Overview of ORD NO_2, NO_x and NO_y Measurement Research

Russell Long
U.S. EPA
Office of Research and Development
National Exposure Research Laboratory

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Outline

1. Introduction
2. Instrumentation and evaluation protocol
3. Ambient Evaluations
4. Laboratory Evaluations
5. Next Steps
6. Questions

Research Team

<u>Research Team</u>

Melinda Beaver – EPA/OAR/OAQPS

Rachelle Duvall – EPA/ORD/NERL

Jim Szykman – EPA/ORD/NERL

Keith Kronmiller – Jacobs Technology Inc.

Michael Wheeler – Jacobs Technology Inc.

<u>Collaborators</u>

Jim Crawford – NASA LaRC

Penn State University

Maryland Department of the Environment

San Joaquin Valley Air Pollution Control District

Texas Commission on Environmental Quality

Colorado Department of Public Health and Environment

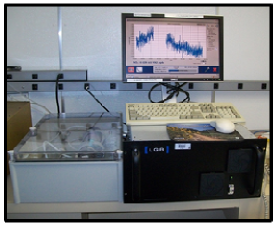
NO_2, NO_x, and NO_y Methods Research

- **Ambient evaluations were performed primarily during DISCOVER-AQ.**
  - **Baltimore, MD – 2 sites**
  - **San Joaquin Valley, CA – 3 sites**
  - **Houston, TX – 3 sites**
  - **Denver, CO – 7 sites**
  - **AIRS (EPA RTP) – between D-AQ deployments**
- **Ambient deployments allowed for the investigation and evaluation of methods for NO_2, NO_x, NO_y.**
- **ORD also evaluated NO_2 and NO_x methods in near roadway settings during the San Joaquin Valley and the Denver DISCOVER-AQ studies.**
- **Laboratory based evaluations are being used to investigate calibration, interference and other method issues.**

NO_2, NO_x Methods

	Operation Principle	*FRM/FEM*
 **Teledyne T200U**  **Thermo 42C, 42i**	**Heated-bed chemiluminescence** • Indirectly measure NO_2 by thermal conversion (molybdenum catalyst) to NO, then NO is detected by chemiluminescence • Chemiluminescence FRM in use since the 1970s (long term record) • Non-specific – Higher oxides of nitrogen also converted to NO and detected as NO_2	**FRM**
 **Teledyne 200EUP, T200UP**	**Photolytic chemiluminescence** • Replace the heated-bed converter with a photolysis cell (high-power light sources) to photolyze NO_2 to NO • More specific to NO_2 • Non-unity conversion efficiency • Indirect	**FEM**

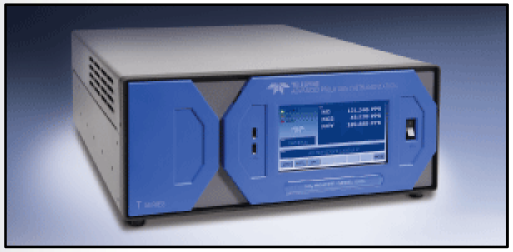
Direct NO_2 Methods

<table>
<tr><th></th><th>Operation Principle</th><th>FRM/FEM</th></tr>
<tr><td>LGR CRDS
</td><td>Cavity ringdown spectroscopy (CRDS)
• 10 s time resolution
• Direct spectroscopic measurement
• Possible interferences from any molecule that absorbs light at 405 nm</td><td>--</td></tr>
<tr><td>Aerodyne CAPS
</td><td>Cavity attenuated phase shift spectroscopy (CAPS)
• 10 s time resolution
• Direct spectroscopic measurement
• Possible interferences from any molecule that absorbs light at ~450 nm</td><td>--</td></tr>
<tr><td>
Teledyne T500U


Environment S.A AS32M</td><td>Cavity attenuated phase shift spectroscopy (CAPS)
• ~15 s time resolution
• FEM
• Direct spectroscopic measurement
• Possible interferences from any molecule that absorbs light at ~450 nm</td><td>FEM</td></tr>
</table>

EPA

NO_y Methods

	Operation Principle	*FRM/FEM*
 **Teledyne T200U NO_y**	**Heated-bed chemiluminescence** • Measures NO, NO_y and NO_y-NO by thermal conversion to NO, then detection by chemiluminescence • External molybdenum converter at ~10 m • Converter temperature set point 315±7 °C	--
 **Thermo 42i-Y**	**Heated-bed chemiluminescence** • Measures NO, NO_y and NO_y-NO by thermal conversion to NO, then detection by chemiluminescence • External molybdenum converter at ~10 m • Converter temperature set point 325 °C	--
 **Ecotech EC9843**	**Heated-bed chemiluminescence** • Measures NO, NO_y and NO_y-NO by thermal conversion to NO, then detection by chemiluminescence • External molybdenum converter at ~10 m • Converter temperature set point 375 °C	--

