Monitoring True NO2

Experience at Great Smoky Mountains with an LED Photolytic Converter

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Discussion Topics

- Site and station information
- Instrument design and layout
- Some data and comparisons
- Instrument assessments

View NW of Look Rock
Great Smoky Mountains NP

Monitoring Station

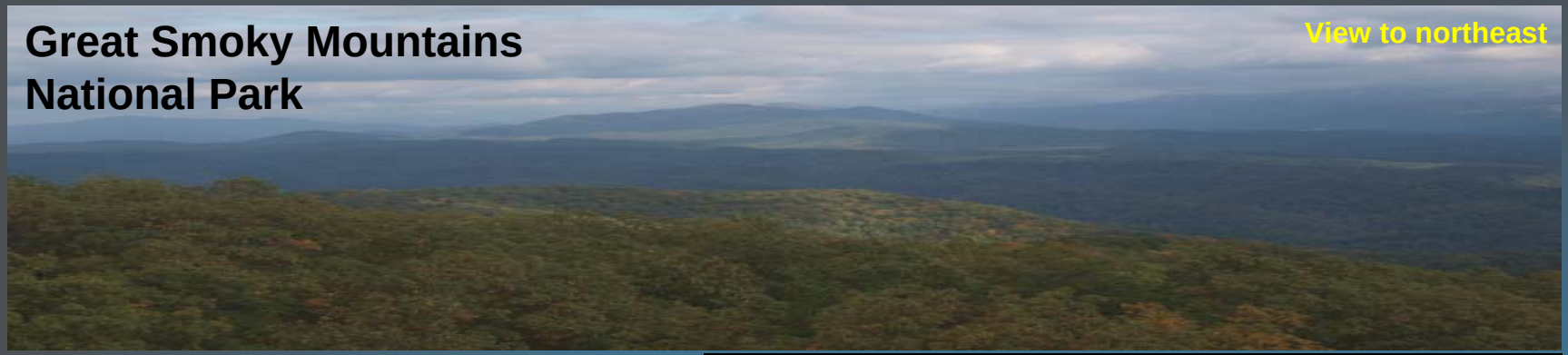
TN

NC

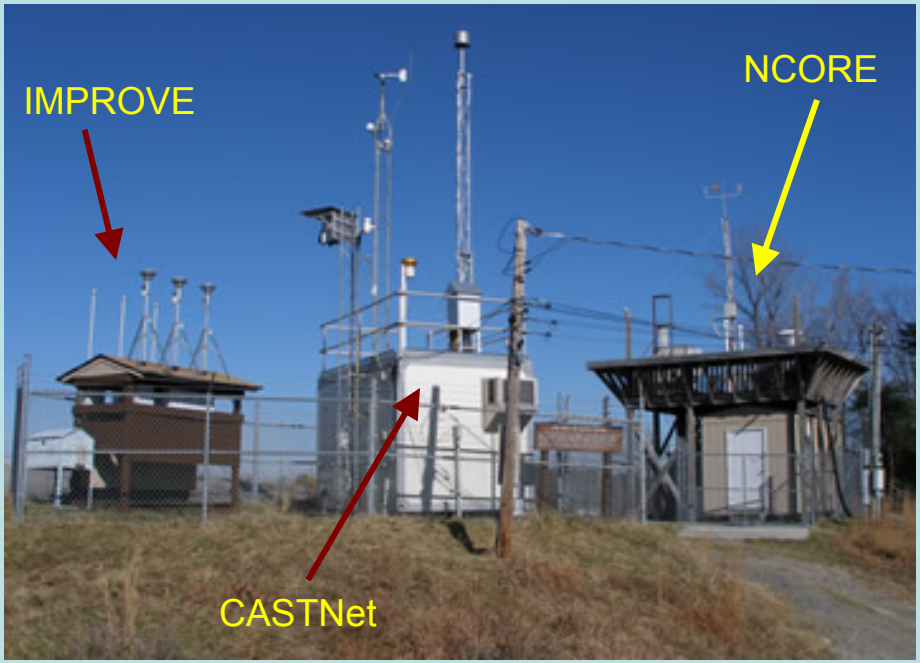
Look Rock

Great Smoky Mountains
National Park

Look Rock Monitoring Station



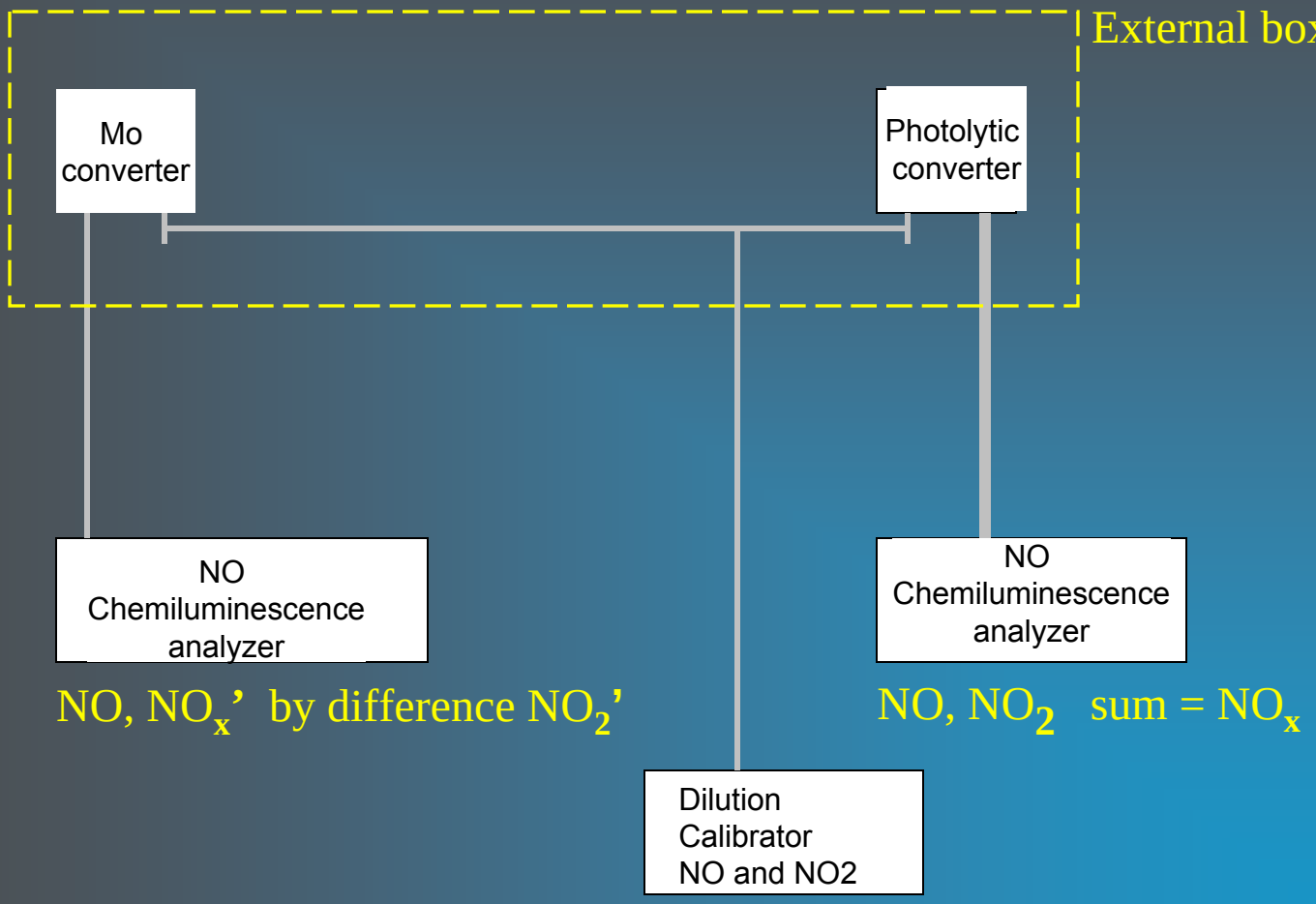
- NCORE: O3, NOy, NO, NO2, SO2, CO, PM2.5, SO4, BC
- CASTNet: filter pack, met
- IMPROVE: fine, course PM filter samples for visibility
- Web camera; nephelometer



