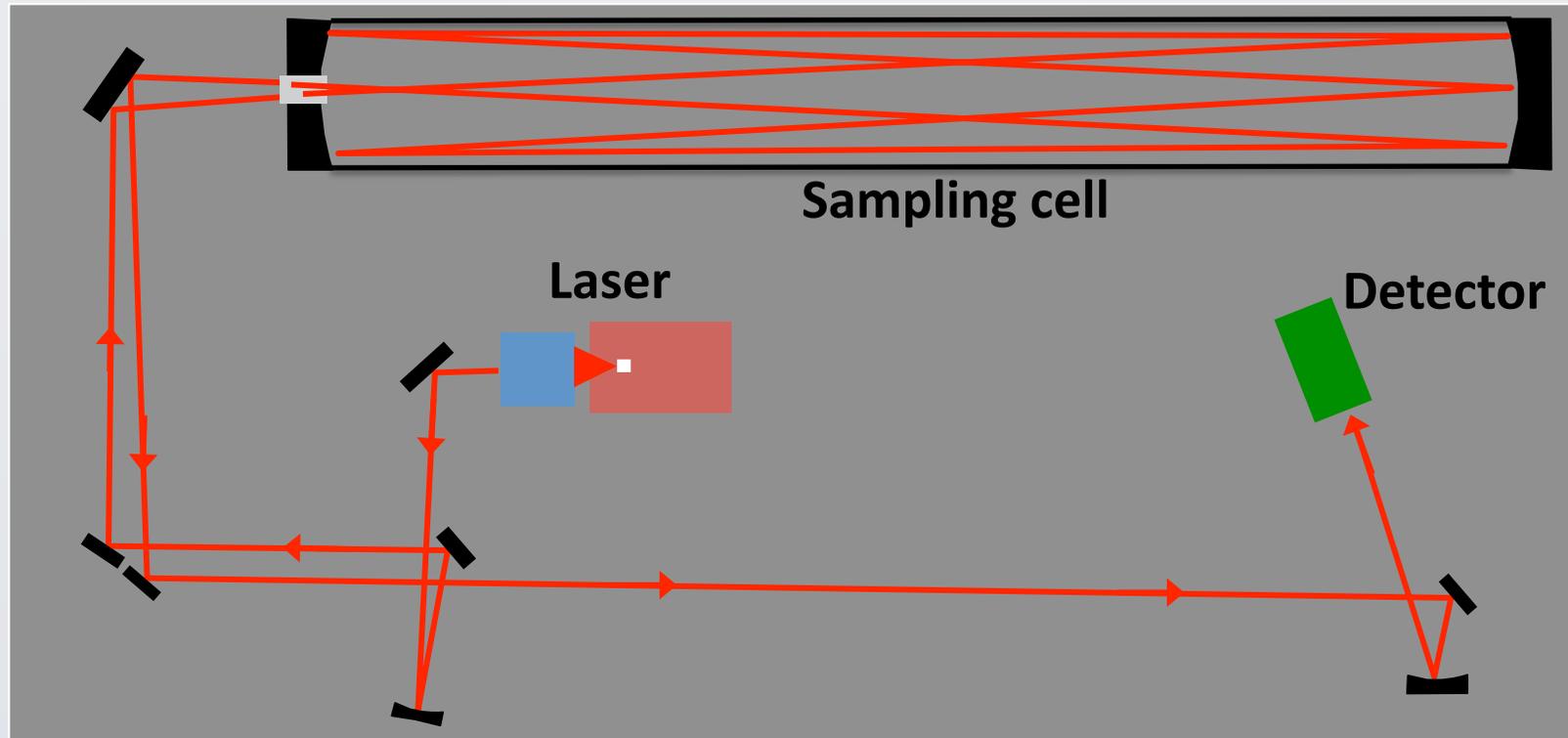
Questions

- What is the contribution of HONO production on atmospheric NO_x and HO_x budgets over a rural forest?
- Which environmental variables are responsible?

Goals for instrument

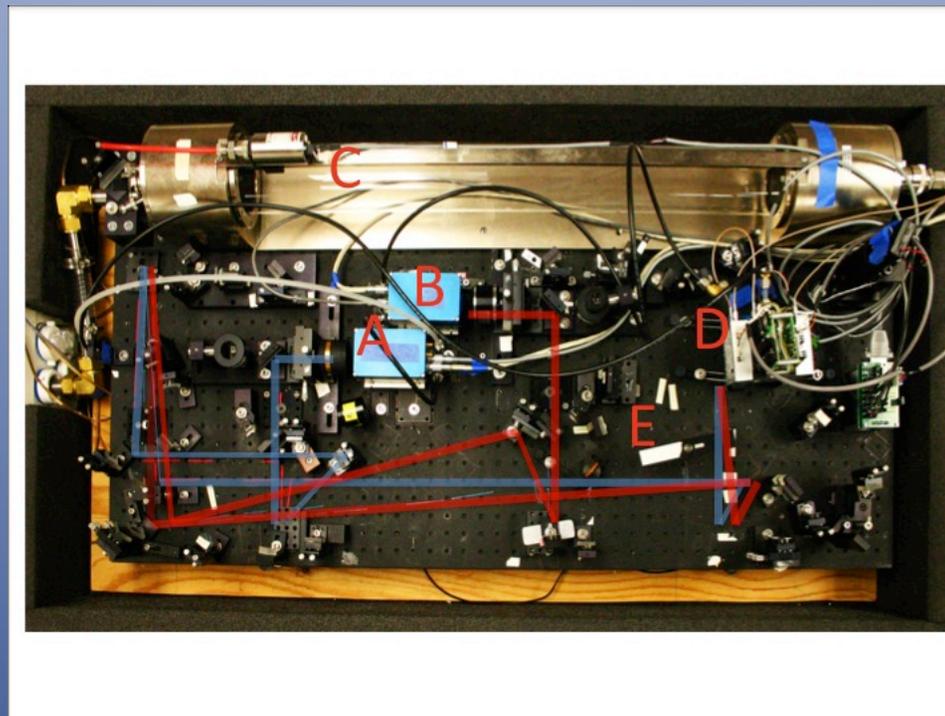
- Direct sampling (no wet chemistry)
- Selectivity (spectroscopic identification)
- Sensitivity (pristine environments & eddy covariance fluxes)
- Long-term deployment (cryogen-free)

