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Ambient Intercomparison of Direct and Indirect Methods for the Measurement of Nitrogen Dioxide (NO_2)

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National Ambient Air Monitoring Conference
Atlanta, GA

Outline

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- Motivation and background
- Overview of methods for NO_2 monitoring
- Deployment of NO_2 analyzers in two environments
  - San Joaquin Valley, CA
  - Research Triangle Park, NC
- Analyzer performance assessments
  - One-minute data
  - Hourly-averaged data
- Brief looks at ongoing analyses: La Porte, TX and Golden, CO
- Next steps

Research Question and Motivation:

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- How do chemiluminescence-based NO_2 measurements (with prior thermal or photolytic conversion) compare with direct, optical analyzers?

- EPA ORD's interest in accurate NO_2 measurements supports:
  - Monitoring networks
  - Reference and equivalent method determinations and evaluations
  - Ground-based satellite validation work with NASA-DISCOVER-AQ

NASA's DISCOVER-AQ Project

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- Deriving Information on Surface Conditions from COlumn and VERtically resolved observations relevant to Air Quality
- How can air quality be reliably informed using non-traditional approaches such as satellite remote sensing?
- Multiyear study:
  - Baltimore/Washington DC → July 2011
  - San Joaquin Valley, CA → Jan/Feb 2013
  - Houston area, TX → September 2013
  - Denver/Front Range, CO → July/August 2014
- EPA ORD has been a collaborator since 2011, and uses deployments as an opportunity to evaluate criteria pollutant monitoring methods.
- http://www-air.larc.nasa.gov/data.htm

How is NO_2 (currently) measured?

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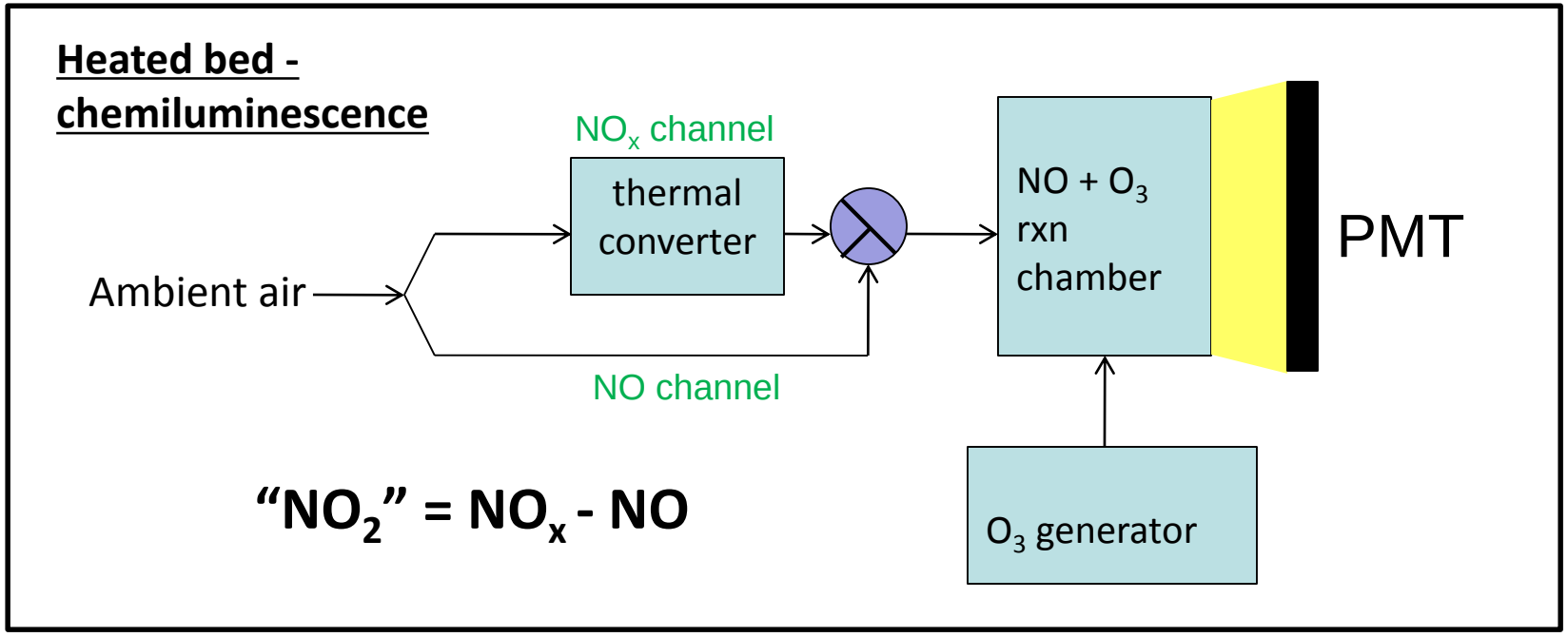
- Federal (Automated) Reference Method (40 CFR, Part 50, Appendix F):
  - **-Gas-phase chemiluminescence**
  - -Indirectly measure NO_2 by conversion to NO, then NO is detected by chemiluminescence ($NO + O_3 \rightarrow NO_2^*$, NO_2^* = excited state);



- -Advantage→ in use since the 1970s (long term record)
- -Disadvantages → non-specific; indirect

FRM has possible interferences

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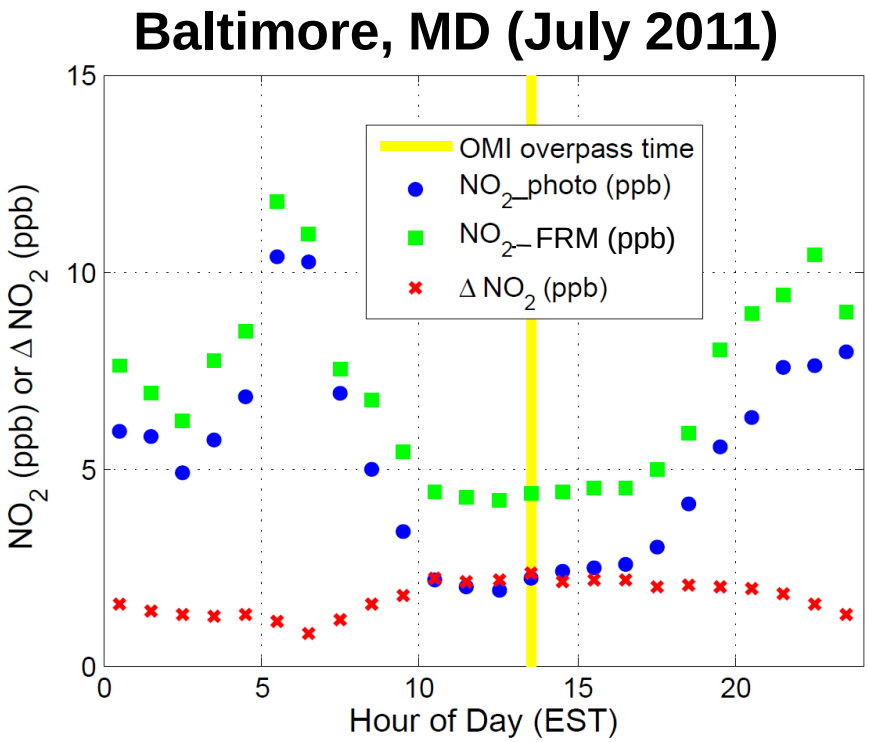
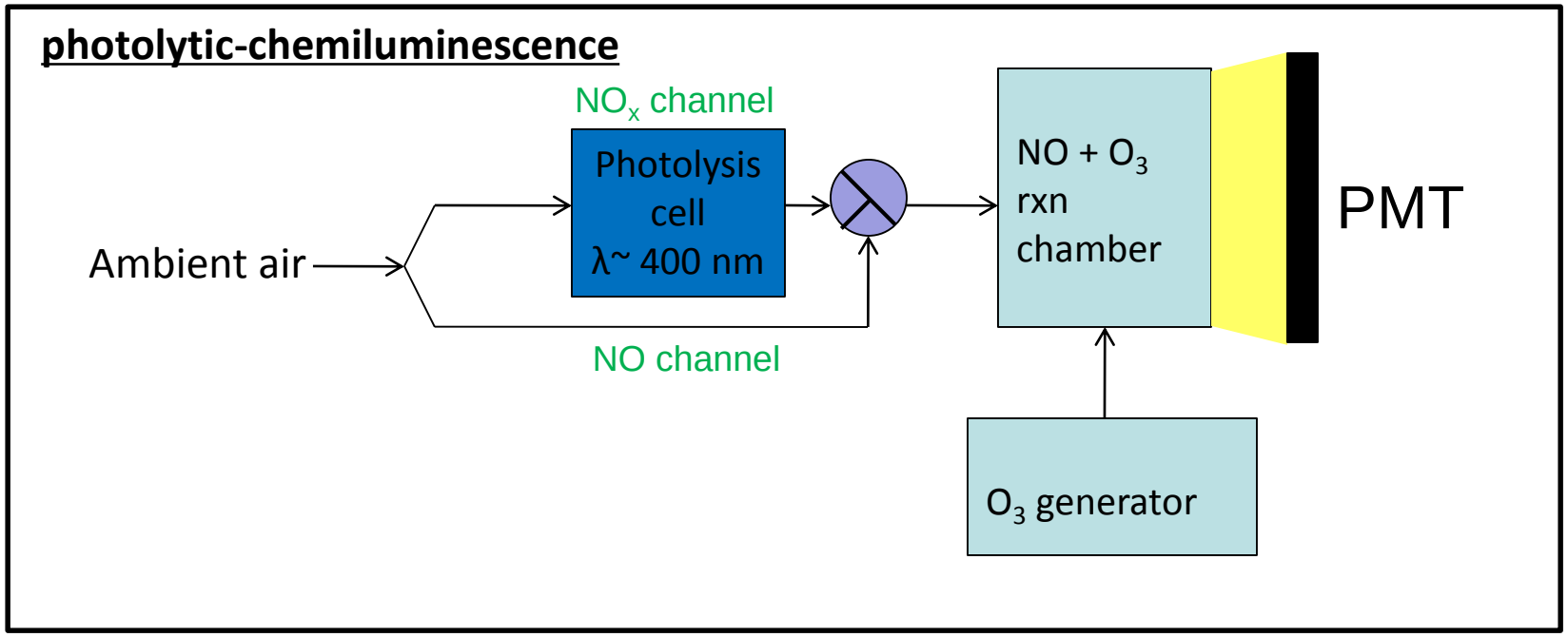