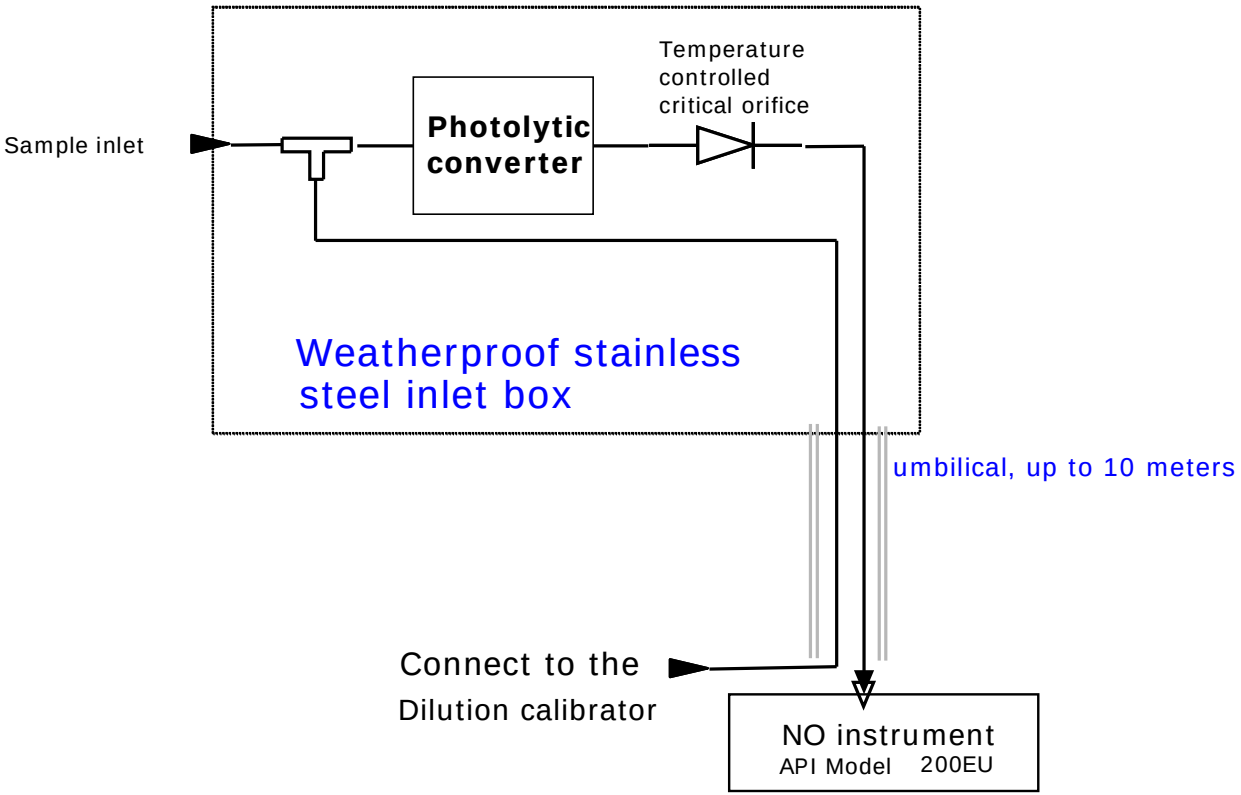
Understanding NO_2: Definitions

- $NO_y = \Sigma$ (NO + NO_2 + HNO_3 + organic nitrates + particulate nitrates + a few others)
- NO_y is the sum of oxidized reactive nitrogen
- NO_x = NO + NO_2 (idealized)
- $NO_z = NO_y - NO_x$

Nitrogen Oxide Measurements at Look Rock



Measurement of NO_2 using Photolysis



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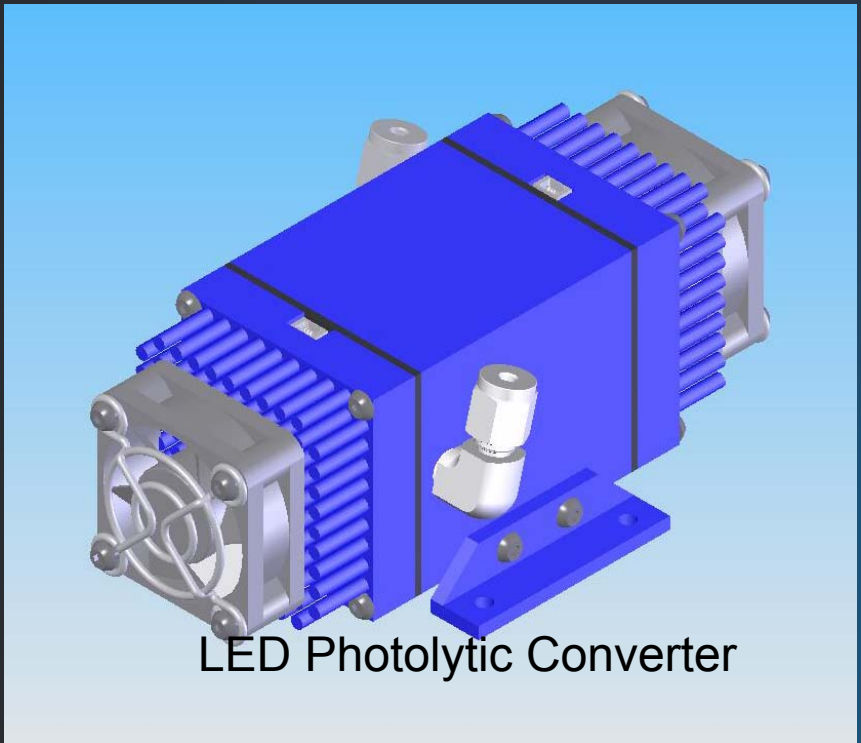
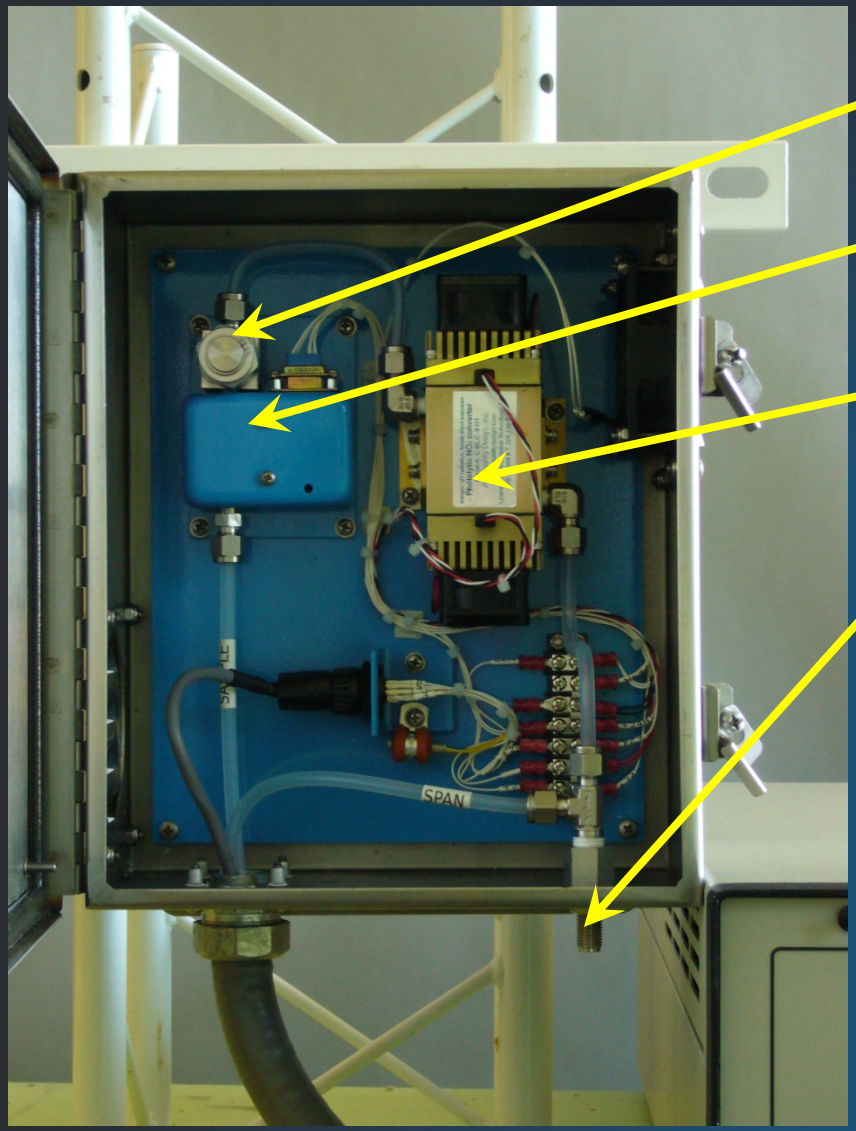

LED Photolytic Converter

- High efficiency (~50-60% NO_2 conversion)
- Highly specific for NO_2
- Negligible radiant heating of the sample gas
- Long light-source life (estimated >5,000 hours)
- Power consumption: 30 W
- Converter size: 5 cm (w) x 5 cm (h) x 15 cm (l)