Tunable Infrared Laser Differential Absorption Spectroscopy



Tunable Infrared Laser Differential Absorption Spectroscopy

Sample out

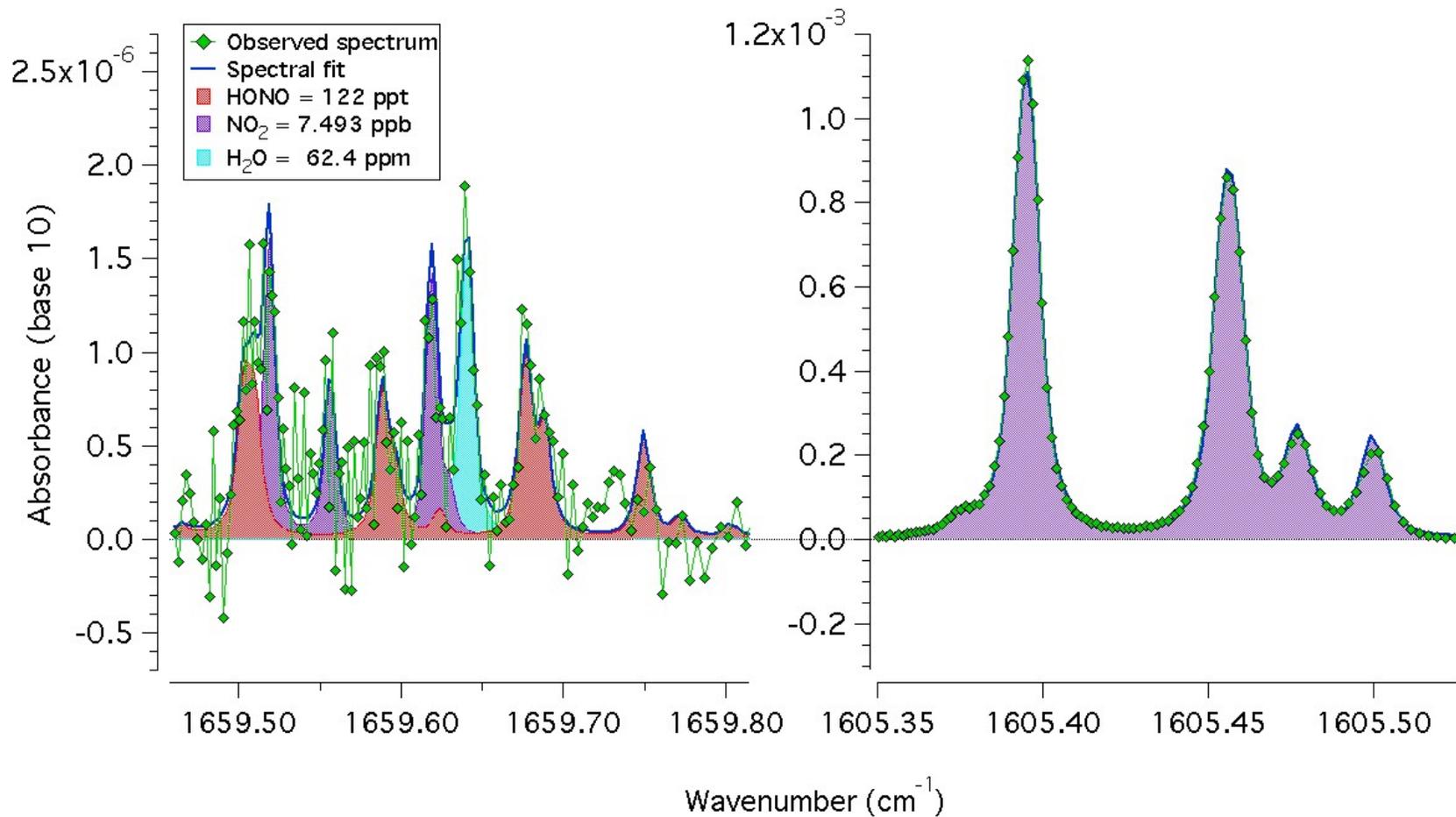


Sample in



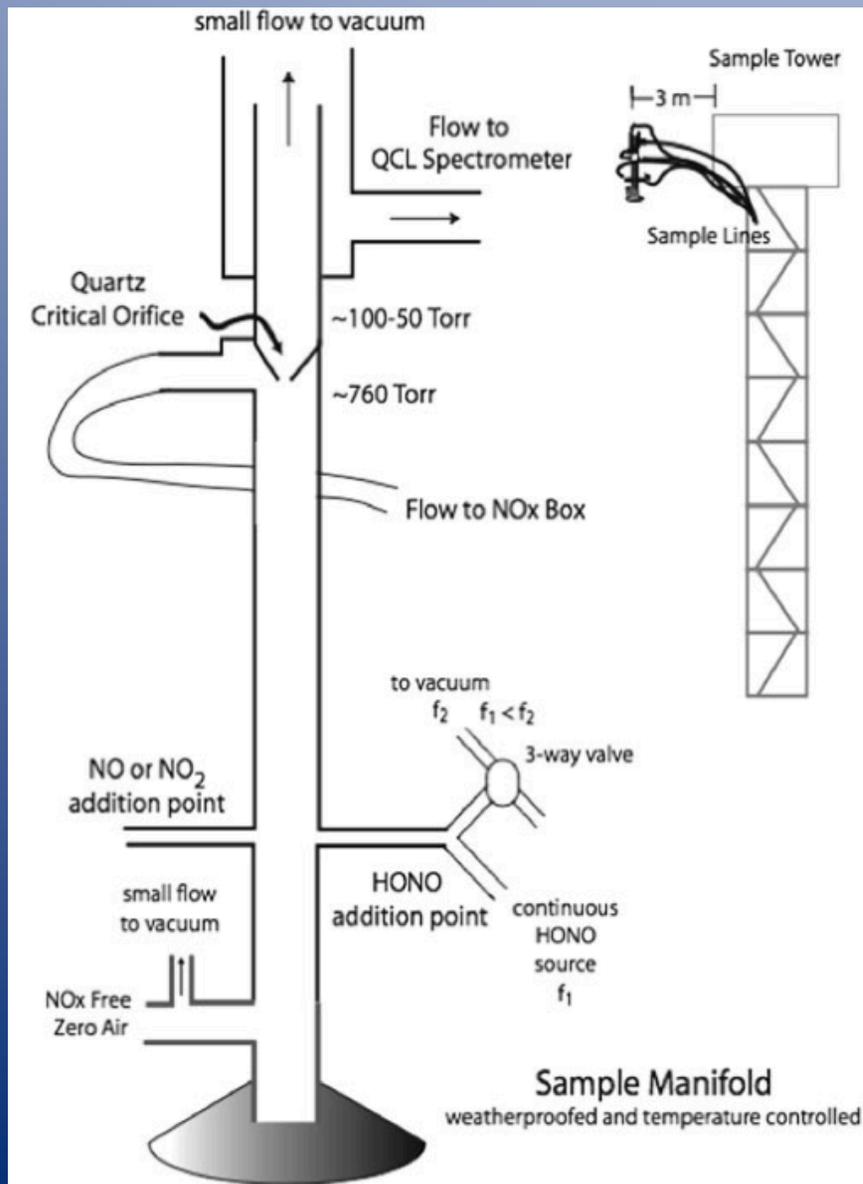
- A) QC laser for HONO (1660 cm^{-1})
- B) QC laser for NO_2 (1604 cm^{-1})
- C) 210-m path-length multi-pass astigmatic cell
- D) Detector

1-hr avg. spectra (6:30-7:30 am on 1/18/2011)



Spectra provide unambiguous identification of HONO

Sampling system



- Routine in-field tests on sampling system to ensure artifact-free measurements
- No particle filters

