Global Analyzer Systems Ltd.

Measurement Errors of NO_2 using Heated Metal Converters in Chemiluminescence Analyzers

A presentation by:

Charles Odame-Ankrah, PhD, PChem

(Research Manager, Global Analyzer Systems Ltd.)

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EnviroTech 2019

Presentation Outline

1) Project Objectives
2) Atmospheric Chemistry of NO_x (Summary)
3) Upgrading a Chemiluminescent Analyzer
4) Field Trials
5) Conclusions

Project Objectives: True NO_2?

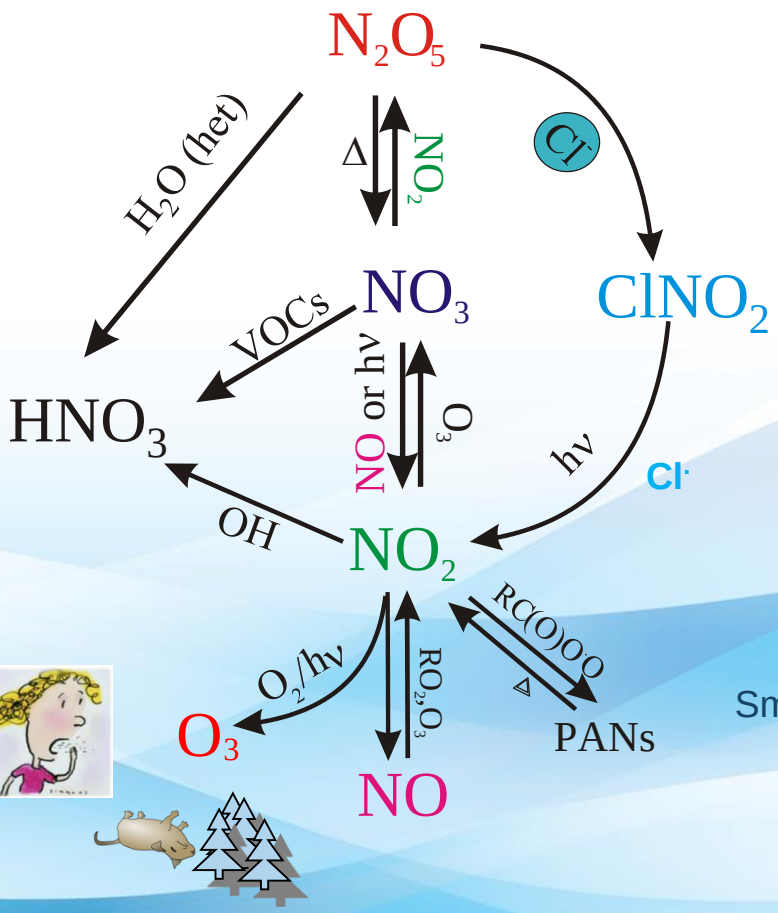
Create a device that enables existing analyzers to SELECTIVELY measure NO_2

- Linear conversion over a wide dynamic range
- Simple external installation
- Fast response & high resolution
- Conversion efficiency >96%

In order to….

- Reduce the potential over-reporting of NO_2/NO_x
- Meet evolving Federal Regulations

Nitrogen Oxides in the Troposphere



Health implications,
Breathing problems

Smog

NO NO_2

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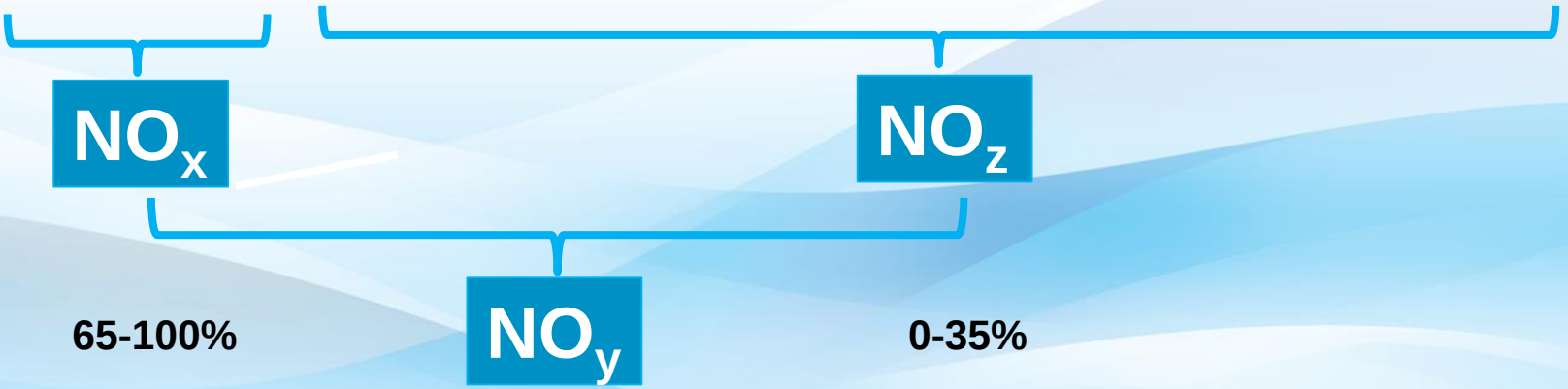
NO_x, NO_y, NO_z & Chemiluminescence



$$NO_y = NO_x + HNO_3 + NO_3^- + PANs + NH_3 + ClNO_2 + 2N_2O_5 \ldots$$

Measuring NO_2 with NO-O_3 CL Method

Common Technique

Indirect Measurement: Convert NO_2 to NO
(detect via Chemiluminescence of ozone and NO)

1) Heated Metal Converters (Mo/SS)
   - + Efficient
   - + Long Life
   - + Reliable
   - - NOT SPECIFIC

2) Photolytic Converter
   - + Selective to NO_2
   - + Efficient
   - + Long Life
   - + Reliable

Heated Metal Converters are not Specific!

- Heated metal catalytic converters are non-selective.
- Can it always measure NO_x accurately?
- Can NO_2 be overestimated?
- What are the implications?