Inside the External Converter Box



Particle filter

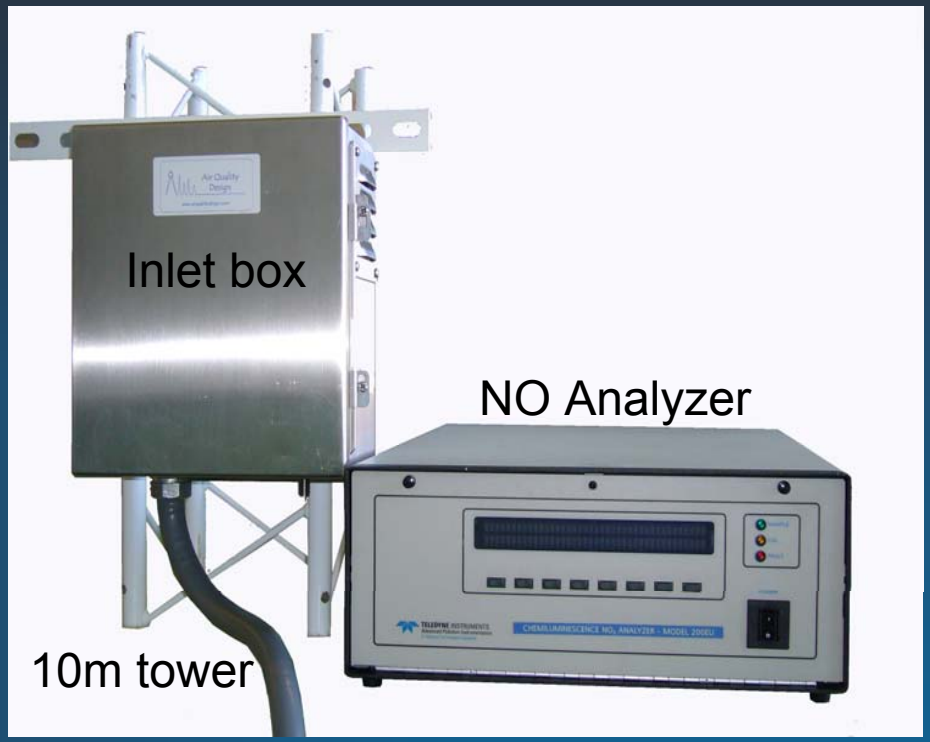
Temperature controlled flow orifice

NO_2 converter

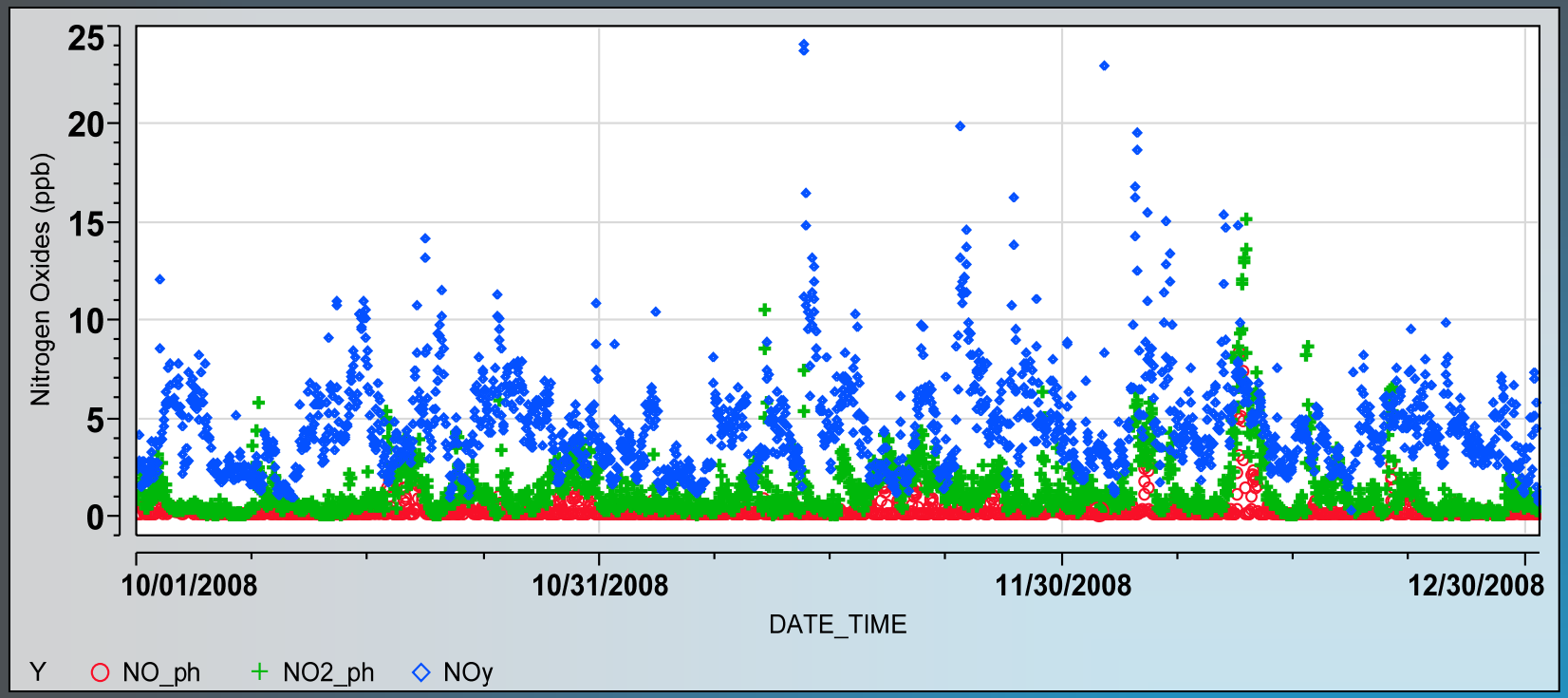
Sample inlet

Implementation of NO_2 Analyzer

- Implementation works best with the converter located at the sample inlet.
- Possible to locate the converter within the NO monitor, but must minimize the residence time of the ambient sample

