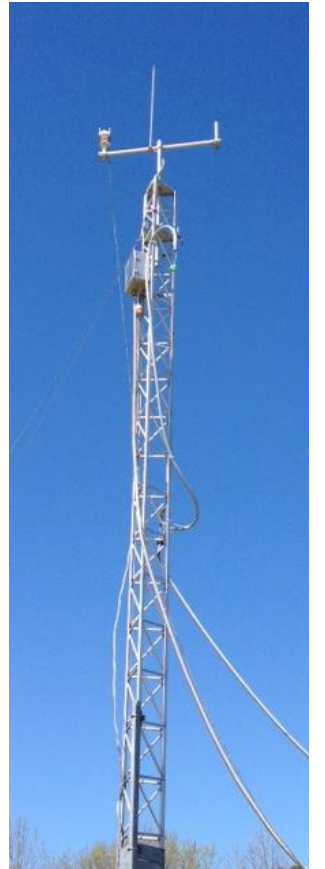


Assessment of NO_y and True NO₂ Measurements Denver CO, San Jose CA, & RTP NC

Tim Hanley, EPA – OAQPS
National Ambient Air Monitoring Conference
August 10th, 2016



Locations with NO_y and collocated NO_y/NO_x

NO_y

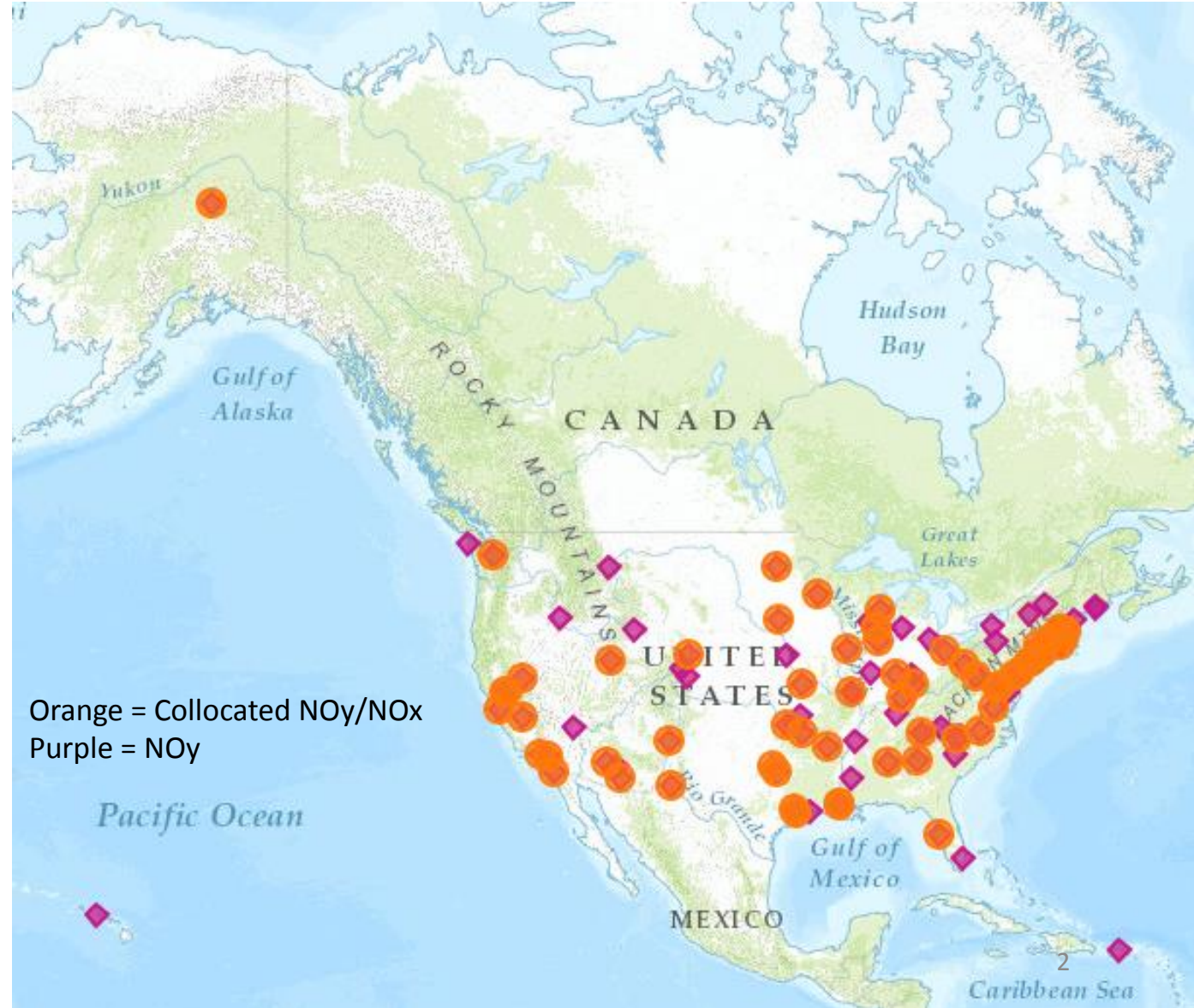
- NO_y is required at NCore and PAMS
- 99 NO_y monitors

Collocated NO_y and NO_x

- 60 collocated stations

NO₂ and NO_x

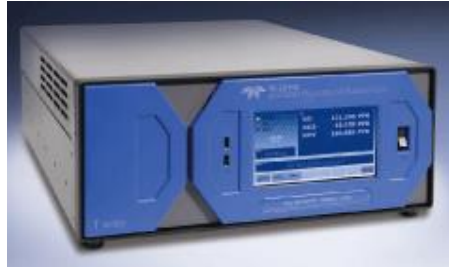
- 475 NO₂ monitors
- NO₂ is required in areas over 1 million in Population, plus near-road
- most NO₂ analyzers provide NO_x
- “True NO₂” required at PAMS by July 1, 2019.
- 22 Photolytic (NO, NO₂, NO_x) and 8 CAPS (NO₂ only) reported to AQS in 2015



Key Features and Differences in Ambient NO/NO₂/NO_x/NO_y Measurements

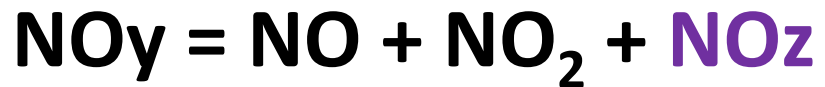
| Method | Channels | Detection Limit | Key Features/issues |
|---|--|--|---|
| Chemiluminescence (chemical reaction that creates light) NO _x | NO NO ₂ NO _x | 5 ppb (conventional) 50 ppt (trace level) | <ul style="list-style-type: none"> - Most widely used NO₂ method - Thermal converter (315C) is used to convert NO₂ to NO; detection of NO is made by its chemiluminescence reaction with an excess of O₃. - NO is measured by bypassing the converter - Known to have interference with part of NO_z |
| Chemiluminescence NO _y | NO NO _y | 50 ppt (trace level) | <ul style="list-style-type: none"> - Electronics run the same as a NO_x; - Molybdenum converter externally located on 10 M tower to minimize the surfaces available that can absorb reactive nitrogen. - Converter is operated higher than NO_x (350C) |
| Cavity Attenuated Phase Shift (CAPS) NO ₂ | NO ₂ | 40 ppt | <ul style="list-style-type: none"> - High sensitivity and highly specific measurement of NO₂ with negligible interference's. - Good experiences with ease of operation |
| Photolytic NO _x | NO NO ₂ NO _x | 100 ppt | <ul style="list-style-type: none"> - Utilizes photolytic LED to separate NO₂ followed by chemiluminescence. |

