Surface Measurements (NO_2 & O_3) at Padonia, MD During July 2011 DISCOVER-AQ Field Campaign

Office of Research and Development
National Exposure Research Laboratory

14 Feb 2012

Participants and Measurement Methods

United States Environmental Protection Agency

EPA /Contractor Participants

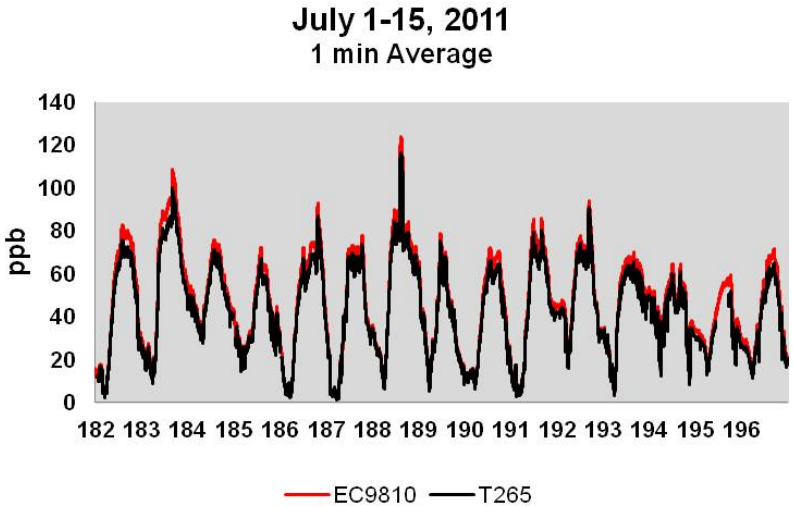
- Russell Long – ORD/NERL/HEASD
- Jim Szykman – ORD/NERL/ESD
- Keith Kronmiller – Alion Science and Technology
- Mike Wheeler – Alion Science and Technology
- Melinda Beaver – ORD/NERL/HEASD

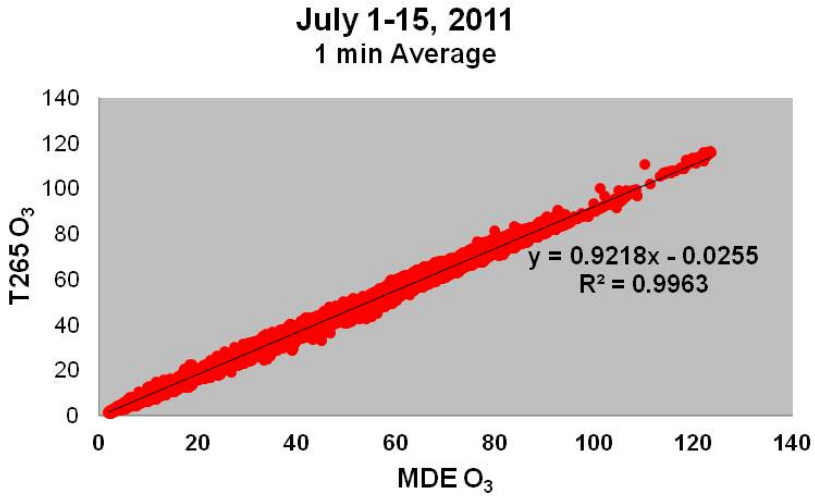
Measurment Methods

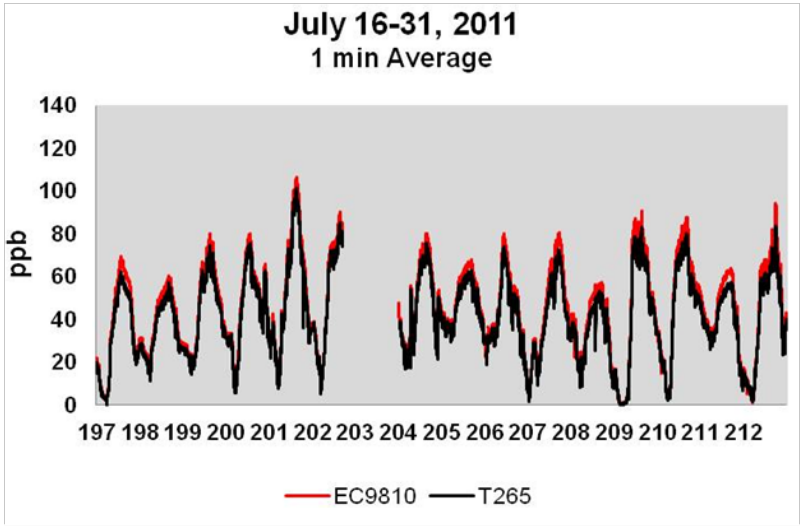
- Ozone (O_3)
  - Teledyne-API T265 (U.S. EPA FEM) – NO chemiluminescence
  - Ecotech EC9810 (U.S. EPA FEM) – UV photometric – data provided by MDE
- Nitrogen Dioxide (NO_2)
  - Thermo 42C (U.S. EPA FRM) – HB conversion → O_3 chemiluminescence
  - Teledyne-API 200EUP – Photolytic conversion → O_3 chemiluminescence
- Total Reactive Oxides of Nitrogen (NO_y)
  - Thermo 42iy – HB conversion (external 10m) → O_3 chemiluminescence
  - Ecotech EC9843 – HB conversion (external 10m) → O_3 chemiluminescence

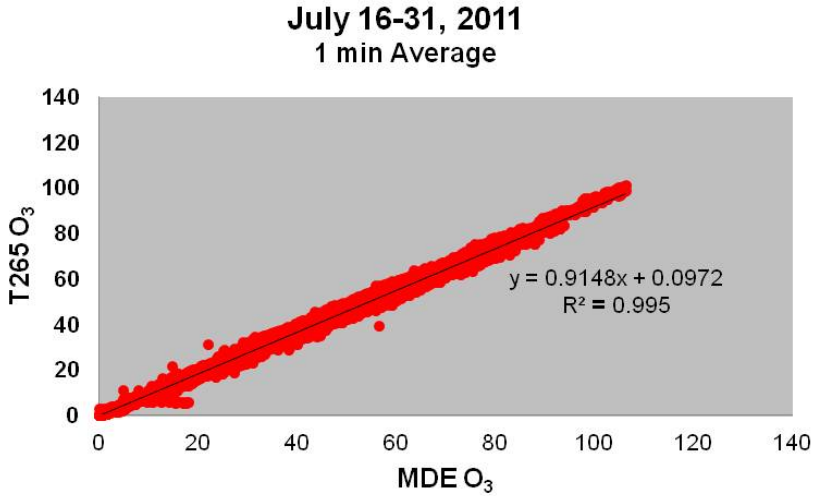
Data from Russell Long and Keith Kronmiller