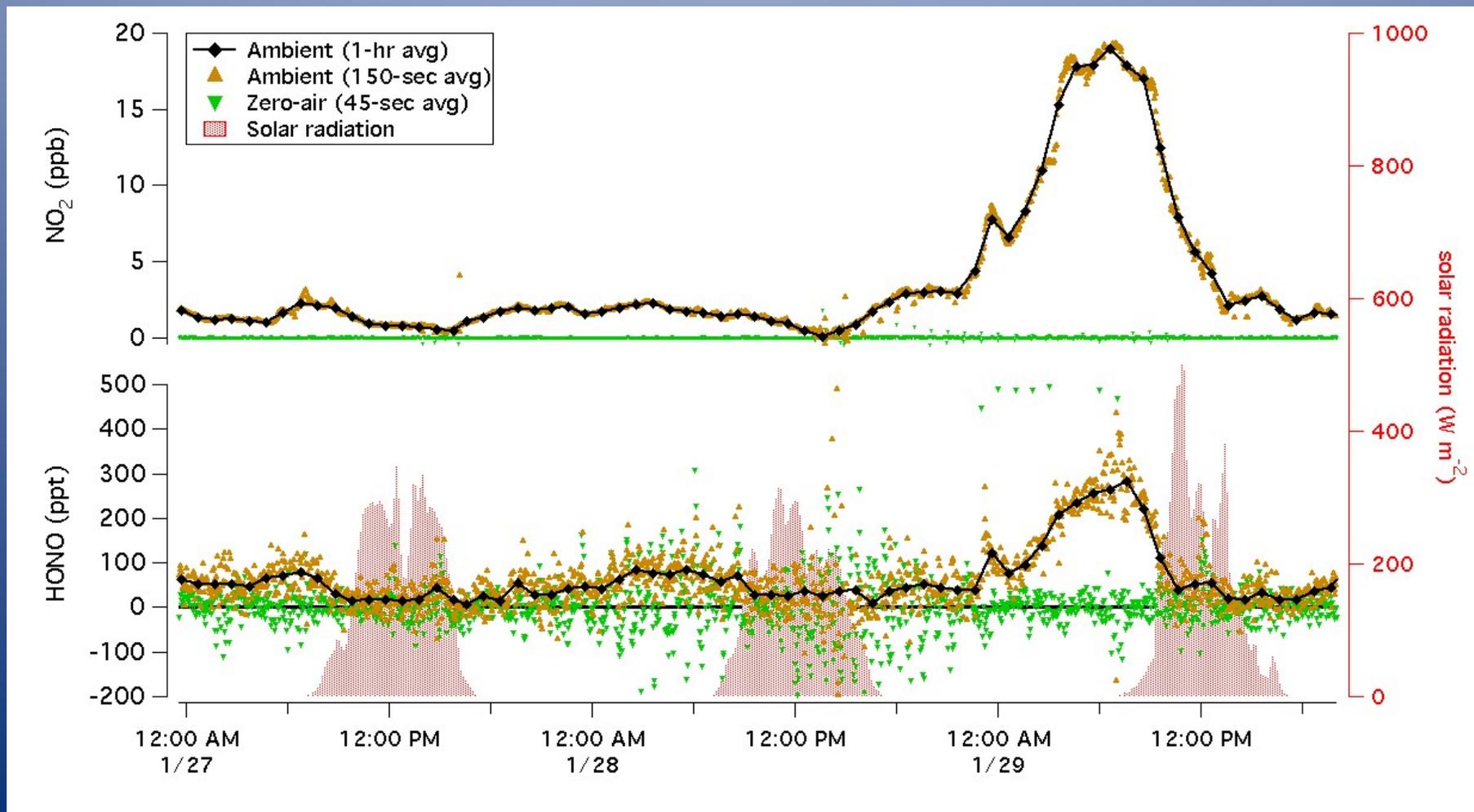
Sampling system



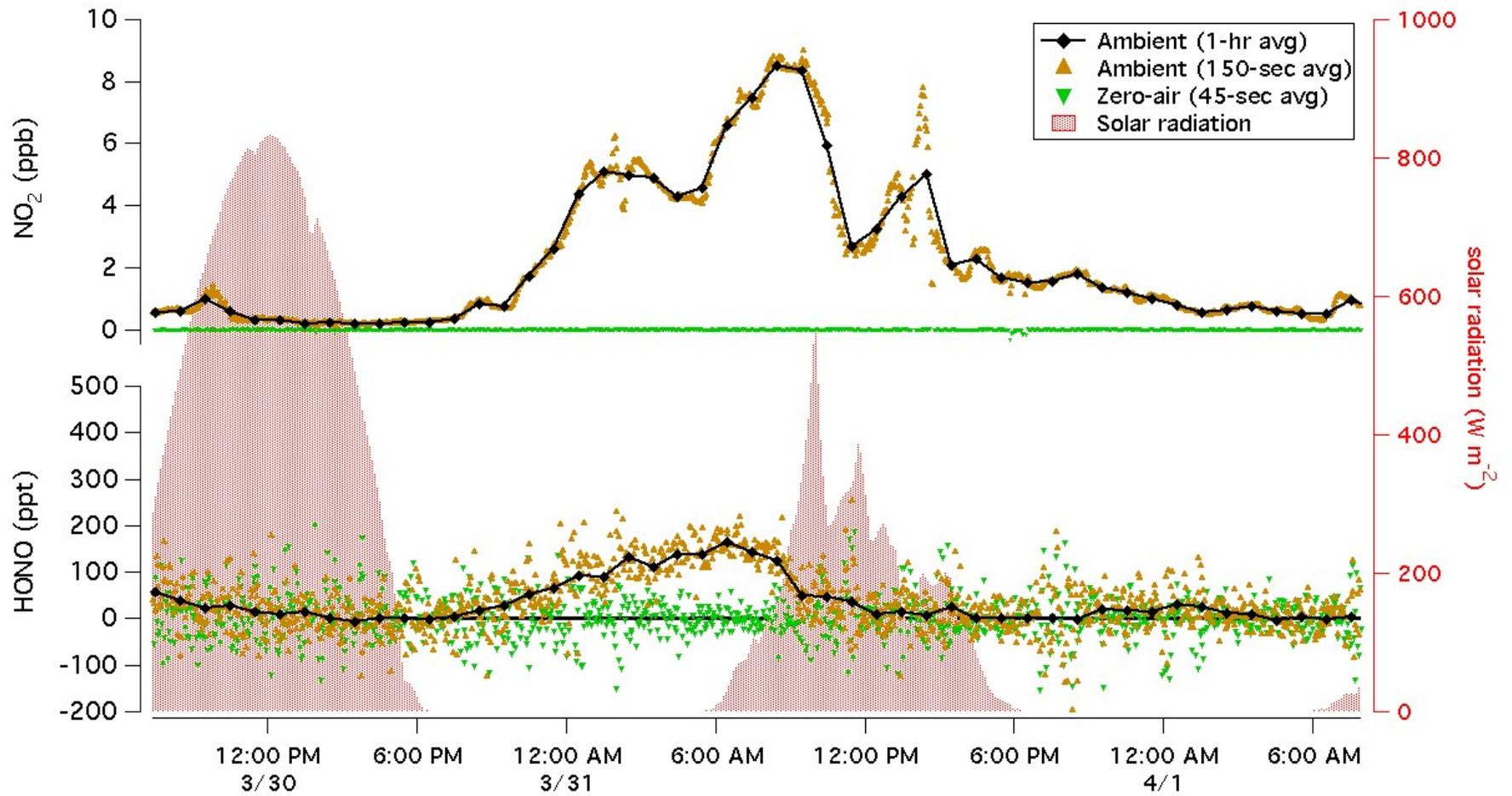
- Routine in-field tests on sampling system to ensure artifact-free measurements
- No particle filters