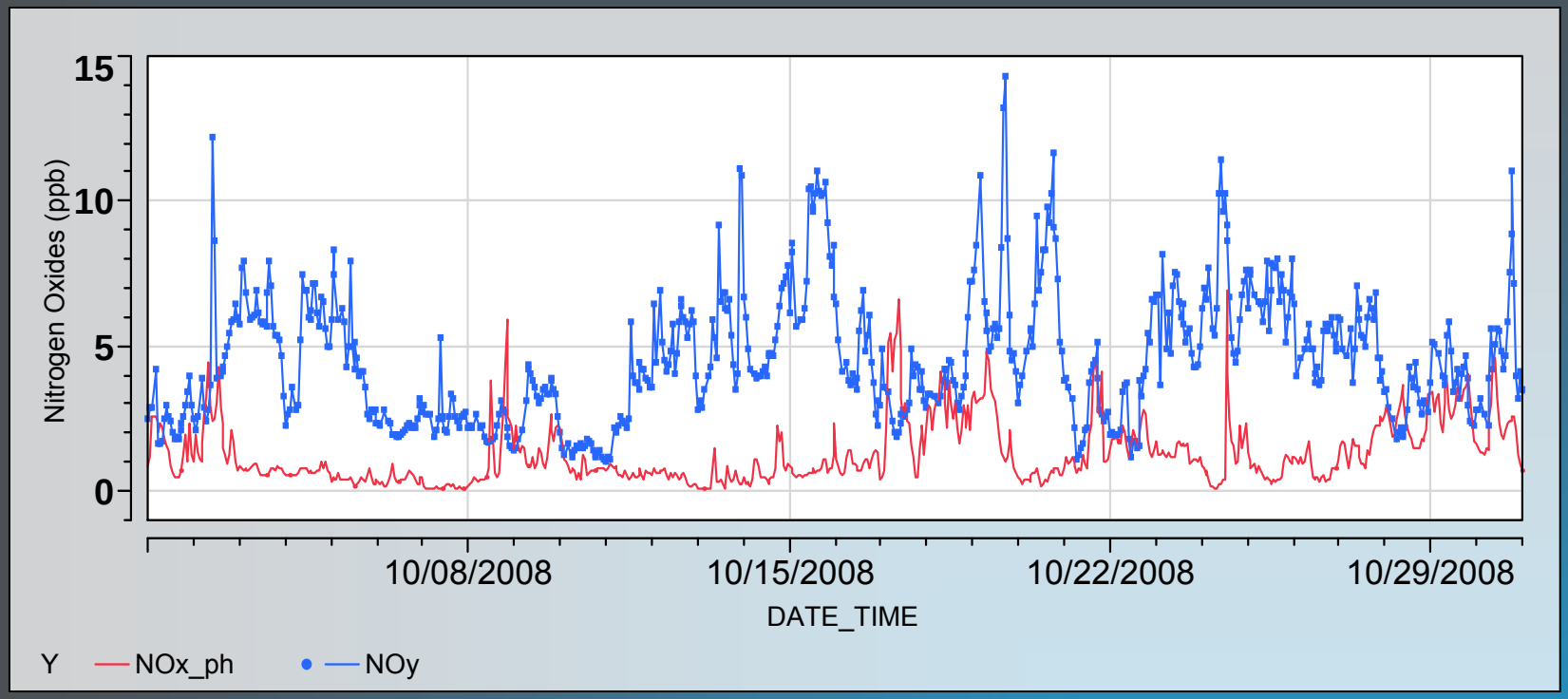


Nitrogen Oxides for Oct. to Dec. 2008



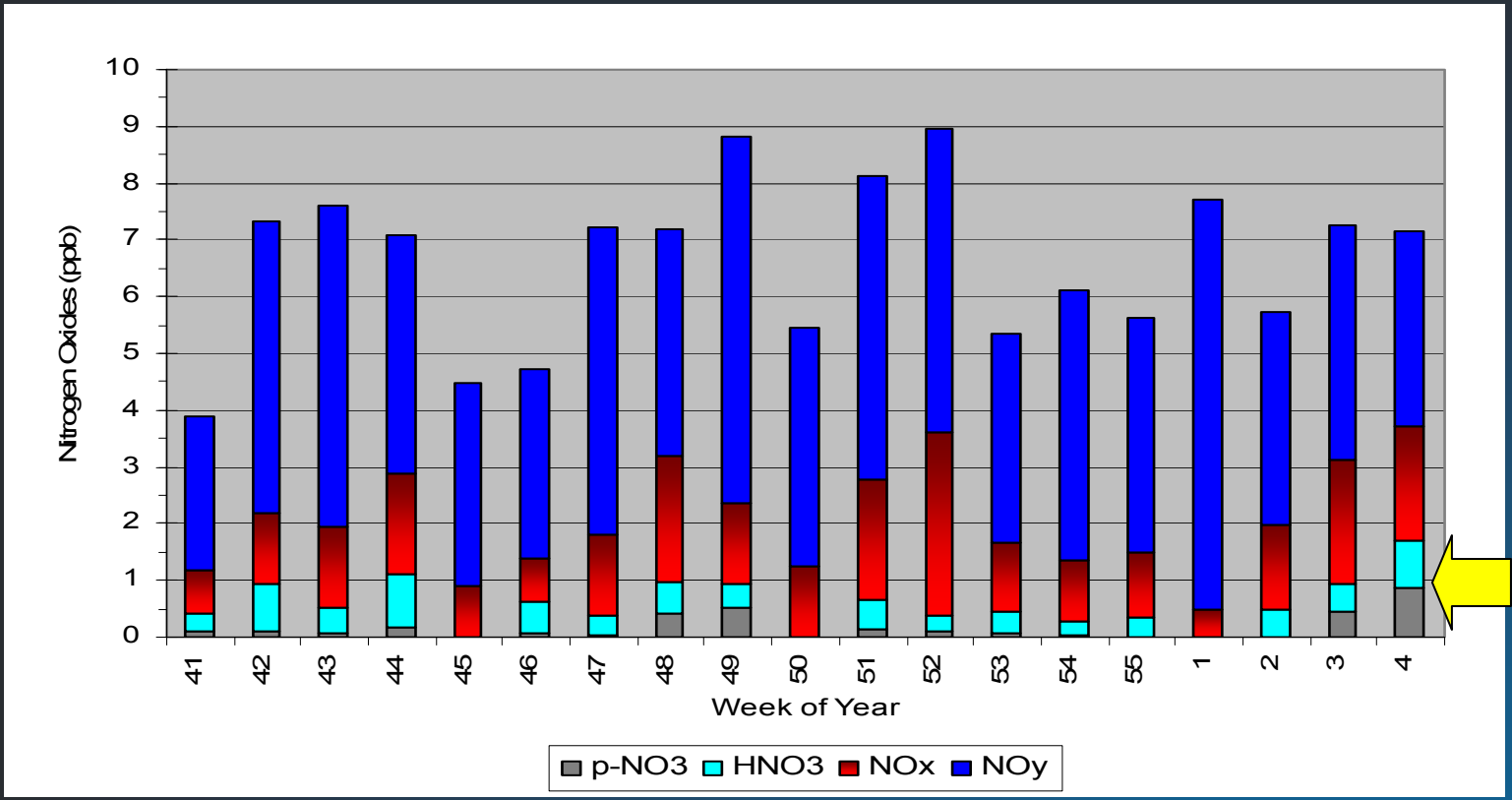
- Data generally as expected. $NO_y > NO_2 > NO$
- Couple problem areas observed.
- Difference between NO_y and NO_2 is variable.

Compare NOy and NOx for Oct. 2008



- NO_x represents “fresh” emissions. Photochem active.
- NO_y – NO_x (called NO_z) is “aged” oxidized species

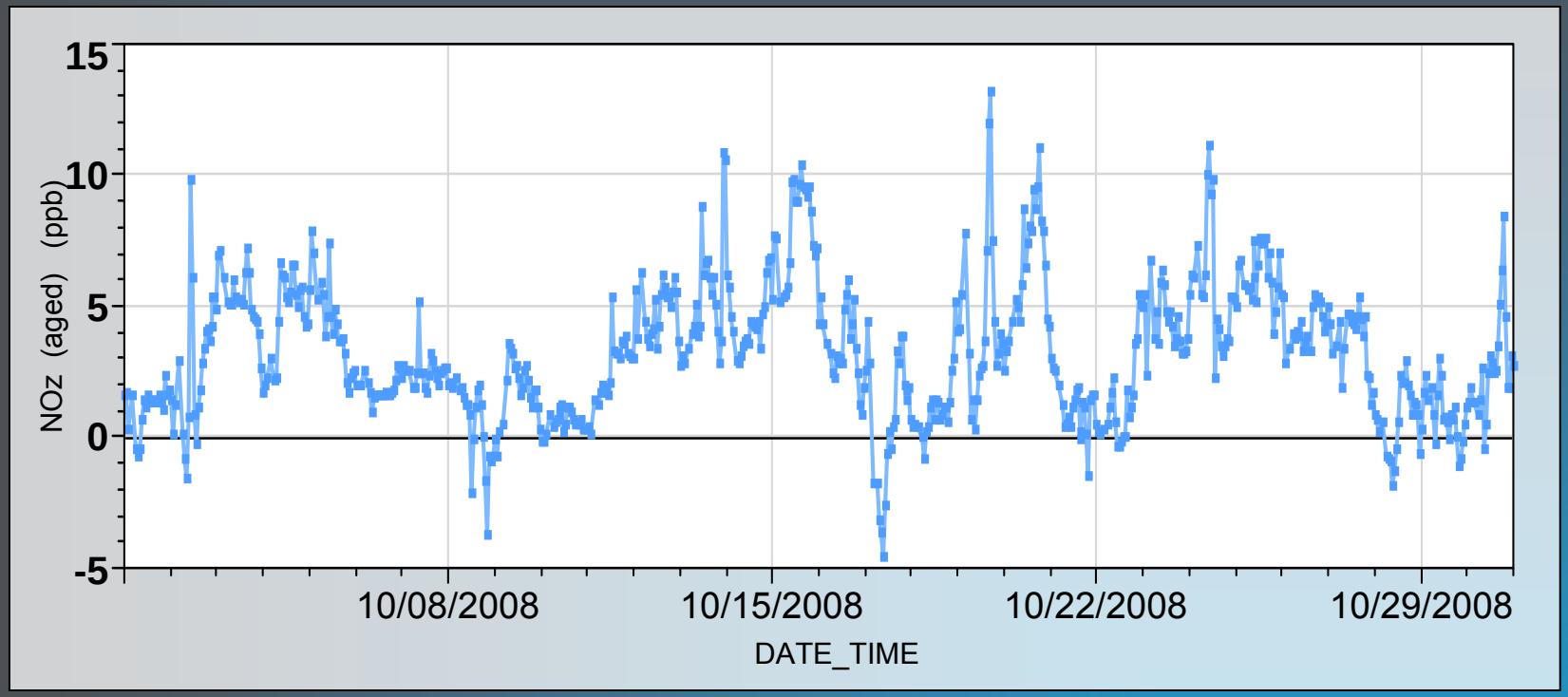
Component Fractions of NOy



Over period Oct. 2008 to Jan. 2009: Mean component % of NOy

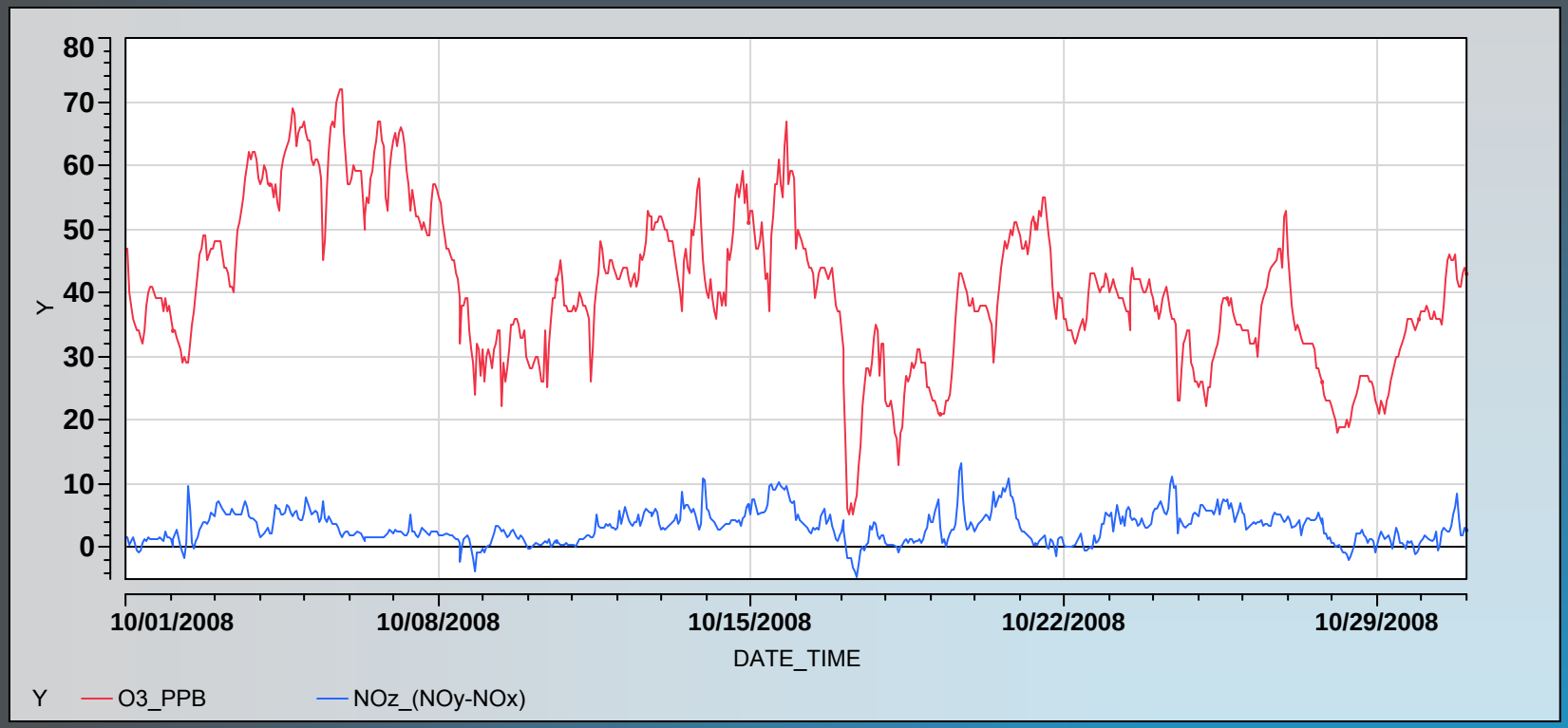
NOx	34%		
HNO3	12%	NOy of other	49%
p-NO3	5%		