Preliminary O_3 Results from Padonia, MD Ground Site



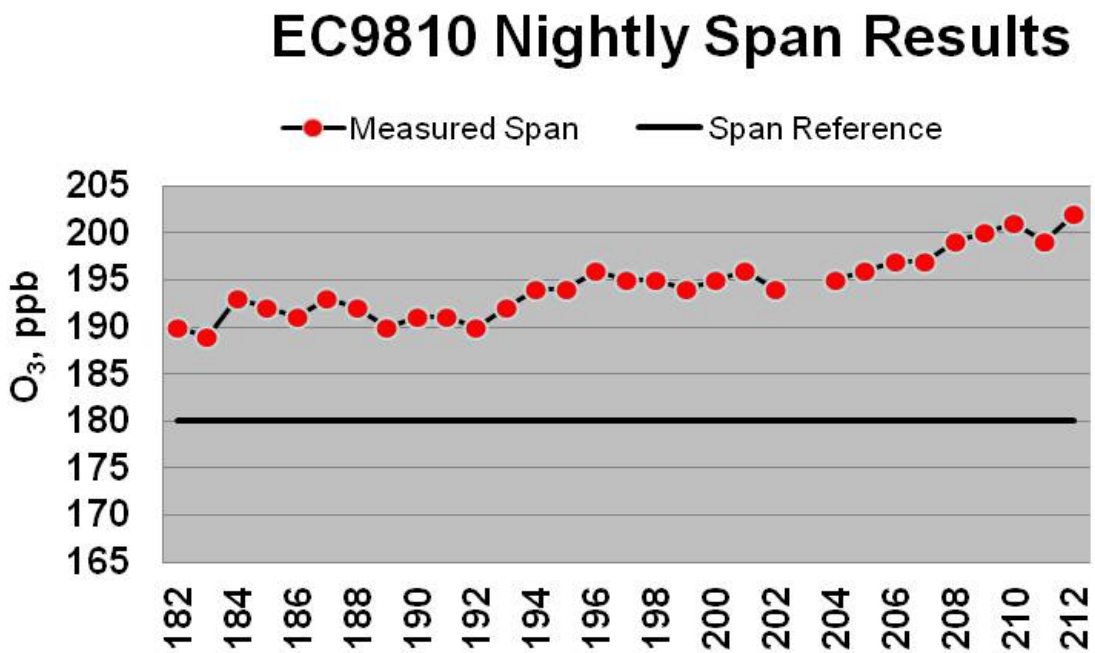






- 1 minute average O_3 results highly correlated
- EC9810 (MDE) O_3 results ~ 8% higher than T265 (EPA) results

Preliminary O_3 Results from Padonia, MD Ground Site



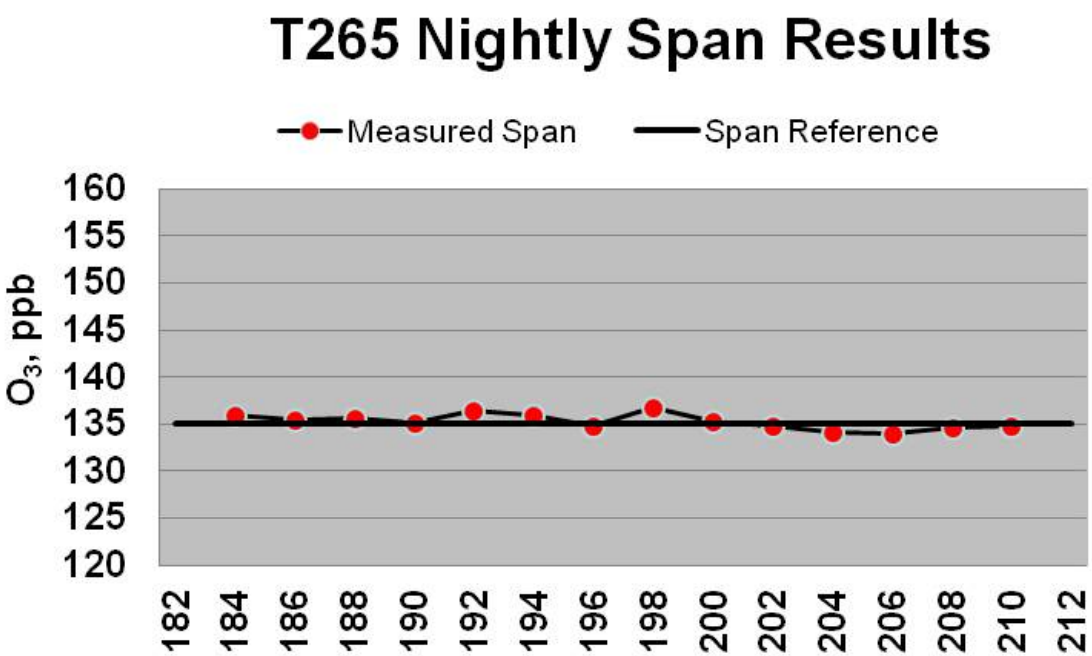
Span correction factor

- 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 O_3 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