Typical NO_x analyzer

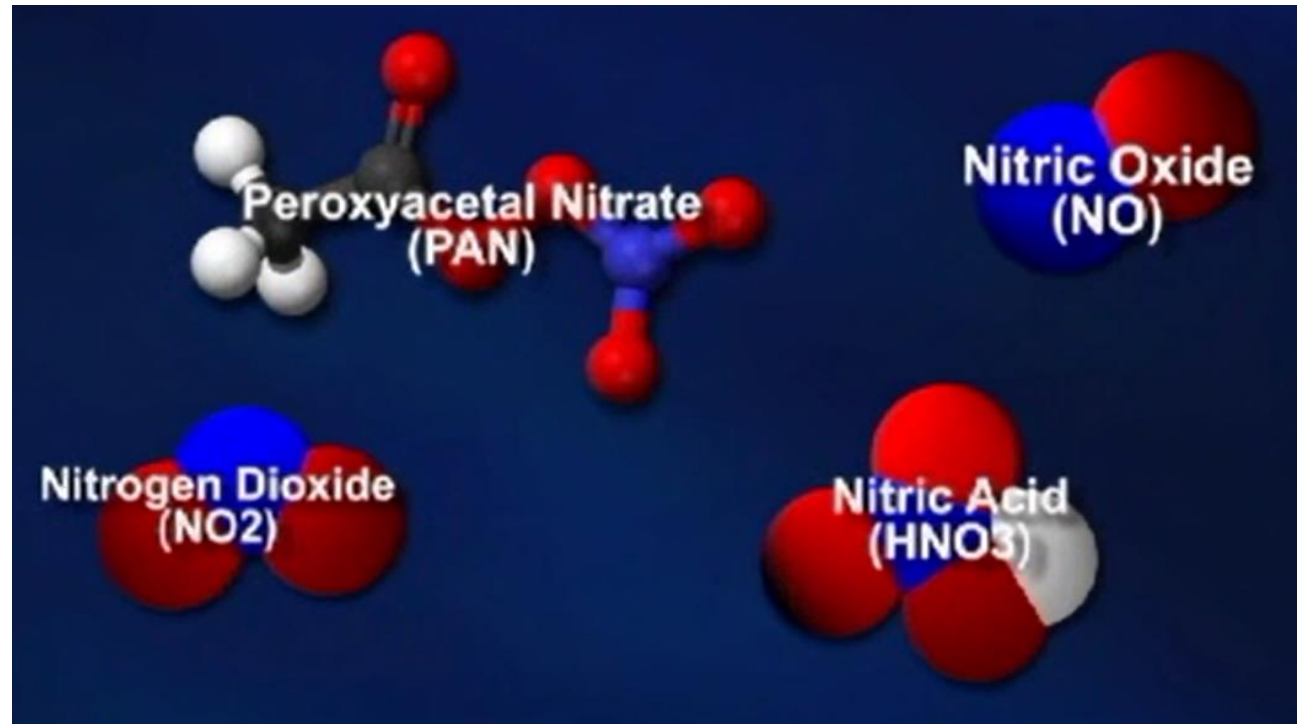


NO_y Converter at 10 meters



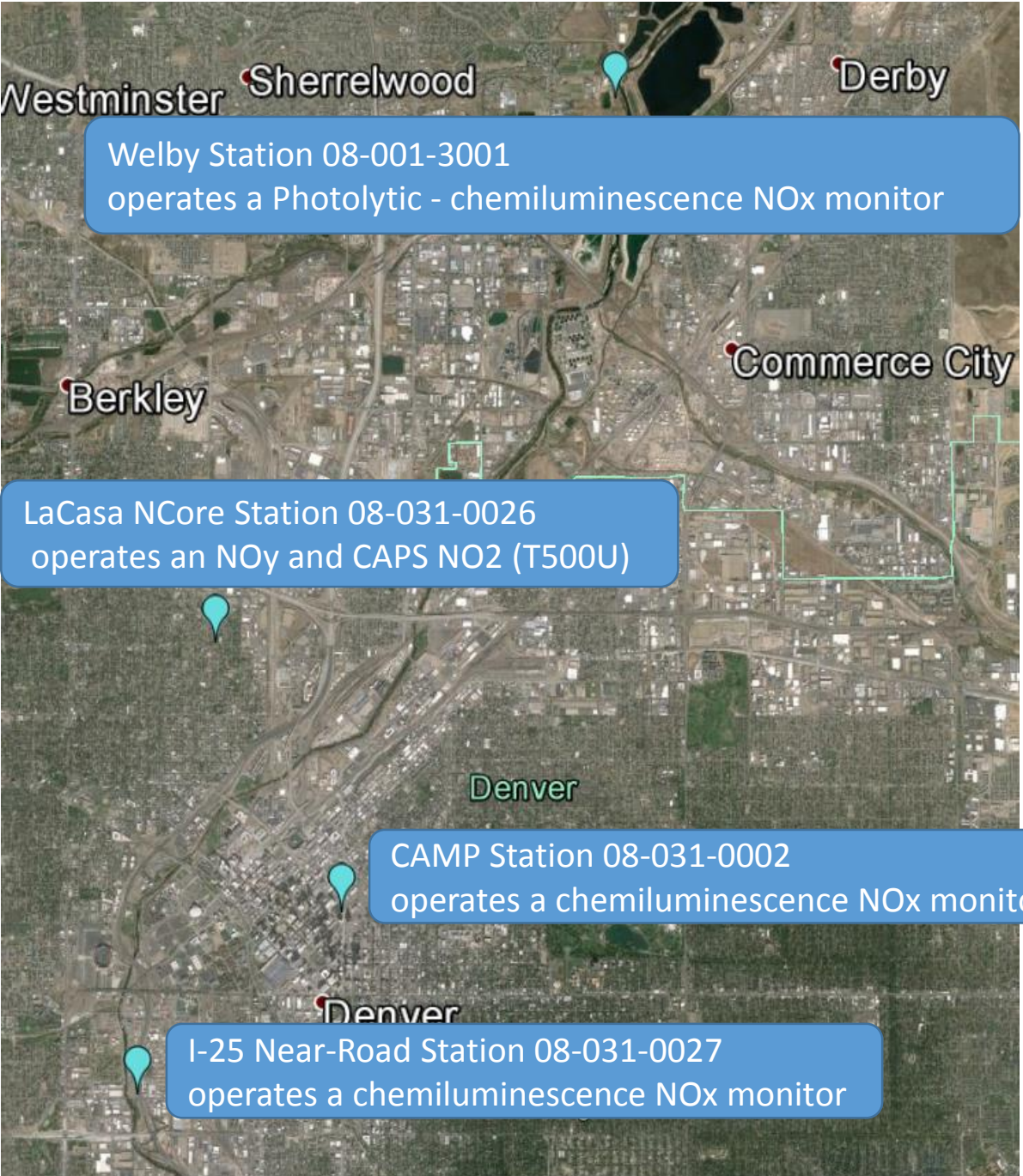


NO_y includes:



Interferences may include NH_3 , which can be minimized with good siting (e.g., away from agricultural feed lots)

Key Denver Colorado Monitoring Stations with active nitrogen measurements



Welby Station 08-001-3001
operates a Photolytic - chemiluminescence NO_x monitor

LaCasa NCore Station 08-031-0026
operates an NO_y and CAPS NO₂ (T500U)

CAMP Station 08-031-0002
operates a chemiluminescence NO_x monitor

I-25 Near-Road Station 08-031-0027
operates a chemiluminescence NO_x monitor

Chemiluminescence NO_x monitors provide measurement of:

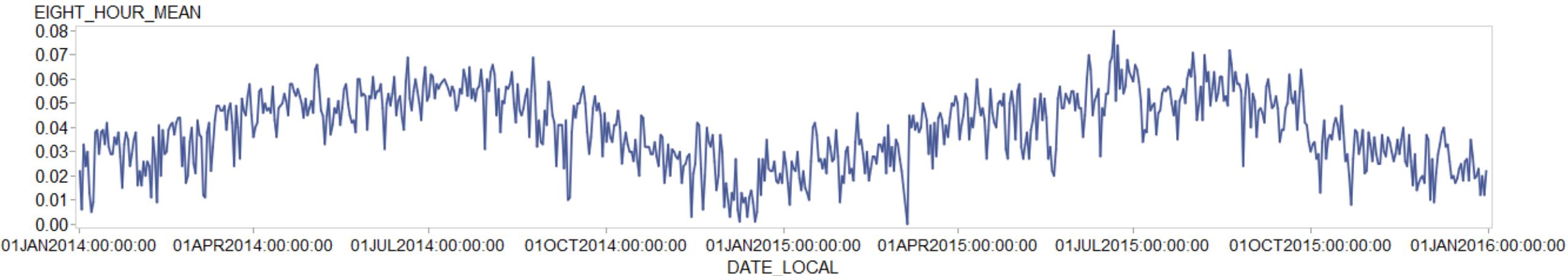
- NO
- NO₂
- NO_x

Direct NO₂ Cavity Attenuated Phase Shift Spectroscopy (CAPS) provides a measurement of:

- NO₂

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

| | 6/17/15 | 6/18/15 | 6/19/15 | 6/20/15 | 6/21/15 | 6/22/15 | 6/23/15 | 6/24/15 | 6/25/15 | 6/26/15 |
|----------------|---------|---------|---------|---------|--------------|---------|--------------|---------|---------|---------|
| LaCasa Station | 0.054 | 0.054 | 0.067 | 0.069 | 0.080 | 0.051 | 0.074 | 0.056 | 0.064 | 0.054 |
| CAMP Station | 0.053 | 0.052 | 0.061 | 0.067 | 0.077 | 0.049 | 0.067 | 0.055 | 0.063 | 0.052 |
| | 7/28/15 | 7/29/15 | 7/30/15 | 7/31/15 | 8/1/15 | 8/2/15 | 8/3/15 | 8/4/15 | 8/5/15 | 8/6/15 |
| LaCasa Station | 0.05 | 0.06 | 0.064 | 0.061 | 0.071 | 0.061 | 0.043 | 0.049 | 0.057 | 0.043 |
| CAMP Station | 0.047 | 0.054 | 0.059 | 0.053 | 0.066 | 0.057 | 0.04 | 0.045 | 0.05 | 0.037 |
| | 8/16/15 | 8/17/15 | 8/18/15 | 8/19/15 | 8/20/15 | 8/21/15 | 8/22/15 | 8/23/15 | 8/24/15 | 8/25/15 |
| LaCasa Station | 0.061 | 0.051 | 0.053 | 0.049 | 0.072 | 0.066 | 0.055 | 0.063 | 0.058 | 0.058 |
| CAMP Station | 0.055 | 0.046 | 0.052 | 0.05 | 0.067 | 0.062 | 0.055 | 0.061 | 0.056 | 0.03 |



What do we see in the nitrogen measurements during an ozone episode?

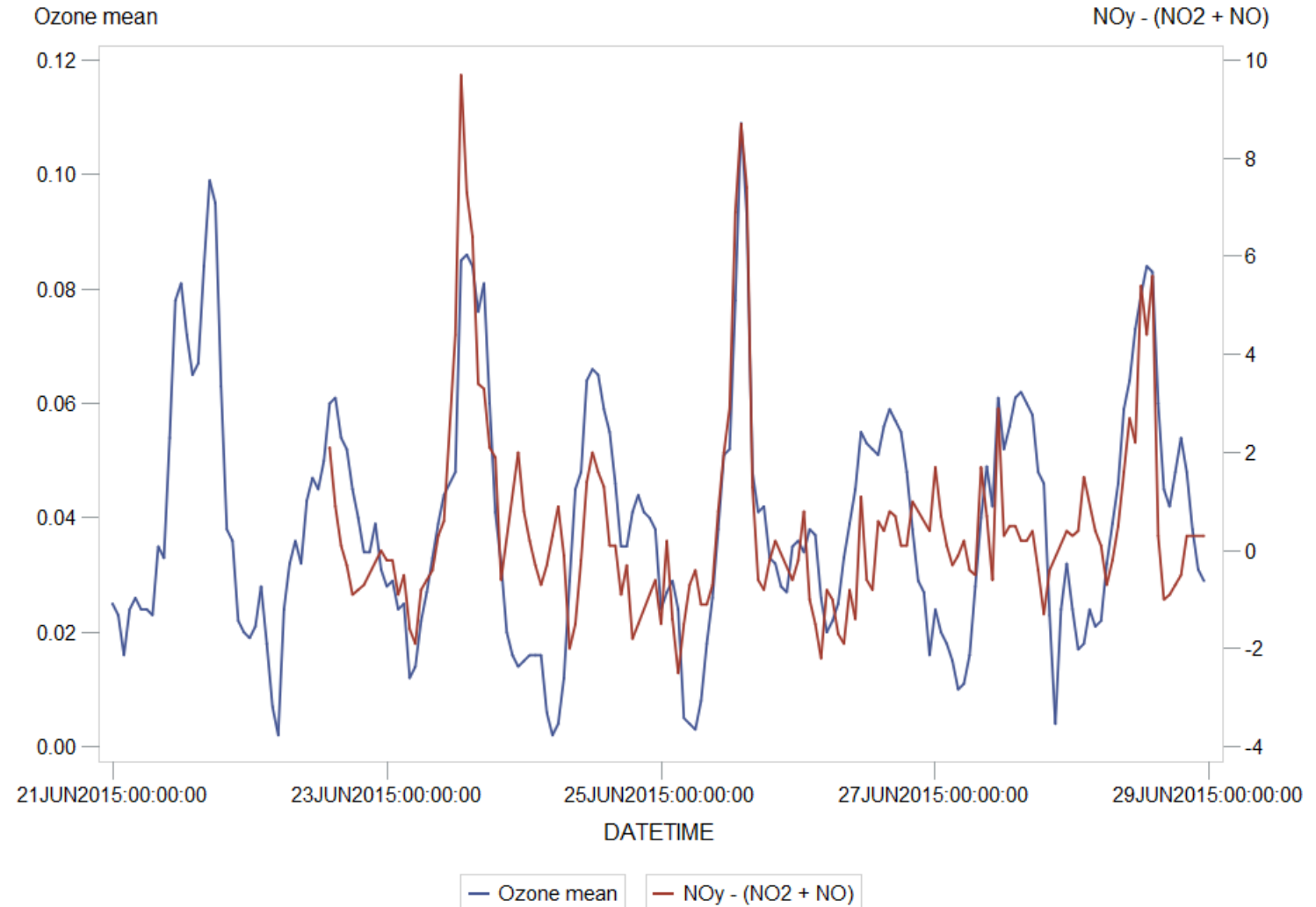
What's measured and what can we calculate?