Evaluation Protocols

Ambient Method Evaluations

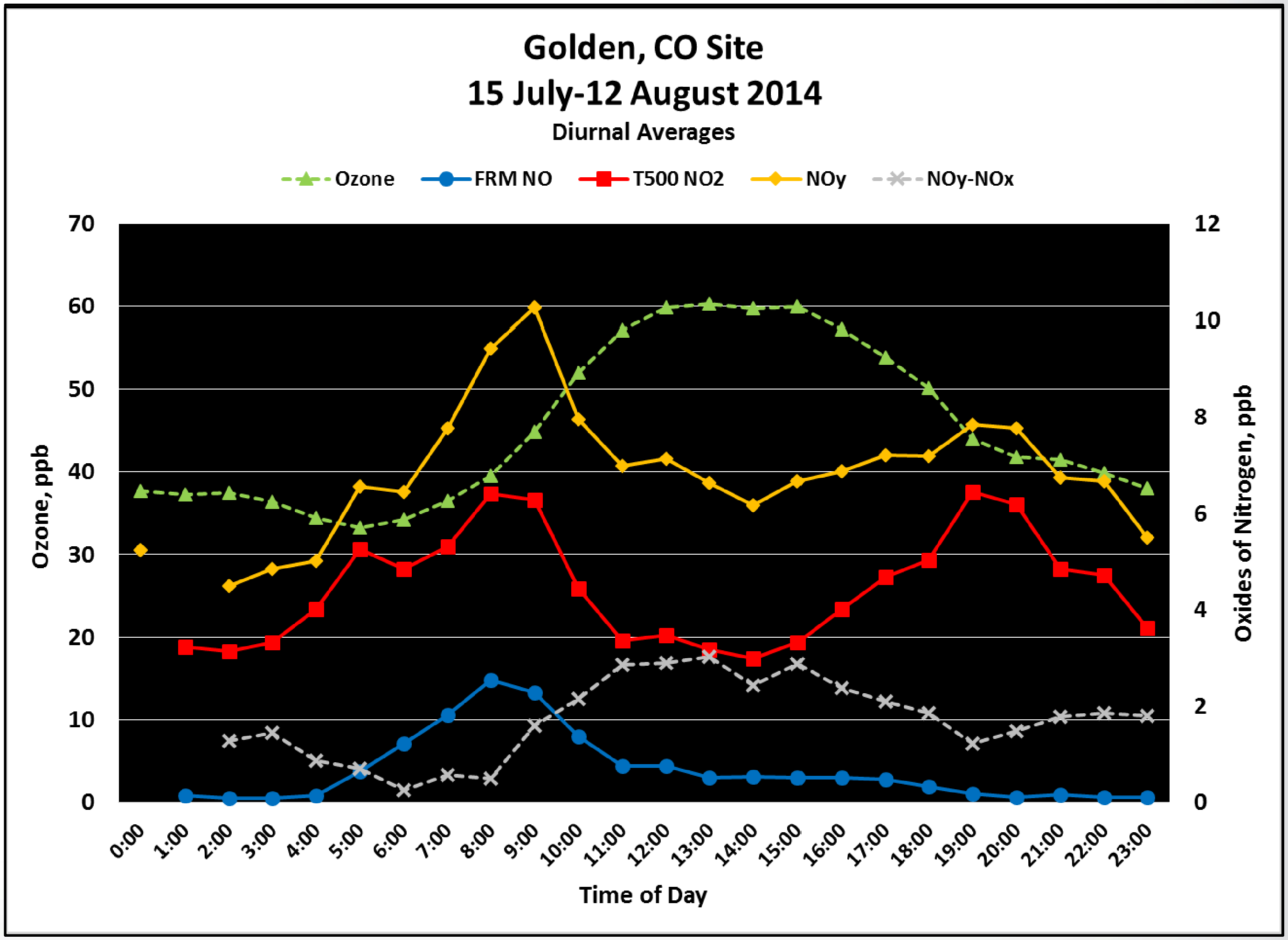
- All instruments housed within environmentally controlled sampling shelters
- Instruments calibrated according to operation manuals in accordance with FRM/FEM requirements
- Nightly, automated zero and span checks
- Glass inlet with sampling height @ 3-5 m agl and common glass sampling manifold
- Envidas Ultimate data acquisition system used to log data
- Ambient Met data and manifold T and RH also collected and logged