ΔNO_2 = FRM_NO_2 – photo_NO_2

- The interference in the FRM monitor over predicts by ~50% during the hours surrounding noon.
- Difference is correlated with ozone → implies interference is related to photochemical activity
- Dunlea et al. (2007) *Atmospheric Chemistry and Physics* - also observed this in Mexico City.

Alternative Technique: Photolytic-chemiluminescence

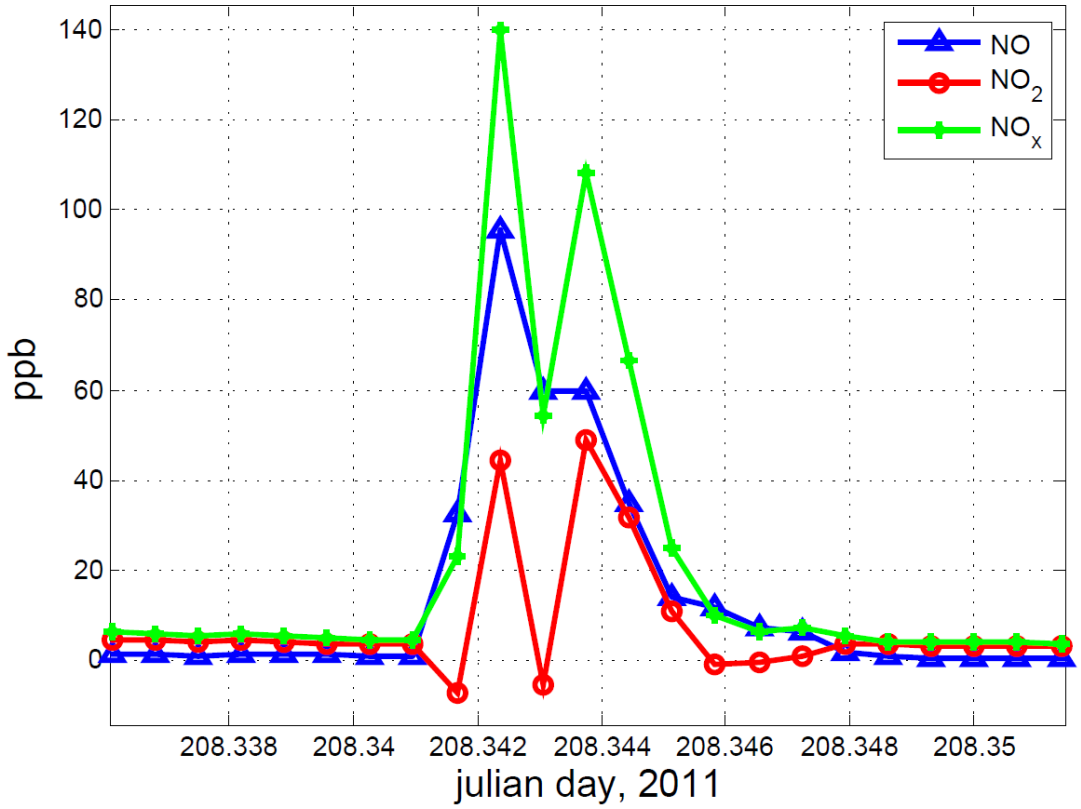
- Replace the metal bed reducer with a photolysis cell to photolyze NO_2 to NO ($NO_2 + h\nu \rightarrow$ **NO** + O; 350-420nm).
  - -Use high-power light sources to maximize conversion to NO.
- Federal Equivalent Method (FEM); designated in June 2012



- Advantage → more specific to NO_2
- Disadvantages → non-unity conversion efficiency; still indirect

Indirect methods have possible interferences

- NO spikes → The indirect determination requires the NOx distribution to change slower than the measurement cycle, otherwise, negative or positive spikes of NO_2 are possible:



Direct, Optical Analyzers Investigated

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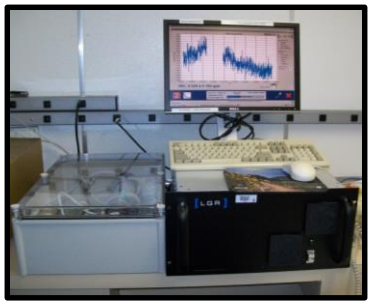
Manufacturer and Model	*Operation Principle*	*FRM/FEM status*
Los Gatos Research NO_2 	Cavity ringdown spectroscopy (CRDS)	--
Teledyne T500U 	Cavity attenuated phase shift spectroscopy (CAPS)	FEM application approved (*designated May 2014)
Environnement SA AS32M 	Cavity attenuated phase shift spectroscopy (CAPS)	FEM application approved (*designated Nov 2013)