Quick glance by season

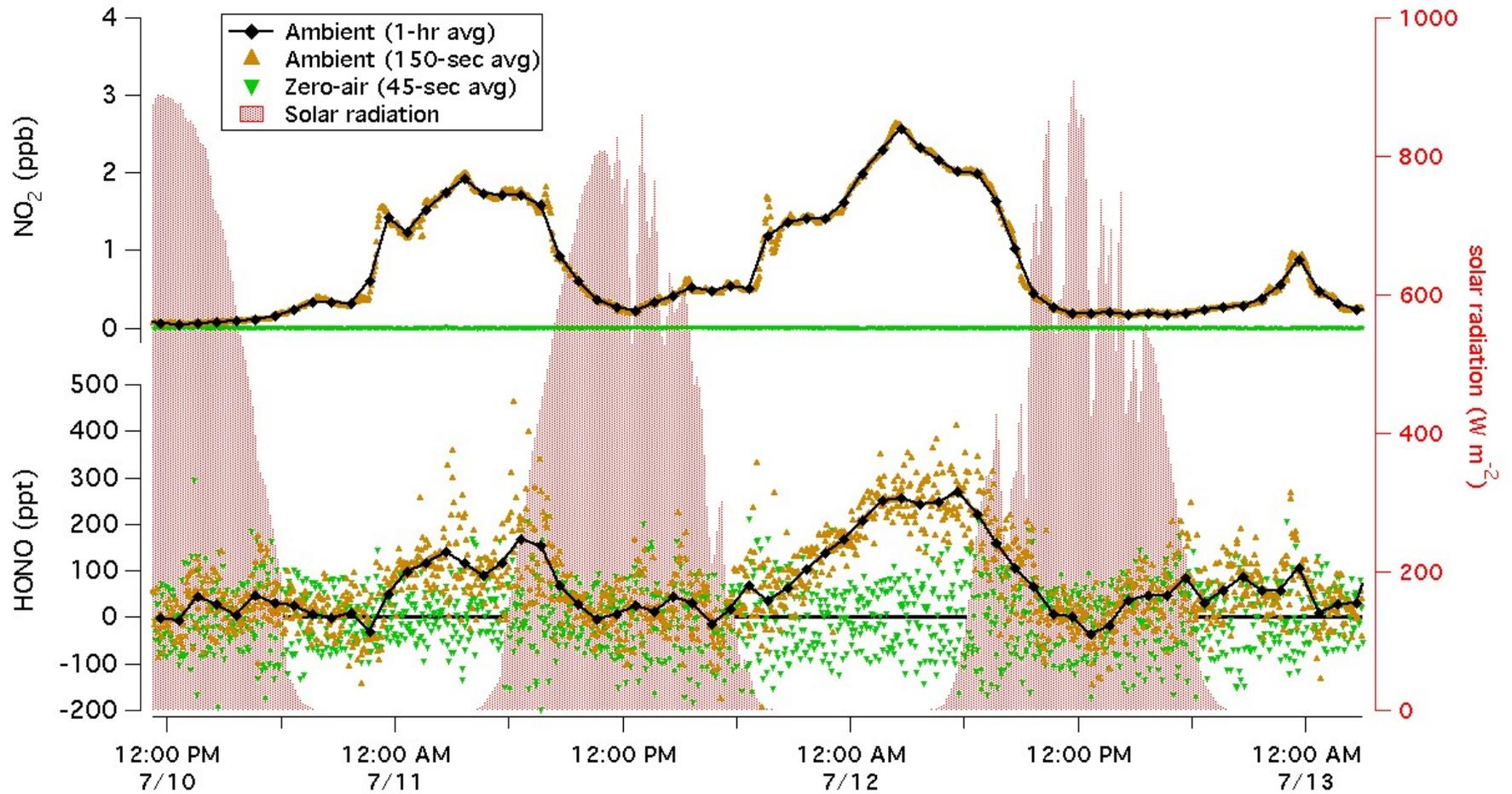
Winter