Laboratoru Method Evaluations

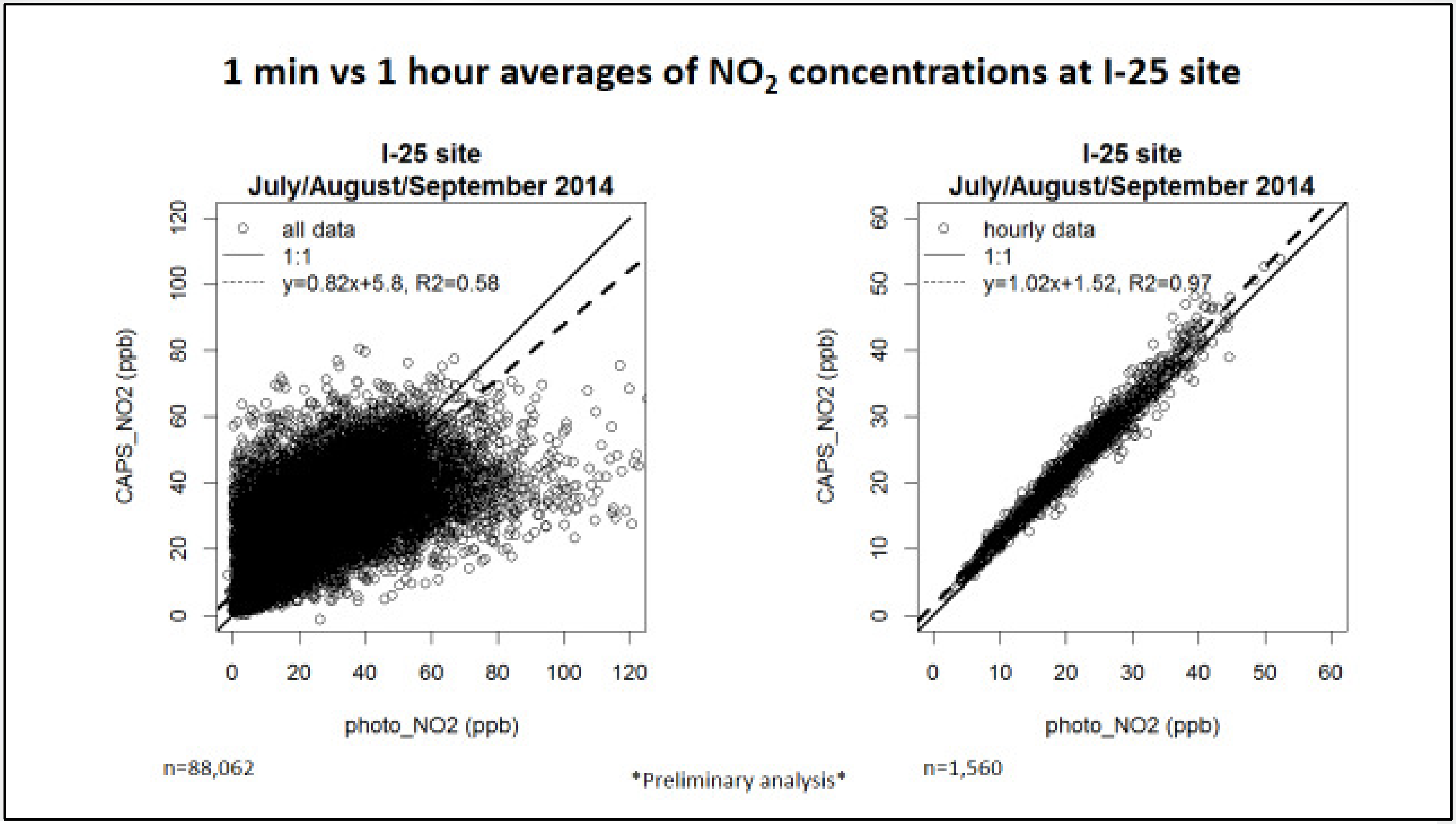
- All instruments housed within environmentally controlled laboratory
- Instruments calibrated according to operation manuals in accordance with FRM/FEM requirements
- Nightly, automated zero and span checks
- Common glass sampling manifold
- Envidas Ultimate data acquisition system used to log data
- Laboratory and manifold conditions (T and RH) collected and logged
- Test atmospheres provided by dynamic dilution system (capable of controlling pollutant concentrations, temperature and RH)

Oxides of Nitrogen Measurements Golden, CO Site

- **Peaks in 1 Hr NO, NO_2, and NO_y concentrations are observed during periods generally associated with local traffic patterns.**
- **Differences between NO_y and NO_x (NO_y-NO_x=NO_z) are correlated (similar diurnal patterns) with ozone. Both ozone and NO_z are photochemically formed.**
- **Hourly average results (for each hour of the day) averaged over the month long study period further show the traffic impacts on peak NO, NO_2 and NO_y concentrations and the similar diurnal patterns of NO_y-NO_x and ozone.**