Direct Optical Techniques

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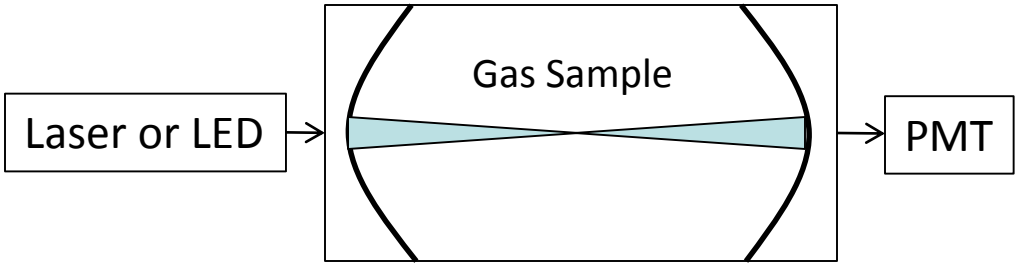
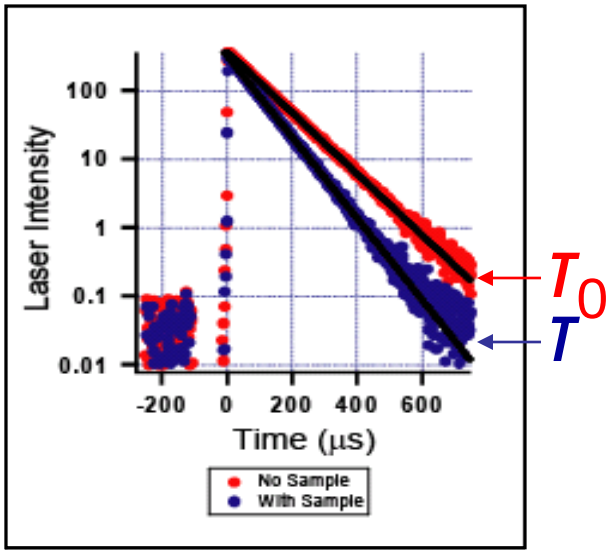
- Cavity ringdown spectroscopy (CRDS)
  - instrument manufactured by Los Gatos Research, Inc.



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



- 10 s time resolution
- Advantage → DIRECT measurement
- Disadvantages → not-necessarily specific to NO_2, but to any molecule that absorbs light at 405 nm

Direct Optical Techniques

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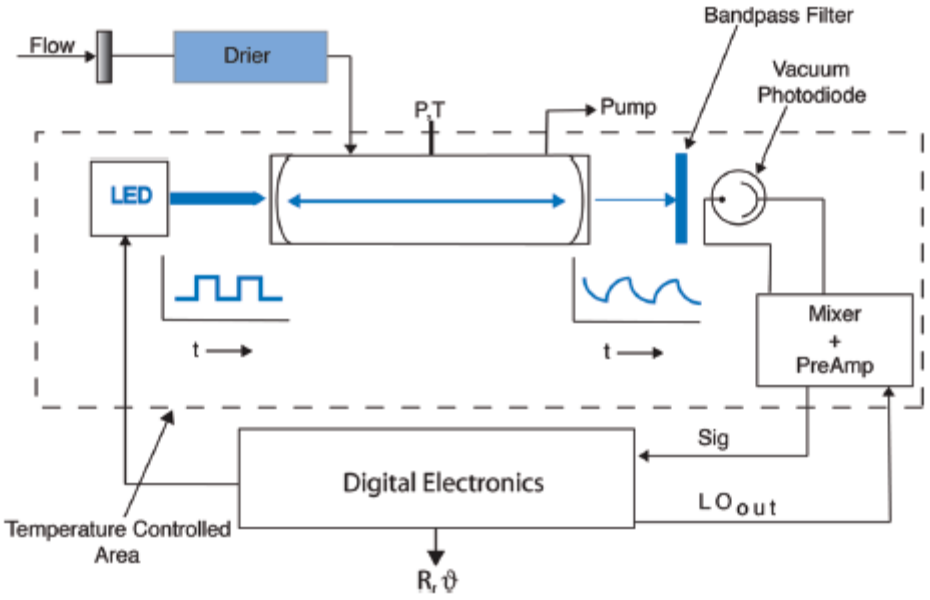
- Cavity attenuated phase shift spectroscopy (CAPS)
  - instrument manufactured by Teledyne API and Environnment SA



- 5 s time resolution
- Advantage → DIRECT measurement
- Disadvantage → not-necessarily specific to NO_2, but to any molecule that absorbs light at ~450 nm

Kebabian et al. ES&T 2008

Two Ambient Evaluations

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Visalia, CA

- Visalia Municipal Airport
- NASA DISCOVER-AQ collaboration
- Jan – Feb 2013
- inlets ~35m from I-99 (60,000 AADT); 17% heavy duty truck traffic
- Thermal conversion, Photolytic conversion, and CRDS analyzers compared

RTP, NC

- EPA RTP, on-site ambient measurement site
- SOAS-RTP collaboration
- August 2013
- background/regionally influenced site
- Thermal conversion, Photolytic conversion, and CRDS, and CAPS analyzers compared

Sampling and Calibration

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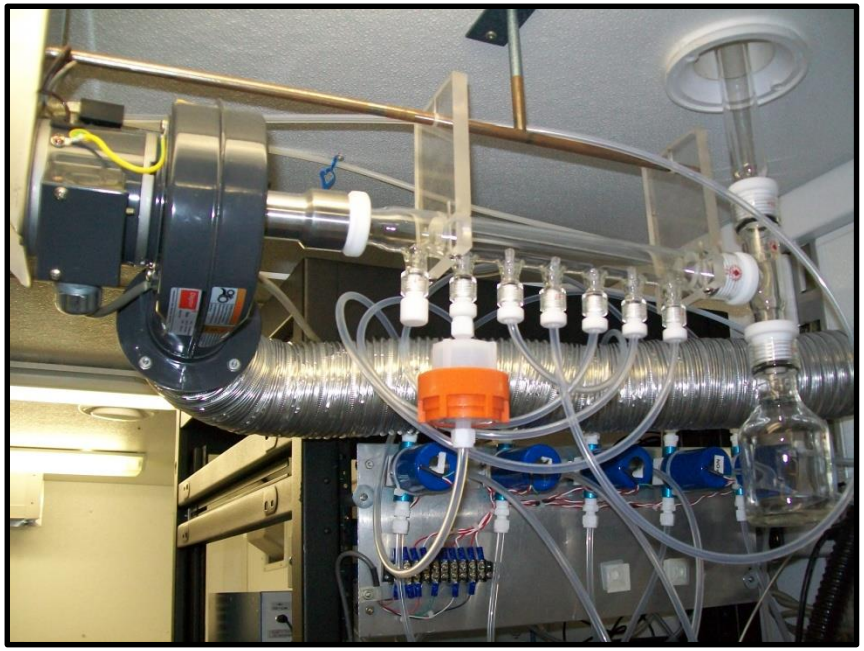
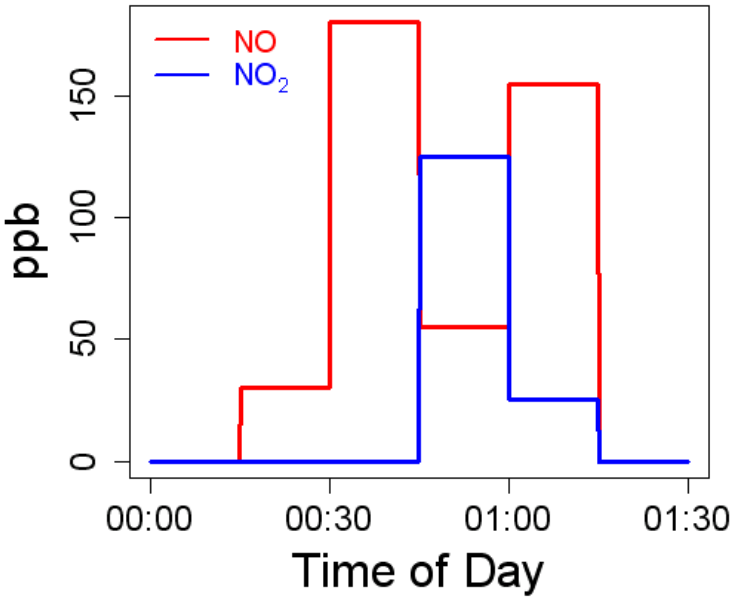


Gas-phase titration of NO (excess) with O_3



- If response is outside ±10% of the expected response, data are excluded from the analysis.