Aged Nitrogen Oxides for Oct. 2008



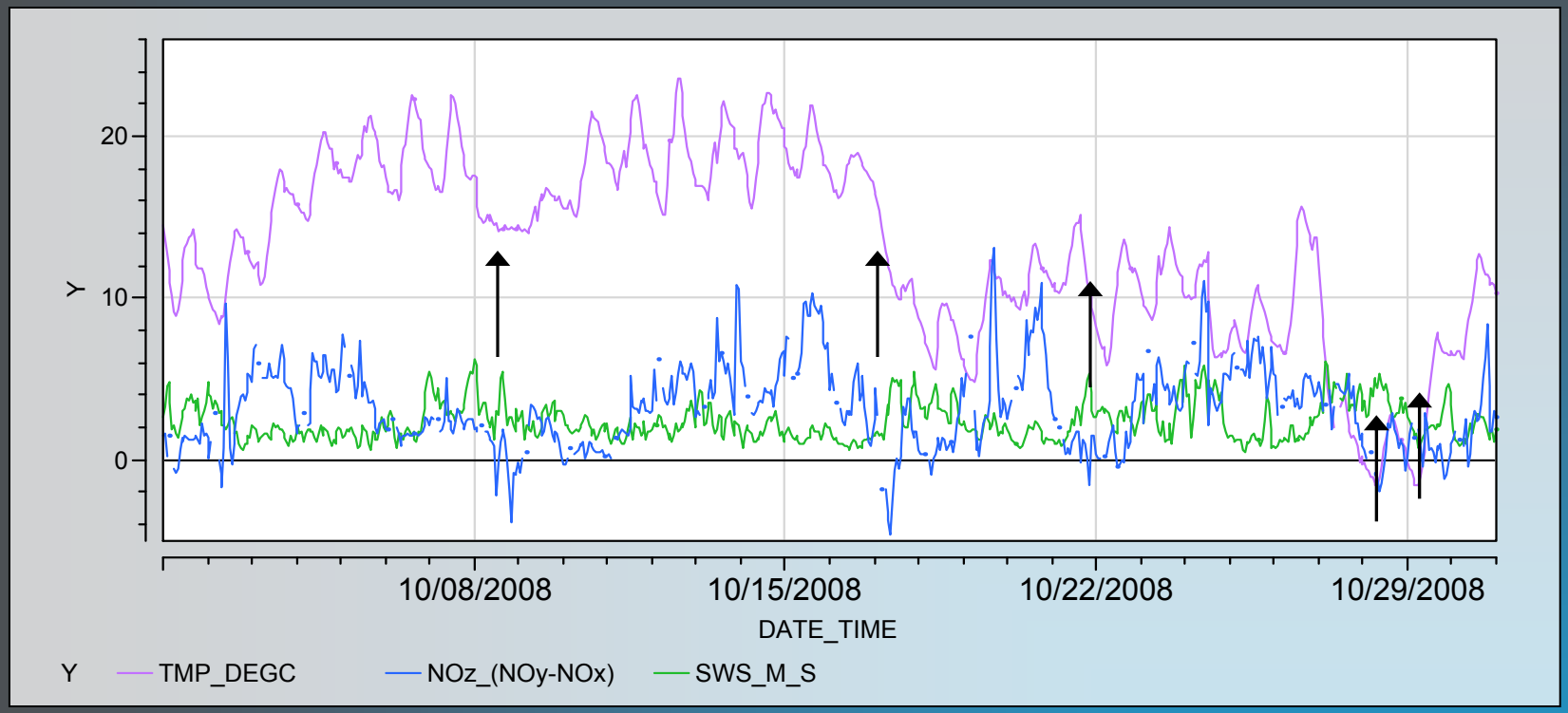
- At Look Rock, most of the NOy is aged
- NOz is episodic; events lasting several days.
- Negative NOz a problem. Instrument balance?

Ozone and NOz for Oct. 2008



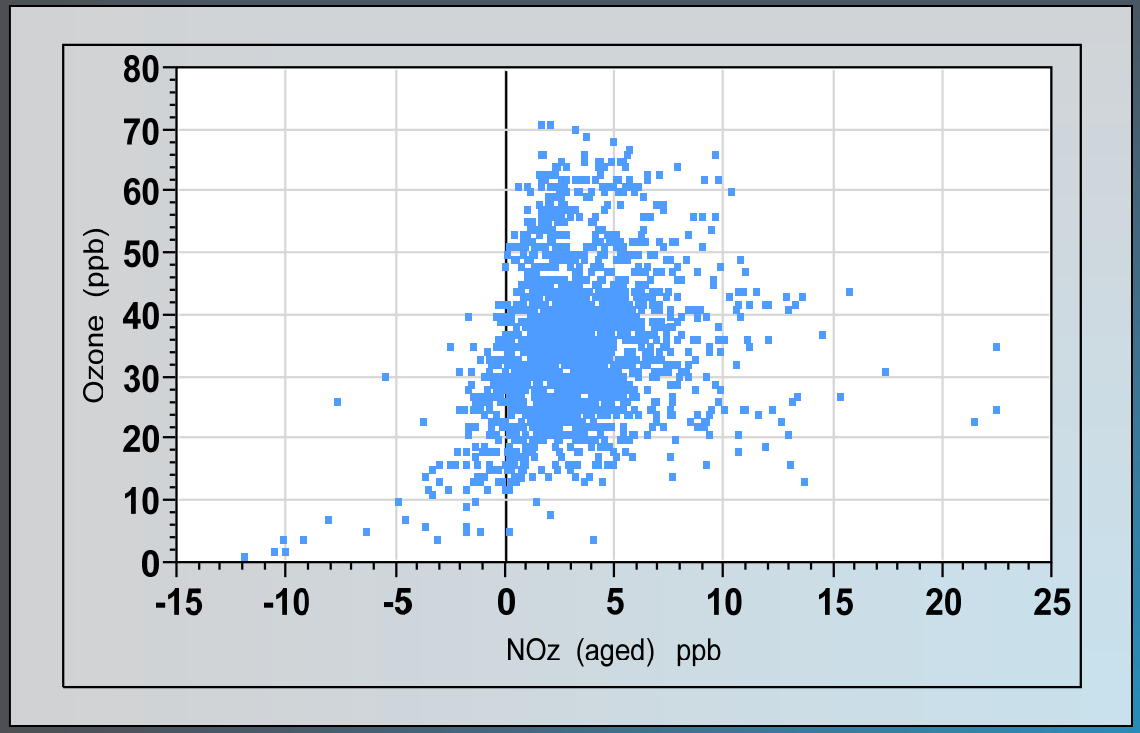
- Ozone and NOz follow synoptic weather

Weather Data for Oct. 2008



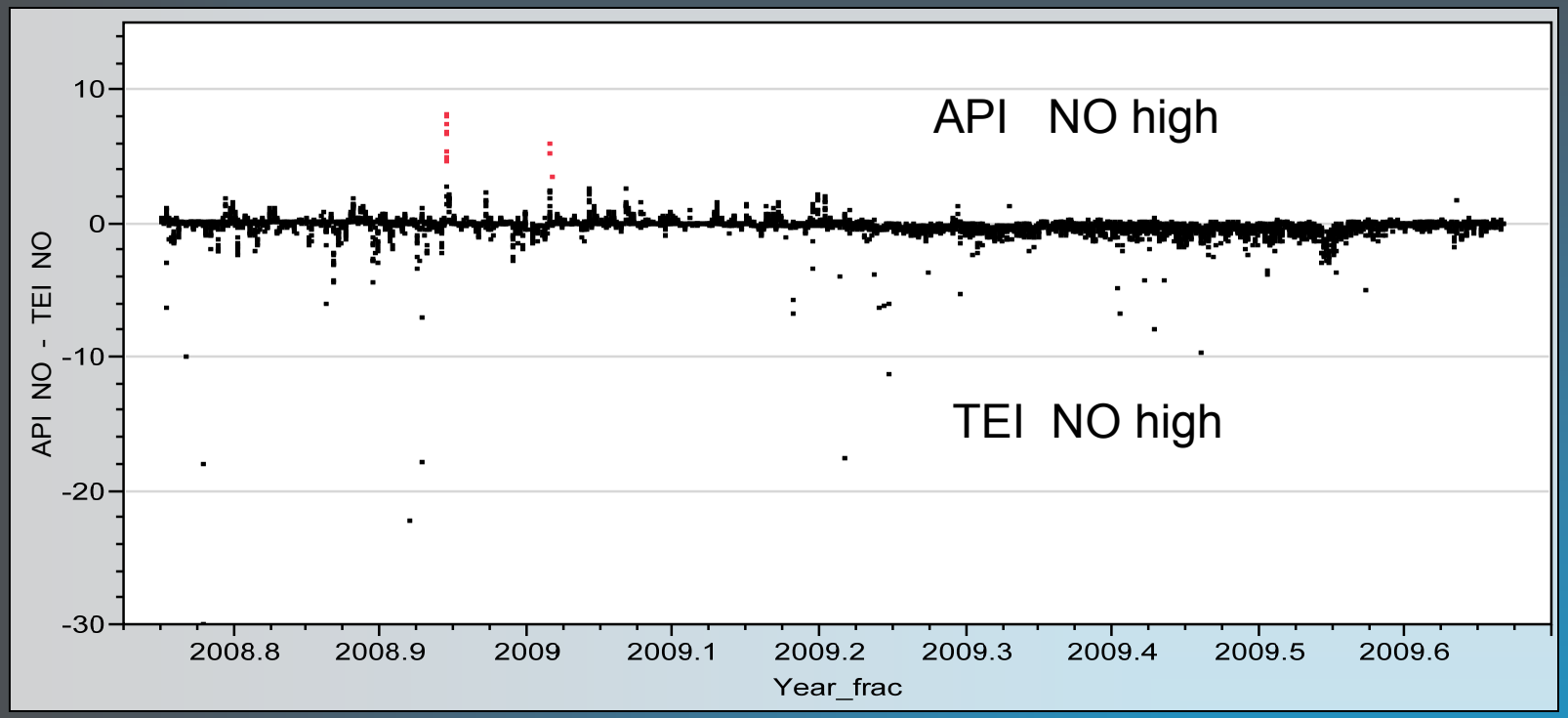
- Incorrect NOz happens during rapid changes of synoptic weather