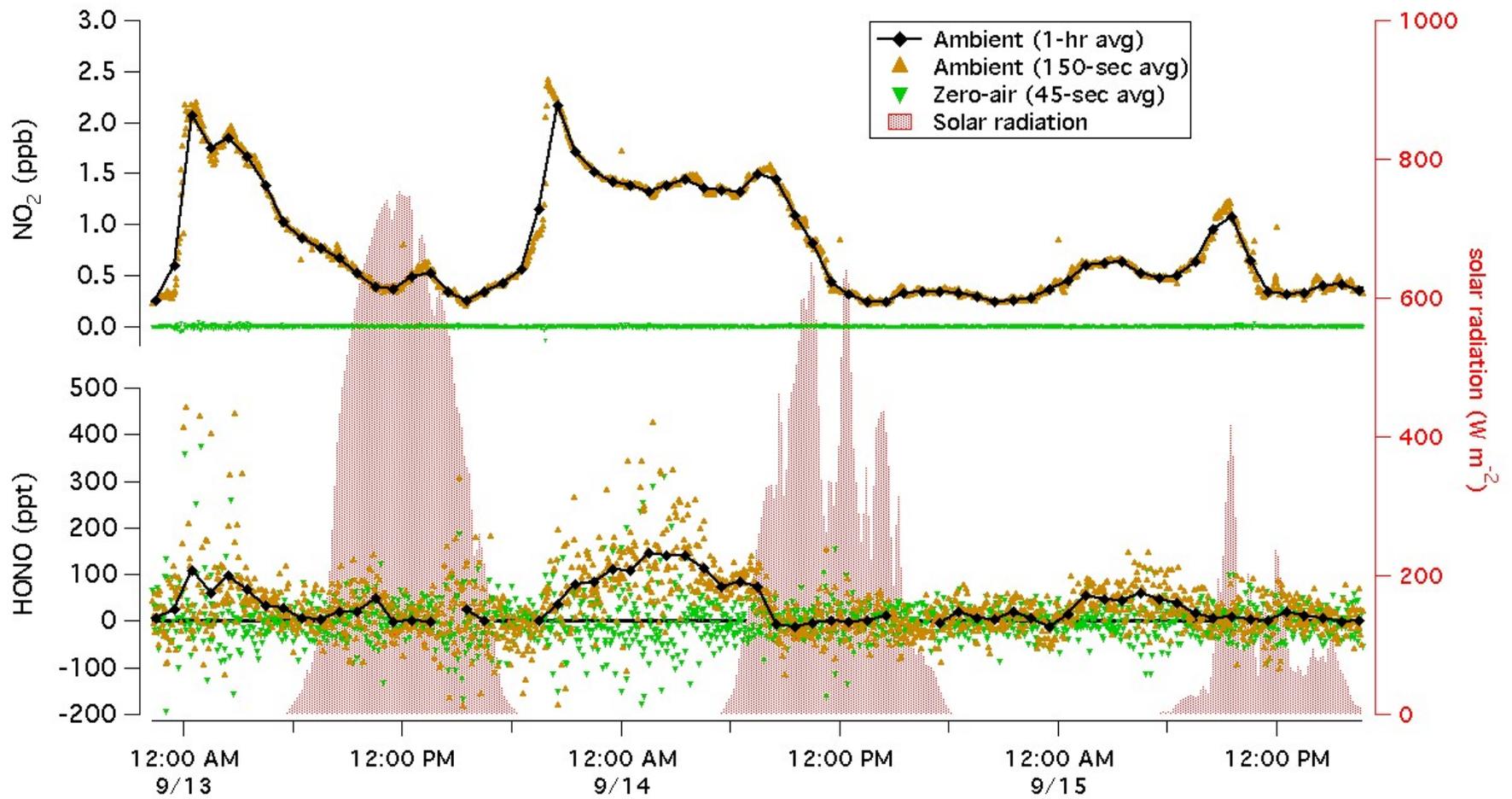
Spring



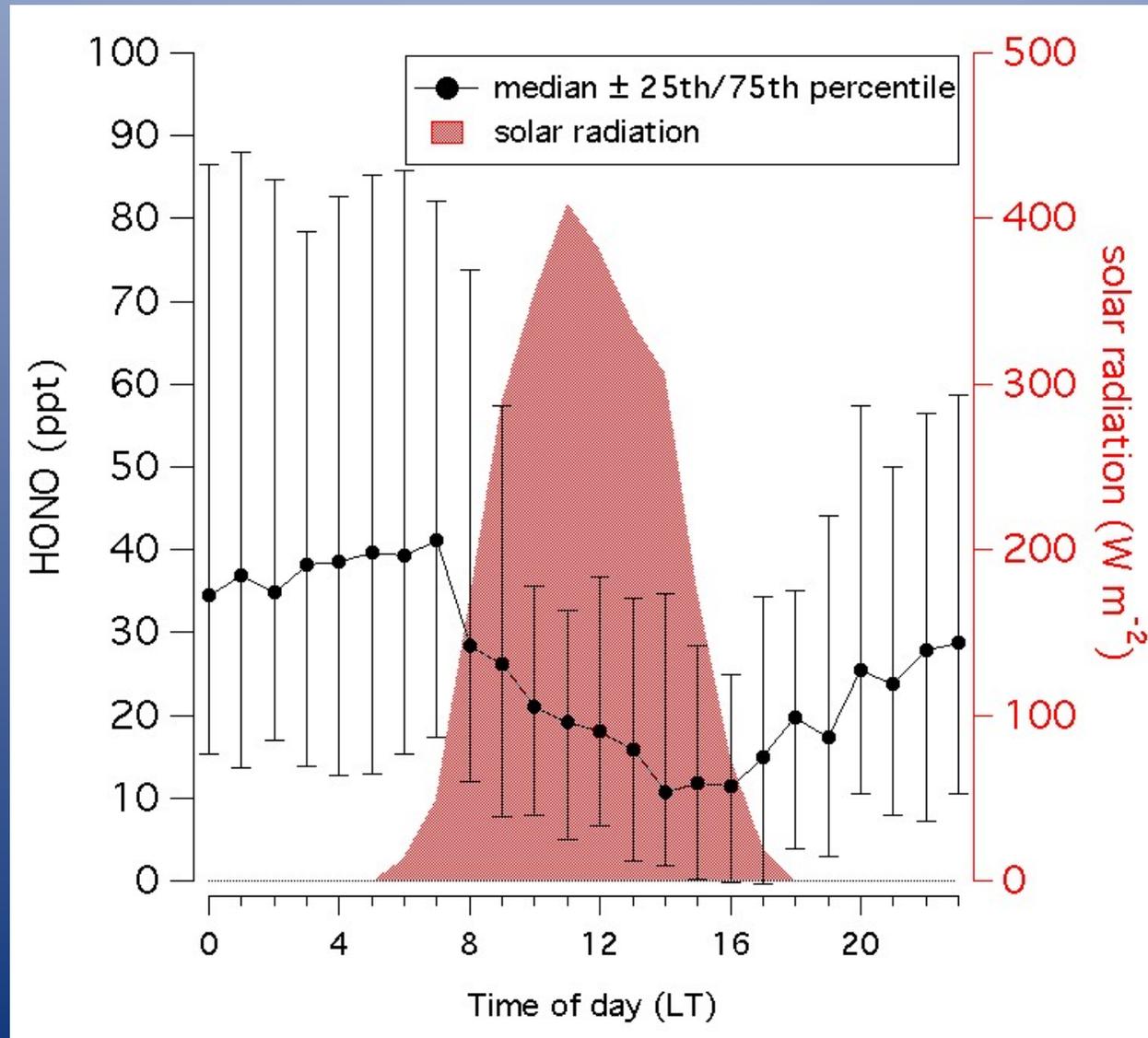