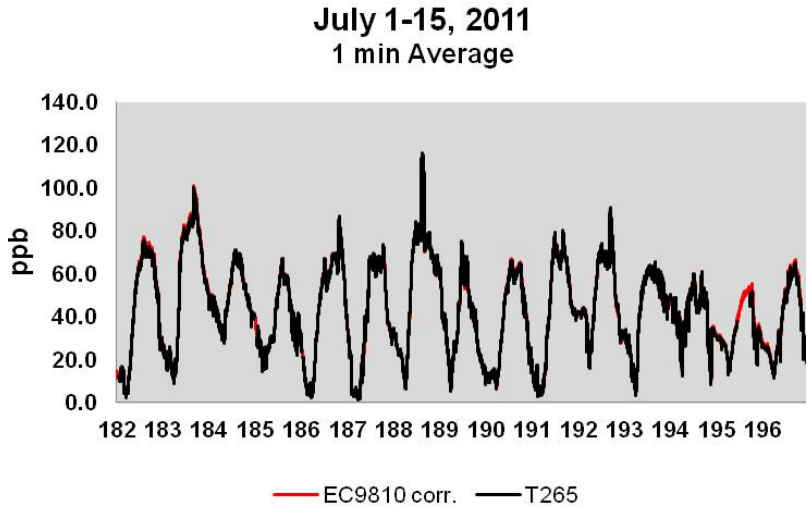


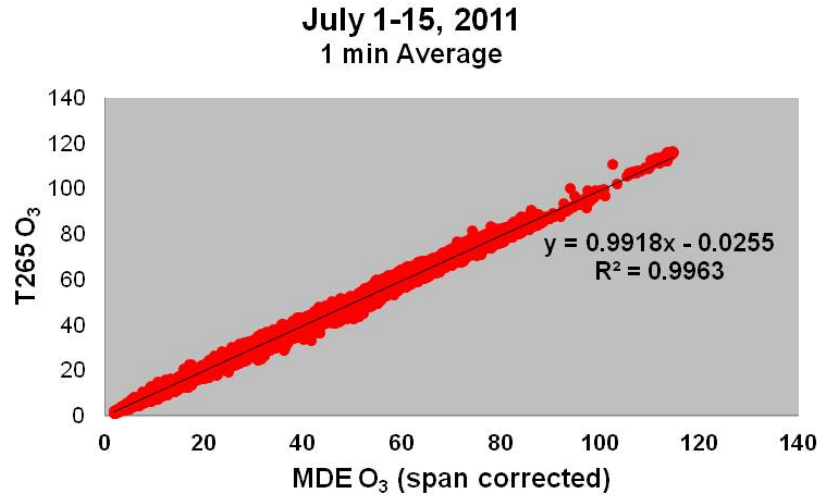
T265 span results

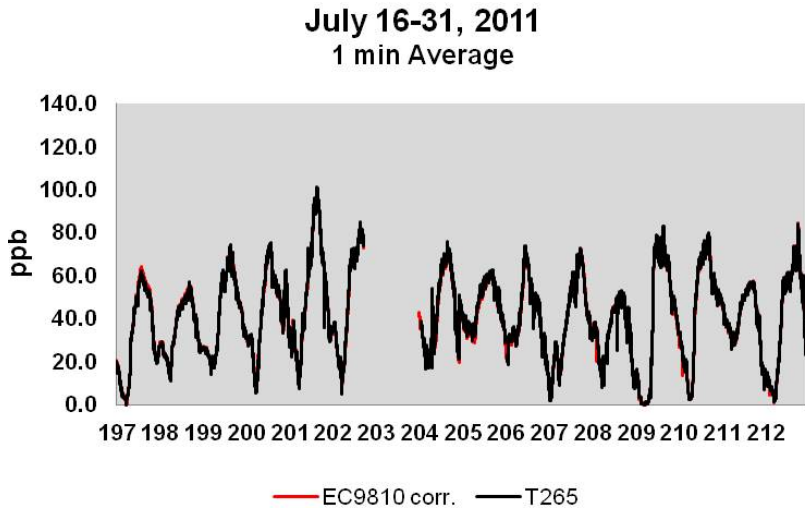
- Nighttime zero and span checks performed every other night
- Span value near expected daily high concentrations (135 ppb O_3)
- Zero drift was negligible
- No Span drift observed over 1-month period
- No data correction for T265 O_3 results

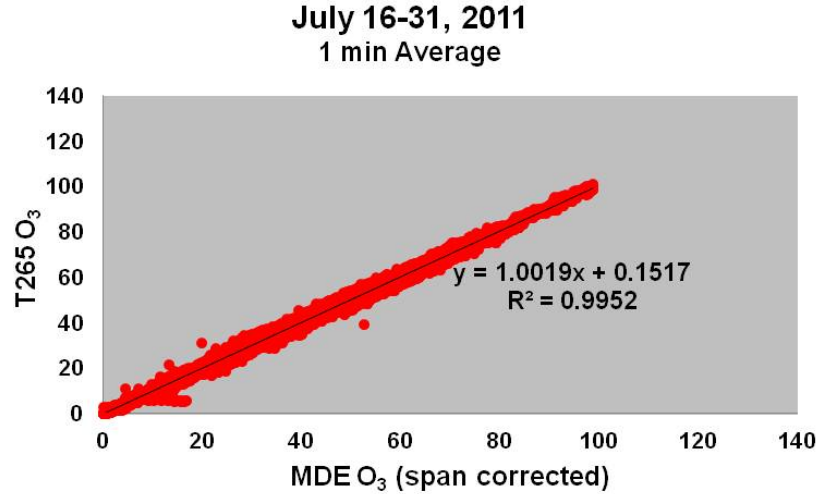
Data courtesy of Jenifer Hains, Maryland Department of the Environment