Visalia, CA (winter)

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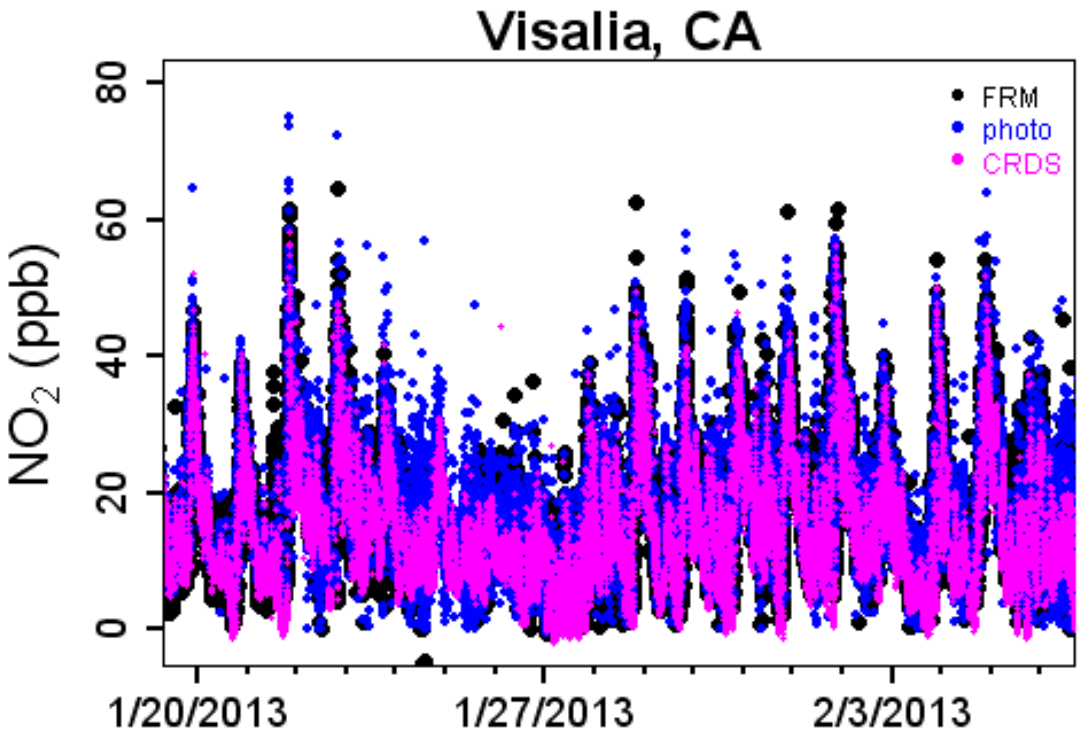

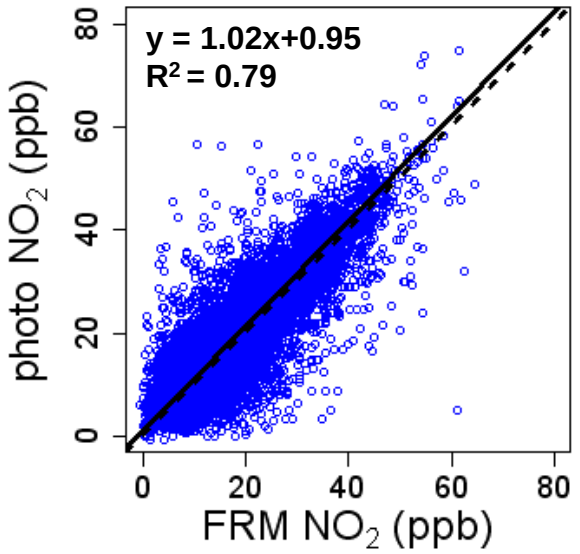

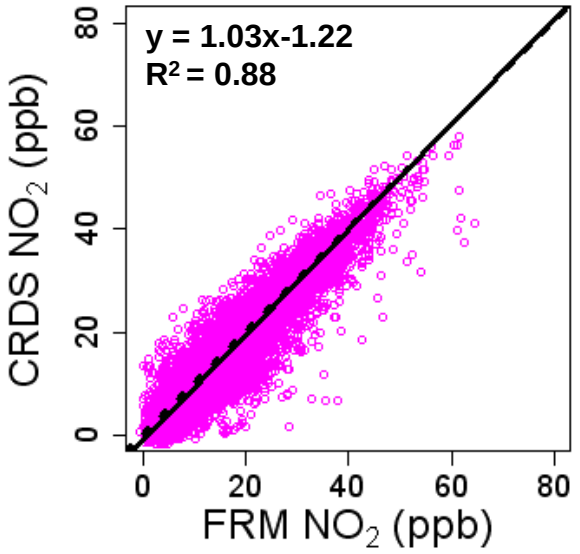

- 18 days, 1 minute data
- Overall, good agreement
- More scatter between indirect methods than between direct and indirect

RTP, NC (summer)

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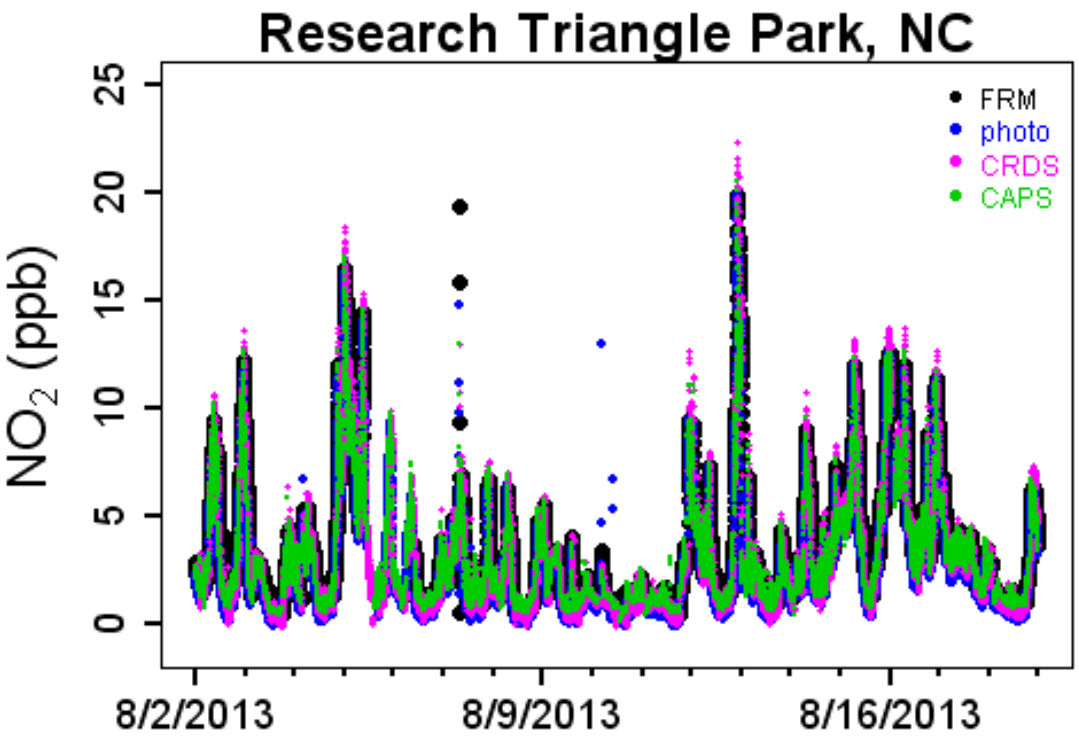
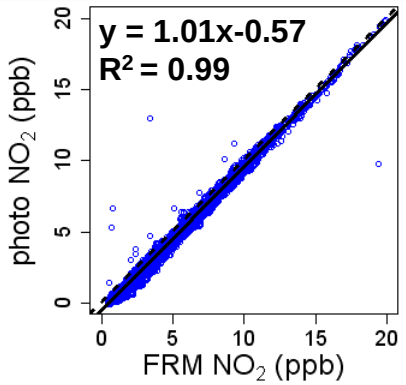
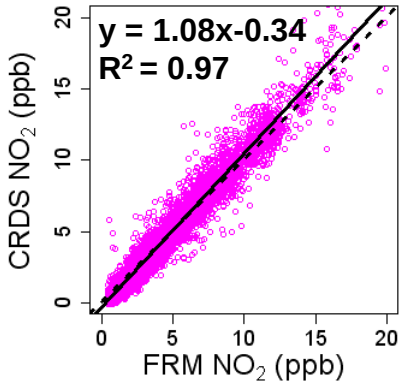
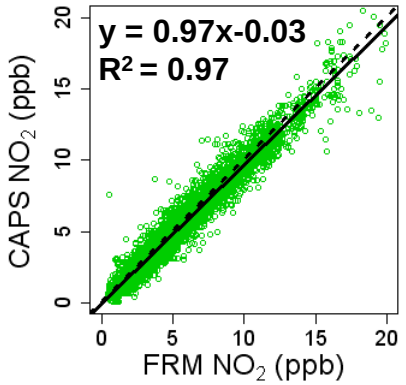