Detected as light

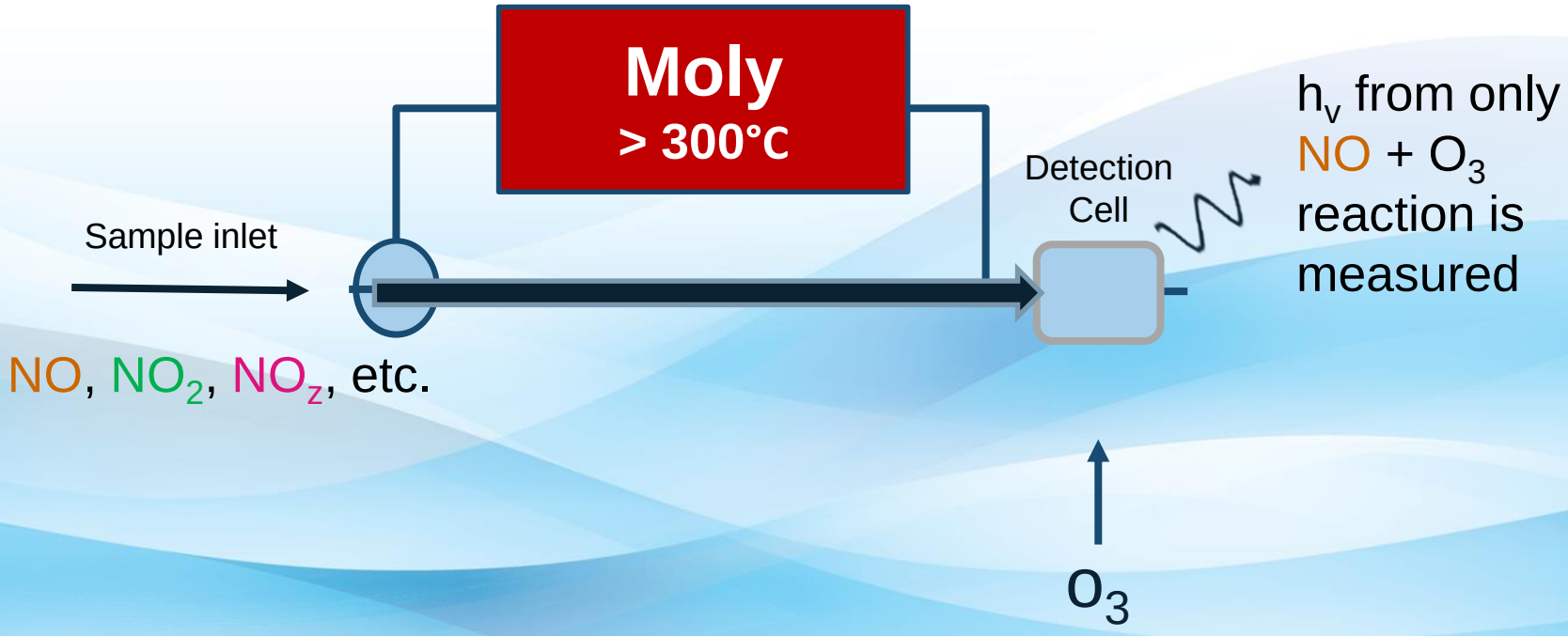
(Chemiluminiscence)

$$+ O_3 \rightarrow NO_2^* \rightarrow NO_2$$

NO_2 may be overestimated

Chemiluminescence - Principle of Operation

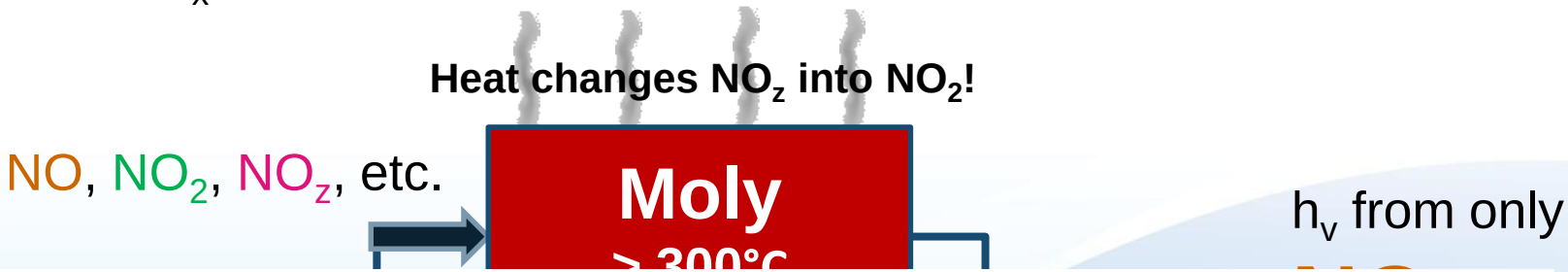
State 1: NO Measurement Mode



Reported as NO Measurement

Chemiluminescence - Principle of Operation

State 2: NO_x Measurement Mode



NO_x and NO_2 can be overestimated by up to 50%[1]

O_3

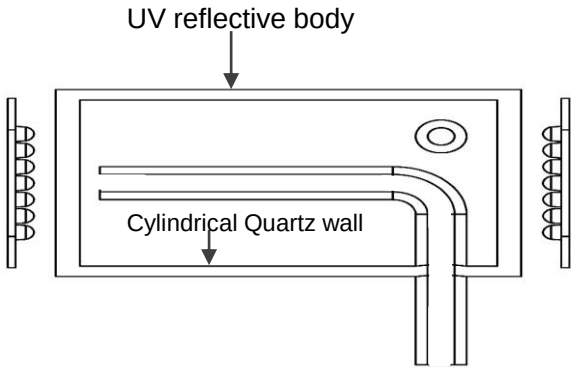
Reported as NO_x Measurement… but is it?

"NO_x" Measurement – NO Measurement = NO_2 + NO_z

Reported as NO_2!

[1]E.J. Dunlea et al. *Atmos. Chem. Phys.*, **7**, 2691-2704 (2007)