➤ LaCasa NCore Station - What's measured and reported:

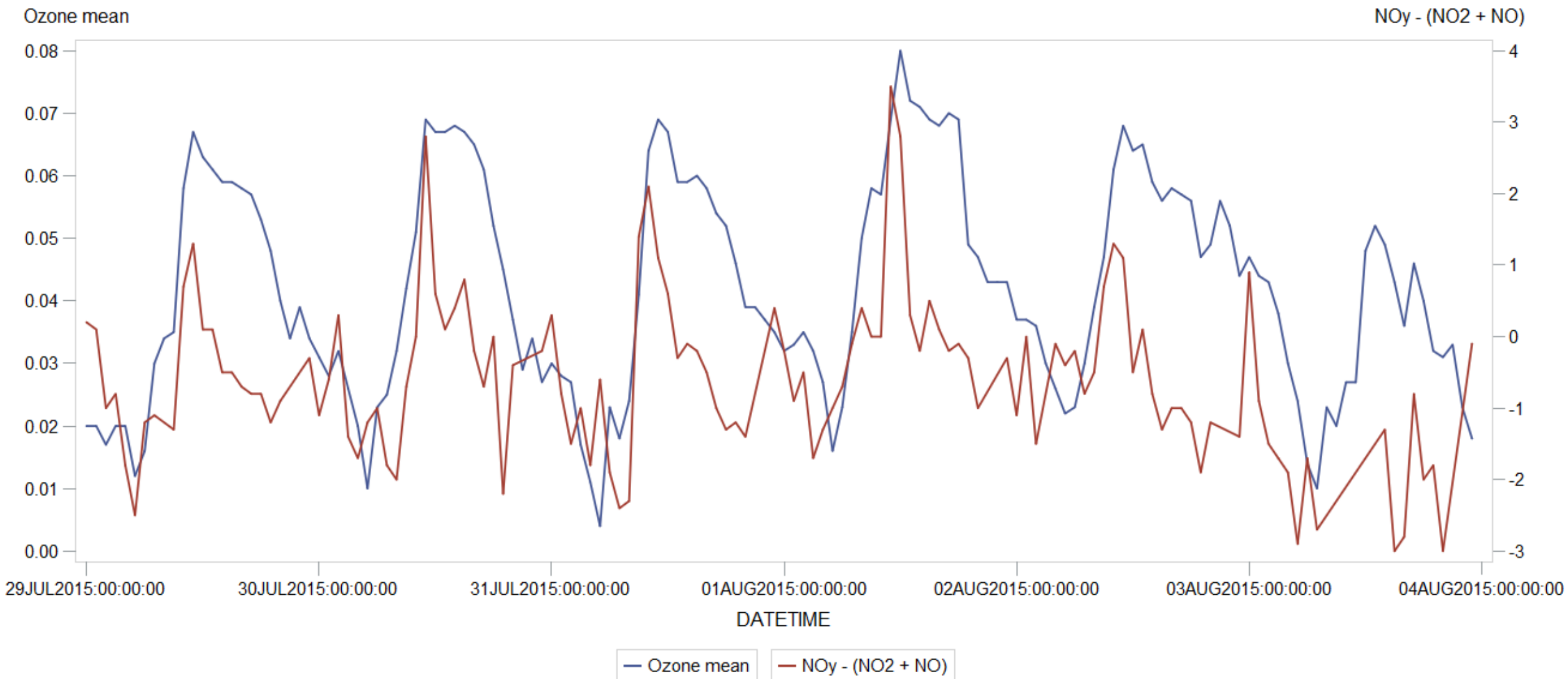
- NO and NO_y on one monitor.
- Direct NO₂ on CAPS

➤ What can we calculate?

- $\text{NO}_y - (\text{NO} + \text{NO}_2) = \text{NO}_z$
- **In these data we see 9-10 ppb of NO_z on high ozone days.**

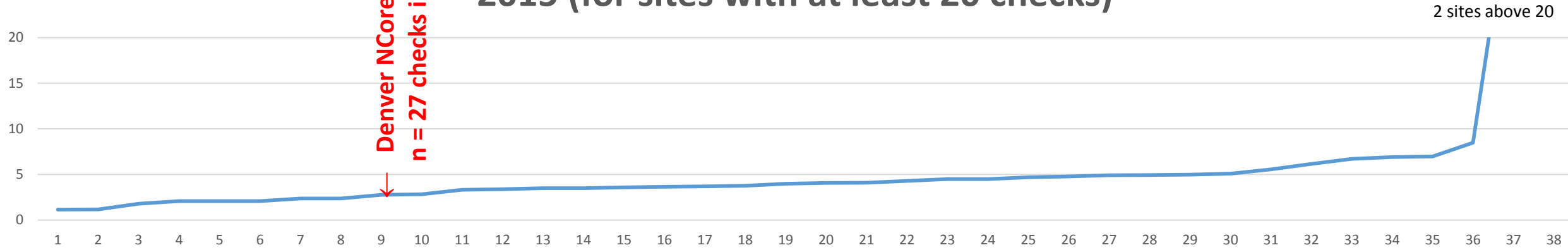


What do we see in the nitrogen measurements during an ozone episode?

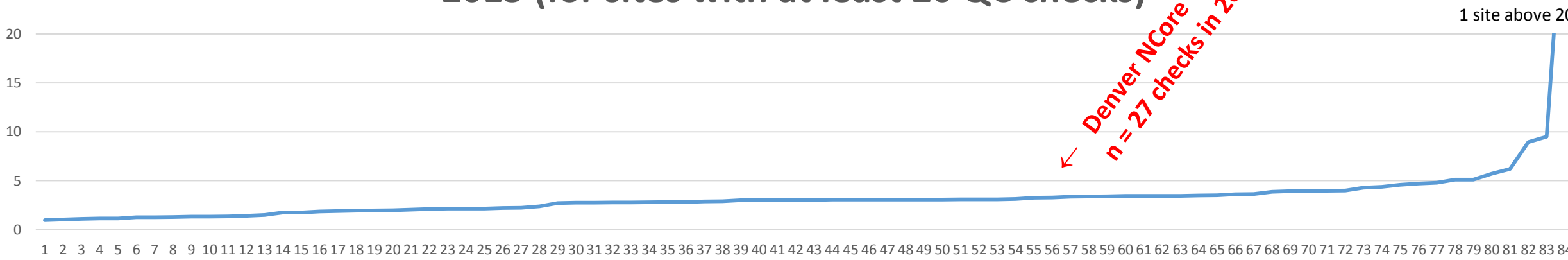


What do the reported QC checks look like for the Denver NCore station compared to the rest of the country?

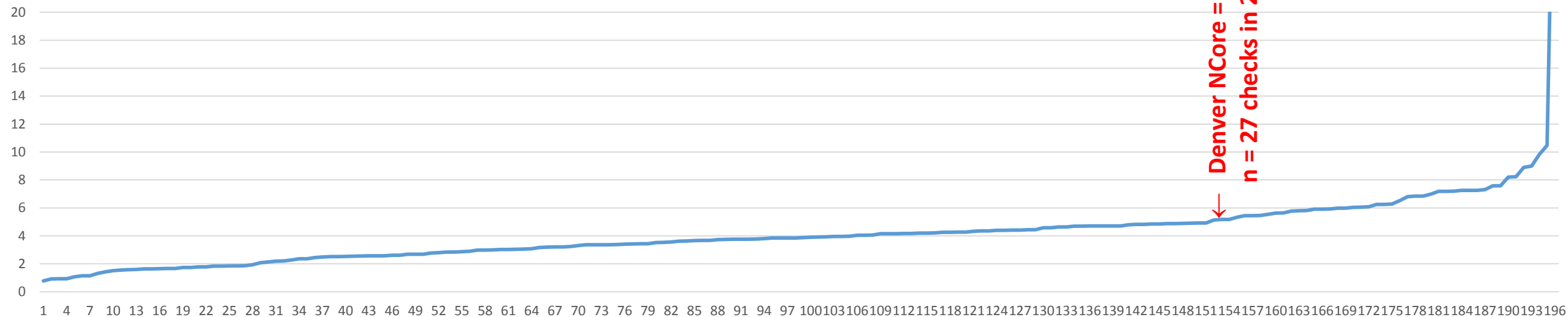
NOy CV Upper Bound 2015 (for sites with at least 20 checks)