Preliminary O_3 Results from Padonia, MD Ground Site



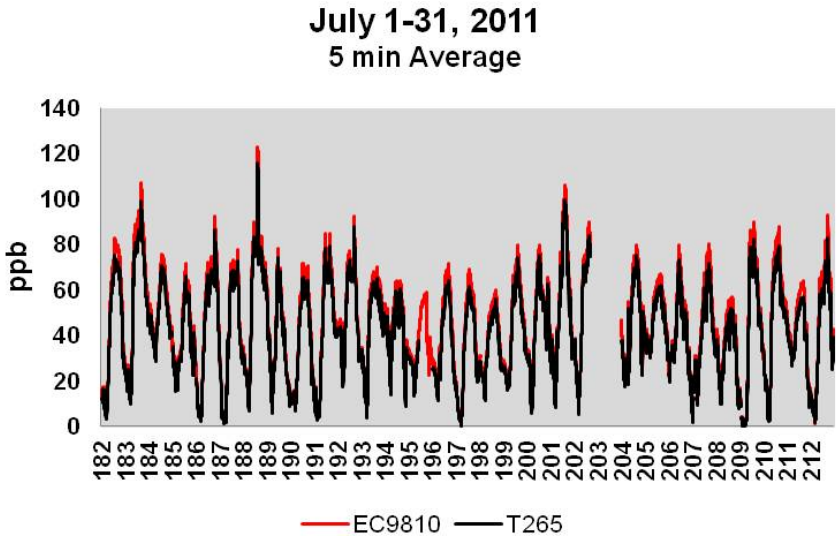


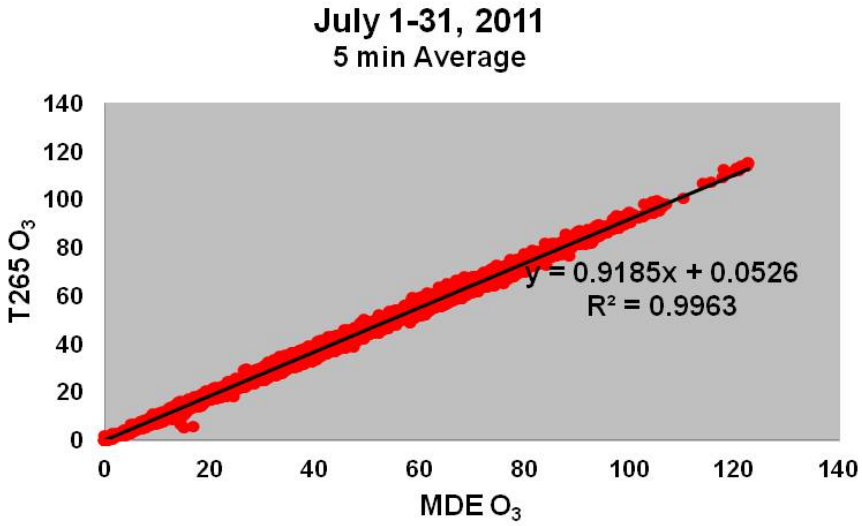


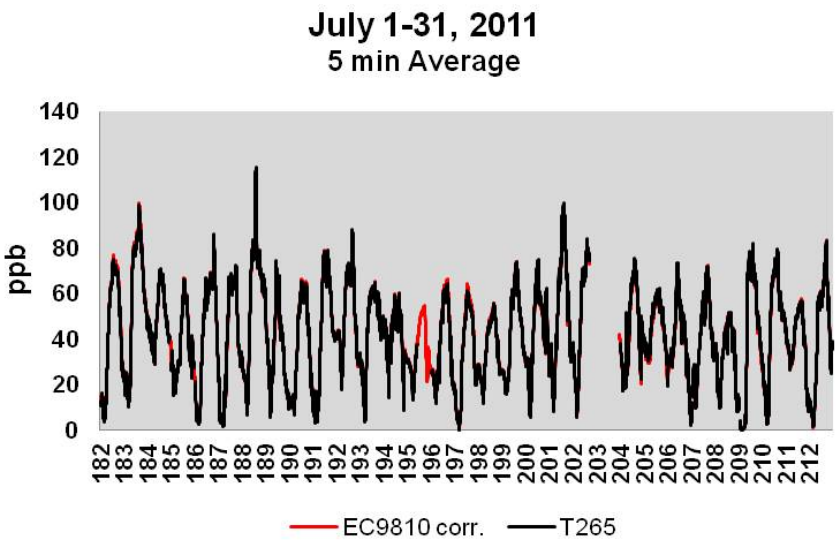


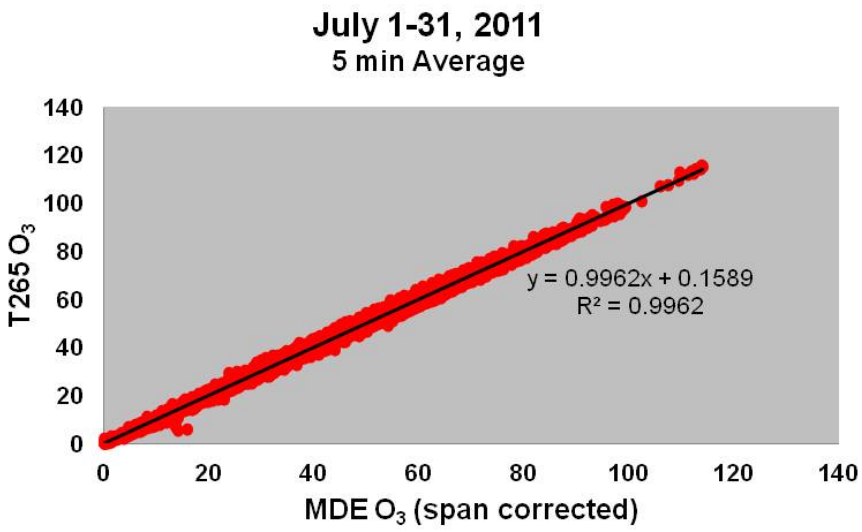
- Comparison of MDE and EPA O_3 results after span correction to EC9810 (MDE) O_3 show excellent agreement for 1 minute averages.