Global's Uniquely designed Photolysis Cell



Unique quartz straw design

Optional
2 LED system

Standalone/External

MiniPhoNO

Patent number:
WO2017173552A1 or
US20190086337

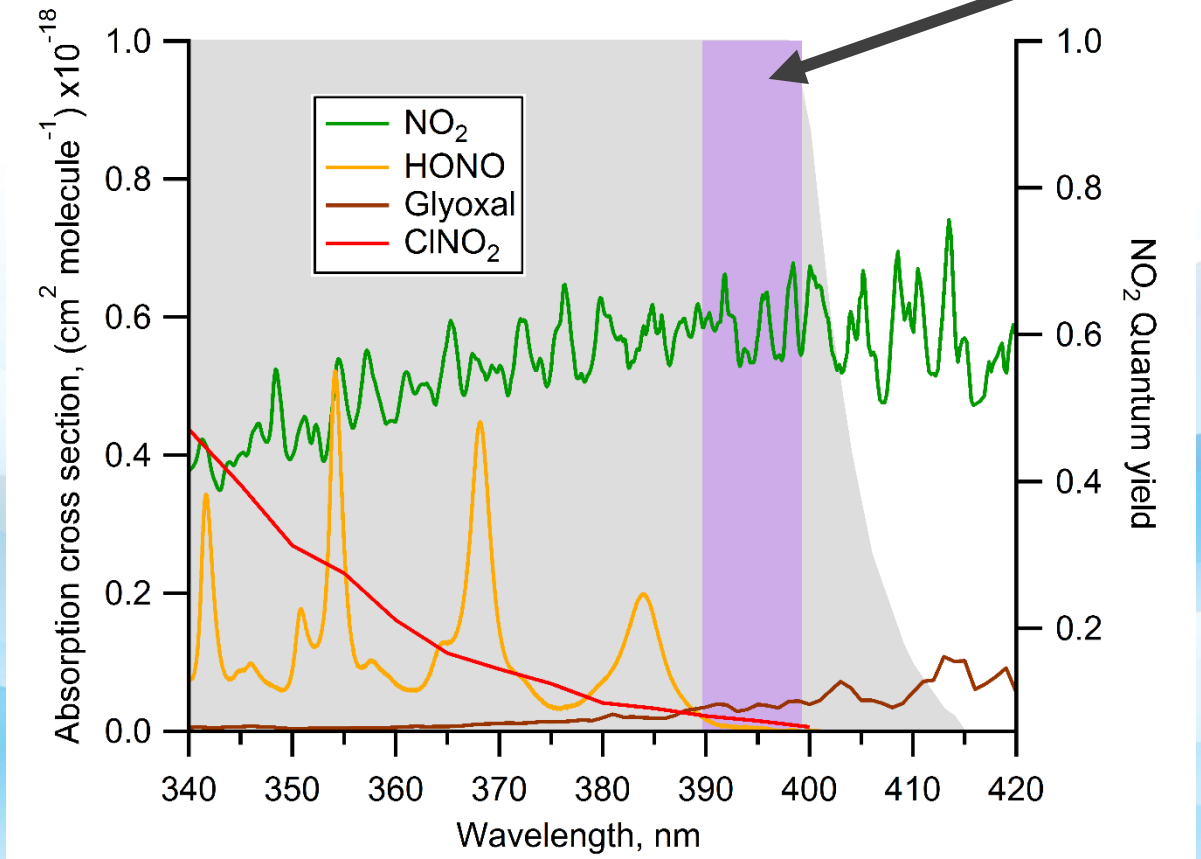
Design benefits

- ✓ This provides a unique flow pattern under reduced pressure
- ✓ Fast response time
- ✓ No memory effects

Selective NO_2 Photolysis

$$NO_2 + h\upsilon \rightarrow NO + O_3$$

Efficient selective NO_2 Photolytic Region ~390-400nm



J.P. Burrows, et al., *J. Quant. Spectrosc. Radiat. Transfer* **60**, 1025-1031 (1998)

J. Stutz, et al., *J. Geophys. Res.* **105**, 14585-14592 (2000)

S.P. Sander, et al., *JPL Publication* **10-6**, Jet Propulsion Laboratory, Pasadena, 2011. http://jpldataeval.jpl.nasa.gov

Challenges of Photolysis of NO_2?

- Light Source Instability
- Back Reactions

$$NO_2 + h_v \rightarrow NO + O_3$$

- Limited Ranges/ Linearity
- Interference Artifacts

Global's Approach

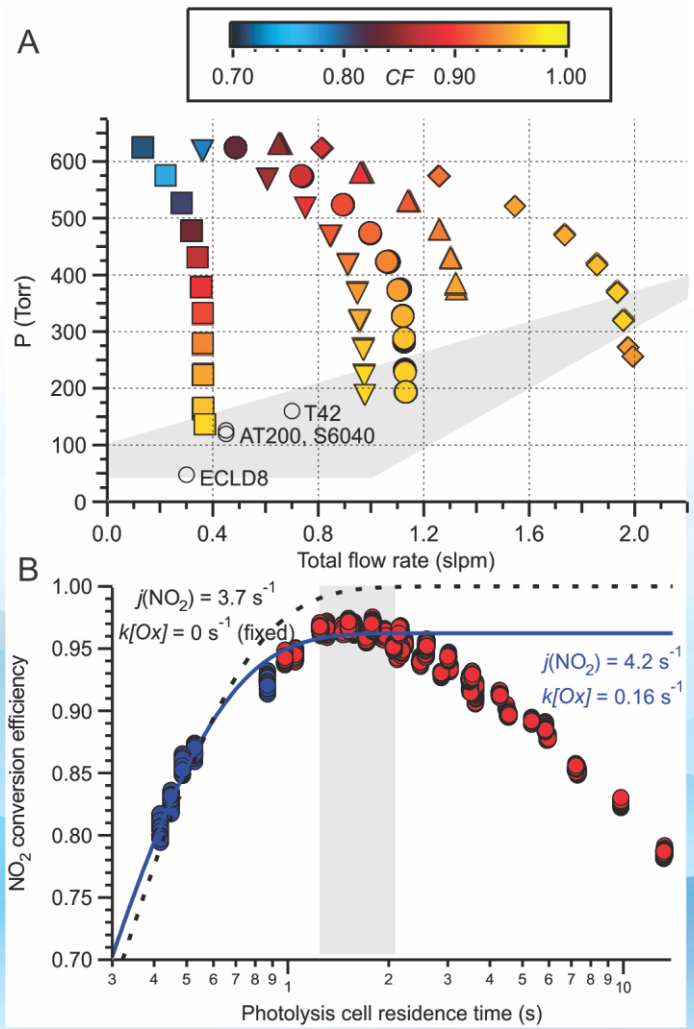
- Patented Technology (**PhoNO**)

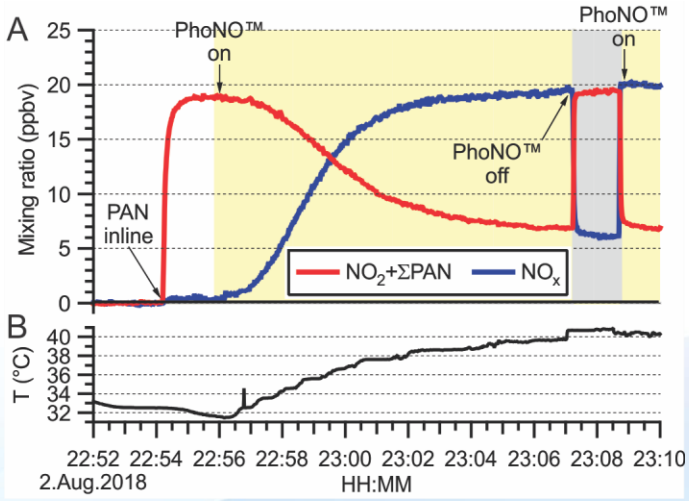
  Patent number: WO2017173552A1
- Stable device
- Real-time data logging
- Defensible data
- Negligible Interference

