

# Direct and Indirect Methods for the Measurement of Ambient Nitrogen Dioxide

Extended Abstract # 57

Melinda R. Beaver<sup>1</sup>, Keith G. Kronmiller<sup>2</sup>, Rachele M. Duvall<sup>1</sup>, Surender M. Kaushik<sup>1</sup>, Timothy Morphy<sup>3</sup>, Patrick King<sup>3</sup>, Russell W. Long<sup>1</sup>

<sup>1</sup>US EPA, Office of Research and Development, National Exposure Research Laboratory, 109 TW Alexander Drive, MC D205-03, Research Triangle Park, NC 27711

<sup>2</sup>Alion Science and Technology, 109 TW Alexander Drive, MC E205-06, Research Triangle Park, NC 27711

<sup>3</sup>Teledyne Advanced Pollution Instrumentation, 9480 Carroll Park Drive, San Diego, CA 92121

## INTRODUCTION

Nitrogen dioxide (NO<sub>2</sub>) is regulated as a criteria pollutant defined by the National Ambient Air Quality Standards (NAAQS) under the Clean Air Act. NO<sub>2</sub> is generally formed in the atmosphere from the photochemical processing of directly emitted nitric oxide (NO), though diesel engines also emit NO<sub>2</sub> directly<sup>1</sup>. Exposure to NO<sub>2</sub> has been linked to human health impacts on the respiratory system due to both short and long-term exposures. To protect against these human health effects, in 2010, the US EPA revised the primary NAAQS for NO<sub>2</sub> to include both 1 hour (100 ppb, 98<sup>th</sup> percentile) and 24 hour (53 ppb, annual mean) standards. NO<sub>2</sub> also plays an important role in radical production and destruction in the tropospheric ozone production cycle. The oxidized nitrogen products which form as a result of these chemical cycles including peroxyacetyl nitrate (PAN), multifunctional organic nitrates (RONO<sub>2</sub>), nitric acid (HNO<sub>3</sub>), and particulate nitrate (pNO<sub>3</sub><sup>-</sup>), deposit to ecosystems and can adversely affect acid sensitive ecosystems.

Because of the importance of NO<sub>2</sub> to human health, ecosystem health, and ozone production, the method for accurate quantification of atmospheric NO<sub>2</sub> is currently a research focus of EPA. The current Federal Reference Method (FRM) indirectly measures NO<sub>2</sub> in two steps: first the thermal conversion of NO<sub>2</sub> to NO, and secondly, the detection of NO by the chemiluminescence which results from the reaction of NO with ozone<sup>2</sup>. The automated FRM has been in place for several decades, and positive interferences in the method have been discussed for nearly as long<sup>3</sup>. These interferences have been attributed to the decomposition of other oxidized nitrogen compounds, such as PAN, other organic nitrogen compounds, and HNO<sub>3</sub> on the heated metal catalyst<sup>4</sup>. These interferences arise from the lack of specificity of the thermal convertor to NO<sub>2</sub>. Another disadvantage of the measurement approach of the FRM is that it is an indirect approach, in that it measures NO<sub>2</sub> as the difference between two channels - an NO channel and a total NO<sub>x</sub> channel. This approach is difficult during periods of rapidly changing NO<sub>x</sub> concentrations. The resulting signal also contains noise induced by the existing noise in each of the two signals used to calculate the difference.

Recently, alternative approaches to the quantification of NO<sub>2</sub> have been produced commercially. These advances, along with the potential for interferences in the FRM support the investigation of methods potentially more specific to NO<sub>2</sub>. Here, we present ambient intercomparisons of NO<sub>2</sub> measurements from a variety of analyzers, including an FRM, a

photolytic convertor chemiluminescence NO<sub>x</sub> monitor (a Federal Equivalent Method; FEM), and two direct optical techniques. The goal of this work is to determine the operating characteristics and data quality resulting from these emerging NO<sub>2</sub> techniques. Intercomparisons between the NO<sub>2</sub> methods during winter 2013 in California's San Joaquin Valley and summer 2013 in Research Triangle Park (RTP), NC are presented. Performance comparisons of these methods with the current FRM are discussed.

## EXPERIMENTAL METHODS

**Table 1.** Instruments and their operating principles used in the investigations presented here.

\*Data from the T500U CAPS are only available from RTP, NC.