Summer



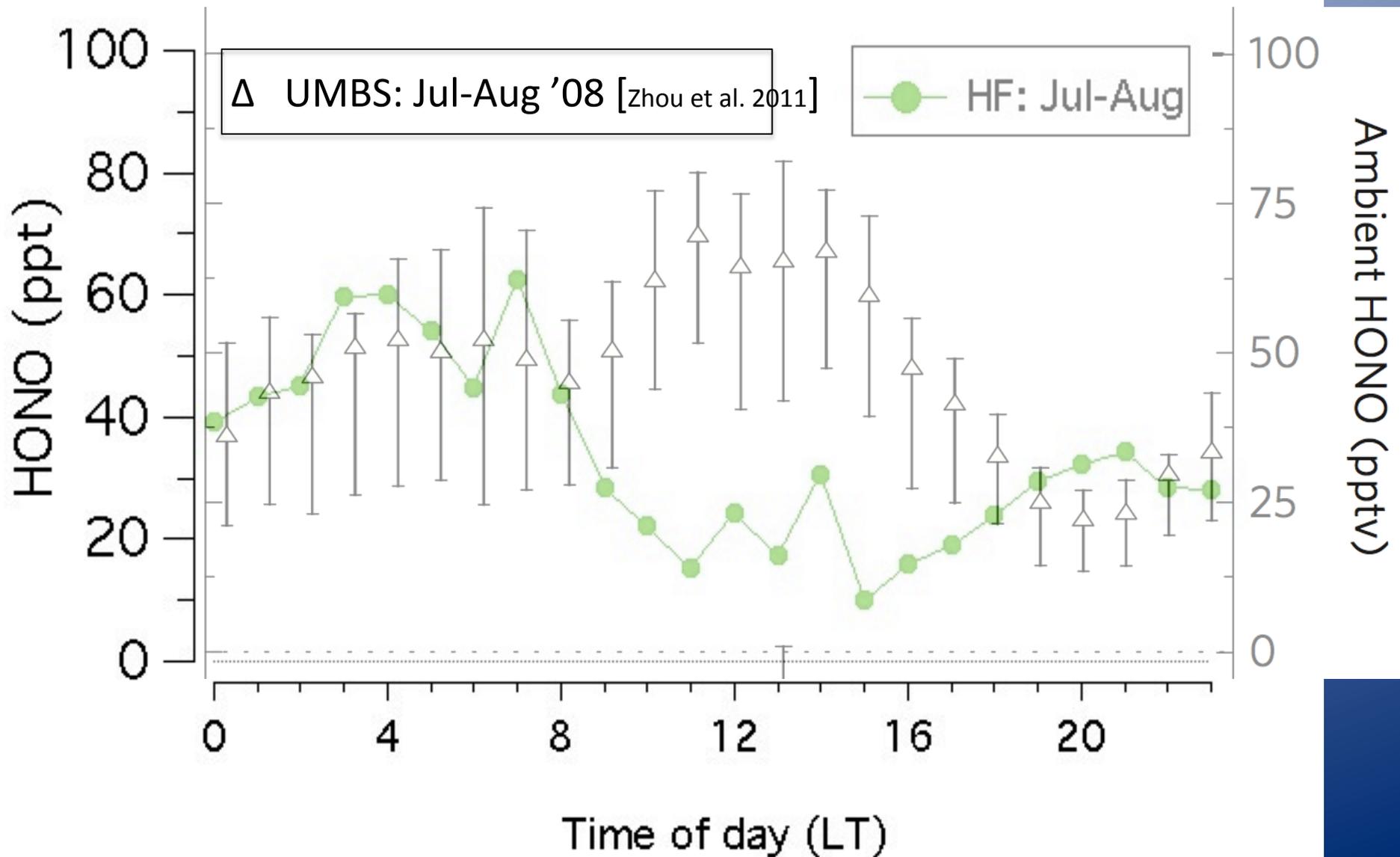
Autumn



