

In This Issue

[Air Pollution News](#)

[Promotion](#)

[Case Study](#)

[Employee
Introductions](#)

[Quick Links](#)

[Get a Quote](#)

[Meet the Staff](#)

[Visit our Website](#)

[Helpful
Downloads](#)

[Past Newsletters](#)



Air Pollution News

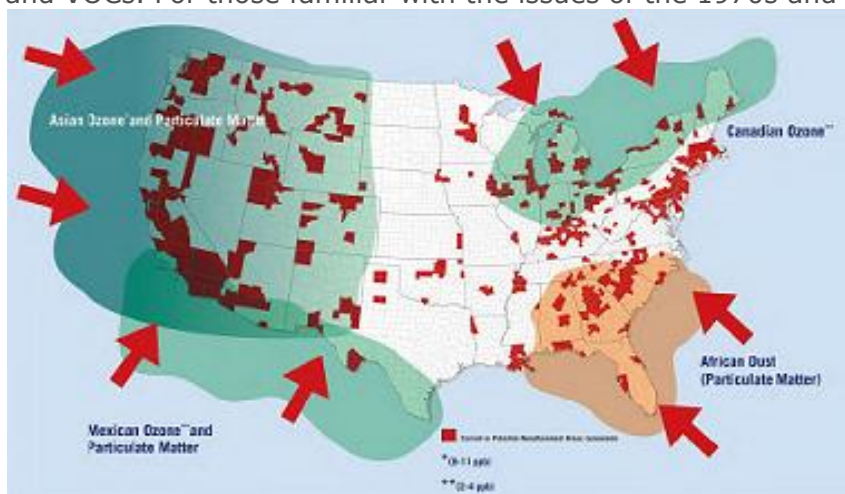
Imported Ozone Pollution: Challenges for Meeting the Stricter Federal Ozone Standard

A stricter U.S. federal standard for ozone, 70 parts per billion (ppb) over an 8-hour period, has replaced the previous 75 ppb/8-hour standard (see [Fall 2015 issue of 2B Buzz](#)). This poses a challenge for air quality managers, as over 200 counties are expected to be above the standard. A few ppb of ozone will increasingly make the difference between compliance and exceedance in this new regulatory context, placing a premium on knowing just where the ozone at a given location is coming from.

Regulatory actions of municipalities, counties, and states can work to reduce the ozone that is formed locally. But some of a location's ozone pollution is "imported" from sources beyond its borders. And ozone's precursors (nitrogen oxides [NO_x] and volatile organic compounds [VOCs]) can also be imported from other regions. Such non-local ozone and emissions cannot be reduced by local or state air quality measures. This nexus of science and policy is an active area of investigation.

Ozone and precursors from different geographic regions

Ozone, NO_x, and VOCs can be literally blown into a region from other states or countries, even crossing oceans. The U.S. West experiences significant influx of ozone and precursors from Asian sources across the Pacific Ocean, for example. Areas downwind of major cities are subject to unwanted imports of ozone, NO_x, and VOCs. For those familiar with the issues of the 1970s and 1980s related to

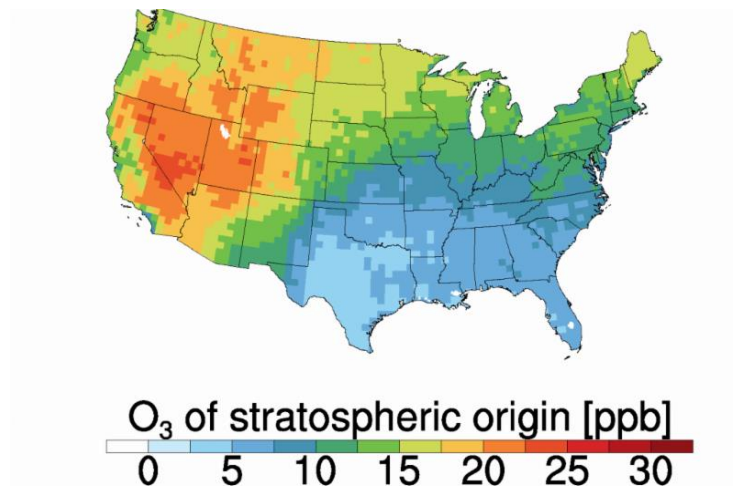


acid deposition, it's "déjà vu all over again" in regions like the more densely populated eastern U.S., where one city's emissions can become another city's pollution problem.