Ozone to NOz Relationship for Oct. 2008



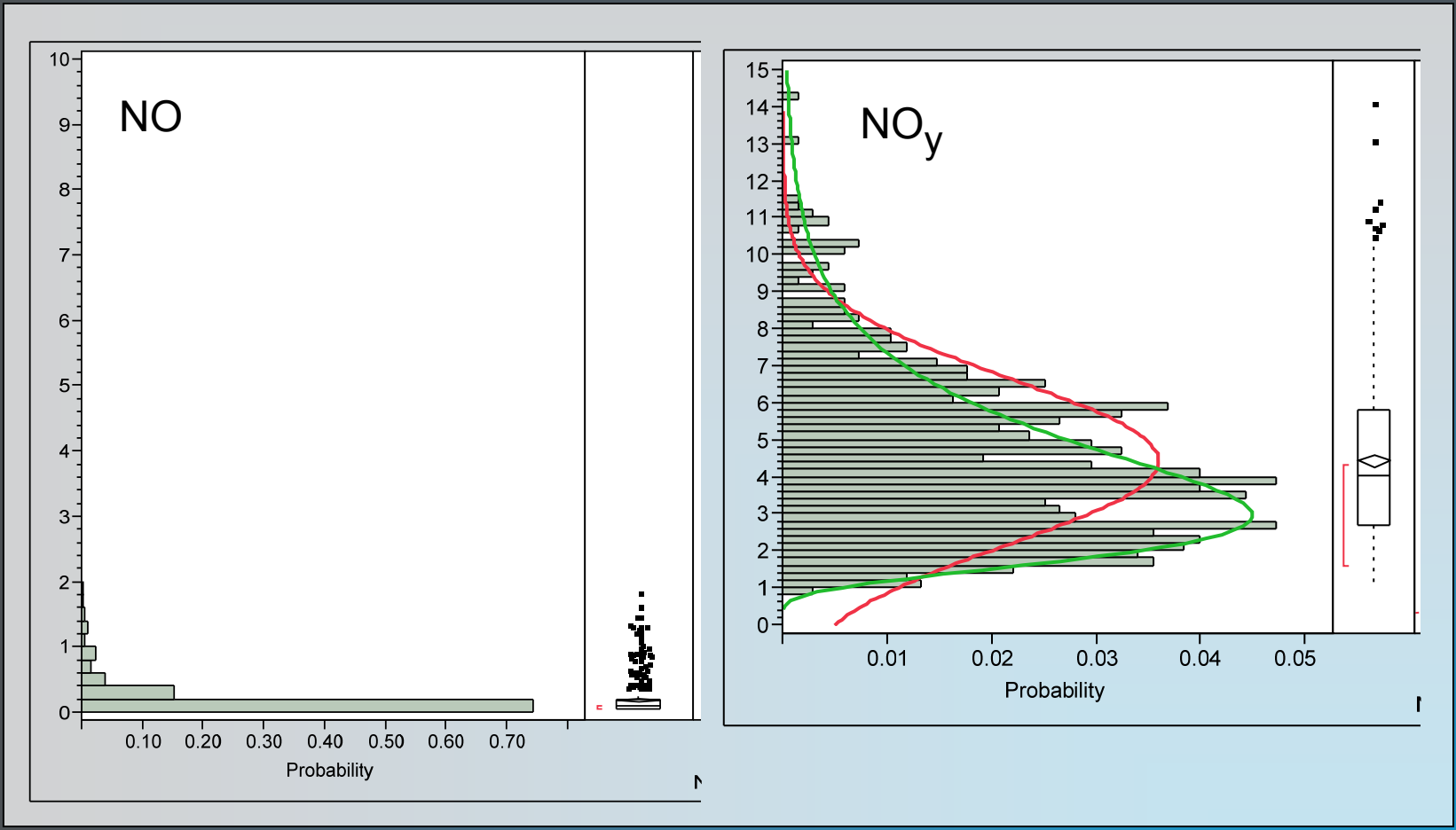
- Weak ozone production from aged NOz air masses
- Incorrect NOz < 0 only when ozone low

Sample Data for Oct.2008 to Aug. 2009



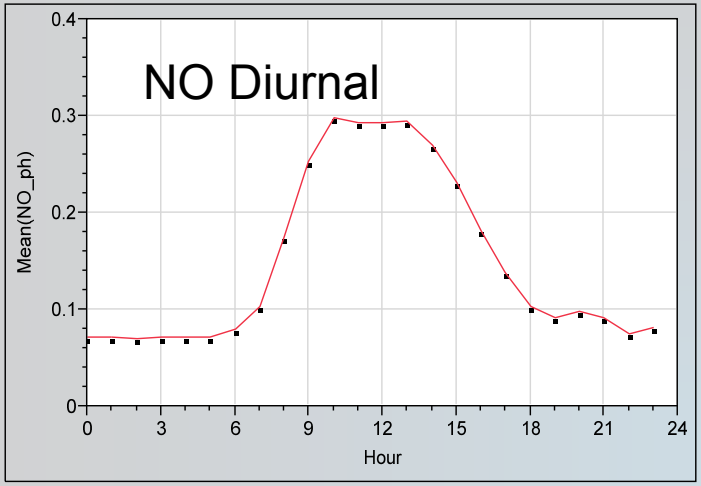
- Agreement in NO is not perfect between analyzers
- Instrument balance, calibrations, validation important