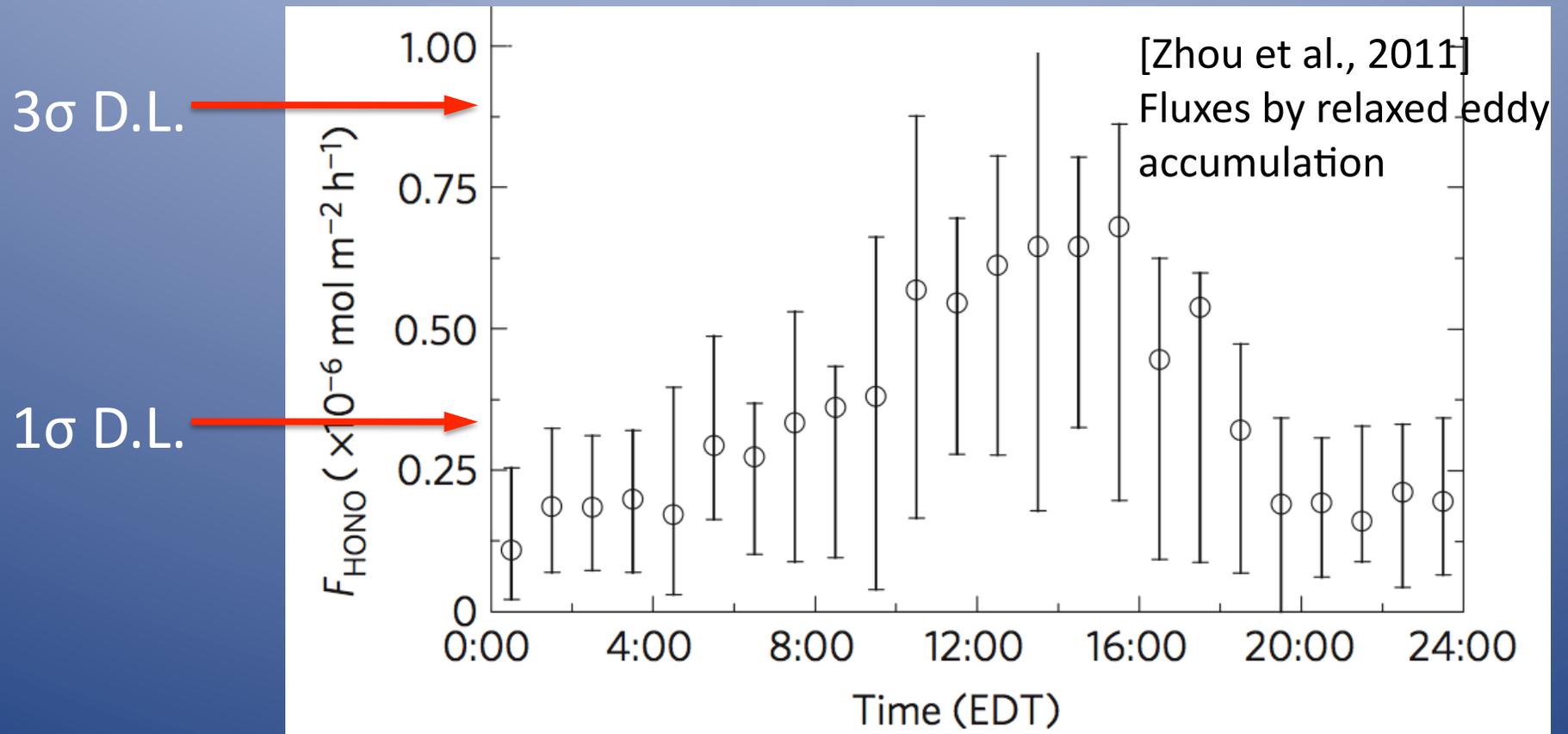
Harvard Forest (Dec '10 to Nov '11)