<b>Instrument</b>	<b>Operating Principle</b>
Teledyne T200U	Thermal conversion, gas-phase chemiluminescence, FRM
Teledyne 200EUP	Photolytic conversion, gas-phase chemiluminescence, FEM
*Teledyne T500U CAPS	Cavity Attenuated Phase Shift (CAPS)
Los Gatos Res., RMT-200	Cavity Ring-Down Spectroscopy (CRDS)

Ambient intercomparisons between the instruments listed in Table 1 have been conducted. The photolytic conversion analyzer (FEM) replaces the heated bed/catalytic conversion module responsible for converting NO<sub>2</sub> to NO with a blue light convertor to achieve a more selective conversion to NO via photolysis. This photolytic convertor based analyzer was designated as a US EPA FEM in June 2012. The CAPS and CRDS techniques are direct, optical techniques that quantify the NO<sub>2</sub> concentration based on the interaction of light with NO<sub>2</sub> molecules in high-finesse (low optical loss) cavities. The CAPS NO<sub>2</sub> analyzer determines the NO<sub>2</sub> concentration from a phase shift calculation based on light attenuation, and operates at a wavelength of ~450 nm<sup>5</sup>. The CRDS analyzer determines NO<sub>2</sub> concentration from the differences in the rate of decay of light within the sample cell in the presence and absence of NO<sub>2</sub>, and operates at a wavelength of ~405 nm.

A month-long intercomparison of the NO<sub>2</sub> analyzers listed in Table 1 was conducted in January and February 2013 in Visalia, CA as part of NASA's DISCOVER-AQ campaign throughout California's San Joaquin Valley<sup>6</sup>. The overall goal of the study is to better predict and measure air quality at Earth's surface. EPA participated by augmenting a San Joaquin Valley Air Pollution Control District (SJVAPCD) surface monitoring site at the Visalia Municipal Airport (36.31411 N, -119.39301 W) with additional air quality instrumentation. This site was located approximately 35 m from the edge of Northbound I-99 (2012 Annual Average Daily Traffic of approximately 59,000<sup>7</sup>). The second intercomparison of the analyzers listed in Table 1 was conducted at EPA's Ambient Air Innovative Research Site (AIRS) in RTP, NC (35.889015N, 78.874626W) for 8 weeks during the summer of 2013. The RTP, NC site is characterized as a background site with limited direct traffic impacts. The T500U CAPS instrument was only available during the summer 2013 study, as noted by the asterisk in Table 1.

During these measurement intensives, all instruments were contained within the same temperature-controlled (~25 °C) measurement shelter. All instruments shared a common inlet (located approximately 5 m above ground) and a common sampling manifold. Each instrument's calibration was verified nightly at ~21:00 EST with NO<sub>2</sub> produced by gas phase titration of NO with ozone; NO was also present during the calibration checks. When an instrument's response

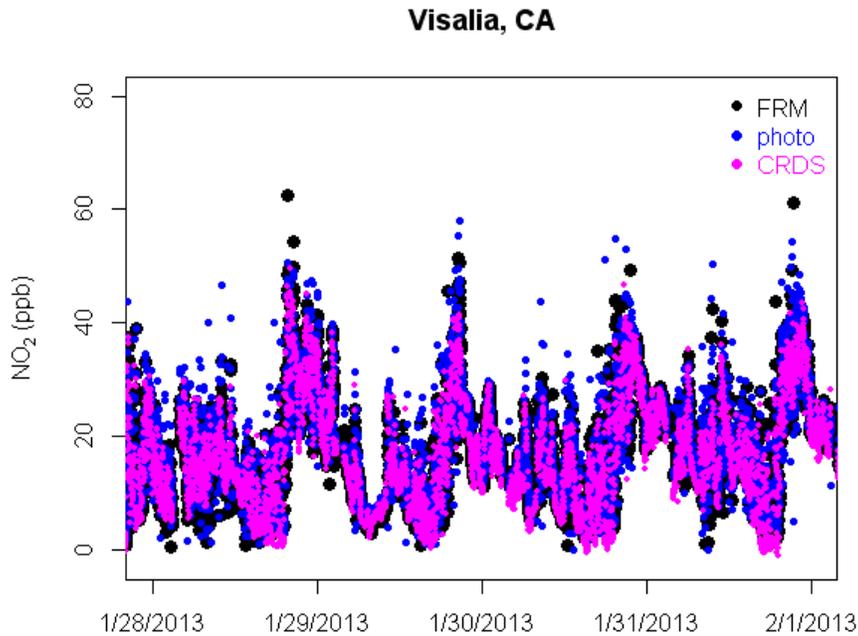
was found to differ by >15% from the audit concentration at both audit levels (20 ppb and 100 ppb NO<sub>2</sub>), data from the instrument was discarded until analyzer recalibration was performed. Instruments were connected to a single data logger to ensure data were time synched.