[Figure adapted from U.S. Chamber of Commerce, <https://www.uschamber.com/issue-brief/ozone-national-ambient-air-quality-standards>]

Intrusive ozone from above

For some regions, it's not only air from upwind that brings in unwelcome ozone; air from high overhead can descend. In this natural phenomenon known as a "stratospheric intrusion," air from the ozone-rich stratospheric ozone layer sometimes brings ozone to the surface. Some regions of the country are more prone to this than others, and there is seasonality to the phenomenon as well. In the Intermountain West, for example, stratospheric intrusions occur more often in springtime, and especially at higher elevations. Stratospheric intrusions make it more difficult for some regions to meet health-based standards for ozone pollution. The map shows results from an atmospheric model of May and June 2010. In dark orange areas, stratospheric intrusions contribute about 20 ppb of ozone at the surface.



The contribution of stratospheric ozone to U.S. surface ozone peaks in the western Rockies during late spring and can push some regions of the Intermountain West above the federal standard. This map shows the mean contribution in parts per billion for May to June. The stratosphere is a region 8-30 miles above Earth that contains over 90 percent of the atmosphere's ozone. It's this ozone layer that's the "good ozone," filtering harmful ultraviolet radiation from the Sun. But lower down, at Earth's surface, excessive ozone is harmful to human health and other living things. [Graphic: [NOAA](#)]

Research to quantify "imported" ozone and precursors

A critical research question for scientists and air quality managers is, "How much of the ozone is made locally, and how much comes from somewhere else?" Recent studies have made inroads into quantifying the two sources of "imported" ozone mentioned above.

For example, research has shown that offshore winds are increasing the baseline ozone concentrations entering California from the west, especially during El Niño years. Baseline ozone is rising at many sites in the western U.S., especially at higher elevations. "How much" has become a key question. During the spring and summer of 2016, NOAA is partnering with the California Air Resources Board in the California Baseline Ozone Transport Study (CABOTS). Researchers will use a lidar to produce daily profiles of ozone from the ground to about 3 kilometers aloft, and a [2B Technologies Model 205 Dual Beam Ozone Monitor](#)[™] colocated with the lidar will make measurements at ground level. The work will help to characterize how much ozone from across the Pacific is mixing down to the surface in the San Joaquin Valley of central California.

In the region near Las Vegas, NOAA's lidar measurements have shown that stratospheric intrusions contributed to three exceedances of the federal standard in May and June of 2013. The results were used by Clark County, Nevada officials in their request for a waiver of the exceedances under the EPA's "exceptional events" rule. The utility of the research has led to an invitation for NOAA to conduct a second study in spring/summer of 2017.

It's one atmosphere

Despite the nation's significant progress in reducing emissions of ozone precursors, meeting the new ozone standard will continue to be a challenge in many areas of the country. The atmosphere knows no boundaries, and getting a handle on ozone "imports and exports" will be an important topic for air quality.

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FEM approval expected soon!



- ✓ Direct measurement of NO₂ by absorbance at 405 nm
- ✓ NO measured by selective conversion using reaction of NO with O₃
- ✓ Range of 0 – 10,000 ppb for NO₂; Range of 0 – 2,000 ppb for NO_x and NO
- ✓ Essentially interference-free; insensitive to other nitrogen-containing compounds
- ✓ Doesn't require an NO₂-to-NO converter; allows measurements with efficiency unmatched by chemiluminescence instruments
- ✓ New design with a folded cell and corner mirrors (~2m path length)
- ✓ Modes: NO₂ only; NO only; NO₂, NO, and NO_x
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Case Study: Roadside NO_x Monitoring with the Model 405 nm

2B Tech's instrument offers higher performance at lower cost

The [2B Technologies Model 405 nm NO₂/NO/NO_x Monitor™](#) was put to the test in a recent side-by-side comparison with two other instruments measuring nitrogen dioxide (NO₂) along busy Colorado roadways. Bottom line:

not only do the Model 405 nm NO₂ measurements compare favorably to the data from the other instruments, but the 2B Tech instrument excels by offering more information (NO, NO_x) in a lighter, more economical package.