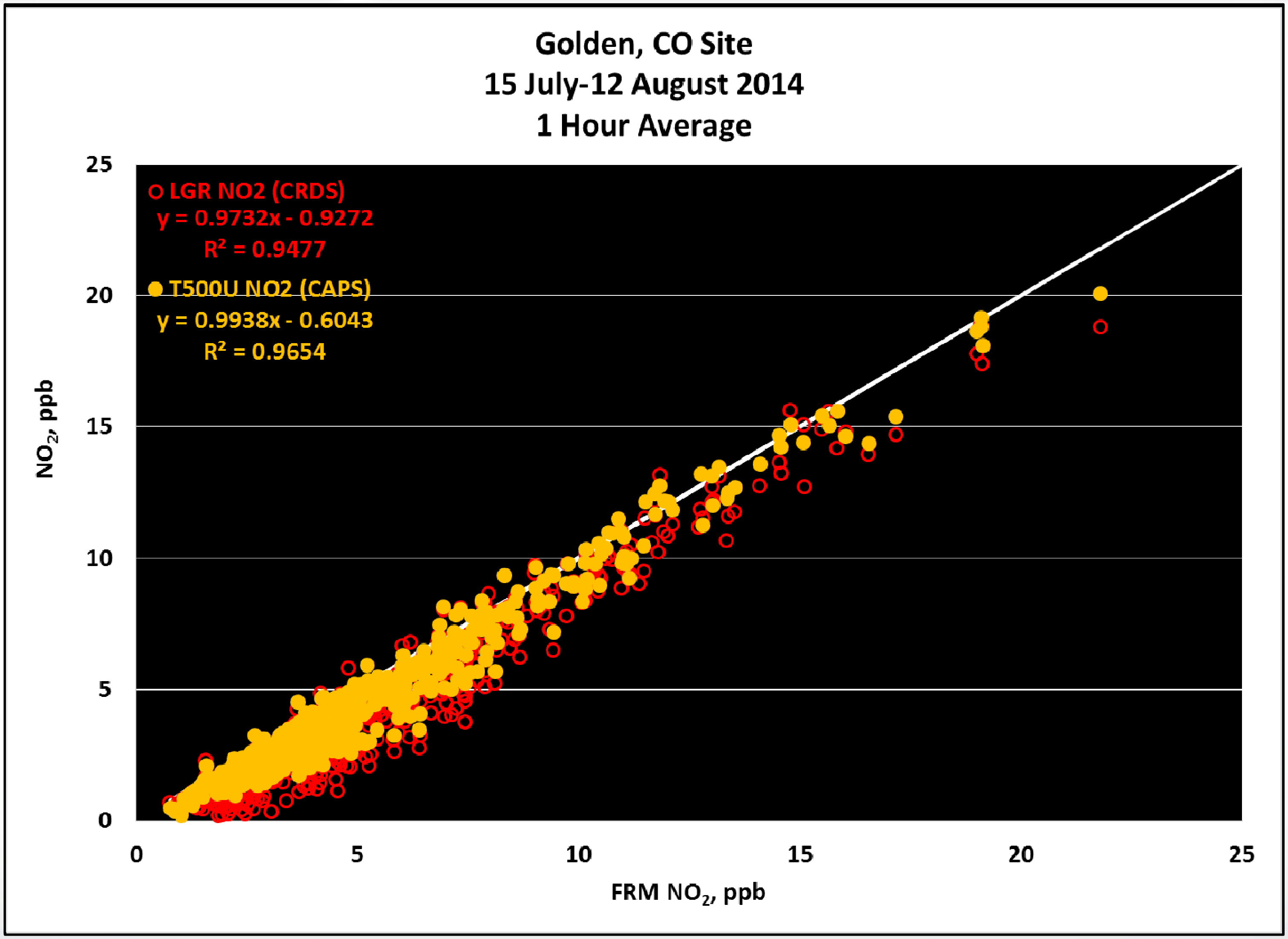


Comparison of NO_2 Measurements Denver I-25 (Near Roadway) Site

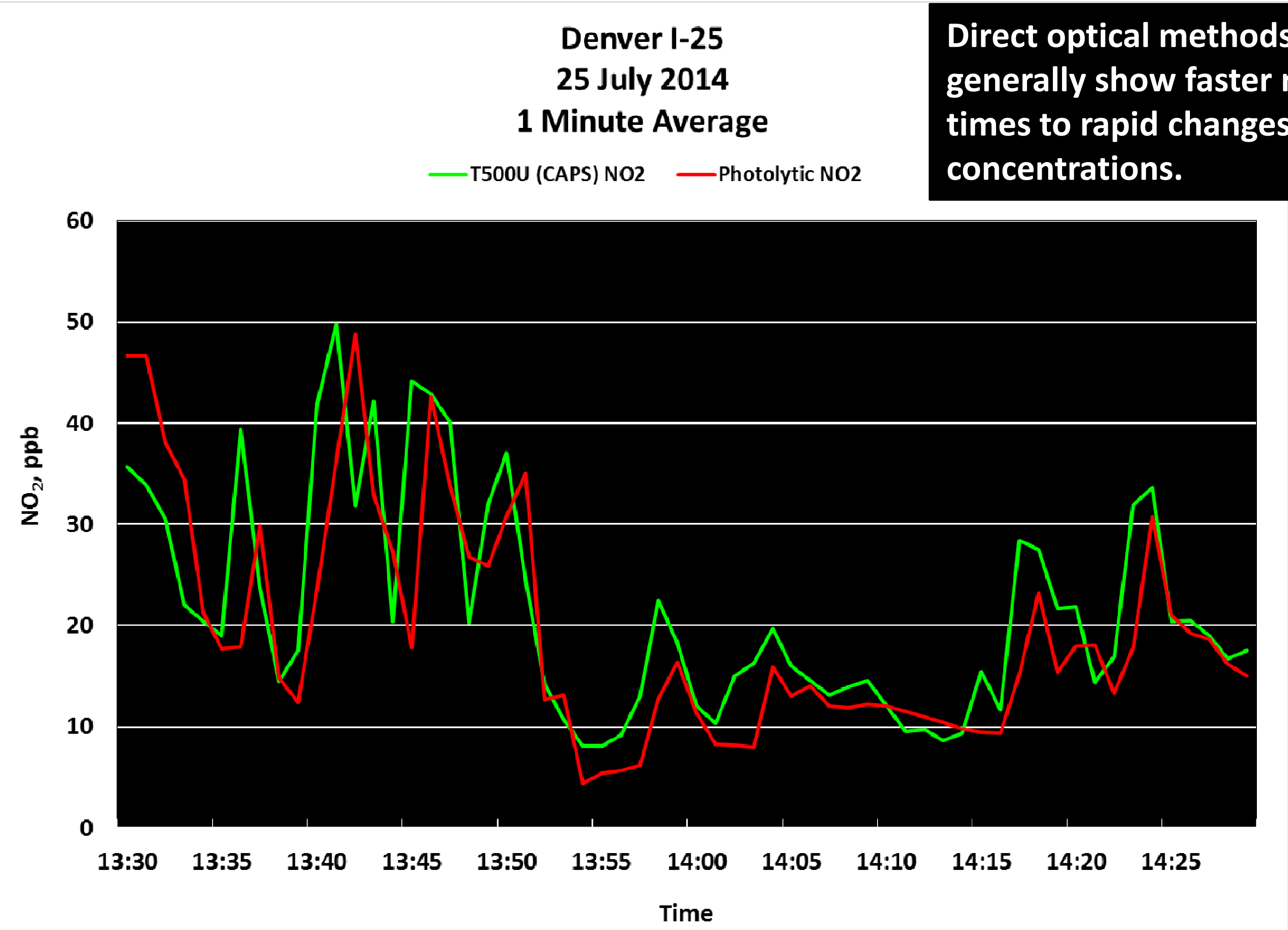


- **Data Averaged to 1 hour show very good agreement.**

Comparison of NO_2 Measurements Golden, CO Site