## RESULTS AND DISCUSSION

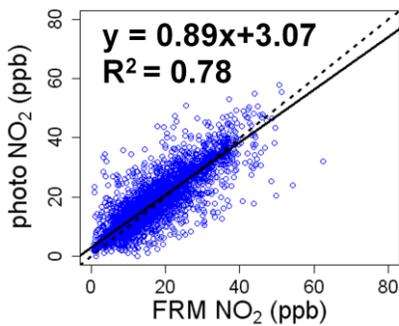
Preliminary analyses of the surface NO<sub>2</sub> datasets from Visalia, CA and RTP, NC are currently underway. Time series plots of two four-day periods from each location are shown in Figure 1 (Visalia, CA) and Figure 2 (RTP, NC). Each data point represents a 1 minute average of data; the FRM is shown in black, the photolytic analyzer (FEM) is shown in blue, the CRDS is shown in magenta, and the CAPS is shown in green. In general, NO<sub>2</sub> concentrations were much higher at the Visalia, CA site (mean of 15.8 ppb vs 3.9 ppb in NC) due to the site's proximity to a roadway, as well as to the meteorology of the winter season in CA's San Joaquin Valley.

NO<sub>2</sub> concentrations in Visalia, CA were also much more variable than in RTP, NC. This variability could be due to the site's proximity to a roadway. The variability could also be due to the higher NO concentrations (mean of 24.8 ppb in CA vs 0.48 ppb in NC) and variability observed at the CA site. For example, the photolytic NO<sub>2</sub> analyzer was highly correlated ( $R^2=0.99$ ) with the FRM NO<sub>2</sub> measurement at the measurement site in NC, while in Visalia CA, the two analyzers were slightly less correlated ( $R^2=0.78$ ). The effect of NO concentrations and NO variability on the correlations between the FRM and the photolytic instruments will be discussed. In RTP, NC, the photolytic NO<sub>2</sub> and FRM NO<sub>2</sub> are very highly correlated ( $R^2=0.99$ ), while the correlation of the FRM NO<sub>2</sub> with the two direct optical instruments is slightly less ( $R^2_{CAPS} = 0.97$ ;  $R^2_{CRDS} = 0.96$ ). This is likely due to true NO<sub>2</sub> variability that the indirect NO<sub>x</sub> monitors do not capture. Overall, good agreement between the different measurement techniques was observed in both locations and seasons. The slopes of all scatter plots vs. the FRM are within the calibration certainty.

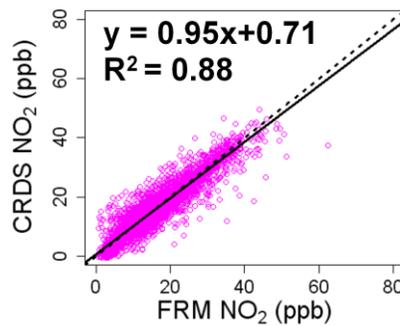
a)



b)