Roadside monitoring both needed and challenging

More than 45 million people in the United States are living, working, or attending school within 300 feet of a major road, airport, or railroad (<https://www3.epa.gov/otaq/documents/nearroadway/420f14044.pdf>). This presents a substantial health risk due to the elevated levels of pollutants as a result of vehicle emissions. Recognizing this risk, the EPA modified the National Ambient Air Quality Standards (NAAQS) in 2010 to include roadside monitoring for criteria pollutants such as nitrogen dioxide (NO₂).

Measurements along highly congested roadways present special difficulties. Many atmospheric pollutants (NO₂, CO, PM_{2.5}) occur simultaneously, are at very high concentrations, and vary quickly as traffic patterns shift. This challenges instrumentation in terms of interferences and time response. 2B Technologies has recently introduced the [Model 405 nm NO₂/NO/NO_x Monitor™](#), which now meets all of these challenges through design features that give it a high sensitivity and fast response time. It is anticipated that the Model 405 nm will soon be designated as a federal equivalent method (FEM) for measuring NO₂ in roadside monitoring and other applications.

The Model 405 nm measures NO₂ by direct long path absorption. Additionally, the Model 405 nm also measures NO by converting it to NO₂ by reaction with excess ozone. Although NO is not listed as a criteria pollutant by the EPA, knowledge of its concentration is critical since it partitions rapidly (few minutes) with NO₂ in the atmosphere and is the primary N-containing constituent in vehicle exhaust.

The Model 405 nm hits the road: Intercomparison testing with FEM and FRM methods for NO₂

In the fall of 2015, we conducted an informal five-day test of the 2B Technologies Model 405 nm at a roadside monitoring site in Denver, Colorado. The site is run by the Colorado Department of Public Health and Environment (CDPHE) and is part of Colorado network of EPA-approved sites. The site is located just to the north of the intersection of two major interstate highways (I-25 and I-70) and within 10 m from the entrance ramp between the two highways. 2B Tech's Model 405 nm shared an inlet line that extended out over traffic with a Teledyne NO₂ federal reference method (FRM) Model 200E NO_x-chemiluminescence analyzer (CL) and a Teledyne NO₂ federal equivalent method (FEM) Model T500U NO₂ analyzer that is based on Cavity Attenuated Phase Shift spectroscopy (CAPS). The Teledyne instruments were operated by CDPHE.

The top left panel of Figure 1 below shows the temporal data for NO₂ from both the Teledyne Model T500U-CAPS and the 2B Technologies Model 405 nm. The

data from both instruments are one-minute averages and are plotted against each other in the right panel. The Model 405 nm exhibited excellent agreement with the T500U-CAPS over the entire time period. Hourly averages (which are recorded for compliance monitoring) were typically within 1.5 parts per billion by volume (ppbv) between the two instruments. The good agreement at the faster time scales, shown in the figure, ensures that important information is not lost in the rapidly changing environment along major roadways.