Preliminary O_3 Results from Padonia, MD Ground Site

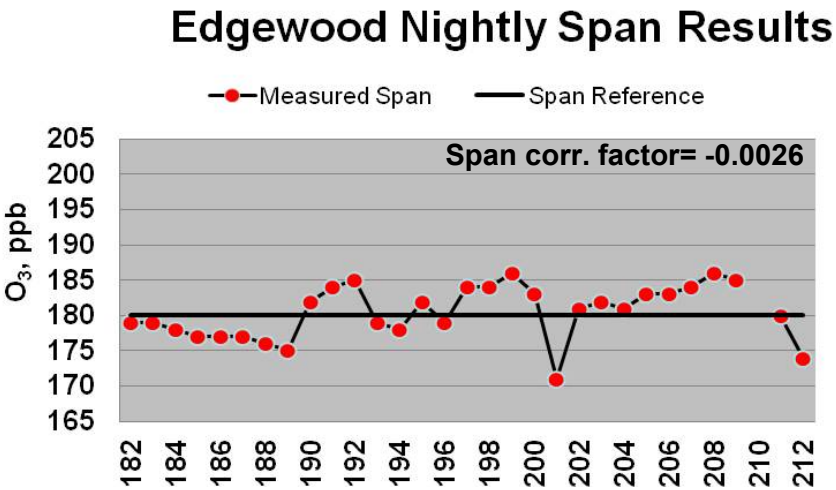


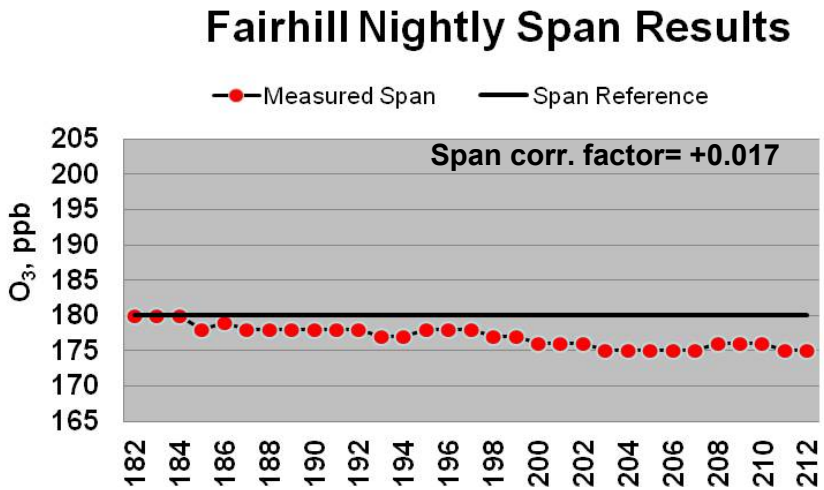


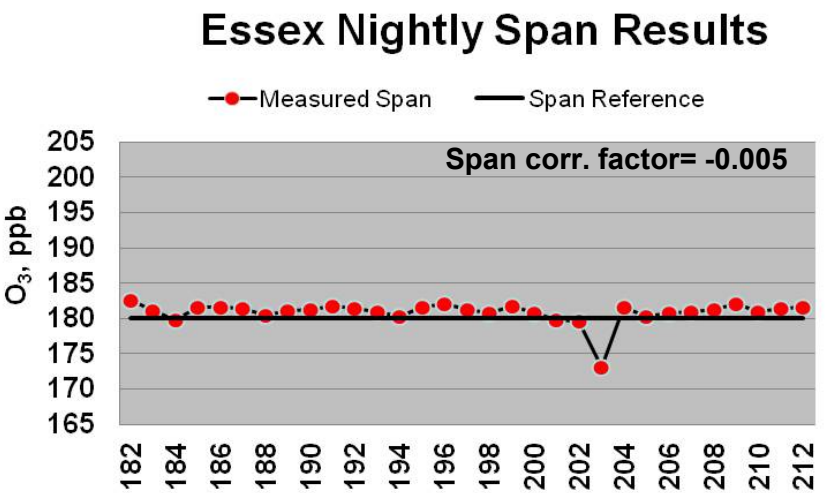


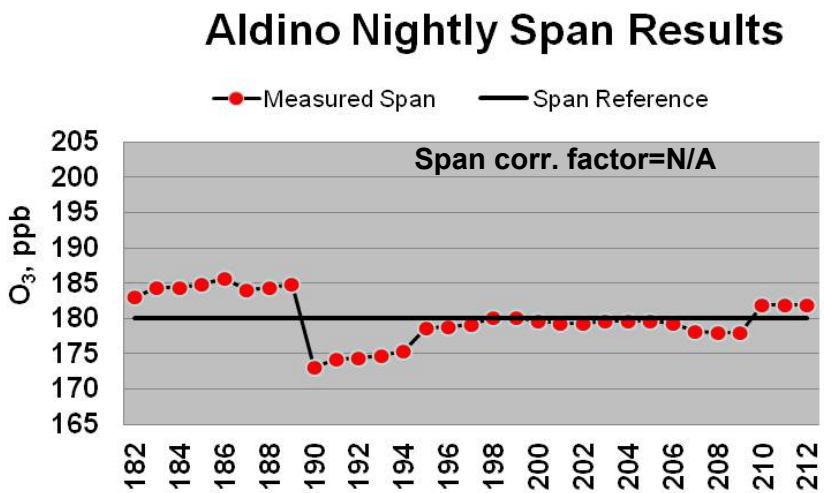


Nightly O_3 Span Results for Other DISCOVER-AQ Ground Site



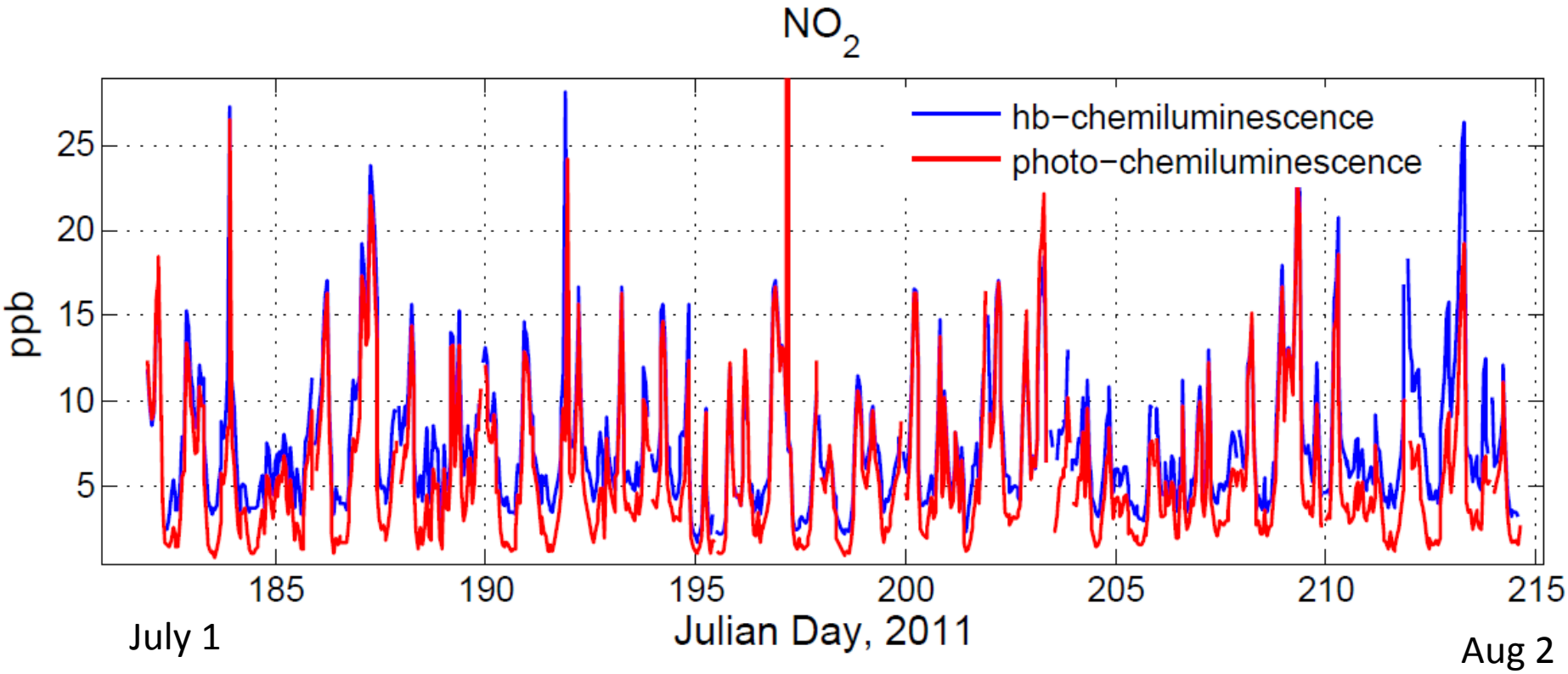




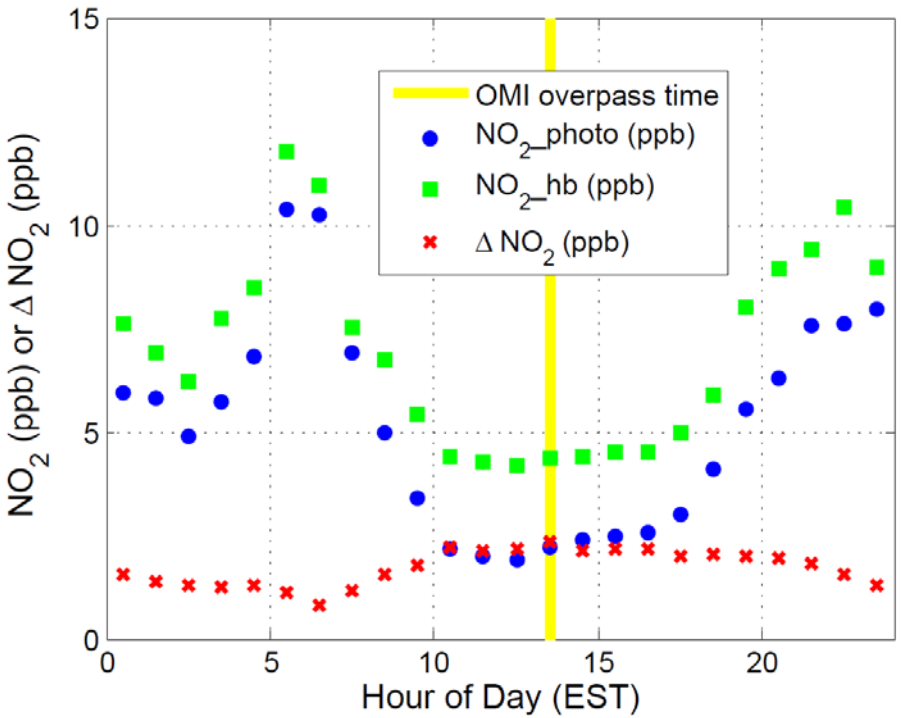


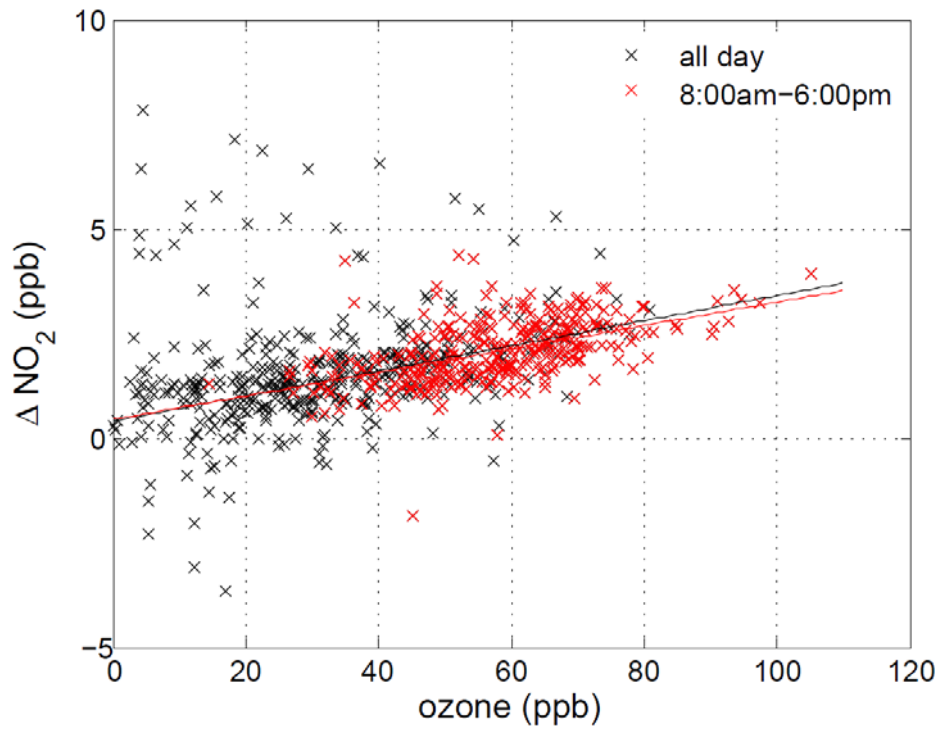
Data courtesy of Jenifer Hains, Maryland Department of the Environment

Preliminary NO_2 Results from Padonia, MD Ground Site



Preliminary Results from Padonia, MD Ground Site





$$\Delta NO_2 = NO_2\,(\text{hb} - \text{chemiluminescence}) - NO_2\,(\text{photo} - \text{chemiluminescence})$$

- The interference in the hb-chemiluminescence monitor over-predicts by ~50% during the hours surrounding noon (peak periods of photochemistry).
- ΔNO_2 correlated with O_3 during daylight hours.