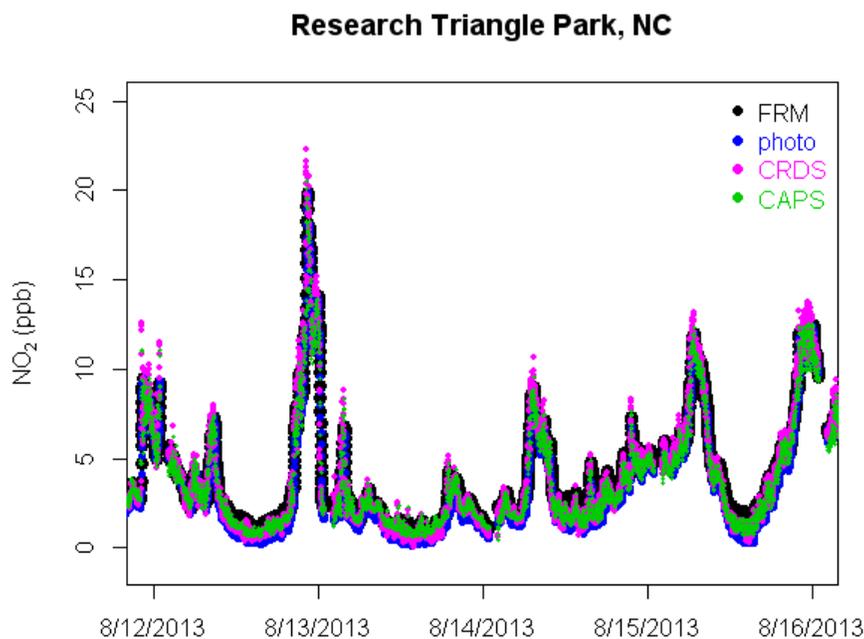


c)

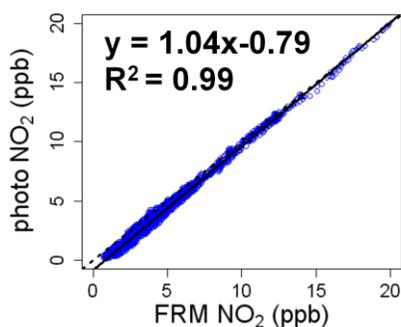


**Figure 1.** NO<sub>2</sub> concentration data from Visalia, CA over a four day period in January, 2013. Panel a) shows the time series of the FRM (black), photolytic (blue), and CRDS (magenta) analyzers. Panel b) shows a scatter plot of the photolytic instrument vs the FRM instrument. Panel c) shows a scatter plot of the CRDS instrument vs. the FRM instrument. The CAPS instrument was not available for this intercomparison.

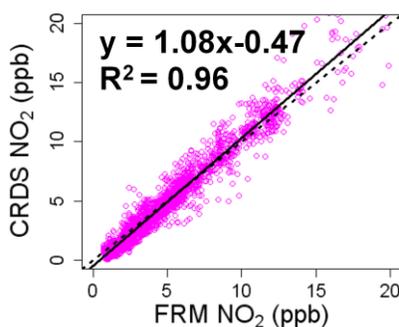
a)



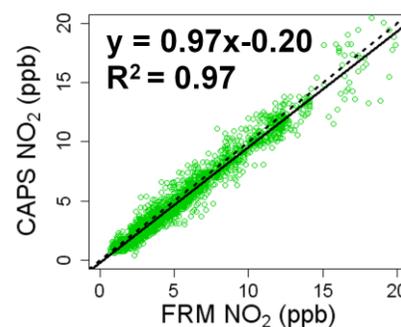
b)



c)



d)



**Figure 2.** NO<sub>2</sub> concentration data from Research Triangle Park, NC over a four day period in August, 2013. Panel a) shows the time series of the FRM (black), photolytic (blue), CRDS (magenta), and CAPS (green) analyzers. Panel b) shows a scatter plot of the photolytic instrument vs the FRM instrument. Panel c) shows a scatter plot of the CRDS instrument vs. the FRM instrument. Panel d) shows a scatter plot of the CAPS instrument vs. the FRM.

## SUMMARY

Here, we have shown ambient data from a suite of NO<sub>2</sub> measurement methods including the FRM, a chemiluminescence analyzer using a photolytic convertor (FEM), and two direct optical techniques (CRDS and CAPS). We have seen very good agreement between the measurement approaches in two locations and seasons. In general, the magnitudes of differences that can occur between various methods for measuring NO<sub>2</sub> are within the calibration uncertainties. There are differences in the correlation between the FRM and photolytic

instruments in the two locations; possible reasons for this difference will be discussed. More intercomparisons, particularly during summer months are needed to further this analysis. Targeted laboratory testing should be conducted to finalize conclusions. Results from this work may be used to inform future FRM and FEM determinations.

## DISCLAIMER

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

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## KEY WORDS

nitrogen dioxide, federal reference methods, gas-phase chemiluminescence, oxides of nitrogen