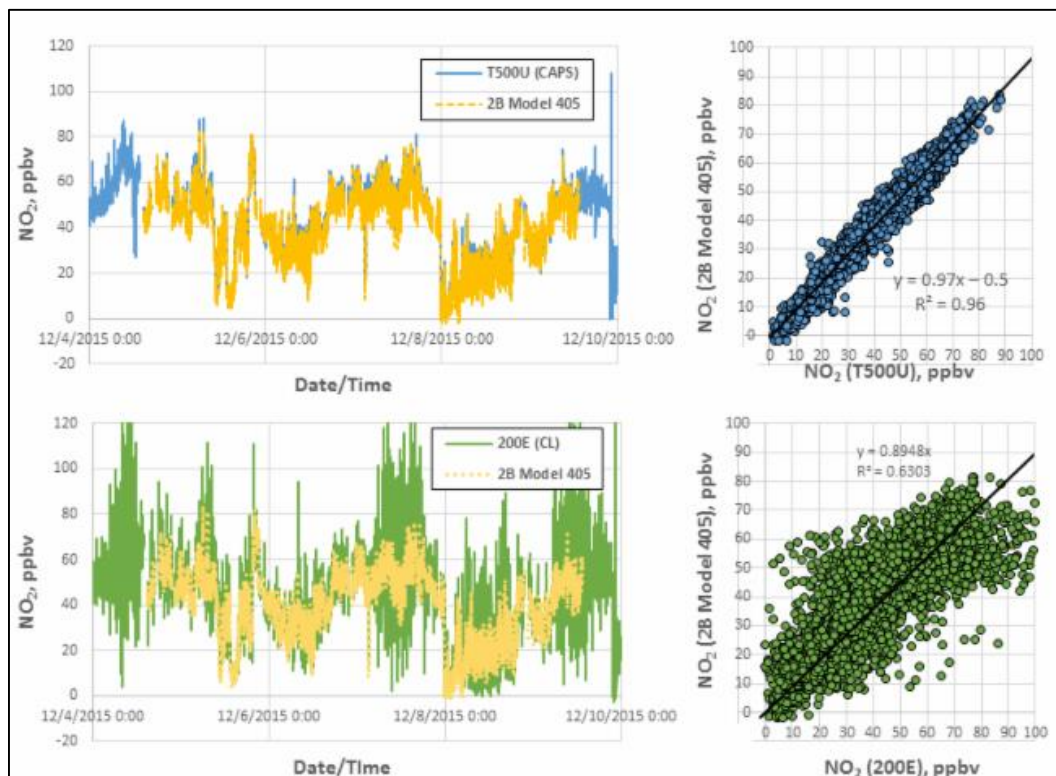


Figure 1. Comparison of NO_2 roadside measurements of the 2B Technologies Model 405 nm $\text{NO}_2/\text{NO}/\text{NO}_x$ Monitor with measurements from the Teledyne T500U Cavity Attenuated Phase Shift spectroscopy instrument (top panels) and the Teledyne 200E chemiluminescence instrument (bottom panels).

The bottom two panels of Figure 1 show NO_2 data for the Teledyne 200E-CL analyzer along with the 2B Technologies Model 405 nm for the same time period. Here, the 200E-CL data has periods of high variability compared to either the Model 405 nm or the T500U-CAPS. These periods of high variability coincide with high traffic periods (i.e., high nitric oxide (NO) concentrations). We hypothesize that the large variability in the data from the 200E-CL instrument is because the NO_2 measurement from this instrument is not a direct measurement. Rather, the sum of $\text{NO} + \text{NO}_2$ (i.e., NO_x) is actually measured by the instrument, and the subsequent NO measurement is then subtracted from this sum to compute NO_2 . However, the NO concentration during high traffic periods is highly variable - often varying more than 20-50 ppbv from minute to minute (see Figure 2 below). Thus subtraction of this large, rapidly varying NO signal causes relatively large biases in the much smaller NO_2 measurement. This illustrates a shortcoming of the indirect CL technique for NO_2 measurement compared to direct techniques such as the Model 405 nm or the T500U-CAPS.

Intercomparison of nitric oxide (NO) measurements

Since NO is primarily emitted from automobiles (and combustion in general), it exhibits even larger and more highly variable concentrations that are directly

related to traffic density. Figure 2 shows a comparison of the NO measured by the 2B Technologies Model 405 nm with the values from the Teledyne 200E-CL instrument (the Teledyne T500U-CAPS instrument does not measure NO). Similar to the NO₂ comparison, excellent agreement is observed between the analyzers - even when NO concentrations are changing dramatically over short time periods.