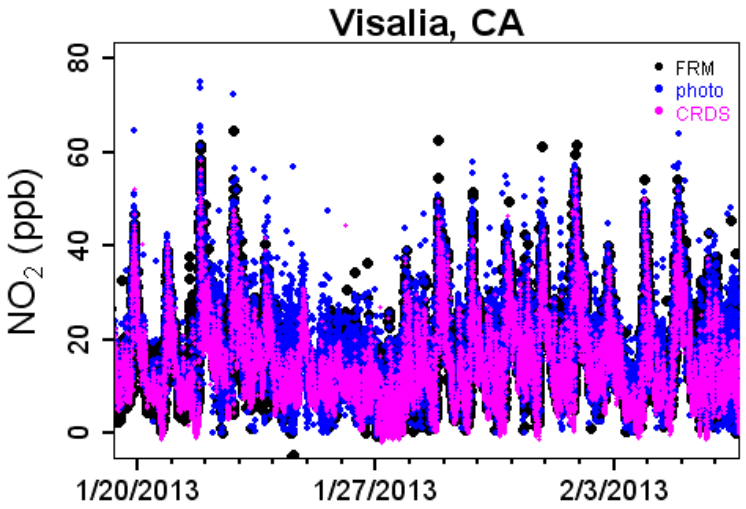


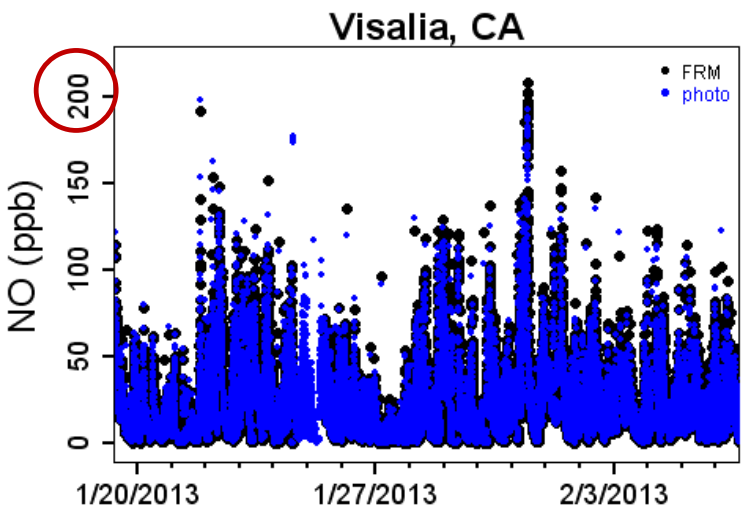


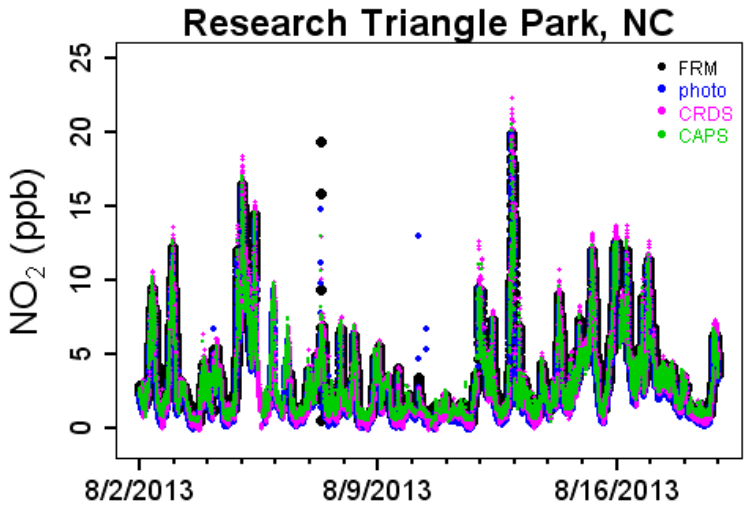


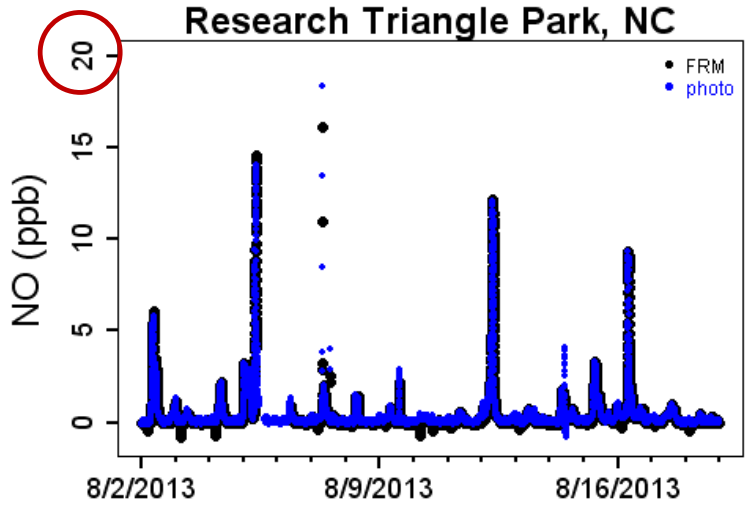
- 18 days, 1 minute data
- CRDS spans were high, but within +/- 10%
- High R^2 between methods

Influence of NO concentrations on correlations?









- NO concentrations in Visalia 10 x higher than in RTP

Influence of NO concentrations?

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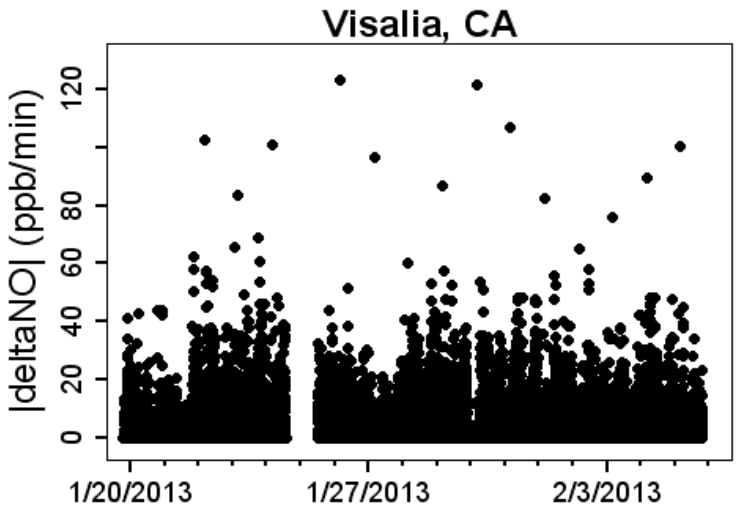
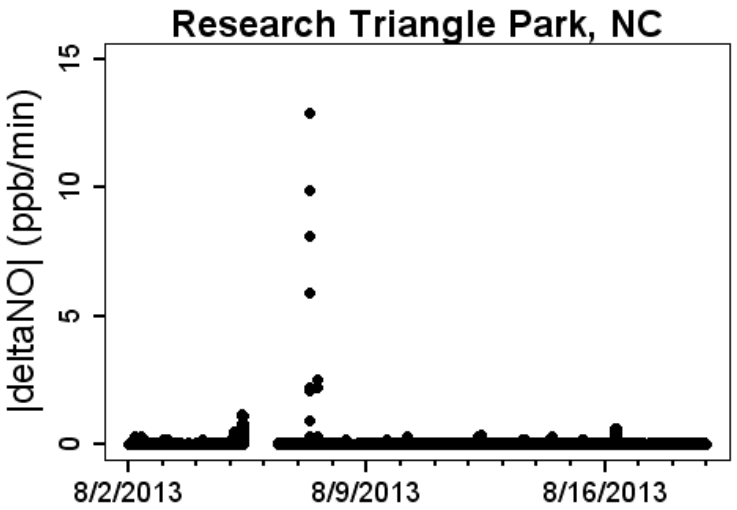
|deltaNO| = absolute value of the diff() between a point and the following point.