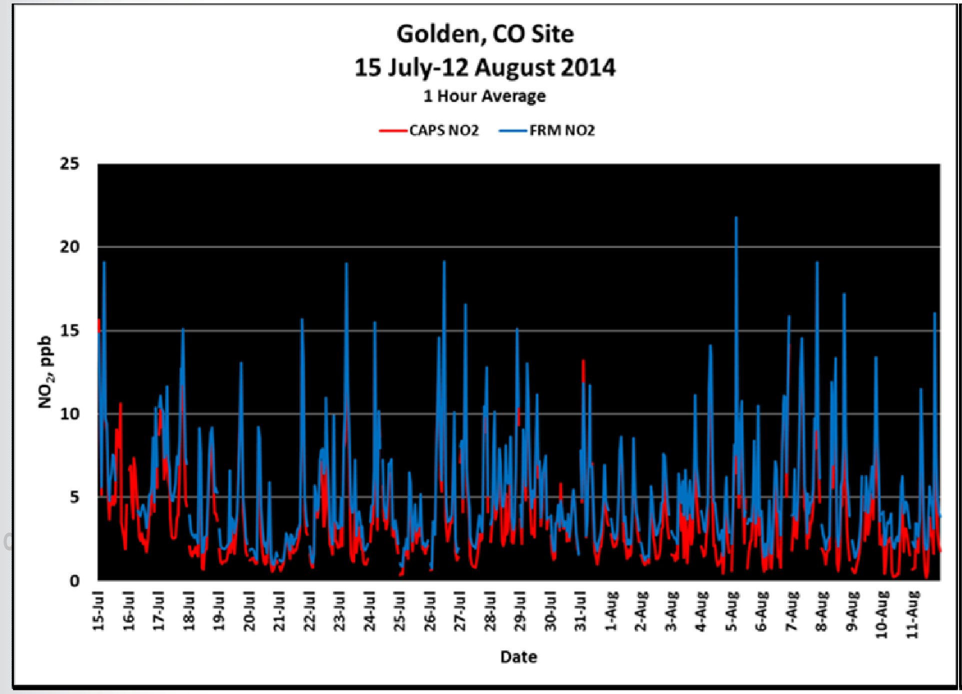


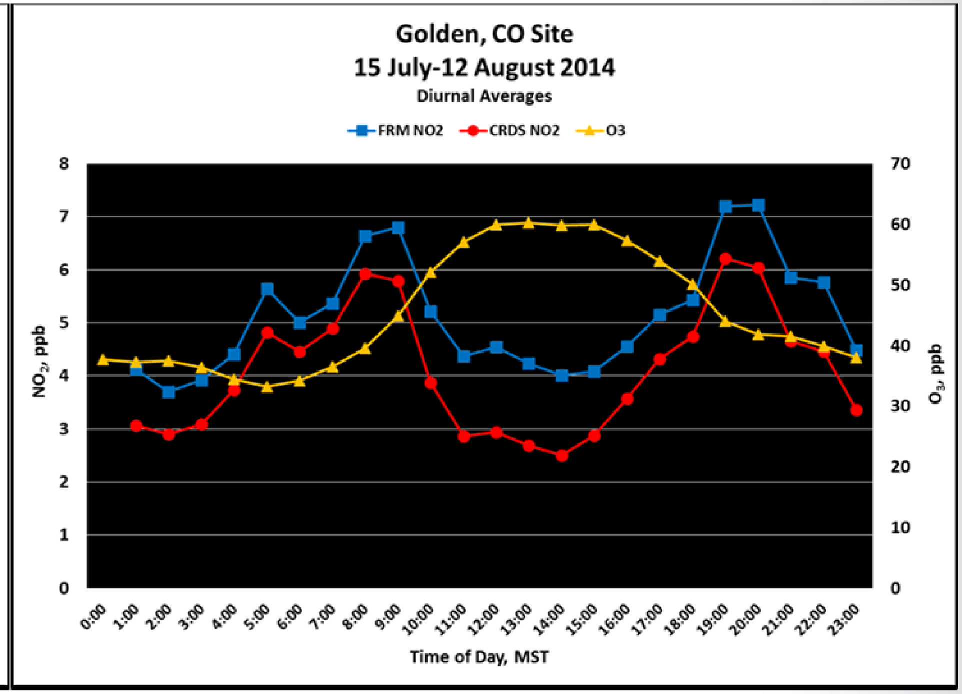
Response Time: Direct vs Indirect



Direct optical methods generally show faster response times to rapid changes in NO_2 concentrations.