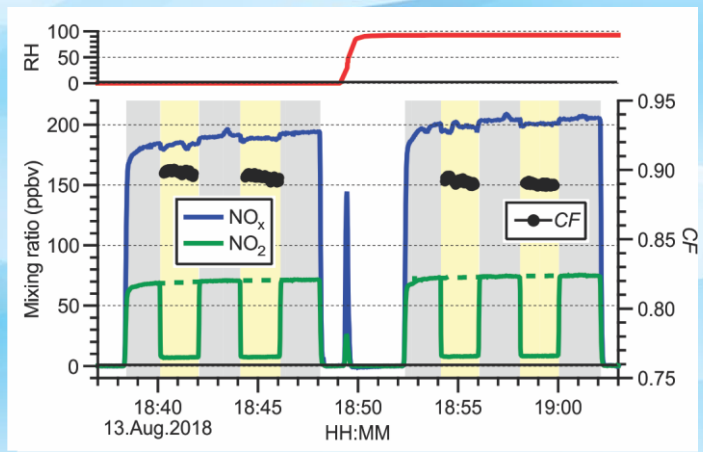
Prototype PhoNO

PhoNO integrated into Thermo 42i

Interference rejection testing

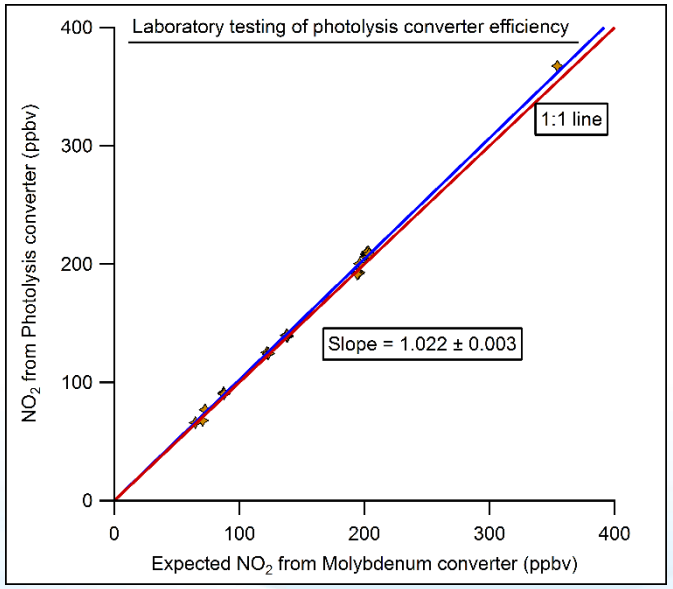




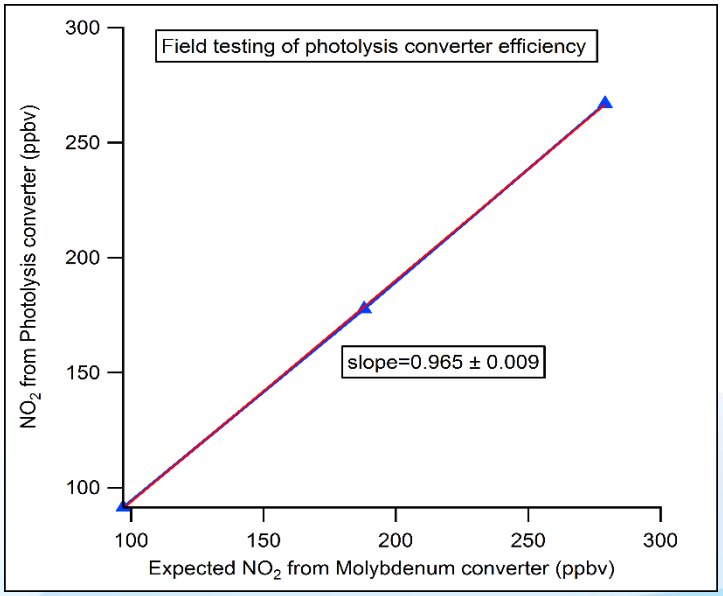


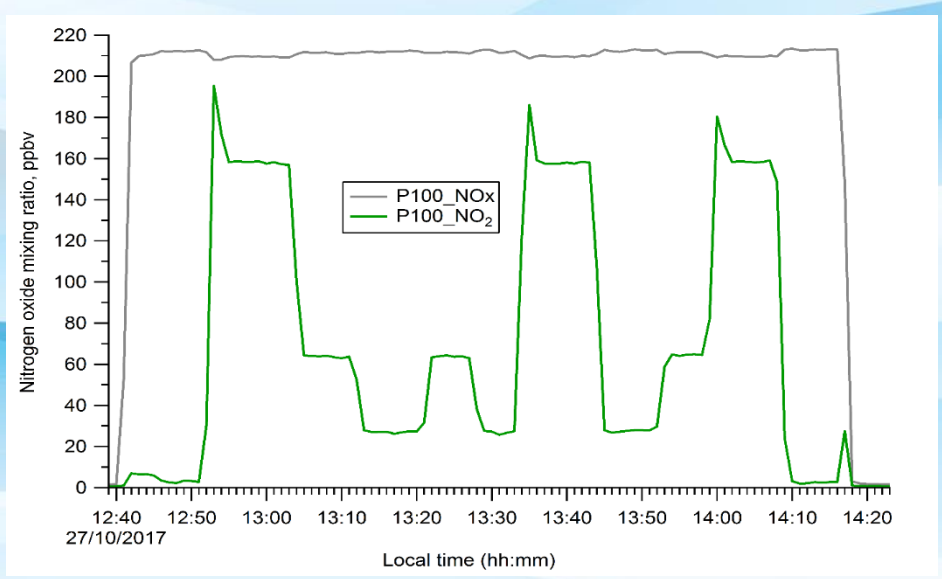
Jordan et al. (2019) Laboratory evaluation of a new photolytic nitrogen dioxide converter for ambient air monitoring. (*submitted*)

