Assessment of NOy and True NO\textsubscript{2} Measurements Denver CO, San Jose CA, & RTP NC

Tim Hanley, EPA – OAQPS
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Locations with NOy and collocated NOy/NOx

NO\textsubscript{y}
- NO\textsubscript{y} is required at NCore and PAMS
- 99 NO\textsubscript{y} monitors

Collocated NO\textsubscript{y} and NO\textsubscript{x}
- 60 collocated stations

NO\textsubscript{2} and NO\textsubscript{x}
- 475 NO\textsubscript{2} monitors
- NO\textsubscript{2} is required in areas over 1 million in Population, plus near-road
- most NO\textsubscript{2} analyzers provide NO\textsubscript{x}
- “True NO\textsubscript{2}” required at PAMS by July 1, 2019.
- 22 Photolytic (NO, NO\textsubscript{2}, NO\textsubscript{x}) and 8 CAPS (NO\textsubscript{2} only) reported to AQS in 2015
<table>
<thead>
<tr>
<th>Method</th>
<th>Channels</th>
<th>Detection Limit</th>
<th>Key Features/issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemiluminescence NOx</td>
<td>NO\nNO\nNOx</td>
<td>5 ppb (conventional)\n50 ppt (trace level)</td>
<td>- Most widely used NO\nmethod\n- Thermal converter (315°C) is used to convert NO\n\nto NO; detection of NO is made by its chemiluminescence reaction with an excess of O\n\n- NO is measured by bypassing the converter\n- Known to have interference with part of NO\n</td>
</tr>
<tr>
<td>Chemiluminescence NOy</td>
<td>NO\nNOy</td>
<td>50 ppt (trace level)</td>
<td>- Electronics run the same as a NO\n- Molybdenum converter externally located on 10 M tower to minimize the surfaces available that can absorb reactive nitrogen.\n- Converter is operated higher than NO\n(350°C)</td>
</tr>
<tr>
<td>Cavity Attenuated Phase Shift (CAPS) NO\n\n2</td>
<td>NO\n2\nNO\nNOx</td>
<td>40 ppt</td>
<td>- High sensitivity and highly specific measurement of NO\n\n2 with negligible interference's.\n- Good experiences with ease of operation</td>
</tr>
<tr>
<td>Photolytic NOx</td>
<td>NO\nNO\nNOx</td>
<td>100 ppt</td>
<td>- Utilizes photolytic LED to separate NO\n\nto followed by chemiluminescence.</td>
</tr>
</tbody>
</table>
NOx = NO + NO₂
NOy = NO + NO₂ + NOz
NOz = PAN + HNO₃ + other

Interferences may include NH₃, which can be minimized with good siting (e.g., away from agricultural feed lots)
Key Denver Colorado Monitoring Stations with active nitrogen measurements

Chemiluminescence NOx monitors provide measurement of:
- NO
- NO$_2$
- NOx

Direct NO$_2$ Cavity Attenuated Phase Shift Spectroscopy (CAPS) provides a measurement of:
- NO$_2$
In the 2014 – 2015 data set there are four ozone episodes where one or more sites in Denver CO has an 8-hour average above 0.070 ppm.

<table>
<thead>
<tr>
<th>Date</th>
<th>LaCasa Station</th>
<th>CAMP Station</th>
</tr>
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<tbody>
<tr>
<td>6/17/15</td>
<td>0.054</td>
<td>0.053</td>
</tr>
<tr>
<td>6/18/15</td>
<td>0.054</td>
<td>0.052</td>
</tr>
<tr>
<td>6/19/15</td>
<td>0.067</td>
<td>0.061</td>
</tr>
<tr>
<td>6/20/15</td>
<td>0.069</td>
<td>0.067</td>
</tr>
<tr>
<td>6/21/15</td>
<td><strong>0.080</strong></td>
<td><strong>0.077</strong></td>
</tr>
<tr>
<td>6/22/15</td>
<td>0.051</td>
<td>0.049</td>
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<tr>
<td>6/23/15</td>
<td><strong>0.074</strong></td>
<td>0.067</td>
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<tr>
<td>6/24/15</td>
<td>0.056</td>
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<tr>
<td>6/25/15</td>
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<td>0.063</td>
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<td>6/26/15</td>
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<tr>
<td>7/28/15</td>
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<tr>
<td>7/29/15</td>
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</tr>
<tr>
<td>7/30/15</td>
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</tr>
<tr>
<td>7/31/15</td>
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<tr>
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<tr>
<td>8/2/15</td>
<td>0.043</td>
<td>0.057</td>
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<td>8/3/15</td>
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</tr>
<tr>
<td>8/4/15</td>
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<td>0.045</td>
</tr>
<tr>
<td>8/5/15</td>
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</tr>
<tr>
<td>8/6/15</td>
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<td>0.057</td>
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<td>8/16/15</td>
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<td>0.055</td>
</tr>
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<td>0.057</td>
</tr>
<tr>
<td>8/25/15</td>
<td>0.03</td>
<td>0.057</td>
</tr>
</tbody>
</table>

The following chart shows the eight-hour mean of ozone levels over time.
What do we see in the nitrogen measurements during an ozone episode?