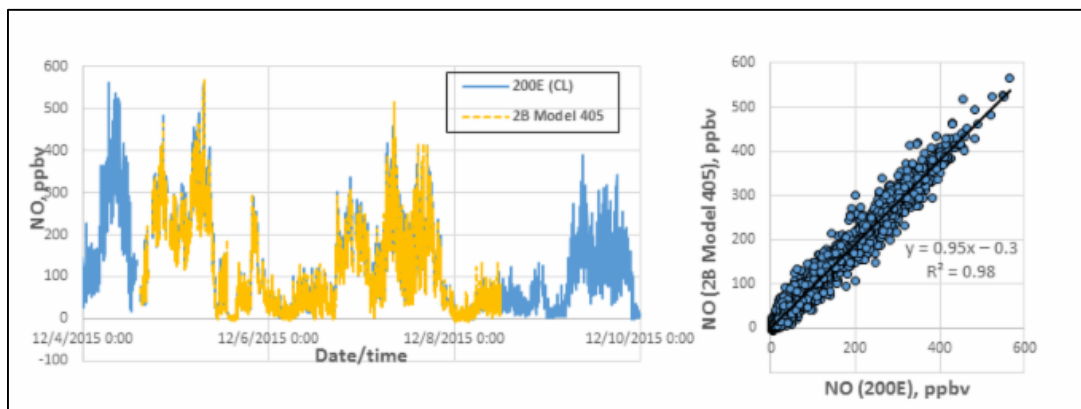


Figure 2. Comparison of NO roadside measurements of the 2B Technologies Model 405 nm NO₂/NO/NO_x Monitor with measurements from the Teledyne 200E chemiluminescence instrument.

Adding it all up

Although this was a relatively short field intercomparison, the initial results indicate that the 2B Technologies Model 405 nm can measure NO₂ with results similar to existing FEM instrumentation (the Teledyne T500U-CAPS), and superior to existing FRM instrumentation (the Teledyne 200E-CL).

Both the 2B Technologies Model 405 nm and the Teledyne T500U-CAPS technique rely on a UV-absorption method that is based on fundamental properties of the NO₂; however, the T500U-CAPS does not measure NO, which is critical for modeling atmospheric air quality. As shown in Figure 2, the Model 405 nm yields NO measurements that are in excellent agreement with an existing instrument.

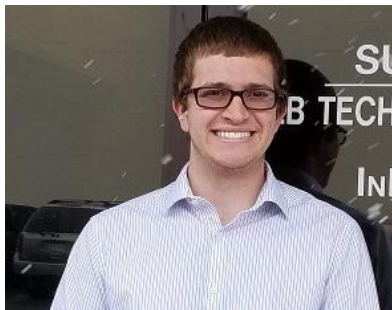
The 200E-CL instrument (an FRM method) can measure both NO and NO₂, but measures NO₂ (the EPA criteria pollutant) indirectly by converting it to NO using a heated solid catalyst; the indirect approach leads to high variability in the measurements especially when concentrations are changing rapidly. In addition, the heated catalysts do not always quantitatively convert NO₂ to NO and are also known to have significant interferences from other N-containing compounds. In contrast, although the Model 405 nm does measure NO by converting the NO₂, this conversion is done with ~100% efficiency using the well-known gas phase titration (GPT) reaction with excess ozone which has essentially no interferences. The validity of using this GPT reaction is seen in the observed excellent agreement with the NO measured by the Model 405 nm and the 200E-CL (which does measure NO directly).

Approval of the [2B Technologies Model 405 nm](#) as a FEM for NO₂ is anticipated later this year.

Acknowledgement: We thank Erick Mattson and the Colorado Dept. of Public Health and Environment for allowing us to work at their monitoring site and for sharing their preliminary data with us.

Employee Introductions

2B Technologies is pleased to announce the addition of Hayden Aubermann and Chris Ennis to our team.



Hayden's passion for science and the environment brought him to 2B Technologies in November 2015 as our Technical Sales Representative. He is responsible for outside sales, marketing, promotions, and outreach at conferences and trade shows. Hayden obtained a B.A in Biochemistry from the University of Colorado Boulder in 2015, where he gained extensive knowledge of both biochemical and environmental applications of analytical instrumentation. He has rapidly developed an encyclopedic knowledge of our products and their applications in the fields of ambient air monitoring, industrial ozone, and environmental education. You can reach Hayden at +1(303) 273-0559 or hayden@twobtech.com to discuss your ozone and NO_x measurement needs.

Chris joined 2B Tech in April 2016 as our Quality Manager. She is responsible for creating and maintaining accuracy of records and documents such as our instrument operations manuals and calibration records, and for writing material for the 2B Tech website, its quarterly newsletter, brochures, research papers, and proposals. Chris obtained her Ph.D. in chemistry from the University of Colorado Boulder in 1985 under the direction of 2B Tech's President, Dr. John Birks. She has worked for 8 years in atmospheric chemistry research at the National Center for Atmospheric Research, and for over 22 years in scientific and technical support and communications at the Cooperative Institute for Research in Environmental Sciences (CIRES) at CU Boulder in conjunction with NOAA's Aeronomy Laboratory and Chemical Sciences Division. chrise@twobtech.com.