Calibration of PhoNO



Up to 37 ppm tested





Raw data from a Thermo 42i analyzer

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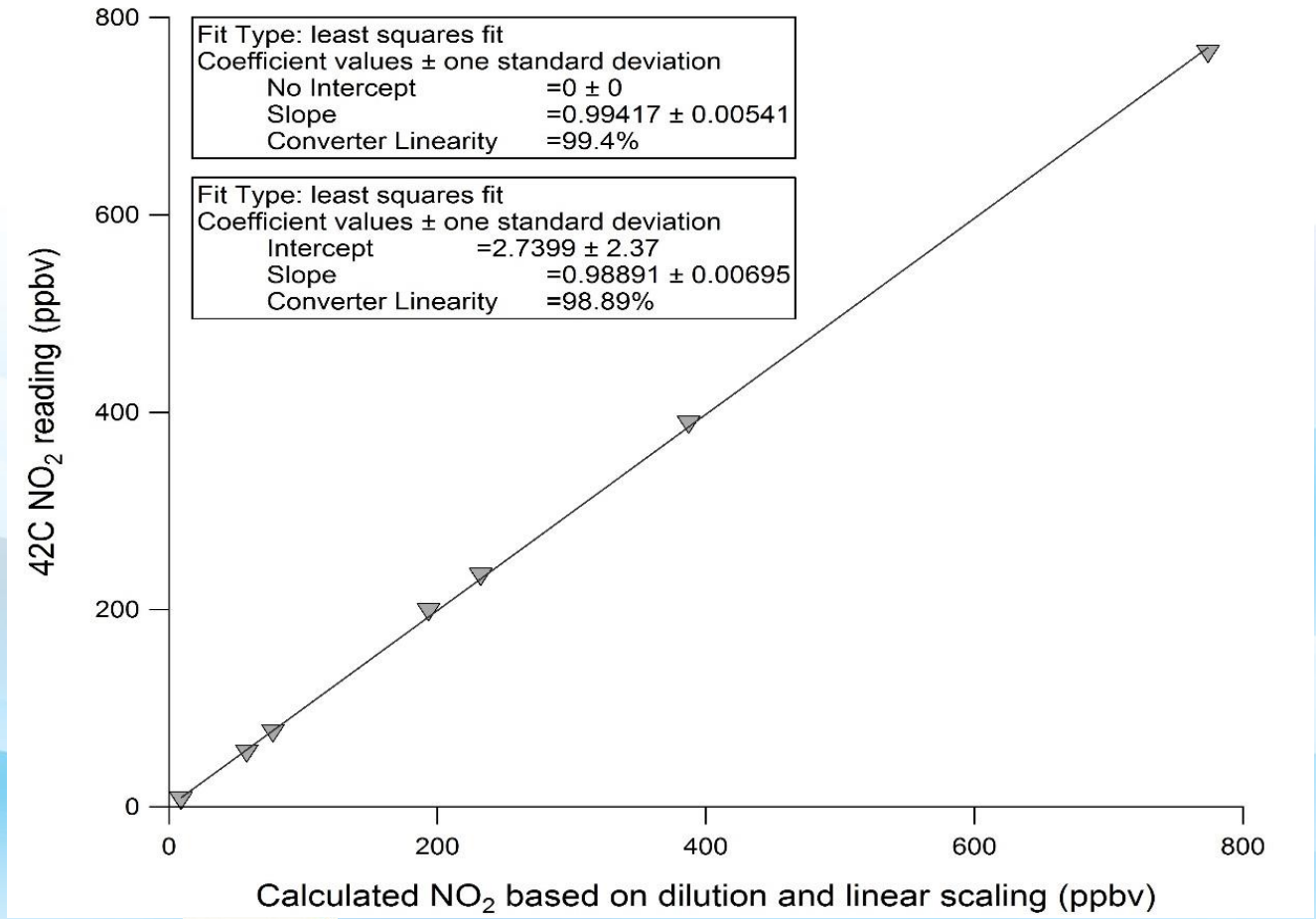
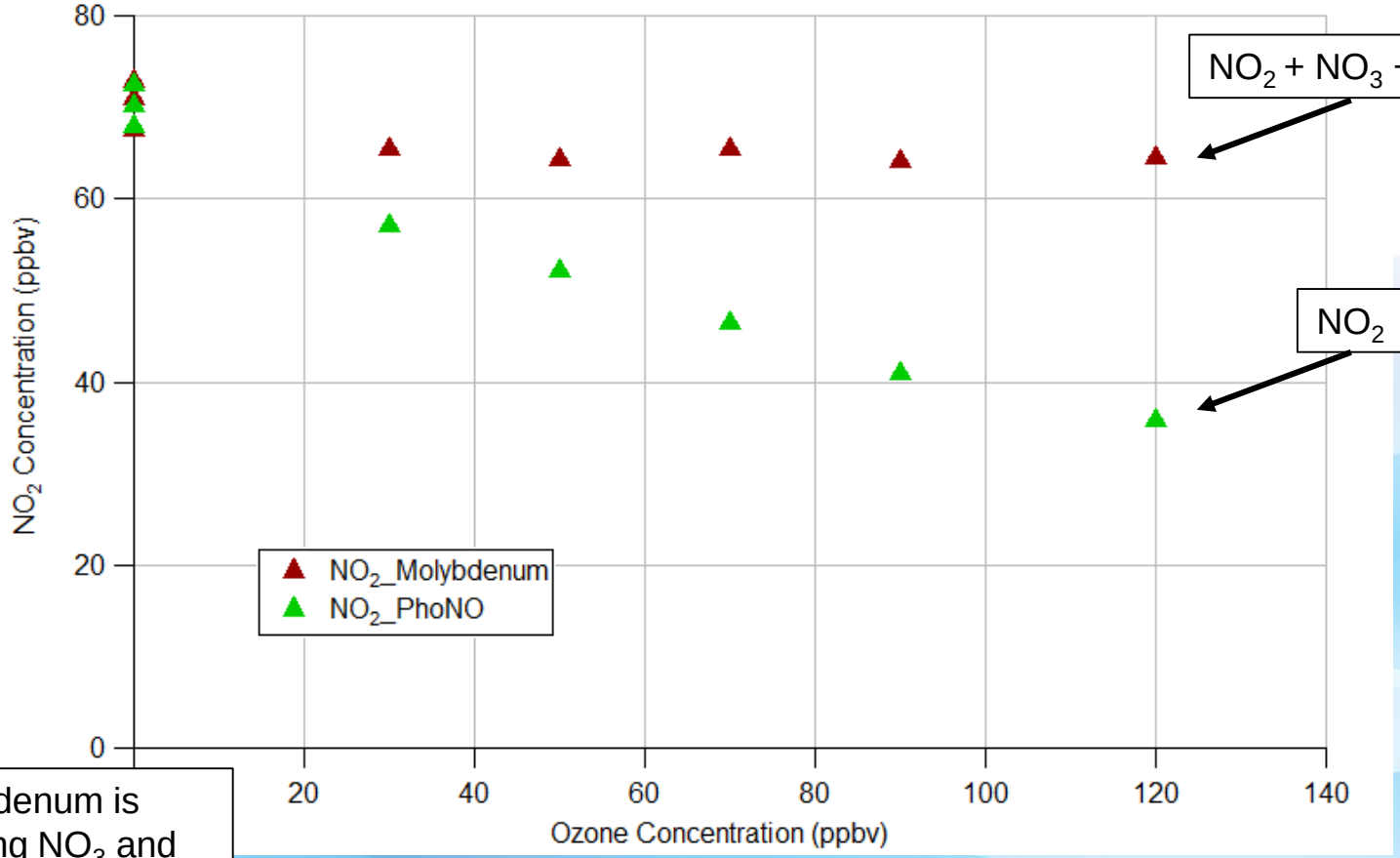
Lab Results – Linearity Testing



Linear over a wide range

Lab Results – NO_z



Molybdenum is measuring NO_3 and N_2O_5 but PhoNO is not!

$$NO_2 \underset{NO/h_v}{\overset{O_3}{\rightleftharpoons}} NO_3 \overset{NO_2}{\rightleftharpoons} N_2O_5$$