Data from Russell Long and Keith Kronmiller

Next Steps

- Complete Baltimore 2011 data analysis/validation:
  - O_3
  - NO_2
  - NO_y
- True NO_2 method evaluation (AIRS sampling site, RTP, NC)
  - Photolytic NO_2
  - CAPS NO_2
  - CRDS NO_2
- 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 O_3 and NO_2
- Future DISCOVER-AQ field deployments:
  - Deploy new optical "true" NO_2 methods in these field intensives

Next Steps: EPA's AIRS site

United States Environmental Protection Agency

Cavity ring-down spectrometer

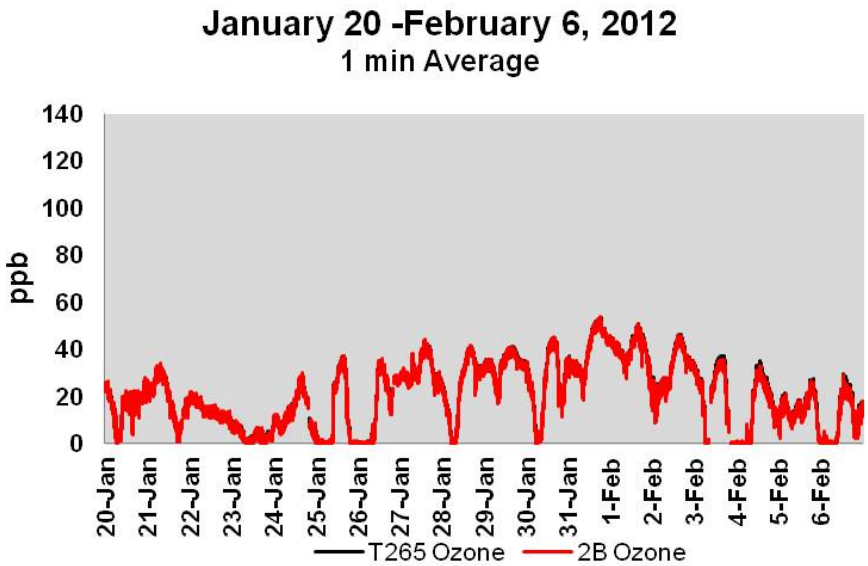
T265 Ozone

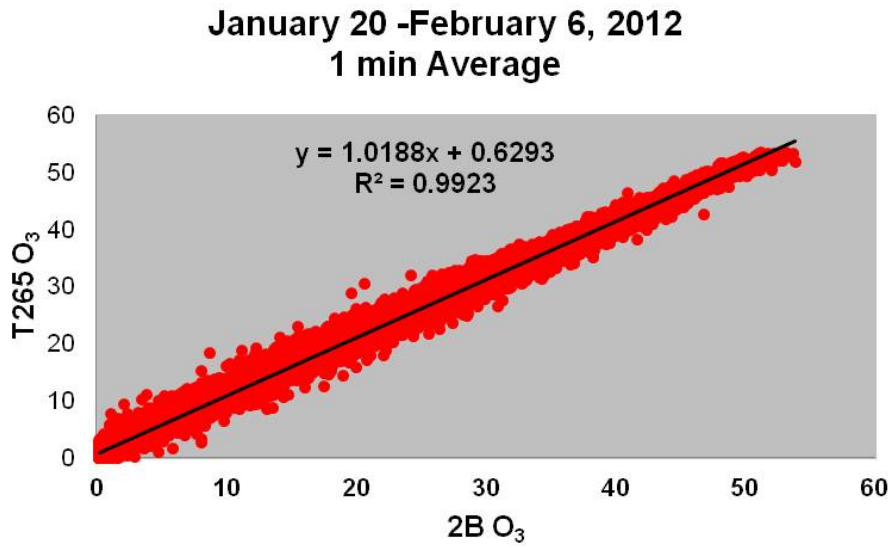
Photo-chemiluminescence

hb-chemiluminescence

- Long term (1 year) comparison

Preliminary O_3 Results, EPA AIRS Site

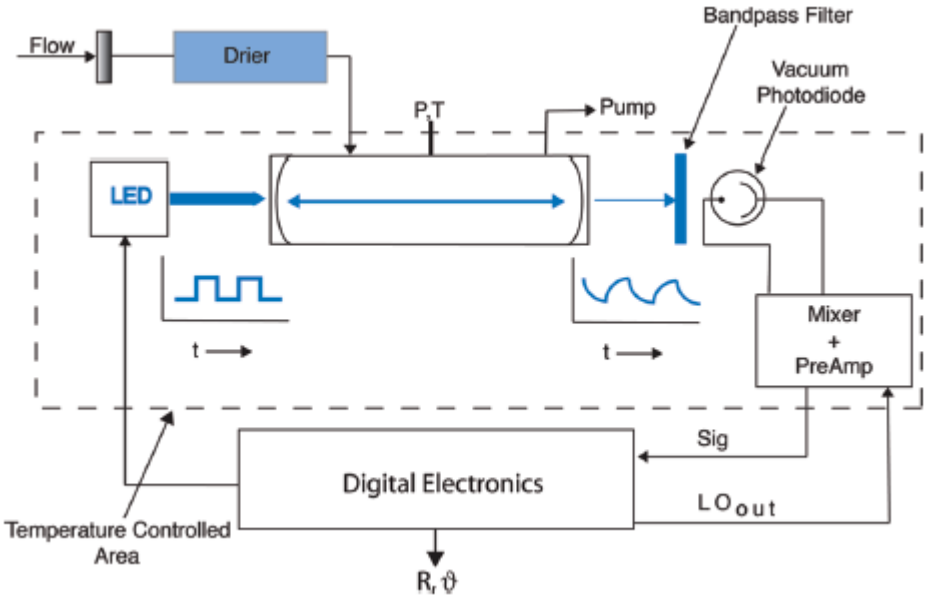




- Good agreement between UV photometric (2B) and NO-Chemiluminescence (T265) methods for 1 minute average ozone
- Additional methods to be evaluated in ambient and laboratory settings

Direct Optical Techniques

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

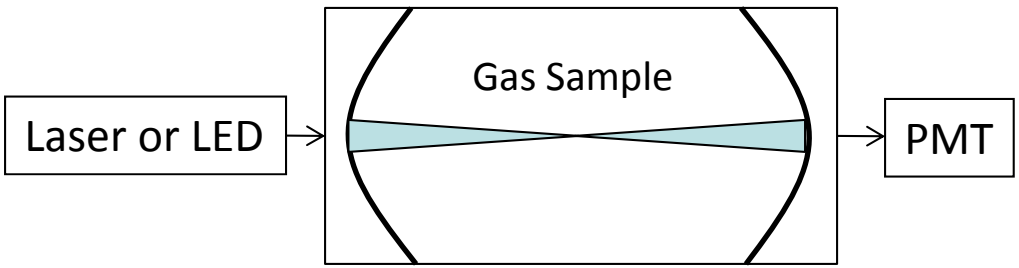


  - advantage → DIRECT measurement
  - disadvantages → not-necessarily specific to NO_2, but to any molecule that absorbs light at ~400nm
  - EPA/ORD has acquired (2) this monitor. CAPS monitor has been operating at AIRS site since December 2011.

