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
Look Rock Monitoring Station

Great Smoky Mountains National Park

- **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

- $\text{NO}_y = \sum (\text{NO} + \text{NO}_2 + \text{HNO}_3 + \text{organic nitrates} + \text{particulate nitrates} + \text{a few others})$

- $\text{NO}_y$ is the sum of oxidized reactive nitrogen

- $\text{NO}_x = \text{NO} + \text{NO}_2$ (idealized)

- $\text{NO}_z = \text{NO}_y - \text{NO}_x$
Nitrogen Oxide Measurements at Look Rock

- Mo converter
- Photolytic converter
- NO Chemiluminescence analyzer
- Dilution Calibrator NO and NO2
- TEI NOy Analyzer
- API NO2 Analyzer

NO, NOx' by difference NO2'

NO, NO2 sum = NOx
Measurement of NO₂ using Photolysis

Sample inlet

Photolytic converter

Temperature controlled critical orifice

Weatherproof stainless steel inlet box

umbilical, up to 10 meters

Connect to the Dilution calibrator

NO instrument
API Model 200EU
Measurement of NO\textsubscript{2} using photolysis

- High efficiency (~50-60\% NO\textsubscript{2} conversion)
- High specificity for NO\textsubscript{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 NO₂ 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. \( \text{NO}_y > \text{NO}_2 > \text{NO} \)
- Couple problem areas observed.
- Difference between \( \text{NO}_y \) and \( \text{NO}_2 \) is variable.
Compare NO\textsubscript{y} and NO\textsubscript{x} for Oct. 2008

- NO\textsubscript{x} represents “fresh” emissions. Photochem active.
- NO\textsubscript{y} – NO\textsubscript{x} (called NO\textsubscript{z}) is “aged” oxidized species
Over period Oct. 2008 to Jan. 2009: Mean component % of NOy

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

![Graph showing weather data for Oct. 2008 with arrows indicating peaks and dips in data]

- Incorrect NOz happens during rapid changes of synoptic weather
• Weak ozone production from aged NOz air masses

• Incorrect NOz < 0 only when ozone low

- Agreement in NO is not perfect between analyzers
- Instrument balance, calibrations, validation important
Frequency Distributions of NO and NO\textsubscript{y}

- NO and NO\textsubscript{x} are nearly lognormal
- NO\textsubscript{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
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.
• 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.
• 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 NO₂ measurements greatly enhance the diagnostic strength of the data set.

- Observed NO₂/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.