Selective

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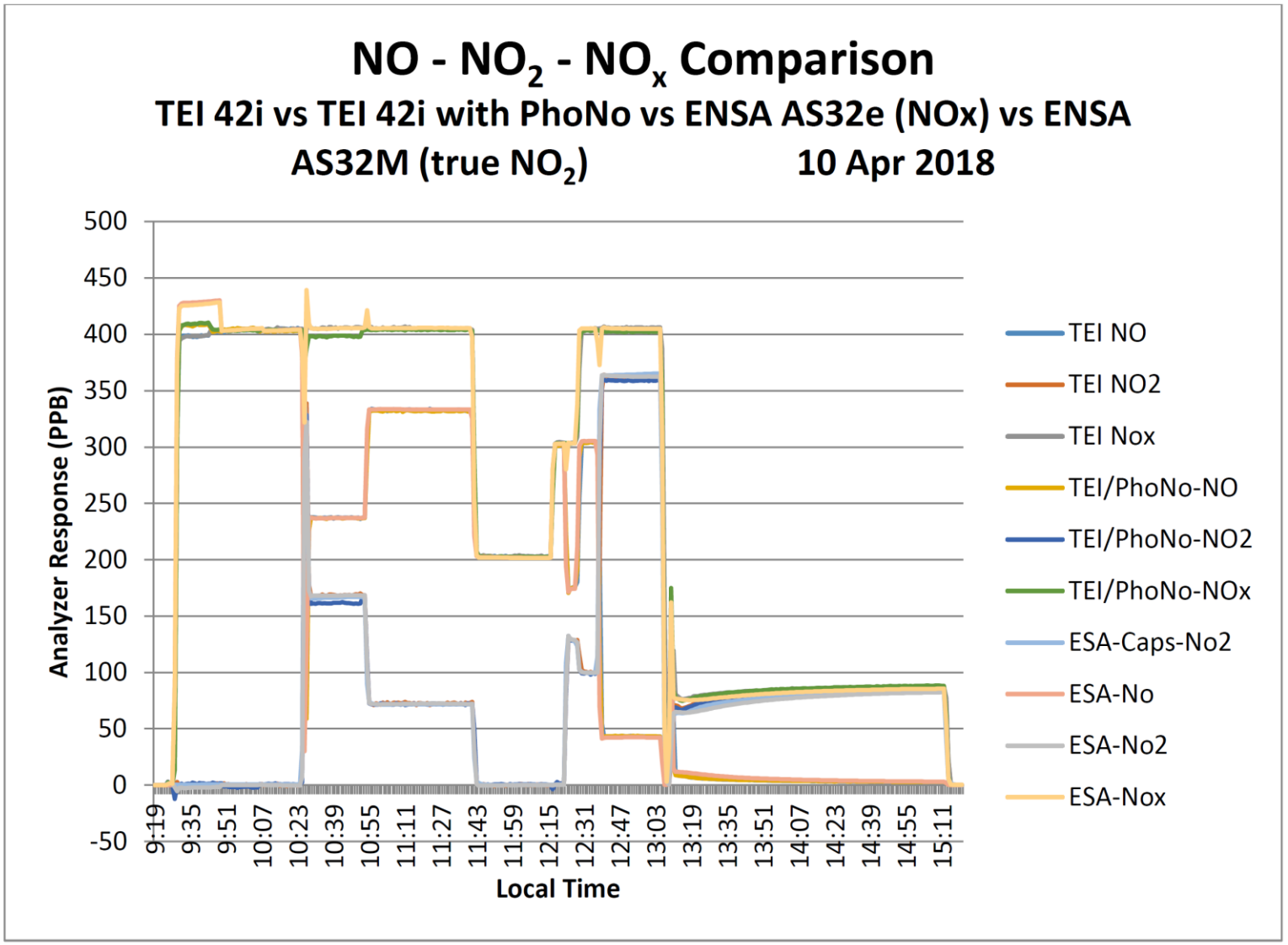
Environment Canada Testing



Field Trials

<u>2016 Field Trial:</u>

CEMs Installation at:

- Fort Saskatchewan

<u>2017 Field Trials:</u>

Ambient Installations at:

- Fort Air Partnership (FAP), Fort Sask. Station
- US EPA, Lake Michigan Ozone Study

<u>Current Field Trial:</u>

Ambient Installation at:

- Calgary Regional Air Zone (CRAZ), Central Station

Fort Air Partnership Field Trial

- Fort Saskatchewan (Old AB Environment Station)
- November 28, 2016 - March 09, 2017
- Average temp: -10^{O}C

No degradation in conversion efficiency

Stable light source

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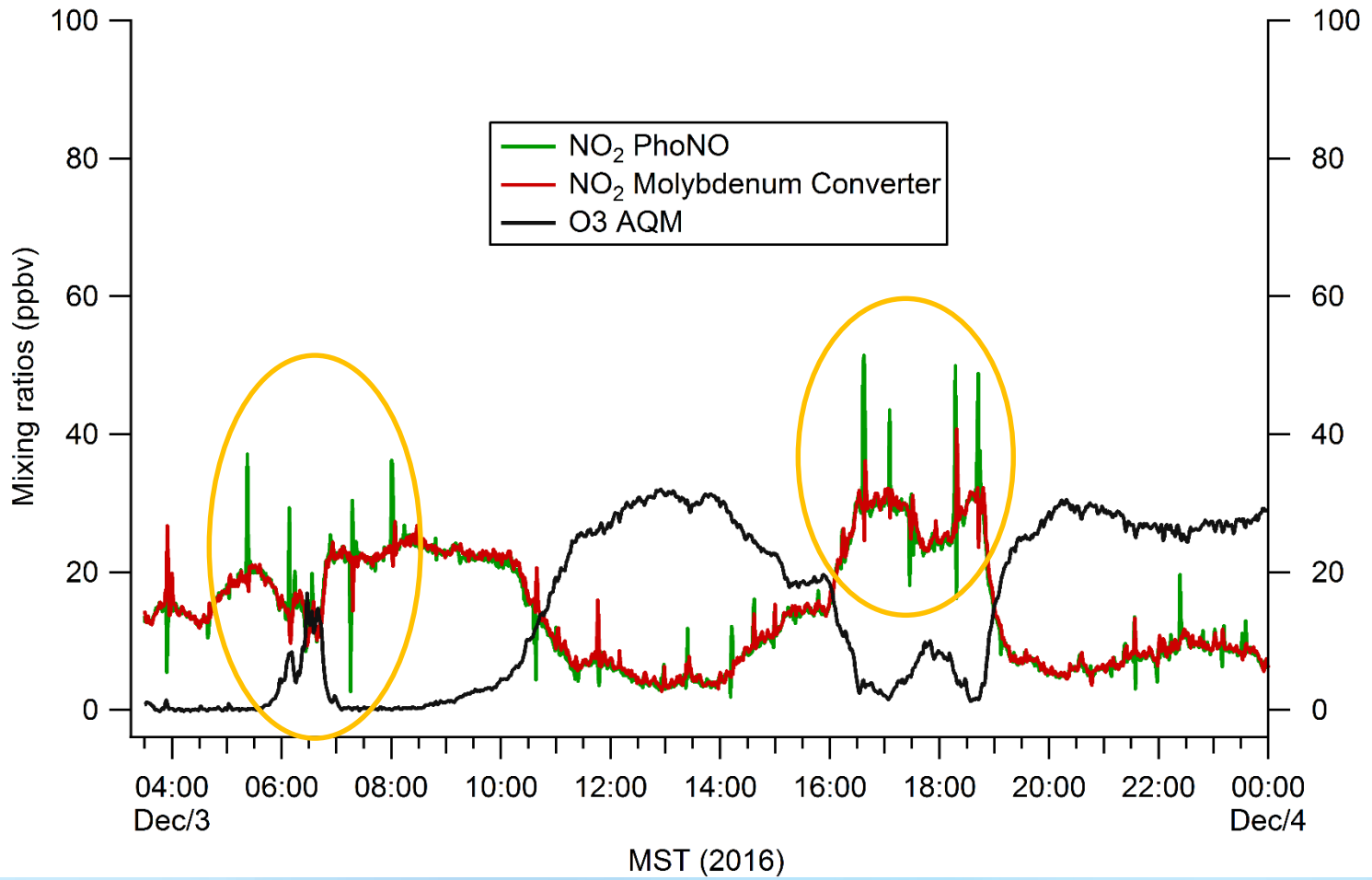
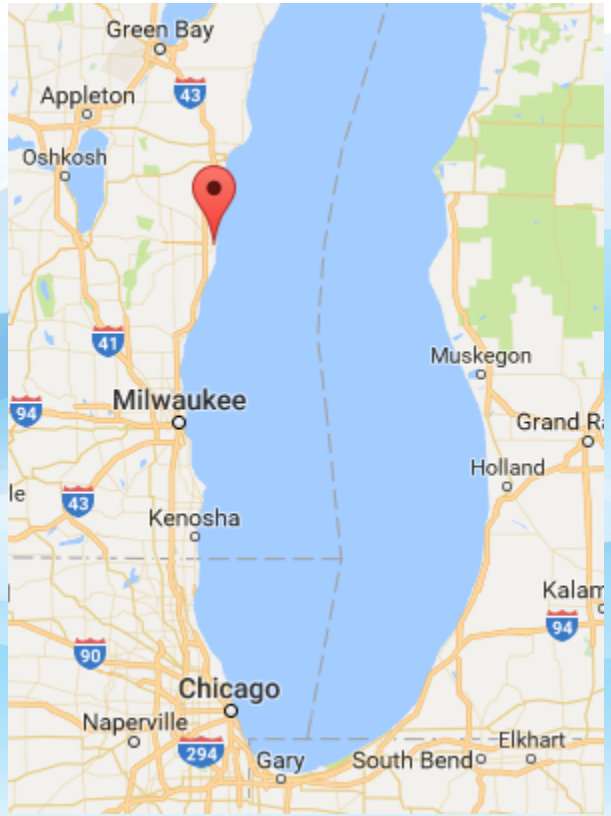
FAP Data – Daytime NO_2 Concentrations