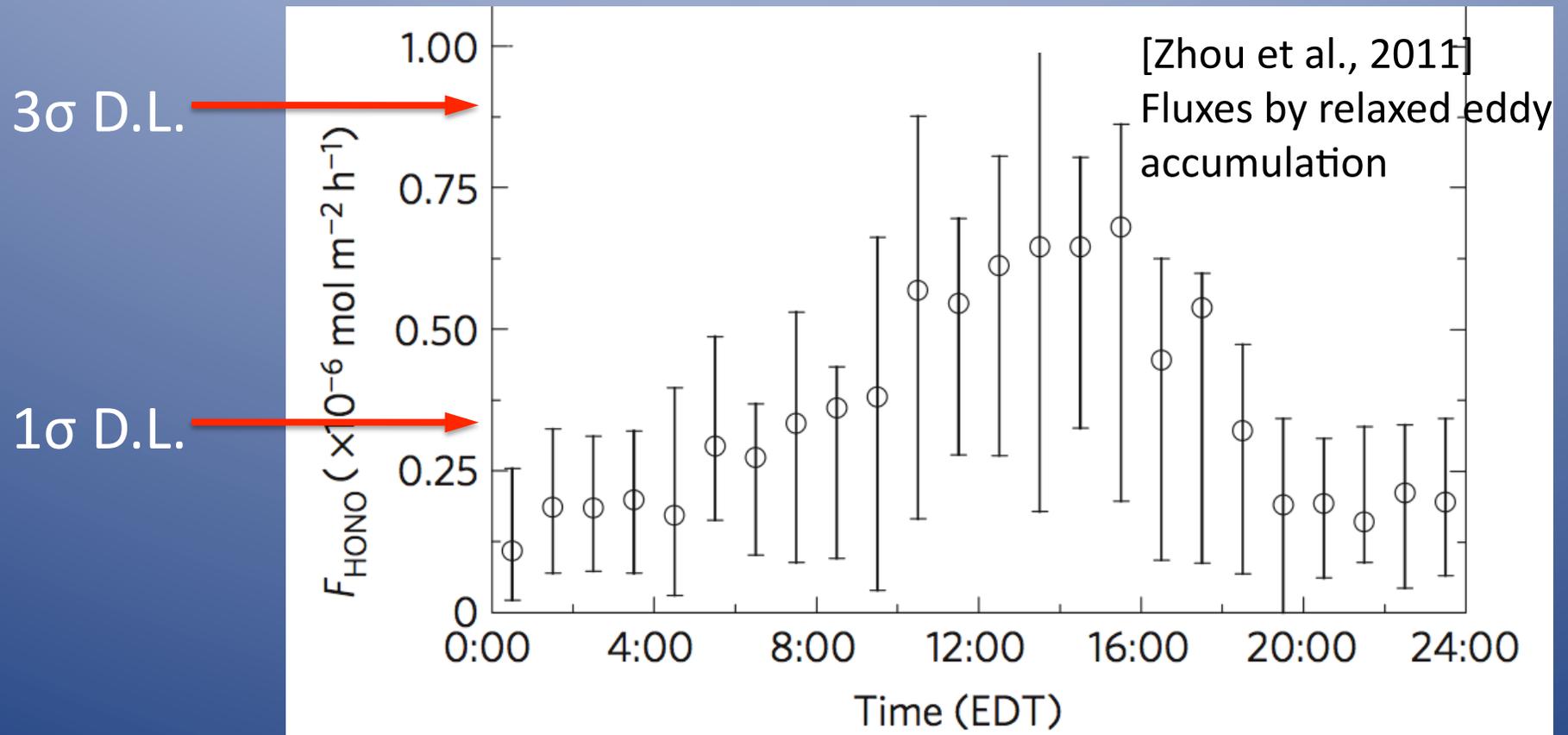
Comparison to previous measurements: mixing ratio



Comparison to previous measurements: fluxes



Comparison to previous measurements: fluxes



Previous rural studies infer daytime HONO flux ranging from 3.6×10^{-6} to $59 \times 10^{-6} \text{ mol m}^{-2} \text{ h}^{-1}$

[Ren et al., 2010; Acker et al., 2006; Kleffmann et al., 2005; Zhou et al., 2002]

Daytime result

Daytime HONO production at Harvard Forest
contributes negligibly to atmospheric HO_x and NO_x
budget over all seasons