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



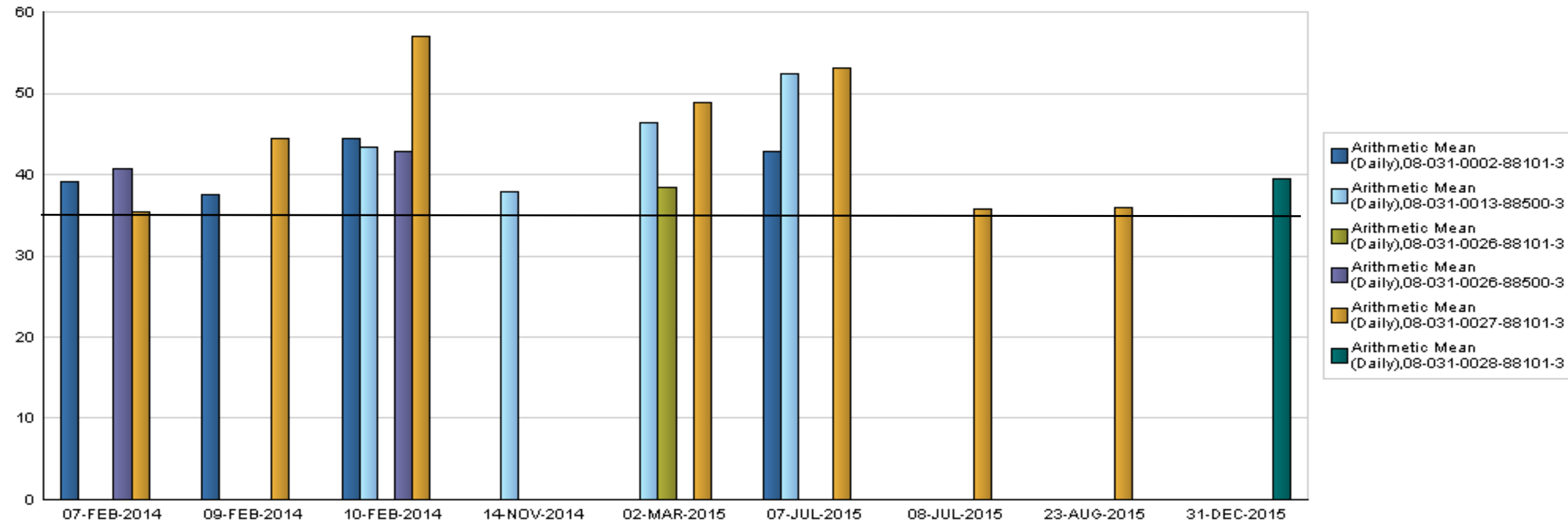
NO₂ CV Upper Bound 2015 (for sites with at least 20 QC checks)



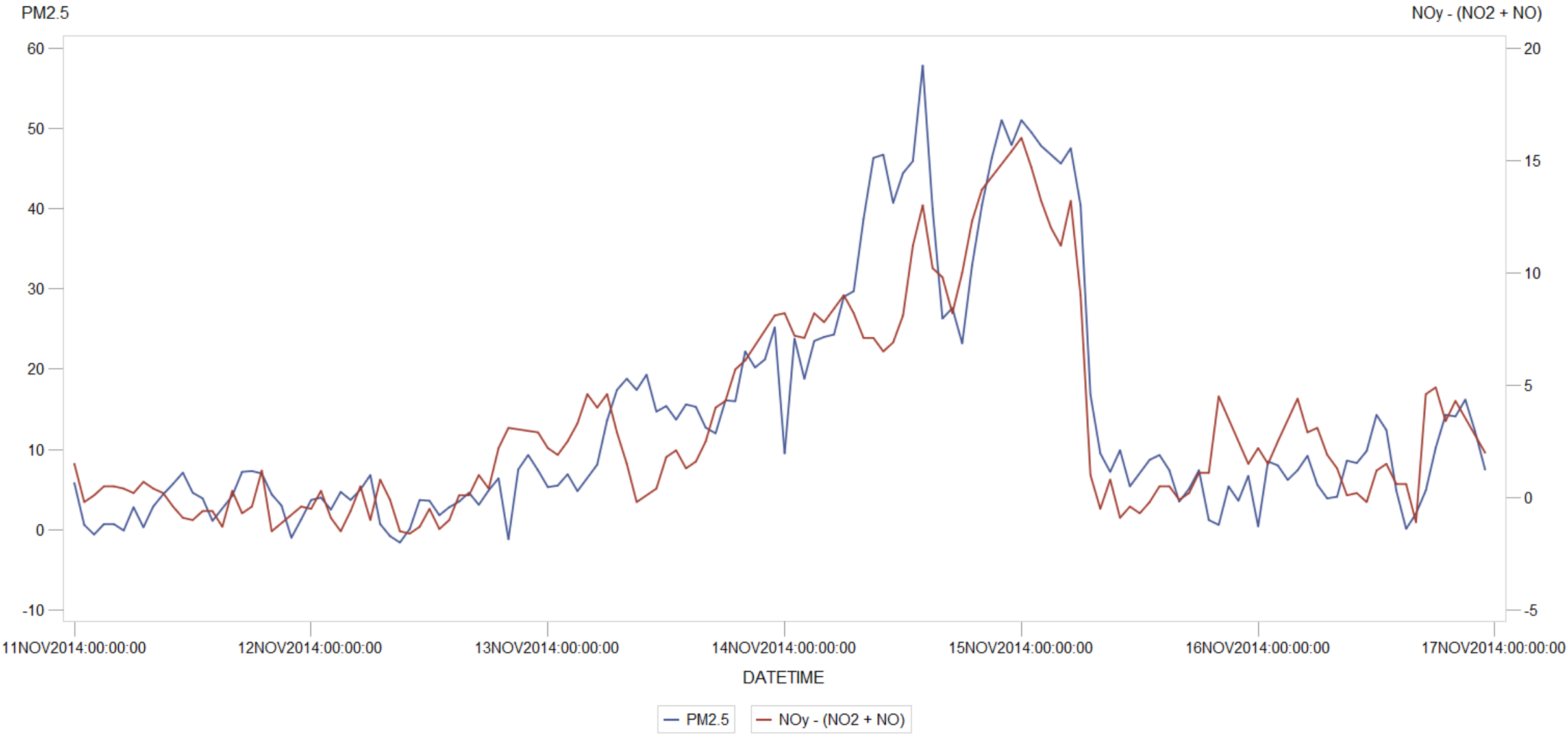
What if we look at PM_{2.5} in Denver?

In 2014-2015 data set, there are several cases where one or more Denver area PM_{2.5} sites are above 35 $\mu\text{g}/\text{m}^3$.