Fast Response

Lake Michigan Ozone Study, 2017

- Sheboygan, Wisconsin, USA
- Collaborated with US-EPA ORD
- May 21, 2017 to June 22, 2017



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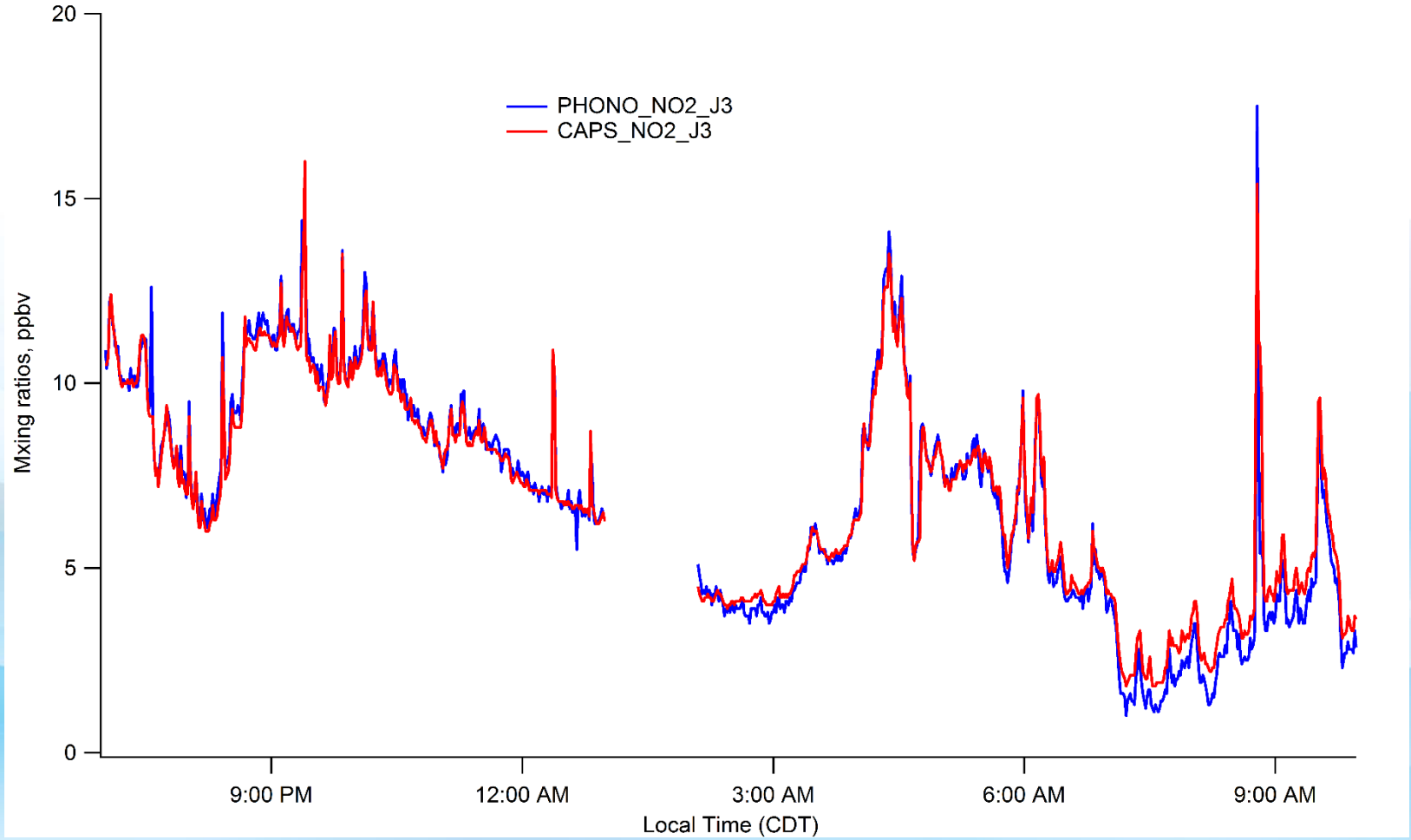
Lake Michigan Ozone Study, 2017