Comparison of NO_2 Measurements FRM vs Optical/Photolytic

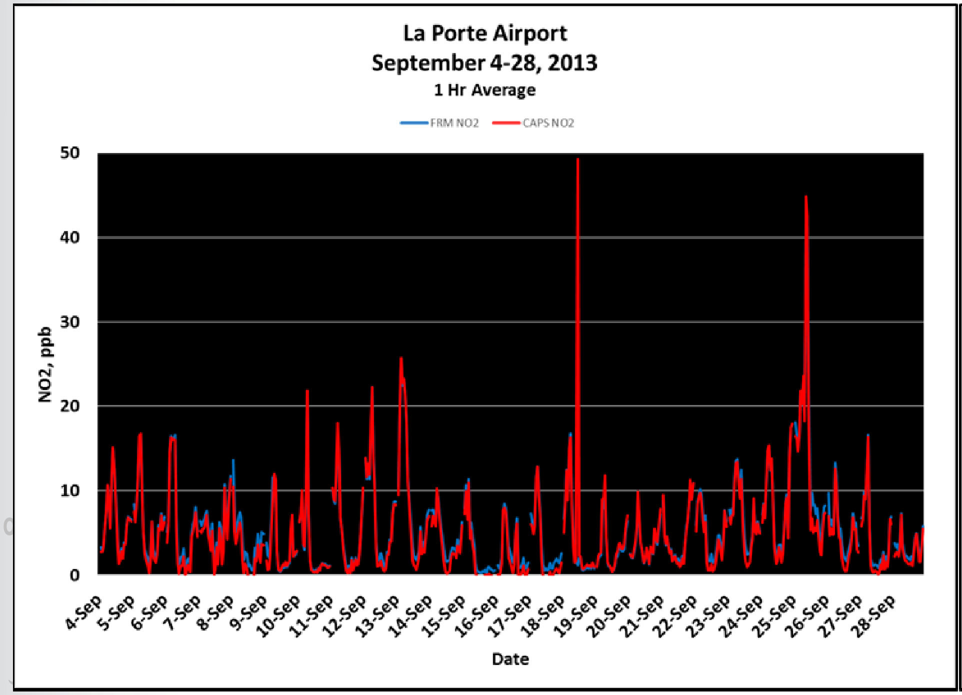


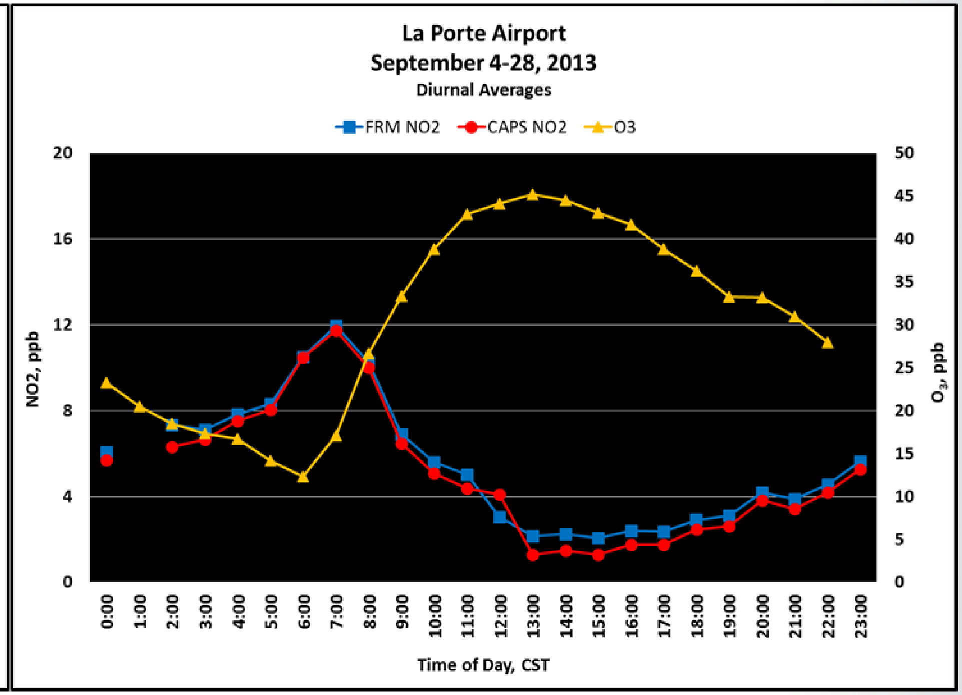


Photochemistry Dominated

- **NO_2 measured by the conventional FRM (Moly converter-chemiluminescence) is overestimated by as much as 50% as compared to more selective (optical, photolytic) NO_2 methods during peak photochemistry hours at sites (Padonia, Golden) that are not dominated by persistent nearby sources.**