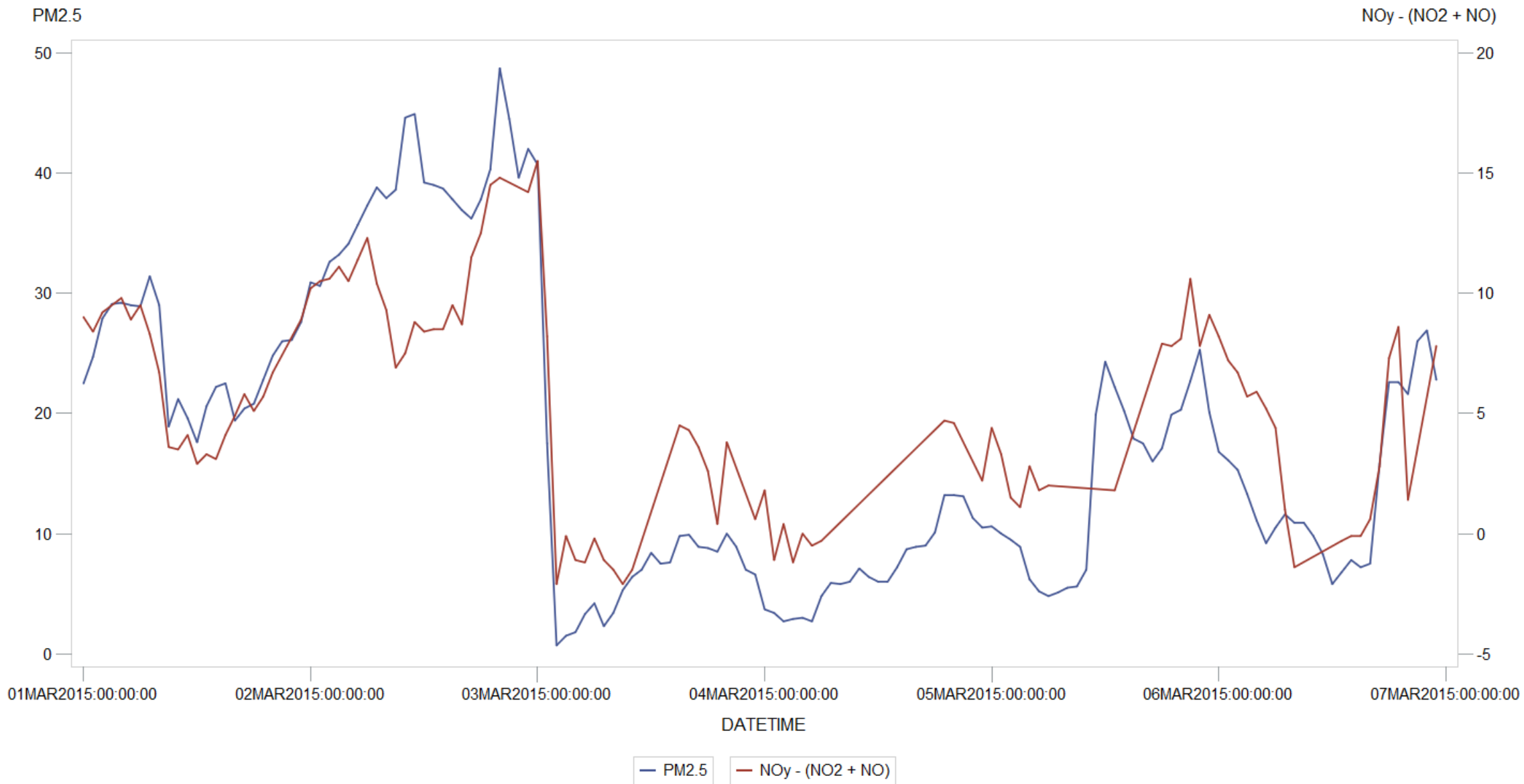
Denver area days in 2014 - 2015 with PM_{2.5} data over 35 $\mu\text{g}/\text{m}^3$



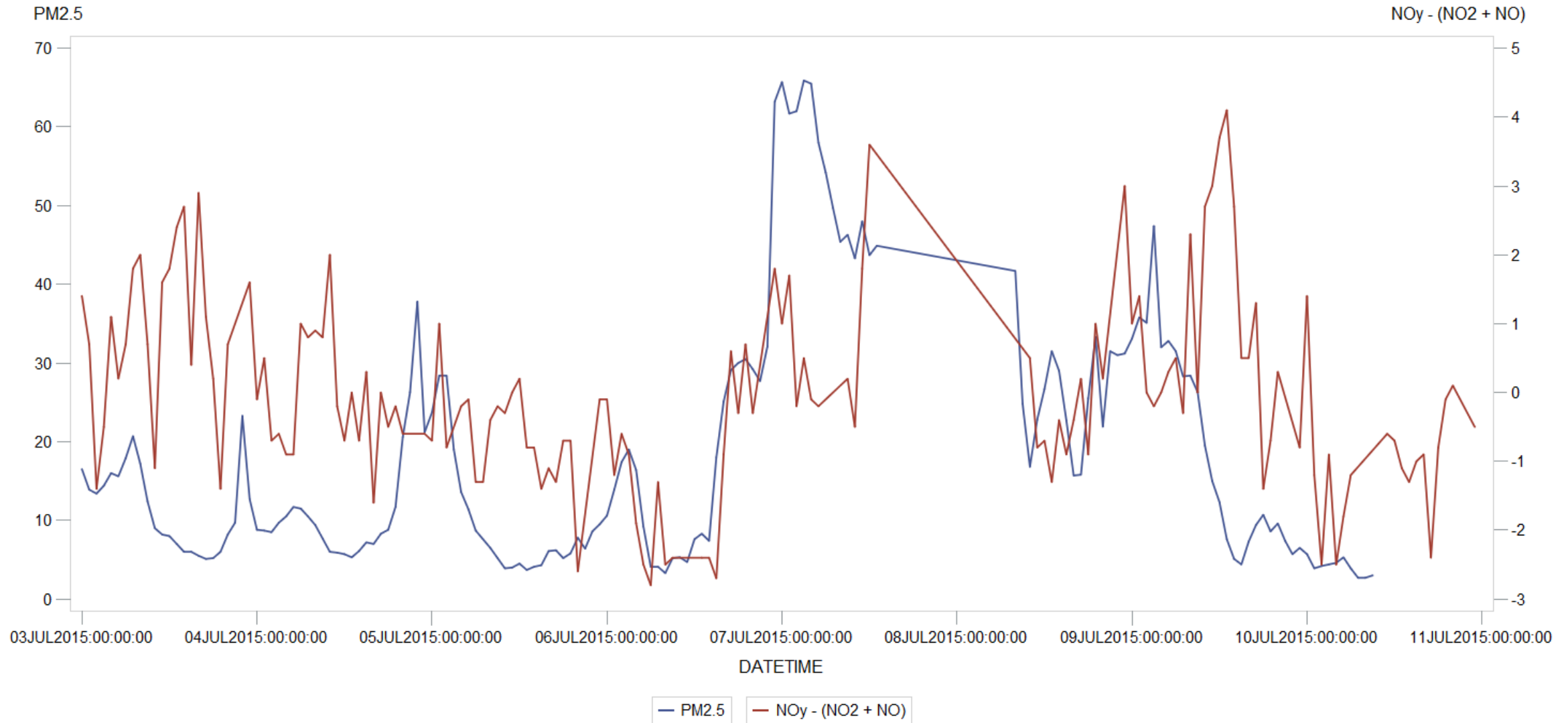
What do we see in the Denver NO_x data during these PM_{2.5} episodes? October 2014



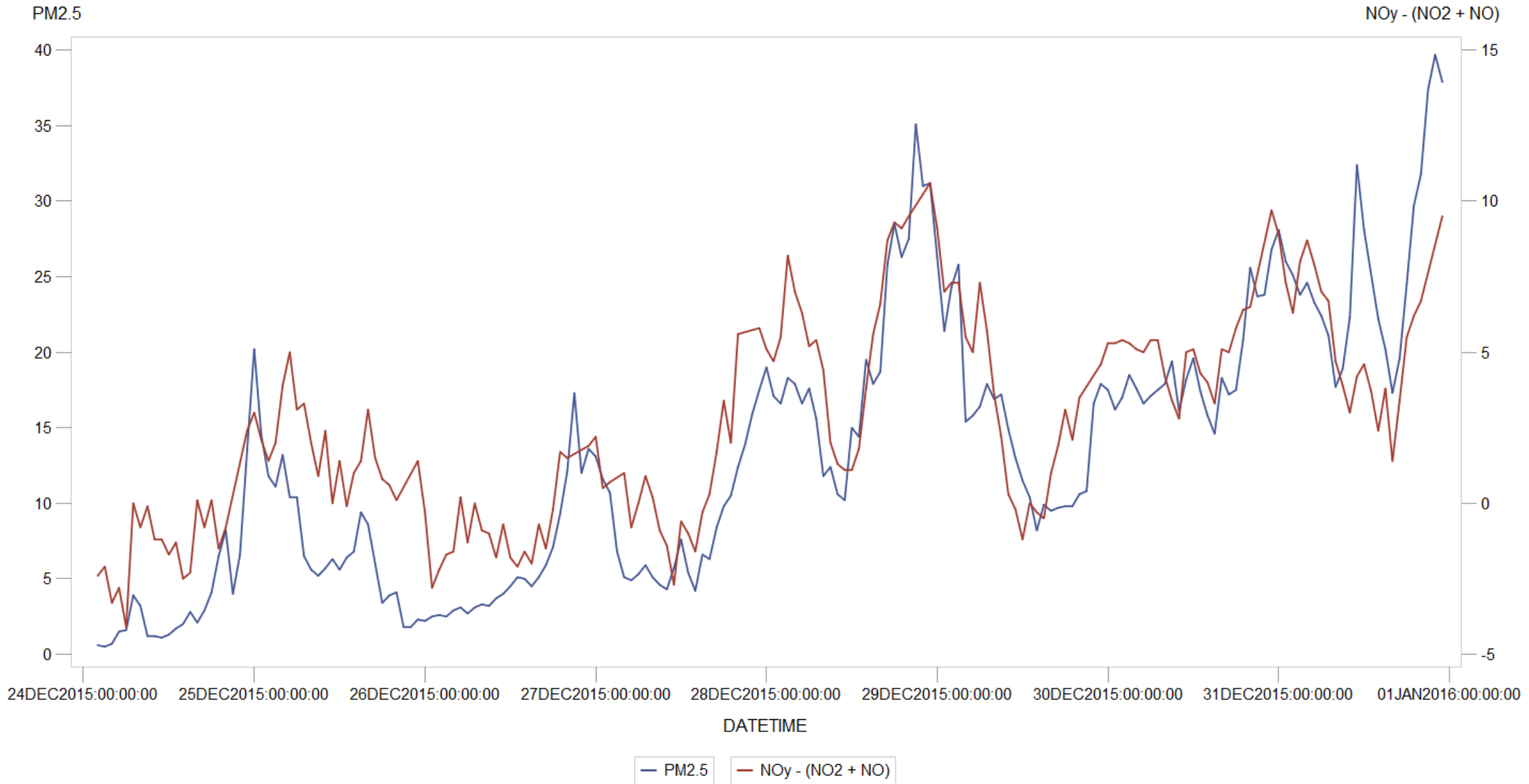
Denver NO_x data during PM_{2.5} episode in March 2015