Preliminary data



Evidence of NO_2 overestimation

Evidence of fast response of PhoNO

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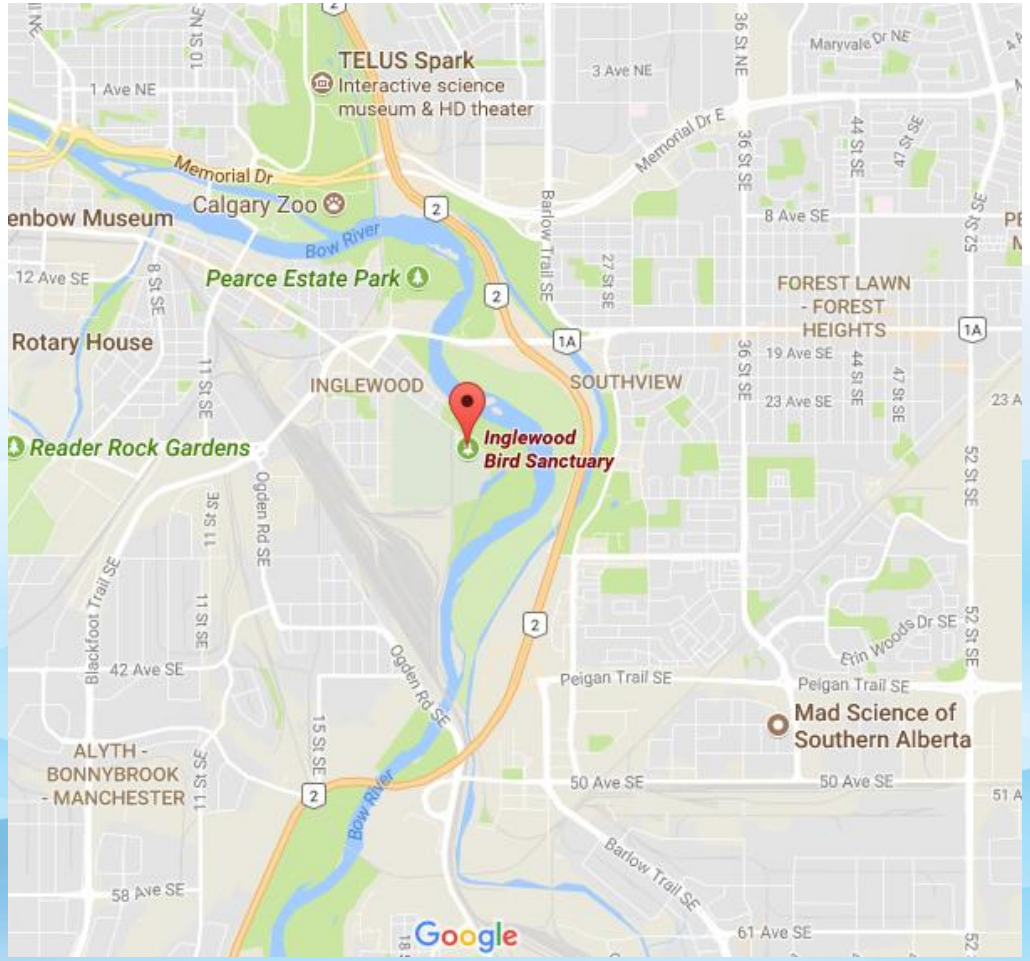
Ongoing CRAZ Co-locate Study



Calgary Central Station
Near Inglewood Bird Sanctuary

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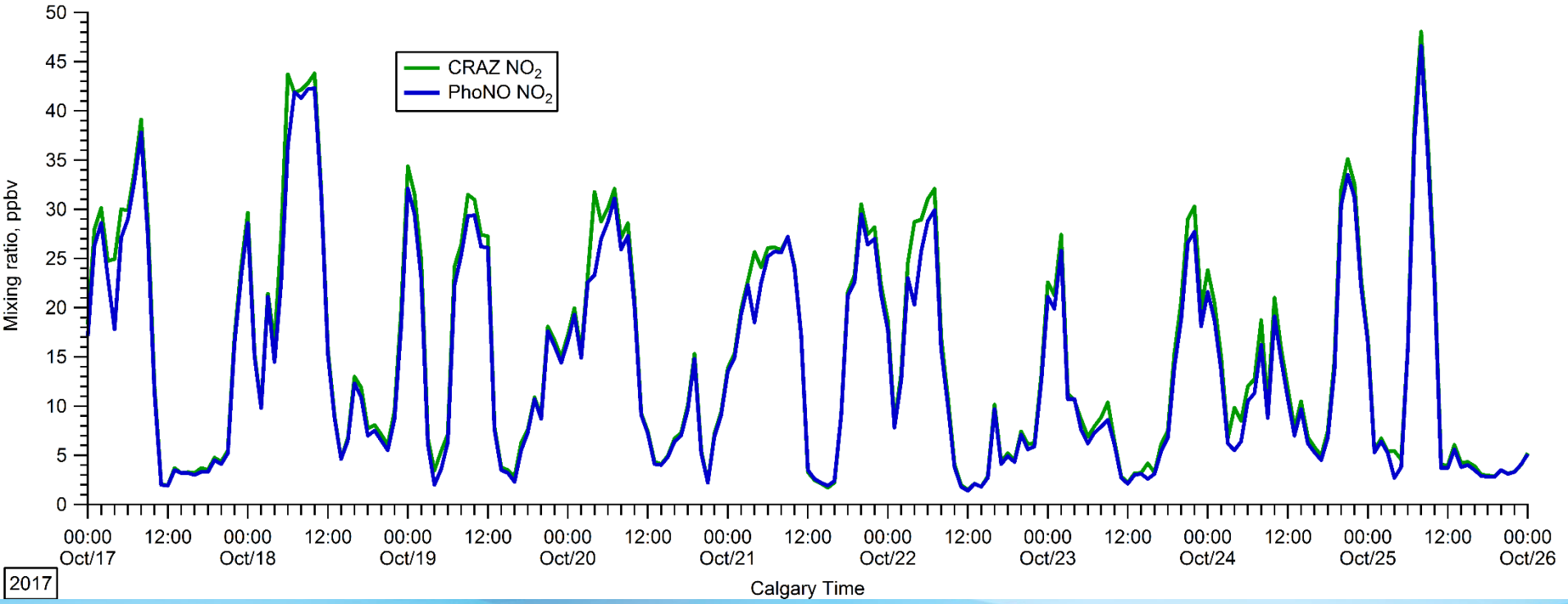
Ongoing CRAZ Co-locate Study

Preliminary data



Evidence of NO_2 overestimation

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What benefits will PhoNO offer?

- No interference from water vapour or ammonia
- Able to handle high concentrations of NO_2
- Real-time monitoring of performance

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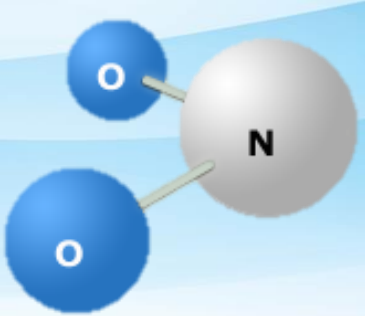
True NO_2 – What's it to you?

- Eliminate over reporting
- Increased understanding of chemical processes (e.g. process optimization)
- Meet evolving Federal Regulations
- Understand the link between NO_2, health effects, and environmental impacts
- Accurate data for modeling emissions and pollution transport



Conclusion

Create a device that enables existing analyzers to SELECTIVELY measure NO_2

- ✓ Linear conversion over a wide dynamic range:
  - ⮡ From low ppb up to as high as 37ppm
- ✓ Simple external installation
  - ⮡ Up to 7′ away from the analyzer
- ✓ Fast response & high resolution
  - ⮡ Making analyzers more robust
- ✓ Conversion efficiency >96% (98-100% typical)
  - ⮡ Achieved up to 100% stable conversion
- ✓ Direct replacement for Mo converters
  - ⮡ Low-cost add-on to existing analyzers

And most importantly….

No extensive analyzer modifications required to install

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Acknowledgements

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UNIVERSITY OF CALGARY

CETAC - WEST

Research and Development Team
Global Analyzer Systems Ltd

FORT AIR PARTNERSHIP
We Monitor the Air You Breathe

ALBERTA INNOVATES

Canada NRC·CNRC

US-EPA ORD

CRAZ
CALGARY REGION AIRSHED ZONE

Other Collaborators:
Dr. Allan Legge

Questions?

PhoNO™
A True NO_2 Converter