Participants and Measurement Methods

EPA /Contractor Participants
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Measurement Methods
• Ozone (O₃)
  • Teledyne-API T265 (U.S. EPA FEM) – NO chemiluminescence
  • Ecotech EC9810 (U.S. EPA FEM) – UV photometric – data provided by MDE
• Nitrogen Dioxide (NO₂)
  • Thermo 42C (U.S. EPA FRM) – HB conversion → O₃ chemiluminescence
  • Teledyne-API 200EUP – Photolytic conversion → O₃ chemiluminescence
• Total Reactive Oxides of Nitrogen (NOₙ)
  • Thermo 42iy – HB conversion (external 10m) → O₃ chemiluminescence
  • Ecotech EC9843 – HB conversion (external 10m) → O₃ chemiluminescence

Data from Russell Long and Keith Kronmiller
Preliminary O$_3$ Results from Padonia, MD Ground Site

- 1 minute average O$_3$ results highly correlated
- EC9810 (MDE) O$_3$ results ~ 8% higher than T265 (EPA) results
Preliminary O₃ Results from Padonia, MD Ground Site

EC9810 Nightly Span Results

- Measured Span
- Span Reference

Span correction factor
- Zero and span checks performed nightly
- Zero drift was negligible
- Span correction based on average results of nightly EC9810 span checks
- Consistent with end of study multi-point calibration results
- Independent of T-265 O₃ results

- Span correction:
  \[ EC9810_{corr} = EC9810 - EC9810(0.0801) \]

Data courtesy of Jenifer Hains, Maryland Department of the Environment
Preliminary $O_3$ Results from Padonia, MD Ground Site

T265 Nightly Span Results

- Nighttime zero and span checks performed every other night
- Span value near expected daily high concentrations (135 ppb $O_3$)
- Zero drift was negligible
- No Span drift observed over 1-month period
- No data correction for T265 $O_3$ results

Data courtesy of Jenifer Hains, Maryland Department of the Environment
Preliminary O₃ Results from Padonia, MD Ground Site

- Comparison of MDE and EPA O₃ results after span correction to EC9810 (MDE) O₃ show excellent agreement for 1 minute averages.
Preliminary O$_3$ Results from Padonia, MD Ground Site

July 1-31, 2011
5 min Average

![Graph 1](image1)

July 1-31, 2011
5 min Average

![Graph 2](image2)

y = 0.9185x + 0.0526
$R^2 = 0.9963$

July 1-31, 2011
5 min Average

![Graph 3](image3)

y = 0.9962x + 0.1589
$R^2 = 0.9962$

July 1-31, 2011
5 min Average

![Graph 4](image4)

y = 0.9962x + 0.1589
$R^2 = 0.9962$
Nightly $O_3$ Span Results for Other DISCOVER-AQ Ground Site

**Edgewood Nightly Span Results**

- Span corr. factor = -0.0026

**Fairhill Nightly Span Results**

- Span corr. factor = +0.017

**Essex Nightly Span Results**

- Span corr. factor = -0.005

**Aldino Nightly Span Results**

- Span corr. factor = N/A

Data courtesy of Jenifer Hains, Maryland Department of the Environment
Preliminary NO$_2$ Results from Padonia, MD Ground Site

![Graph showing NO$_2$ levels from July 1 to Aug 2, 2011, with two methods: hb-chemiluminescence and photo-chemiluminescence.](image)
Preliminary Results from Padonia, MD Ground Site

\[ \Delta \text{NO}_2 = \text{NO}_2 (\text{hb} - \text{chemiluminescence}) - \text{NO}_2 (\text{photo} - \text{chemiluminescence}) \]

- The interference in the hb-chemiluminescence monitor over-predicts by ~50% during the hours surrounding noon (peak periods of photochemistry).
- \( \Delta \text{NO}_2 \) correlated with \( \text{O}_3 \) during daylight hours.

Data from Russell Long and Keith Kronmiller
Next Steps

• Complete Baltimore 2011 data analysis/validation:
  • \( \text{O}_3 \)
  • \( \text{NO}_2 \)
  • \( \text{NO}_y \)
• True \( \text{NO}_2 \) method evaluation (AIRS sampling site, RTP, NC)
  • Photolytic \( \text{NO}_2 \)
  • CAPS \( \text{NO}_2 \)
  • CRDS \( \text{NO}_2 \)
• \( \text{O}_3 \) method evaluation (AIRS sampling site, RTP, NC)
  • Ethylene chemiluminescence (U.S. EPA FRM)
  • UV photometric
  • NO chemiluminescence
• Pandora – column vs surface comparisons of \( \text{O}_3 \) and \( \text{NO}_2 \)
• Future DISCOVER-AQ field deployments:
  • Deploy new optical “true” \( \text{NO}_2 \) methods in these field intensives
Next Steps: EPA’s AIRS site

- Cavity ring-down spectrometer
- T265 Ozone
- Photo-chemiluminescence
- hb-chemiluminescence

• Long term (1 year) comparison
Preliminary O$_3$ Results, EPA AIRS Site

- Good agreement between UV photometric (2B) and NO-Chemiluminescence (T265) methods for 1 minute average ozone
- Additional methods to be evaluated in ambient and laboratory settings
Direct Optical Techniques

- Cavity attenuated phase shift spectroscopy
  - Instrument manufactured by Aerodyne Research, Inc.

  - advantage → DIRECT measurement
  - disadvantages → not-necessarily specific to NO₂, but to any molecule that absorbs light at ~400nm
  - EPA/ORD has acquired (2) this monitor. CAPS monitor has been operating at AIRS site since December 2011.

Kebabian et al. ES&T 2008
Direct Optical Techniques

- Cavity ring-down spectroscopy
  - Instrument manufactured by Los Gatos Research, Inc.

- Advantage: DIRECT measurement
- Disadvantages: not necessarily specific to NO₂, but to any molecule that absorbs light at ~420 nm
- Installed at AIRS February 2012

\[
N(cm^{-3}) = \frac{1}{c \sigma} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right)
\]
Preliminary NO$_2$ Results, EPA AIRS Site

![Graph showing NO$_2$ concentrations over time for different categories: NO$_2$ T200U, NO$_2$ 200EU-P, NO$_y$ -NO eco, and NO$_2$ ARICAPS. The x-axis represents dates from 01/28/12 to 02/07/12, and the y-axis represents NO$_2$ concentrations in ppb.](image-url)