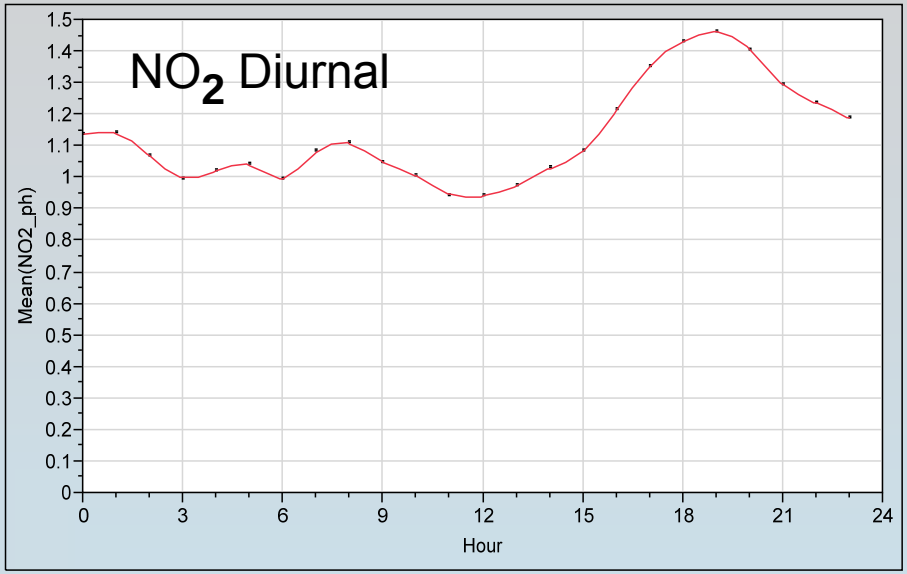
Frequency Distributions of NO and NOy

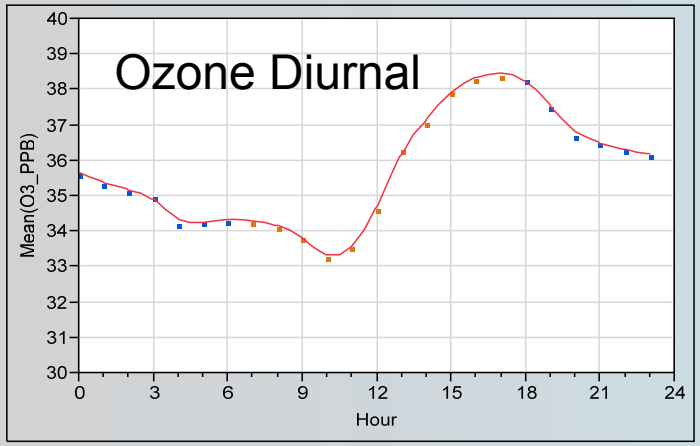


- NO and NO_x are nearly lognormal
- NO_y somewhere between normal and lognormal

Diurnal Patterns for Oct. 2008

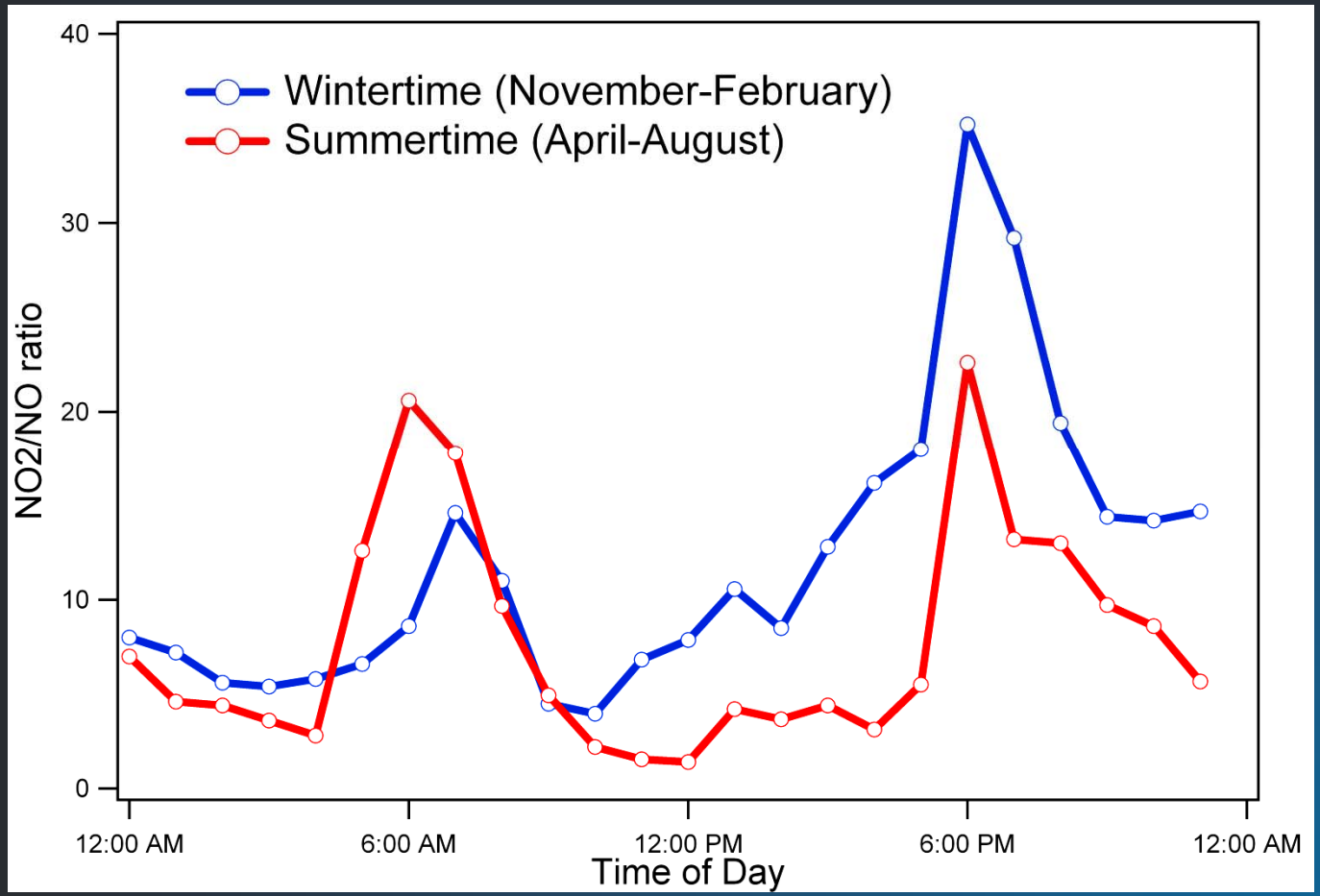






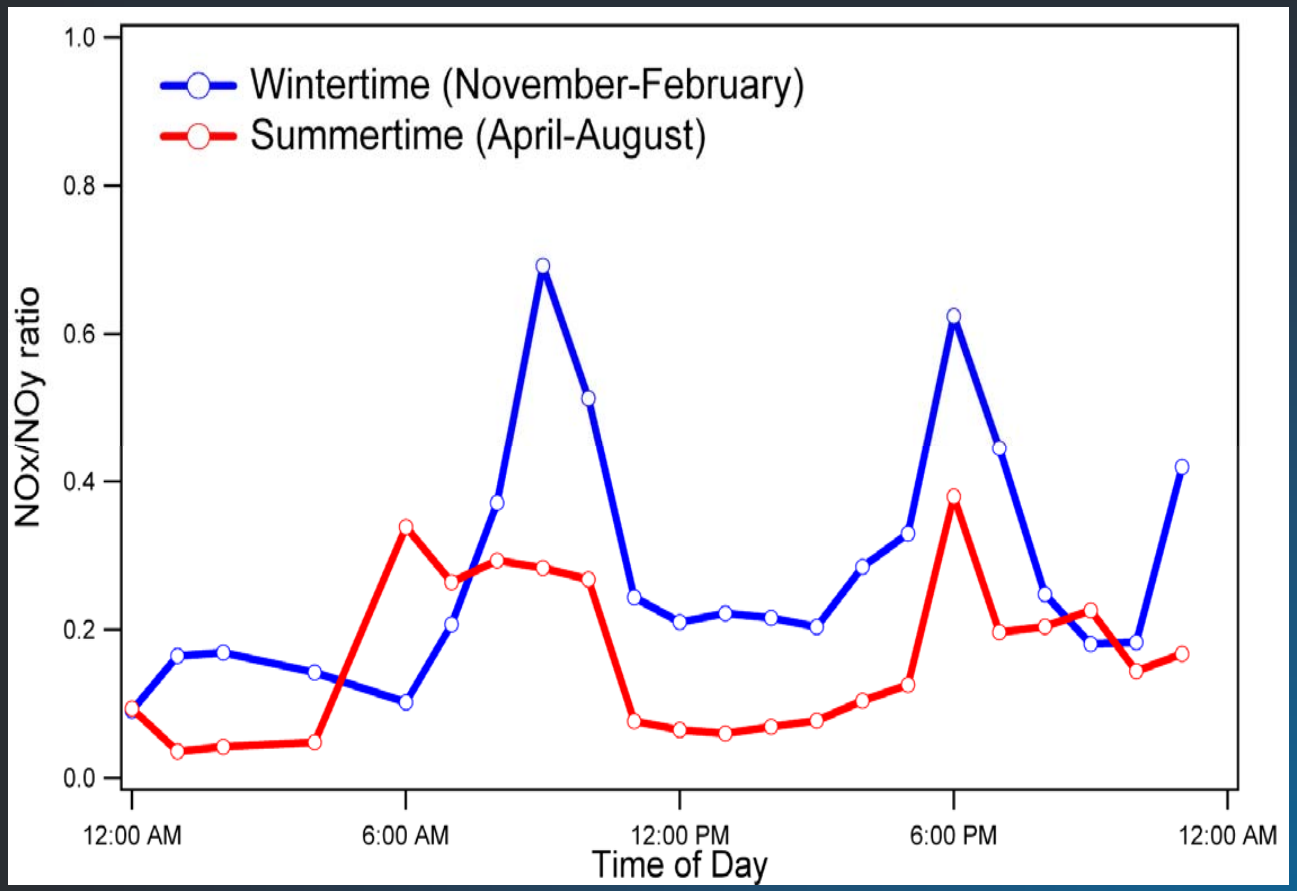
- Ozone and NO peak at different times
- NO_2 and ozone peak in evening