Comparison of NO_2 Measurements FRM vs Optical/Photolytic

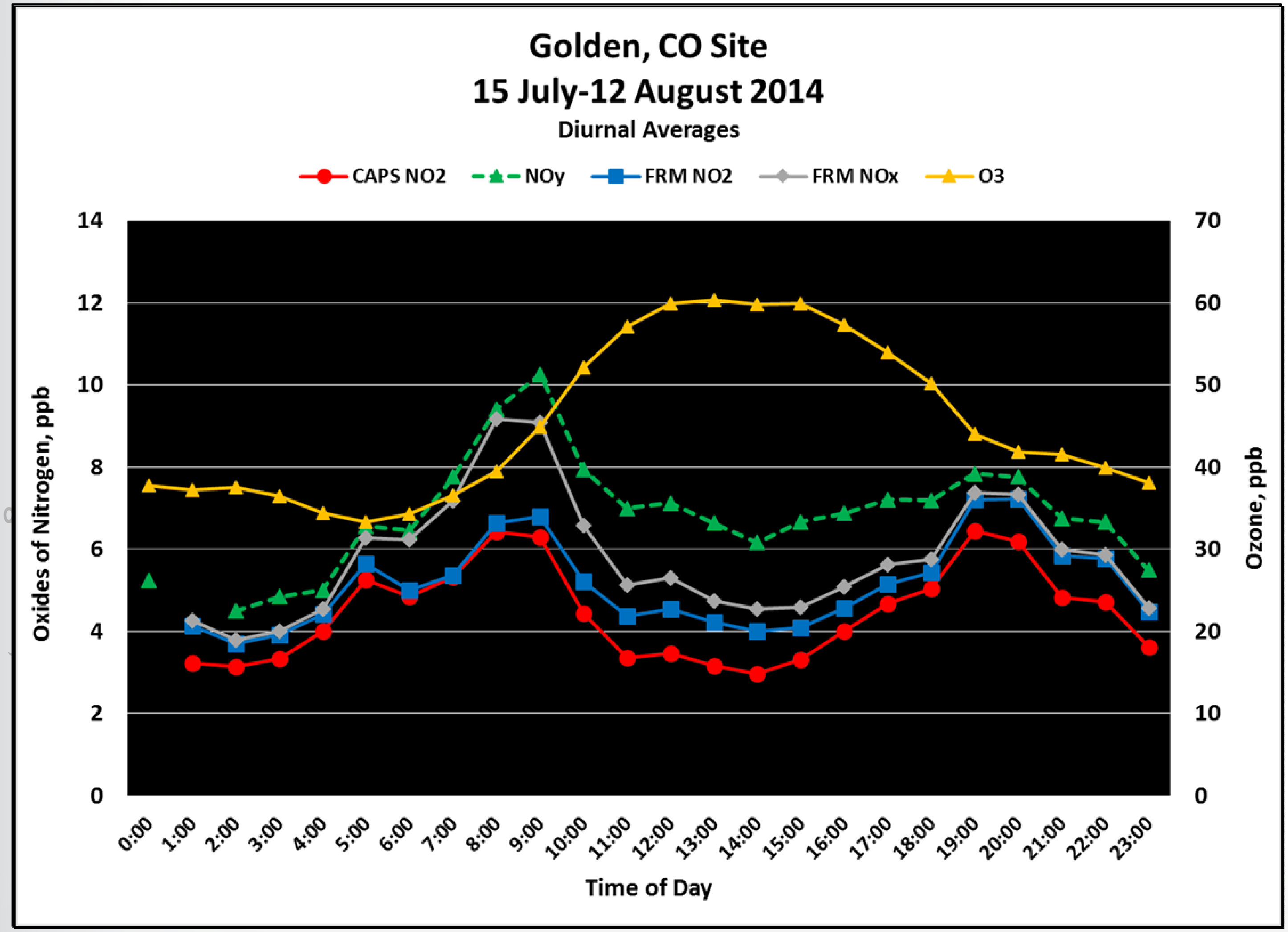




Fresh Emissions Dominated

- **At near source sites (Visalia Airport, La Porte Airport) better agreement is obtained between the FRM and optical/photolytic NO_2 methods.**

Comparison of NO_2, NO_x, and NO_y Measurements



- In general, NO_y results are equal to or greater than FRM NO_x results indication removal of higher oxides of nitrogen (NO_z) in the FRM sample stream.
- Greatest differences between NO_y and FRM NO_x (NO_y-NO_x) are observed during peak photochemistry hours and correlated with ozone concentrations.

Laboratory Studies

Effect of converter temperature on molybdenum converter efficiency

- **Teledyne API T200U FRM – user selectable converter temp. (315 °C default)**
- **Thermo 42iY NO_y Analyzer – user selectable converter temp. (325 °C default)**
- **Determined converter efficiency (NO_2) per 40 CFR Part 50 Appendix F at 3 temperatures**

Analyzer	Converter Temperature °C		
	315	325	340
T200U FRM	98.9%	99.7%	100.0%
42iY NOy	99.8%	99.6%	99.3%

- **Little or no difference was observed in converter efficiency when operating at converter temperatures from 315 to 340 °C.**

Laboratory Studies

Evaluation of calibration/challenge techniques for oxides of nitrogen analyzers

- **Nitrogen dioxide (NO_2) by gas phase titration (GPT, standard method)**
- **N-propyl nitrate (NPN, compressed gaseous standards)**
- **iso-propyl nitrate (IPN, compressed gaseous standards)**
- **NO_2 (compressed gaseous standards)**
- **Teledyne API T200U FRM – 315 °C (default) converter temp**
- **Thermo 42iY NO_y Analyzer – 325 °C (default) converter temp**

Average GPT Calibration Responses

Analyzer	Zero	200 ppb	High GPT	Low GPT	Delta High	Delta Low
42iY NO	0.0	200.2	99.2	165.7		
42iY Diff	0.0	0.2	**101.1**	**34.6**	**100.9**	**34.4**
42iY NO_y	0.0	200.3	200.3	200.3		
T200U NO	-0.1	198.9	96.7	149.1		
T200U NO_2	-0.6	0.1	**103.8**	**51.9**	**102.2**	**49.8**
T200U NO_x	-0.8	199.0	200.5	201		

Laboratory Studies

Average NPN Calibration Responses

Analyzer	Zero	100 ppb	50 ppb
42iY NO	0.0	0.6	0.2
42iY Diff	0.2	98.1	49.0
42iY NO_y	0.2	98.7	49.1
T200U NO	-0.1	1.0	0.4
T200U NO_2	-0.7	97.6	49.1
T200U NO_x	-0.8	98.6	49.4

Average IPN Calibration Responses

Analyzer	Zero	100 ppb	50 ppb
42iY NO	0.0	0.5	0.2
42iY Diff	0.0	98.7	49.4
42iY NO_y	0.0	99.2	49.6
T200U NO	-0.1	0.6	0.3
T200U NO_2	-0.6	100.6	50.4
T200U NO_x	-0.7	101.2	50.8