What’s measured and what can we calculate?

- LaCasa NCore Station - What’s measured and reported:
  - NO and NO\textsubscript{y} on one monitor.
  - Direct NO\textsubscript{2} on CAPS

- What can we calculate?
  - NO\textsubscript{y} – (NO + NO\textsubscript{2}) = Noz
  - In these data we see 9-10 ppb of NOz on high ozone days.
What do we see in the nitrogen measurements during an ozone episode?

In these data we see 3-4 ppb of NOz on high ozone days.
What do the reported QC checks look like for the Denver NCore station compared to the rest of the country?

**NOy CV Upper Bound**
2015 (for sites with at least 20 checks)

Denver NCore = 2.8%

n = 27 checks in 2015

2 sites above 20

**NO CV Upper Bound**
2015 (for sites with at least 20 QC checks)

Denver NCore = 3.3%

n = 27 checks in 2015

1 site above 20
NO$_2$ CV Upper Bound
2015 (for sites with at least 20 QC checks)

Denver NCore = 5.1%
n = 27 checks in 2015
In 2014-2015 data set, there are several cases where one or more Denver area PM$_{2.5}$ sites are above 35 µg/m$^3$.

What if we look at PM$_{2.5}$ in Denver?
What do we see in the Denver NOz data during these PM$_{2.5}$ episodes? 

October 2014

In these data we see ~15 ppb of NOz on the highest PM$_{2.5}$ day.
Denver NOz data during PM$_{2.5}$ episode in March 2015

In these data we see ~15 ppb of NOz on the highest PM$_{2.5}$ day; NOz drops back down to near 0 when PM$_{2.5}$ drops to <10 ug/m$^3$. 

![Graph showing PM$_{2.5}$ and NO$_{y}$ (NO$_2$ + NO) levels during a PM$_{2.5}$ episode in March 2015.](image-url)
Denver NOz data during PM$_{2.5}$ episode in July 2015

In these data we see $\approx 3 - 4$ ppb of NOz on the highest PM$_{2.5}$ days.
Denver NOz data during PM$_{2.5}$ episode in December 2015

In these data we see ~ 10 ppb of NOz on the highest PM$_{2.5}$ days.
What do we see in select chemical speciation data in Denver?

Nitrate dominated episode

Nitrate and Carbon, next slide

Carbon dominated, next slide
What do we see in select chemical speciation data in Denver?

**Denver 2014 Carbon data - Stacked Area**

- Nitrate dominated episode
- More nitrate dominated

**Denver 2015 Carbon data - Stacked Area**

- Nitrate and Carbon
- Carbon dominated episode
What do we see in the nitrogen measurements during an episode in San Jose CA?

• What’s measured and what can we calculate?
  ➢ What’s measured and reported:
    • NO and NO\textsubscript{y} on one monitor.
    • NO, NO\textsubscript{2}, and NO\textsubscript{x} on a second monitor.

  ➢ What can we calculate?
    • NO\textsubscript{y} – NO\textsubscript{x} = NO\textsubscript{z}
    • (NO\textsubscript{y} – NO) – (NO\textsubscript{x} – NO) = NO\textsubscript{z} (normalized for each NO channel)
Comparing (NOy – NO) – (NOx – NO) with Ozone
San Jose NCore station, May 2013

Notes:
• NOz is available leading into ozone episode
• NOz clears out after episode is over
Trend of difference between NOy and NOx compared to PM$_{2.5}$ (24 hour rolling averages) 
San Jose NCore Station 11/20/2013 to 1/28/2014

In these data we see ~4 ppb of NOz on the highest PM$_{2.5}$ day. However, we are likely not measuring all of the NOz.
Comparing ions and Carbon to Mass in CSN

San Jose - November 2013 to January 2014
What do we see in the NOy and NOx data during high ozone in RTP?

Additional NOz calculated using CAPS NO₂
What do we see in the NOy and NOx data during high PM2.5 in RTP?

In early July we have high PM2.5; however, NOz does not appear to correspond to the high PM2.5, but carbon measured by the Sunset does.
Summary and Conclusions:

- Denver NCore station provides first available routine data with collocated NOy and CAPS (direct method) NO₂.
- Difference between NOy and NOx (NO + NO₂) is identified as NOz.
- Denver NOz compares very well on high ozone and high PM₂.₅ days.
- The peak of NOz appears to compare very favorably with the peak of ozone and PM₂.₅.
- These data appear to support the value of true NO₂ collocated with NOy.

Data in San Jose and RTP are similar; except:
- San Jose NOz data is out of phase with ozone, while in Denver it is nearly in phase.
- RTP summer PM₂.₅ appear to be impacted by OC and not NOz. September Ozone data is impacted by NOz.

Related Notes and Next Steps:

- EPA ORD has been investigating optimizing the NOy method calibration procedures and should have useful information in their presentation this week (i.e., St. Louis monitoring conference).
- Requirements for PAMS and NCore nitrogen measurements can be combined at one station:
  - NO and NOy on an NOy analyzer
  - “true” NO₂ on photolytic or CAPS NO₂ analyzer