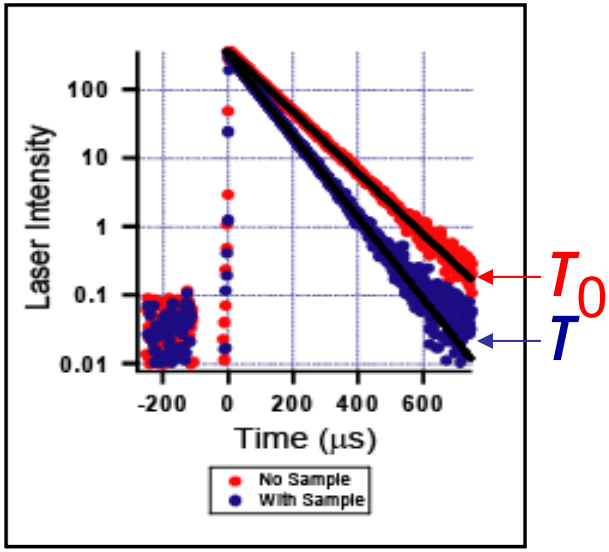
Kebabian et al. ES&T 2008

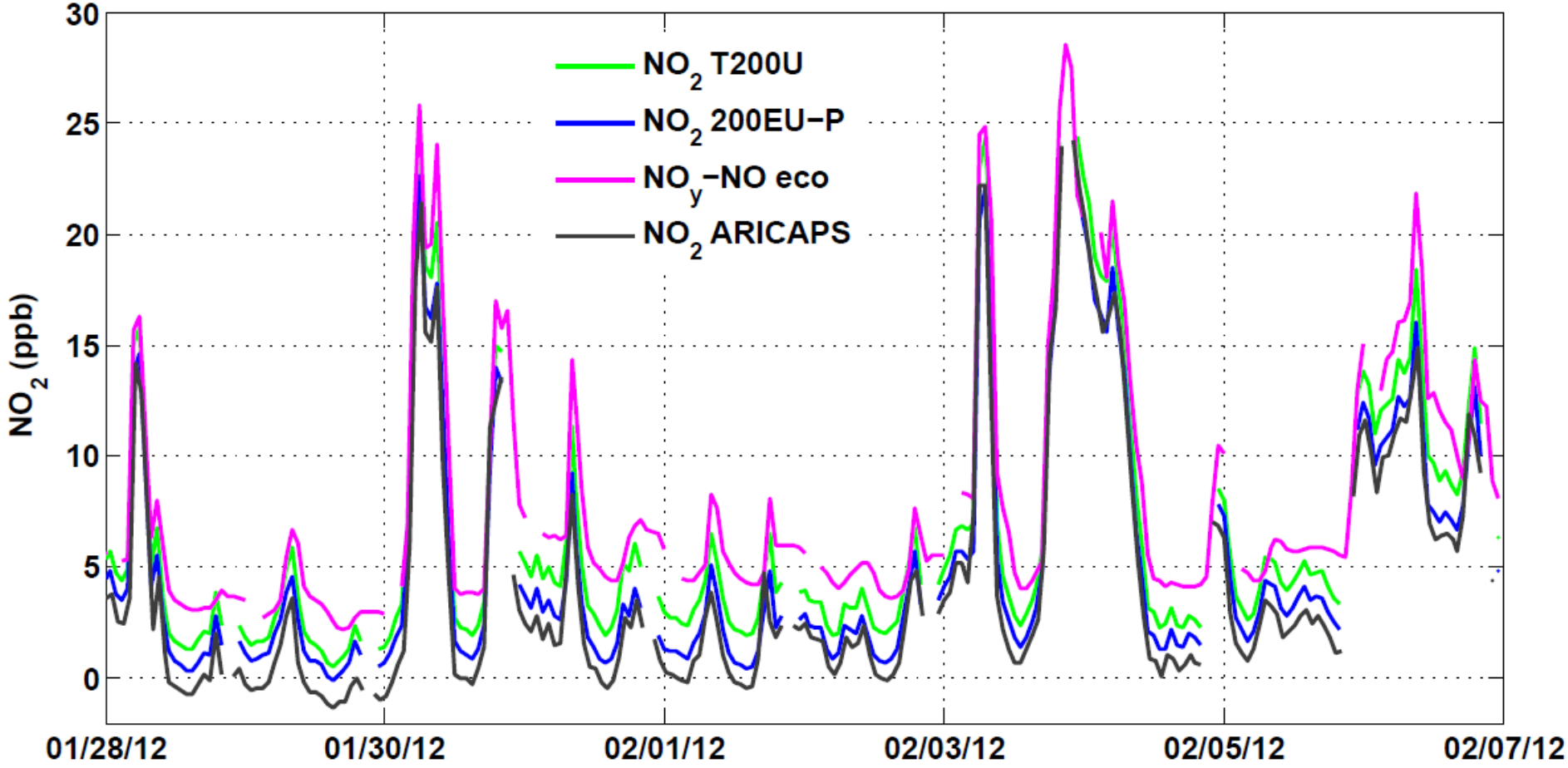
Direct Optical Techniques

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



$$N(cm^{-3}) = \frac{1}{c\sigma}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$$



  - advantage → DIRECT measurement
  - disadvantages → not-necessarily specific to NO_2, but to any molecule that absorbs light at ~420 nm
  - Installed at AIRS February 2012

Preliminary NO_2 Results, EPA AIRS Site