Denver NO_x data during PM_{2.5} episode in July 2015

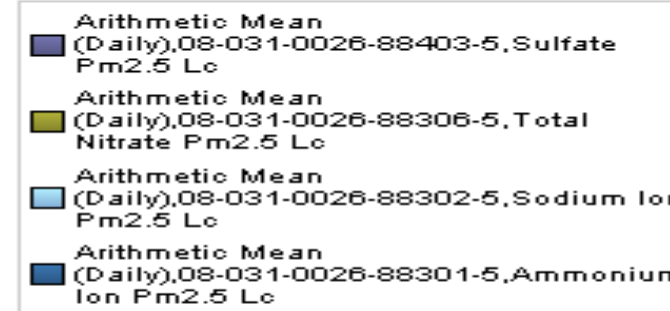
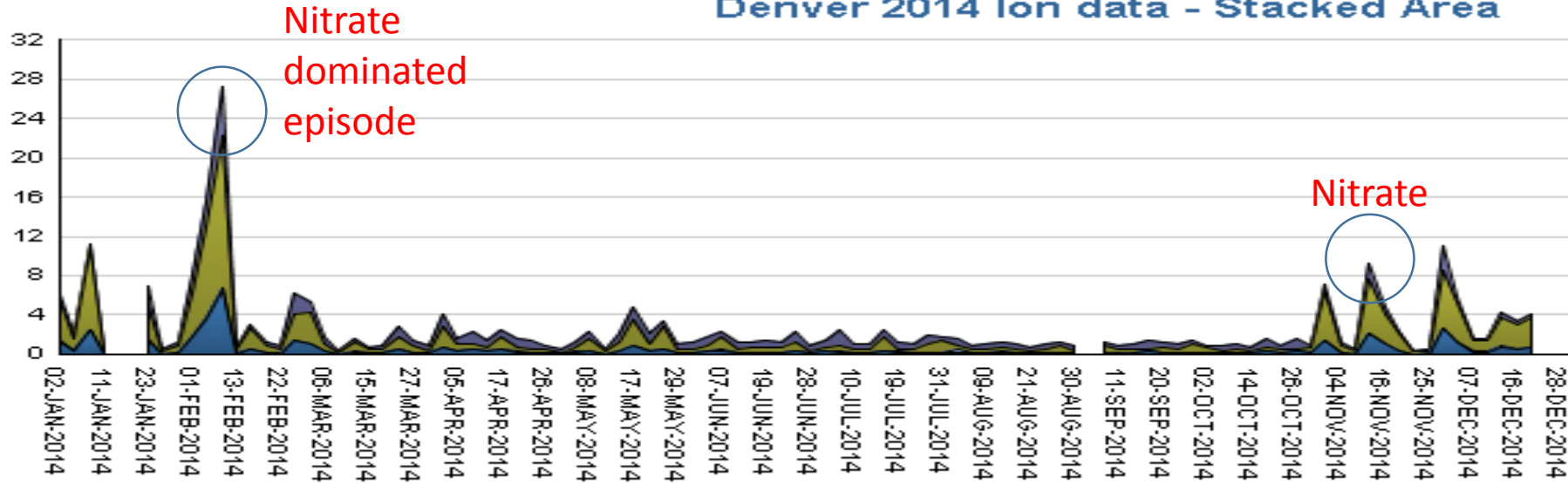


Denver NO_x data during PM_{2.5} episode in December 2015

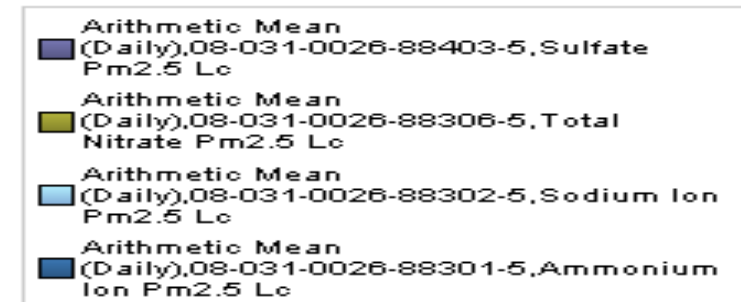
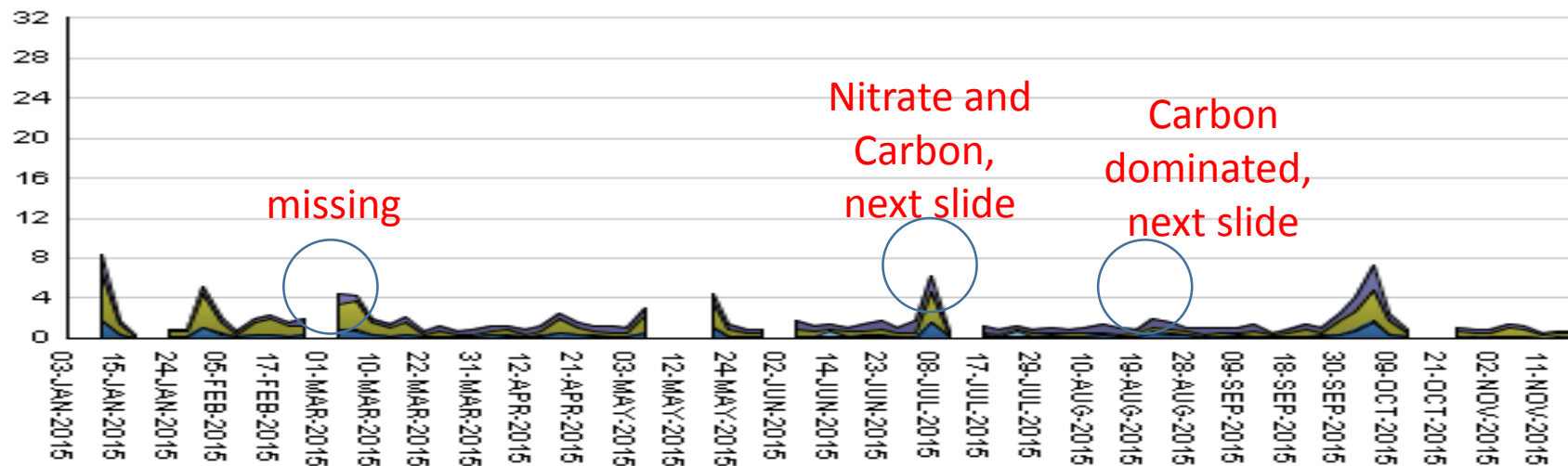


What do we see in select chemical speciation data in Denver?