Influence of NO concentrations on the indirect methods?

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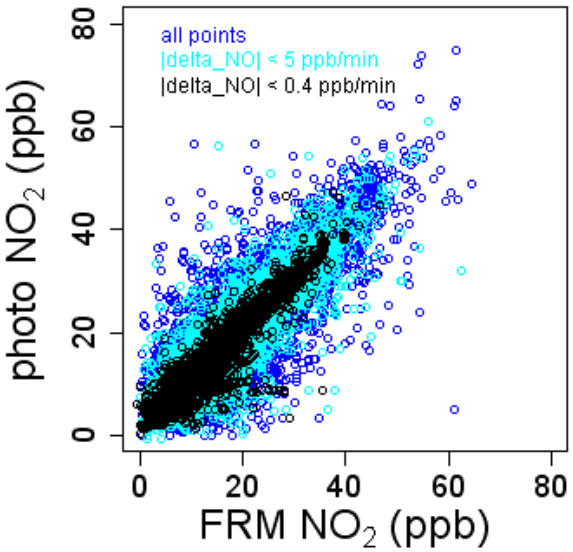
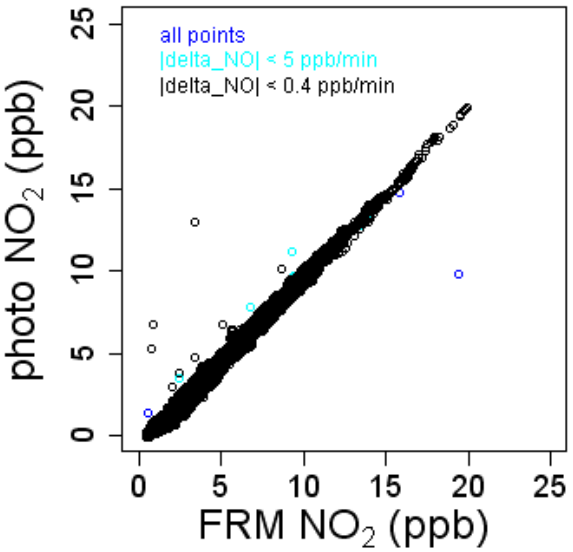
Visalia, CA



	fit	R^2	n
All points	y=1.0x+1.0	0.79	24,468
|ΔNO| < 5ppb/min	y=1.0x+1.3	0.85	15,954
|ΔNO| < 0.4ppb/min	y=0.99x+1.4	0.90	7,900

RTP, NC



	fit	R^2	n
All points	y=1.01x-0.6	0.99	21,701
|ΔNO| < 5ppb/min	y=1.01x-0.6	0.99	21,661
|ΔNO| < 0.4ppb/min	y=1.01x-0.6	0.99	21,608

Influence of NO concentrations on the direct method?

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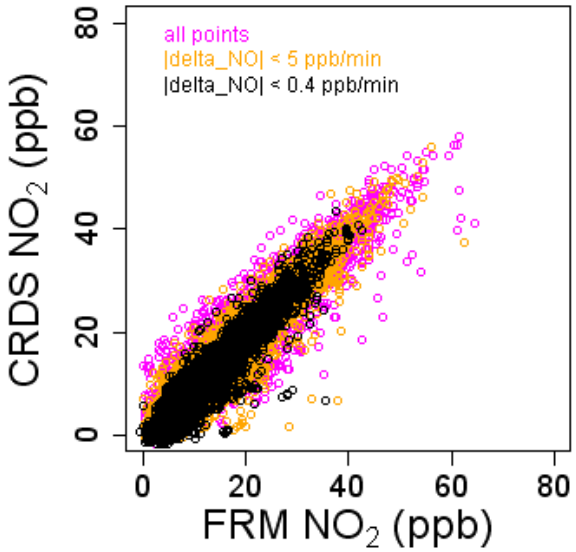
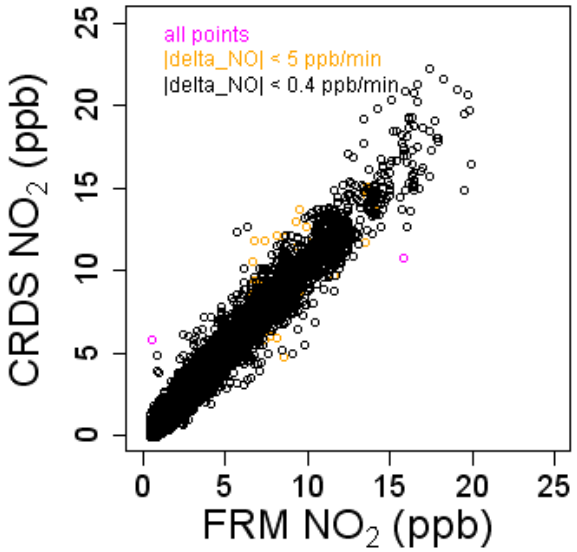
Visalia, CA



	fit	R^2	n
All points	y=1.0x-1.2	0.88	19,000
|ΔNO| < 5ppb/min	y=1.0x-1.5	0.88	13,821
|ΔNO| < 0.4ppb/min	y=1.05x-1.7	0.88	6,851

RTP, NC



	fit	R^2	n
All points	y=1.08x-0.34	0.97	21,701
|ΔNO| < 5ppb/min	y=1.08x-0.34	0.97	21,691
|ΔNO| < 0.4ppb/min	y=1.08x-0.34	0.97	21,678

Does the variability show up in hourly averages?

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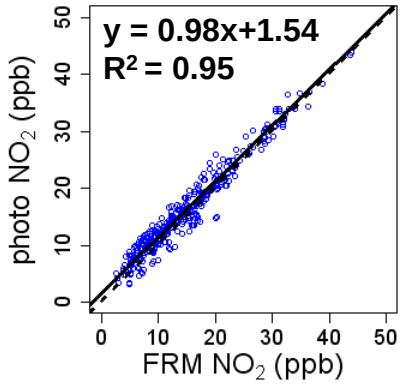
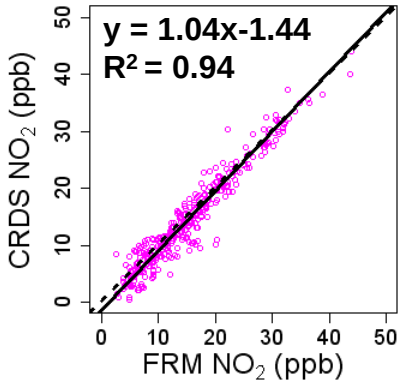
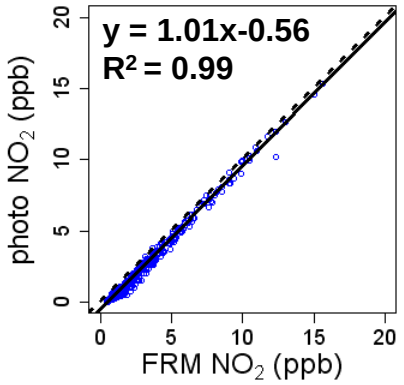
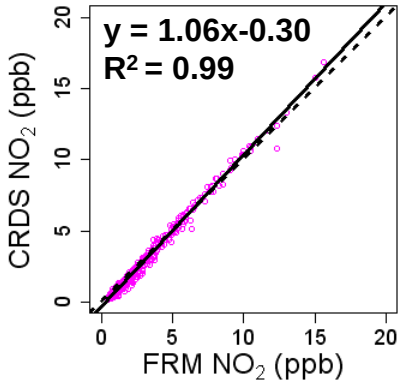
Visalia, CA