Photochem NO_2/NO Diurnal Patterns



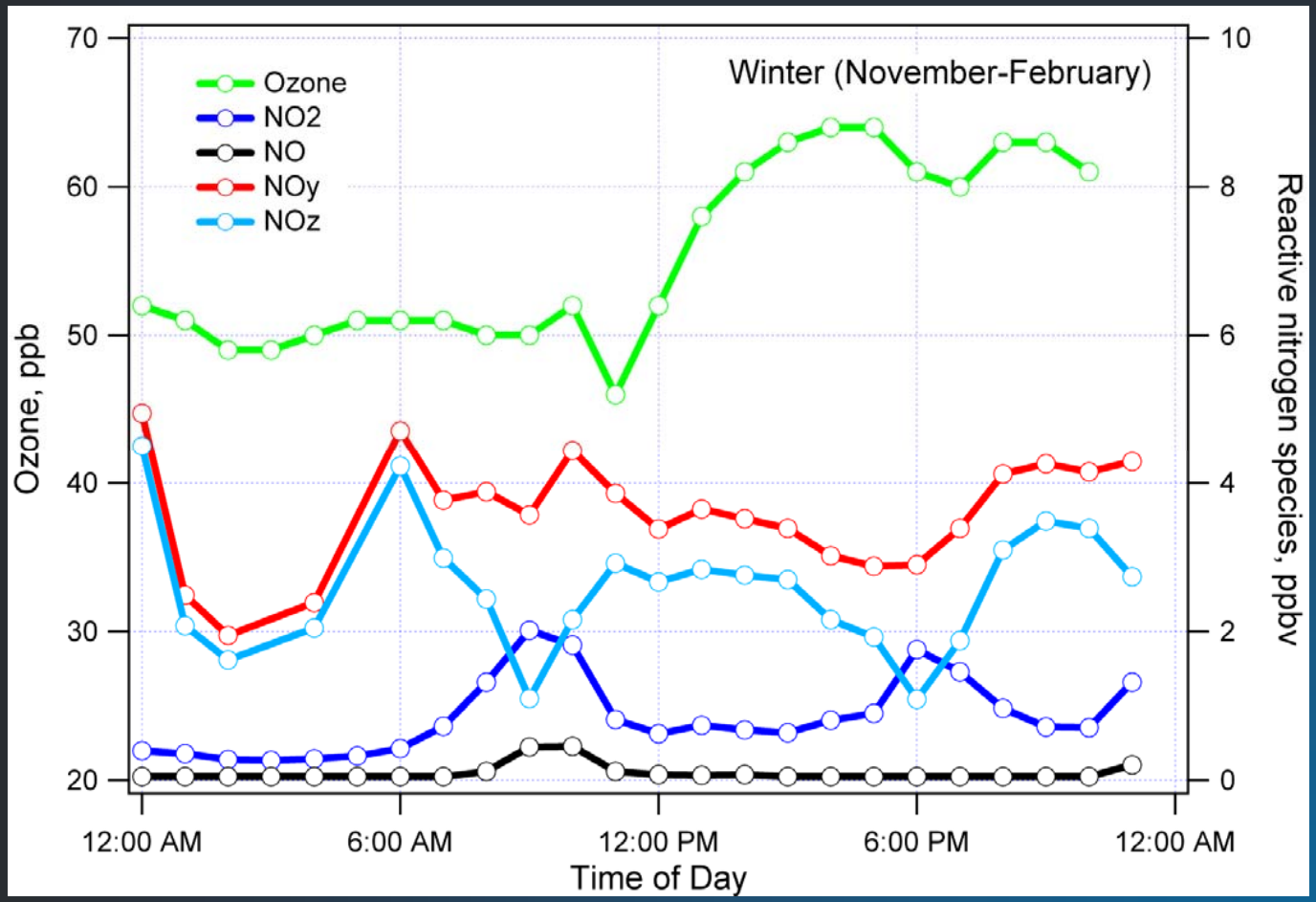
- Winter NO_2/NO ratio shows a daytime minimum of about 5
- Summer NO_2/NO ratio shows a daytime minimum of about 2, consistent with greater solar insolation and photochem.

Diurnal NOx Fraction of NOy



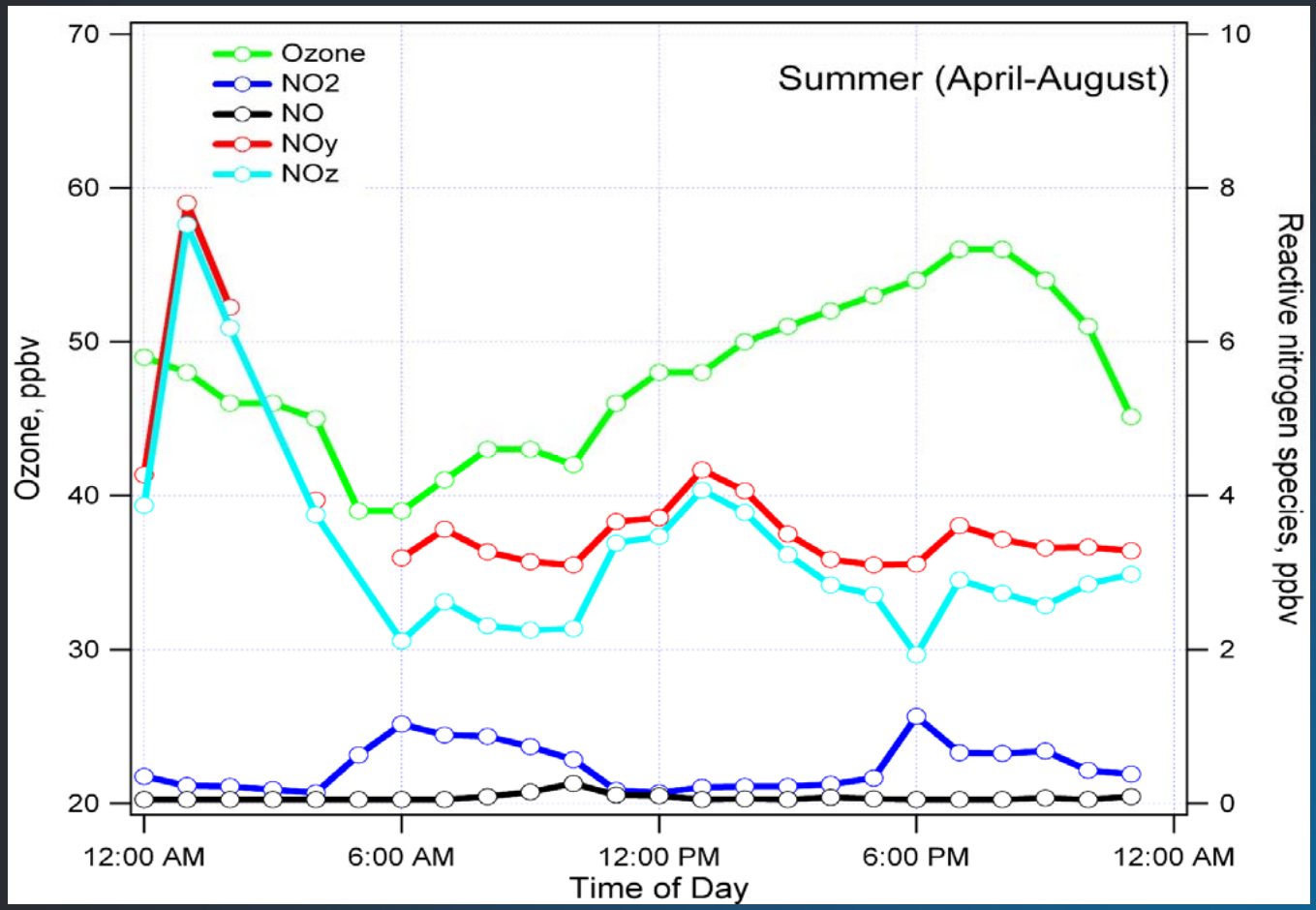
- Winter ratio shows a daytime minimum of about 30%
- Summer ratio shows a daytime minimum of about 10%
- In both seasons, the daytime air masses are photochemically aged, with very aged air masses observed in the summer

Winter 2008-2009 Diurnal Patterns



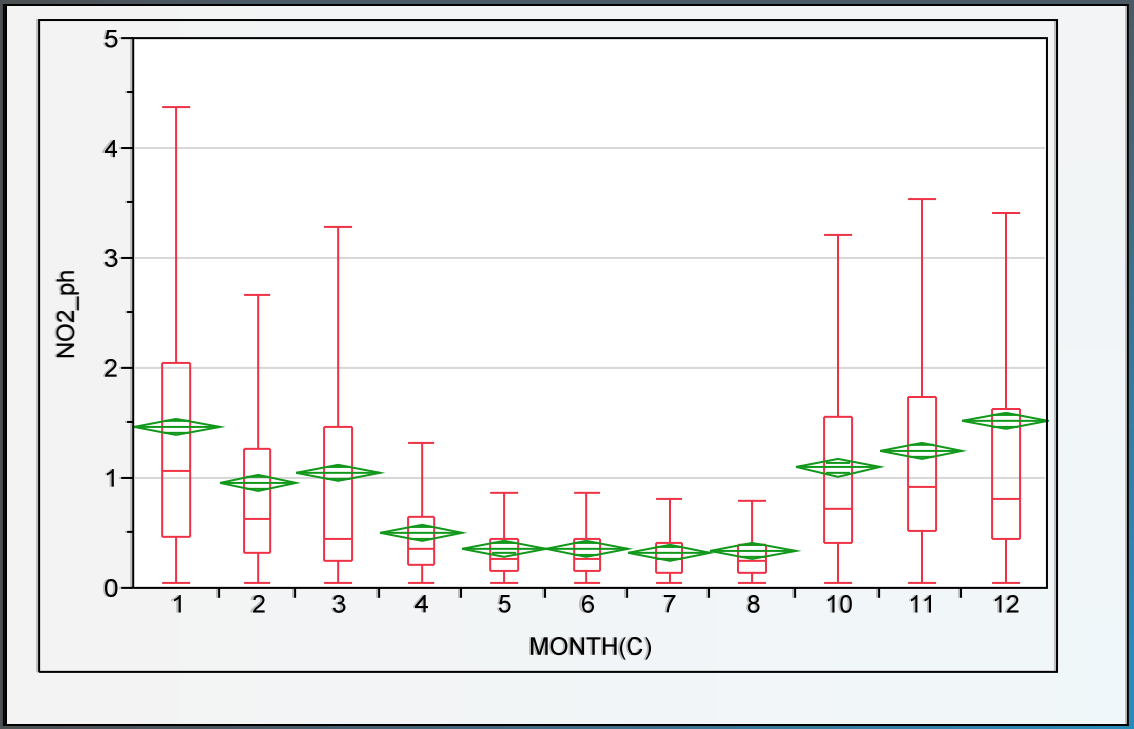
- Variation probably dominated by dynamic effects; some photochemistry.

Summer 2009 Diurnal Patterns



• Local ozone photochem production observed near solar noon, superimposed on a stronger transported ozone signal

Seasonal Variation in NO_2



- NO_2 concentrations are seasonal
- Dependent on solar radiation

Summary

- Photolytic NO_2 measurements greatly enhance the diagnostic strength of the data set.
- Observed NO_2/NO ratios are consistent with our understanding of photochemistry; should serve as a good diagnostic for modeling efforts.
- Summertime observations suggest that at least a portion of the observed ozone is produced locally.
- Attention required to balance the independent systems.