Laboratory Studies

Average NO_2 Calibration Responses

Analyzer	Zero	100 ppb	50 ppb
42iY NO	0.0	0.5	0.2
42iY Diff	0.0	96.7	49.0
42iY NO_y	0.0	97.1	49.1
T200U NO	-0.1	1.0	0.4
T200U NO_2	-0.5	97.6	49.1
T200U NO_x	-0.7	98.6	49.4

Average percent difference between expected value and analyzer response

Analyzer/Cal method	High	Low
42iY/GPT	0.5	0.7
42iY/IPN	-1.9	-3.0
42iY/NPN	-1.3	-2.7
42iY/NO_2	-2.5	-3.7
T200U/GPT	2.1	4.7
T200U/IPN	2.4	1.5
T200U/NPN	-1.6	-1.2
T200U/NO_2	-1.2	-1.7

Regardless of the calibration/challenge method (i.e., GPT vs. IPN vs. NPN vs. NO_2), very similar results were obtained in instrument response.

Next Steps

- **Continue ambient and laboratory based evaluations of NO_2, NO_x and NO_y methods to support NO_2 and NO_x/SO_x Secondary NAAQS reviews.**
  - **Investigation and revision of calibration/challenge procedures**
  - **Investigation of interferences in the NO_x and NO_y determination using HB-converters**
    - **NH_3 interference in NO_2 FRM and NO_y**
    - **Effect of converter temperature on interferences (i.e., NH_3, NO_z)**
- **Continued analysis of data and results from previously completed field studies.**
  - **DISCOVER-AQ**
    - **Direct Optical NO_2 vs FRM NO_2, NO_x and NO_y**
    - **Near roadway applications of NO_2 methodology**
  - **AIRS RTP**
  - **KORUS-AQ**

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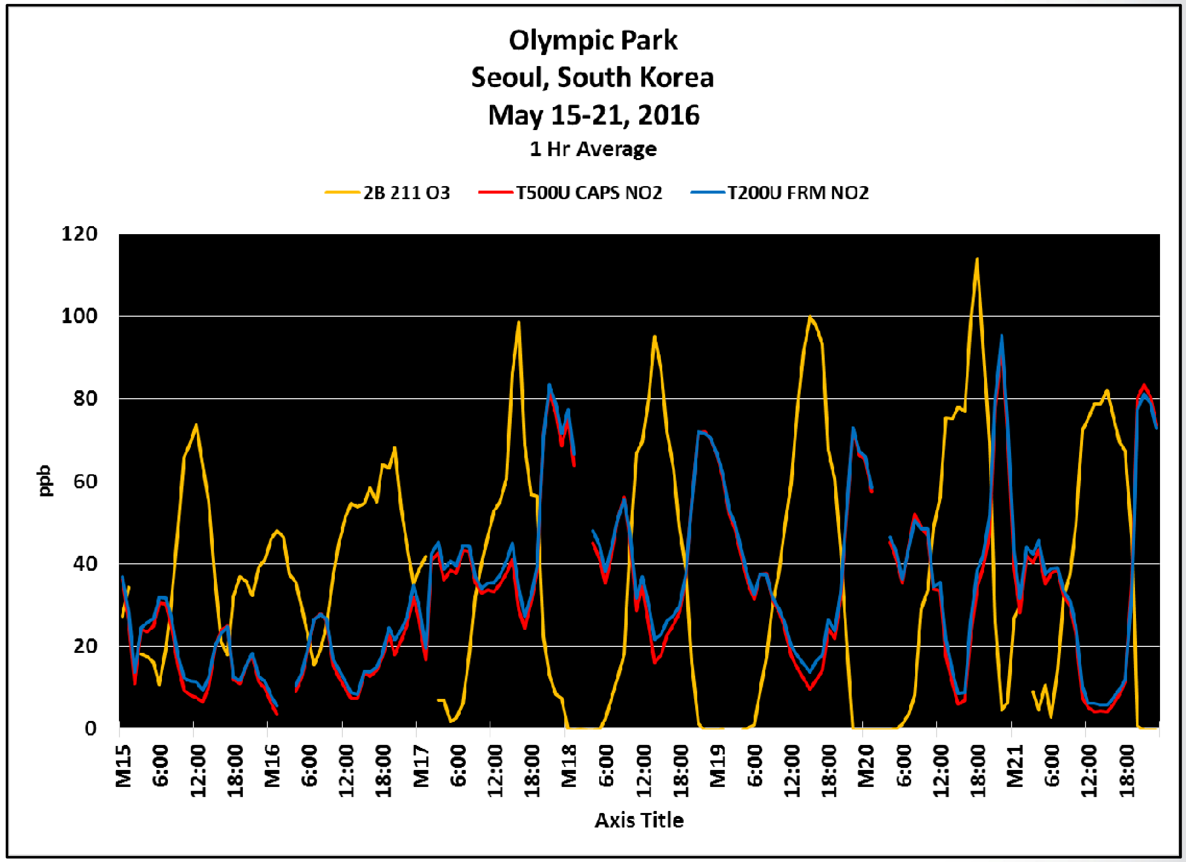
Next Steps



NO_2 methods evaluations performed in Seoul, South Korea during KORUS-AQ Study

Disclaimer

Although this work was reviewed by EPA and approved for presentation, it may not necessarily reflect official Agency policy.

Questions

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