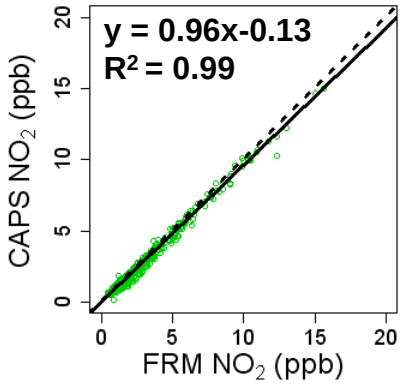




RTP, NC







- When using hourly averaged data, differences between direct and indirect methods are minimal

Ongoing analyses from Houston area DISCOVER-AQ

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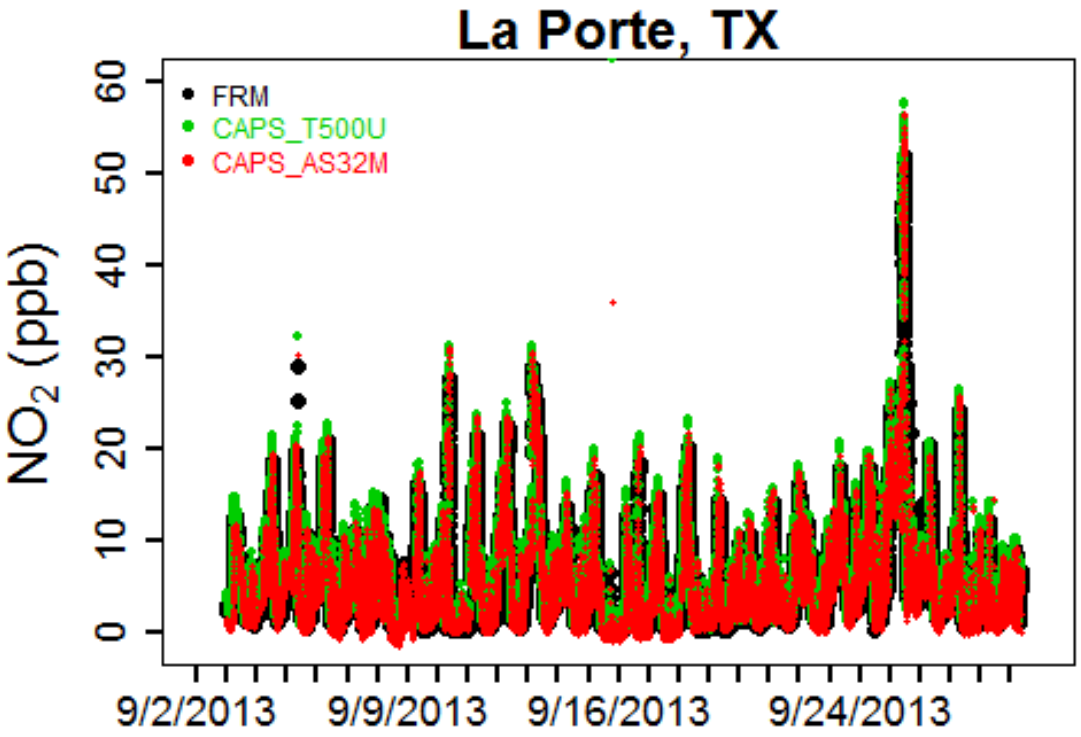
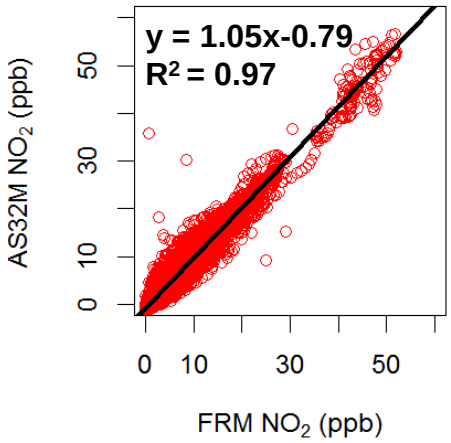
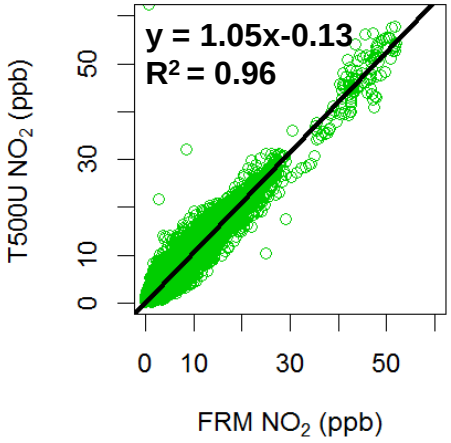
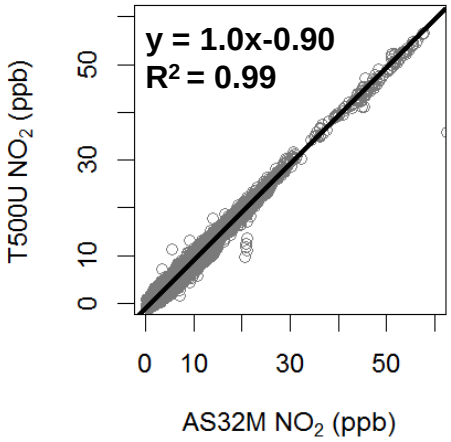




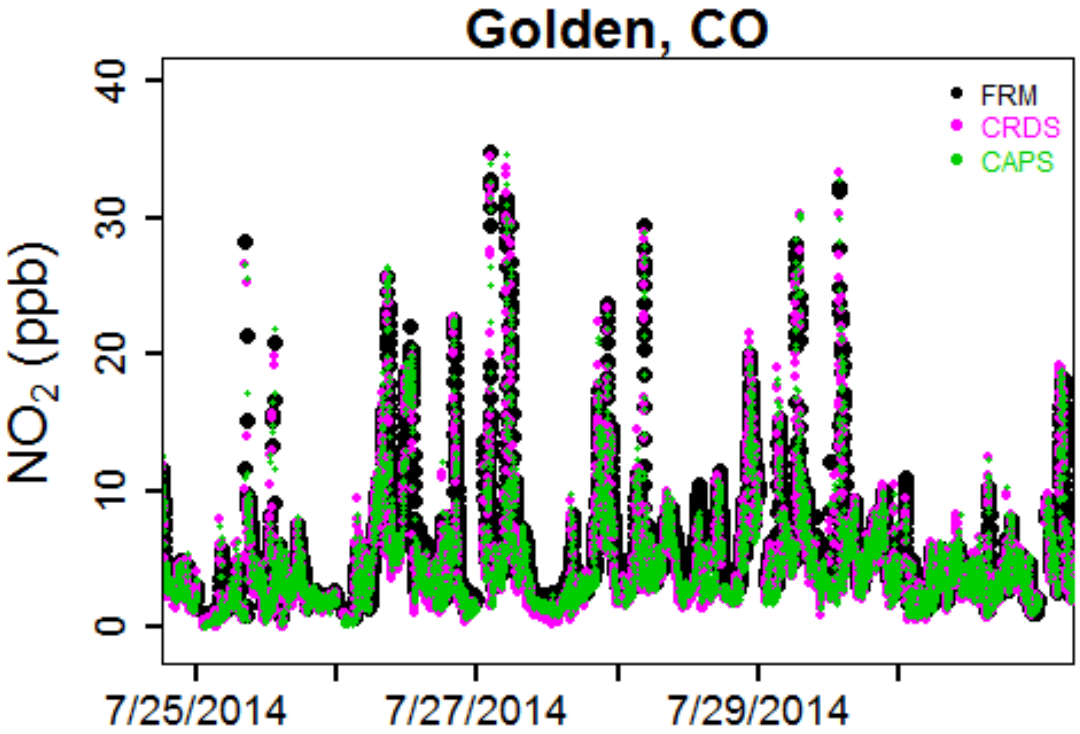




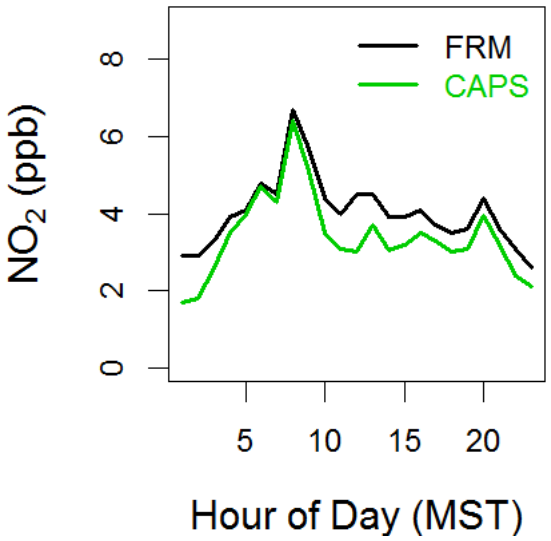
- 26 days, 1 minute data
- both direct analyzers slightly higher than FRM, but within the span tolerance
- Very high R^2 between direct methods

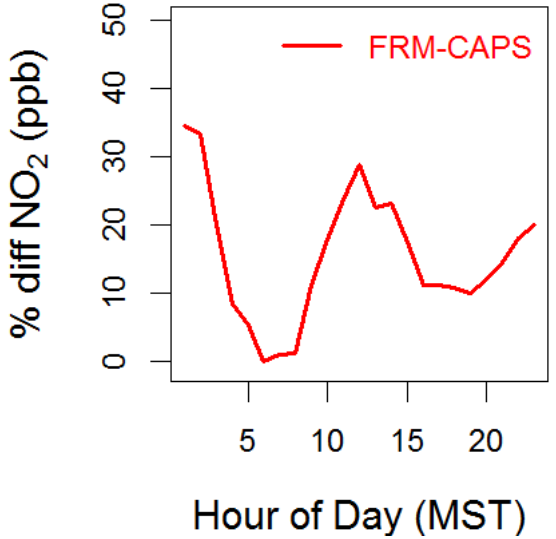
Ongoing work in Golden, Colorado with DISCOVER-AQ

- VERY PRELIMINARY!
- Co-located FRM, CAPS, and CRDS analyzers



- 6 days, 1 minute data





NO_2 Research Initiatives and Next Steps

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- Currently evaluating NO_2 FRM, FEM, and direct optical methods to support EPA's reference and equivalent method determinations
- Ambient datasets are currently being analyzed for their performance under a variety of atmospheric conditions (downwind of an urban area – Baltimore; background site – RTP, NC; near roadway – Visalia, CA; industrial/urban – LaPorte, TX).
- Direct optical methods may be preferable in near-roadway locations
- No significant interferences from NOy compounds were observed in CA or NC.

- Continue collecting ambient NO_2 and NO_y data in Denver, CO 2014 in collaboration with NASA DISCOVER-AQ
- Laboratory testing for NO_2 methods to include extended noise and stability testing; interference tests with H_2O and NO; calibration procedure recommendations

Acknowledgements

- Jim Szykman (EPA/NASA liaison)
- NASA (Jim Crawford, Mary Kleb, Luci Crittenden)
- MDE (Jennifer Hains, Ryan Auvil)
- SJVAPCD (Nathan Trevino)
- City of Visalia (Mark Bettencourt)
- TCEQ (Raj Nadkarni, Mark Estes)
- CDPHE (Gordon Pierce, Greg Harshfield, Erick Mattson)

- Mark Chamberlin, Altech/Environment USA

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

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Supporting Slides

UV/Vis Spectroscopy of NO_2

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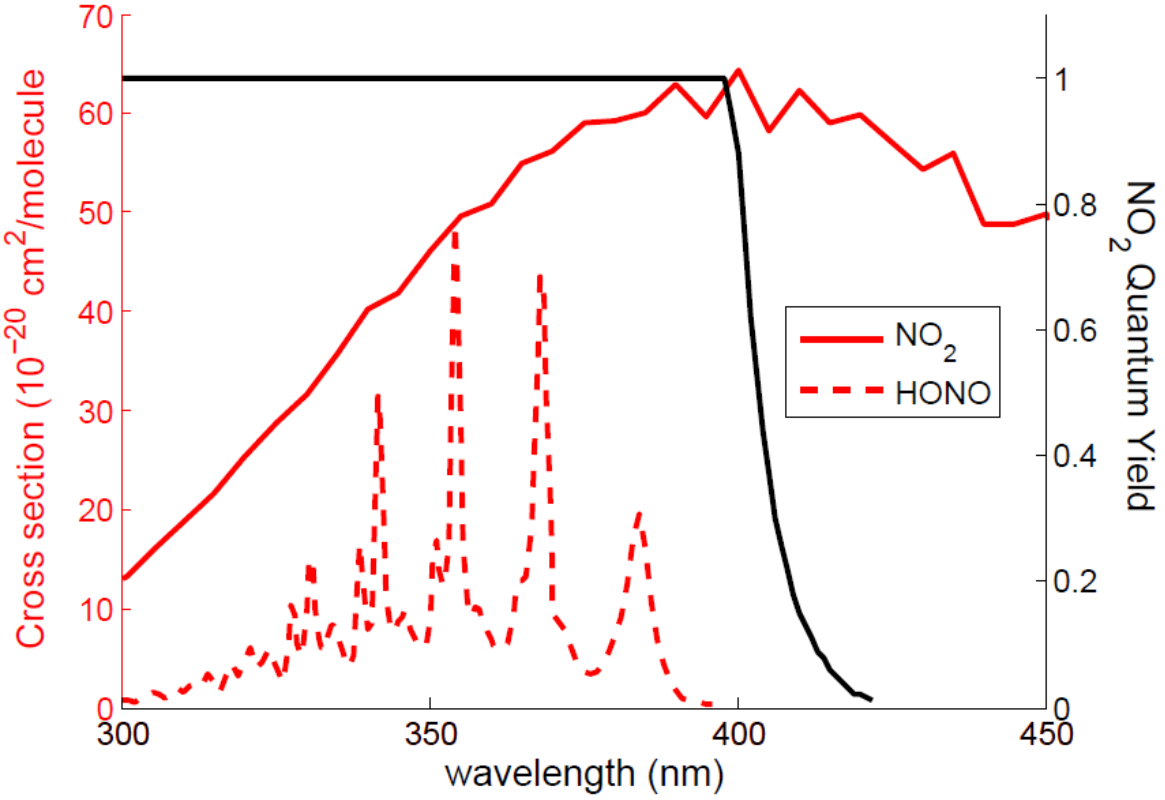

Data from Sander et al. (2006)

Nightly Span/Zero Checks

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Manufacturer and Model	*Size (h x w x l)*	*weight (lbs.)*	*Power (W)*	*Sample flow, vol (Lpm)*	*Cost ($USD)*
Teledyne T200U	7”x 17”x 24”	~55	500	1.0	~16K
Teledyne 200EUP	7”x 17”x 24”	~55	600	1.1	~25K
Teledyne T500U (CAPS)	7”x 17”x 24”	33	80	0.9	~18K
Los Gatos Research NO_2 (CRDS)	7”x 19”x 24” (plus external drier)	60	100	0.9	~30K

Current NO_2 Regulations

United States Environmental Protection Agency

- The Clean Air Act requires EPA to set National Ambient Air Quality Standards (NAAQS) for criteria pollutants:

NO_2 Primary Standards		
level	*averaging time*	*year implemented*
53 ppb	Annual	1971
100 ppb*	1 hr	2010

* The monitoring locations for the Jan 2010 primary standard are to be sited in near roadway locations to capture areas of maximum concentration. (http://epa.gov/ttn/amtic/nearroad.html)