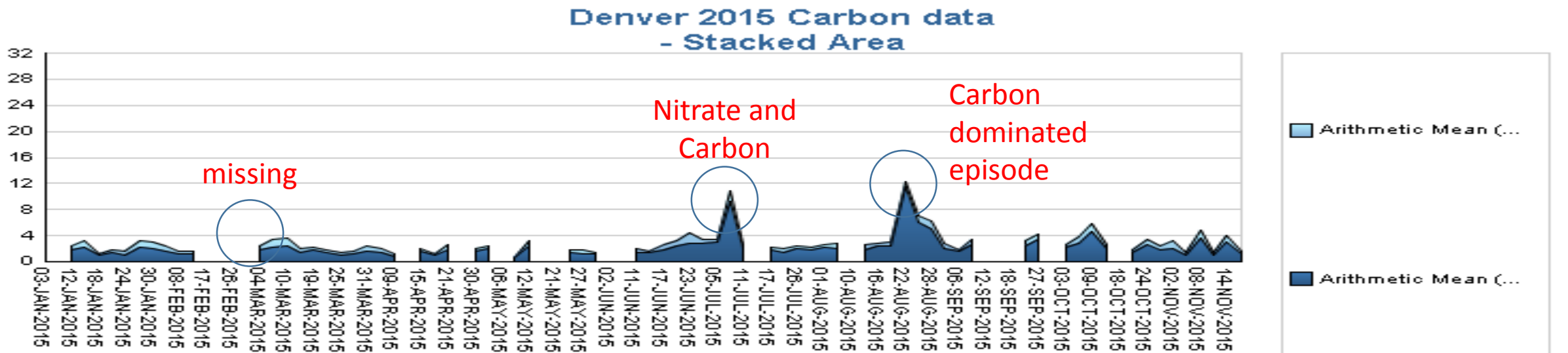
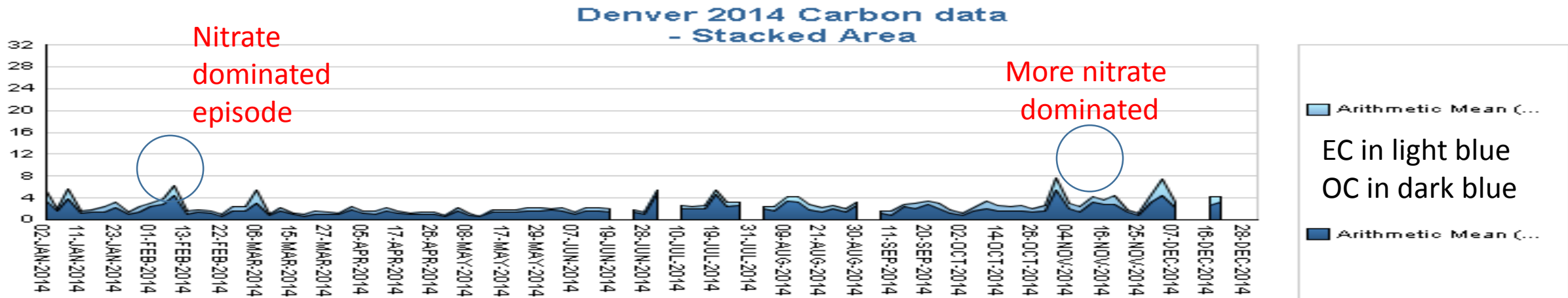
Denver 2014 Ion data - Stacked Area



Denver 2015 Ion data - Stacked Area

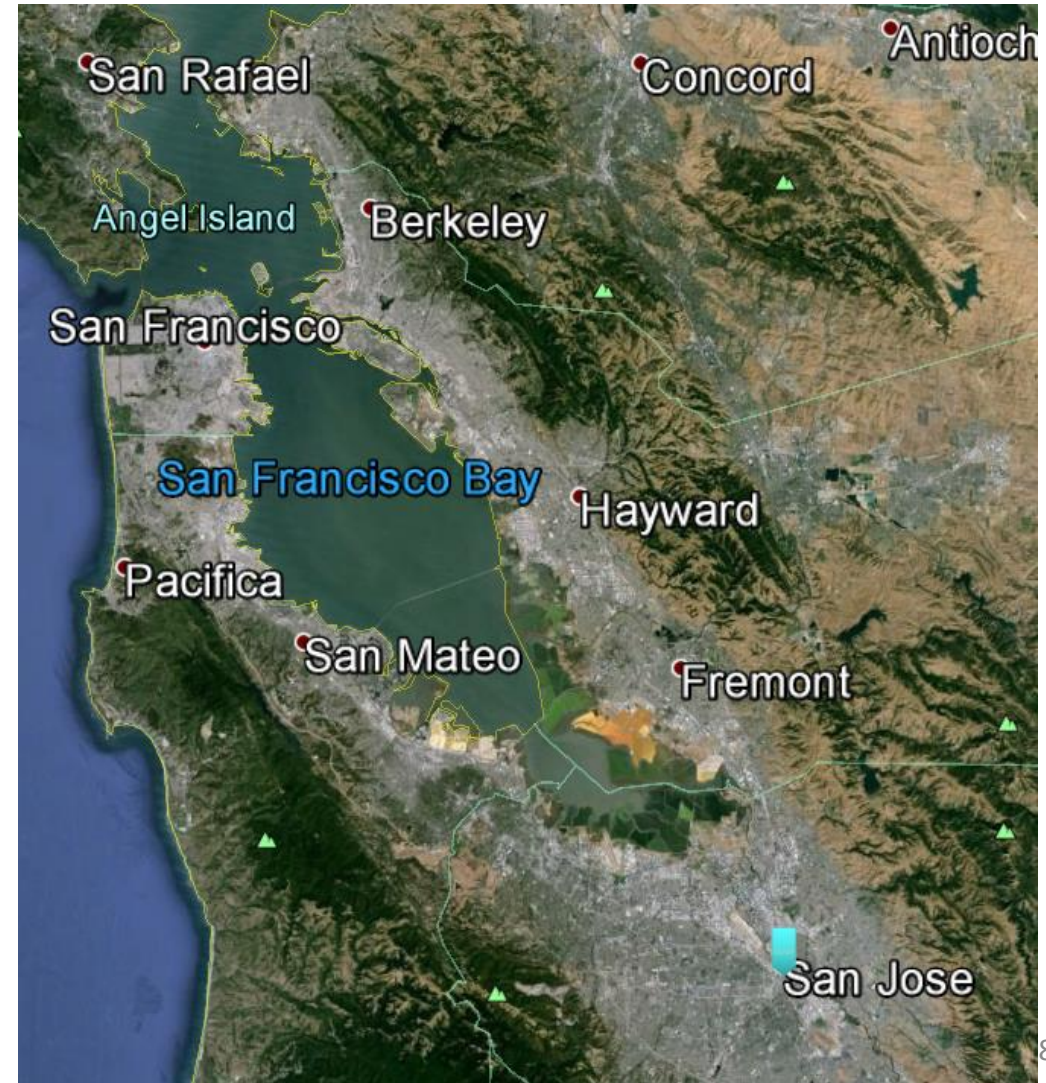


What do we see in select chemical speciation data in Denver?



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_y on one monitor.
 - NO, NO₂, and NO_x on a second monitor.
 - What can we calculate?
 - NO_y – NO_x = NO_z
 - (NO_y – NO) – (NO_x – NO) = NO_z
(normalized for each NO channel)

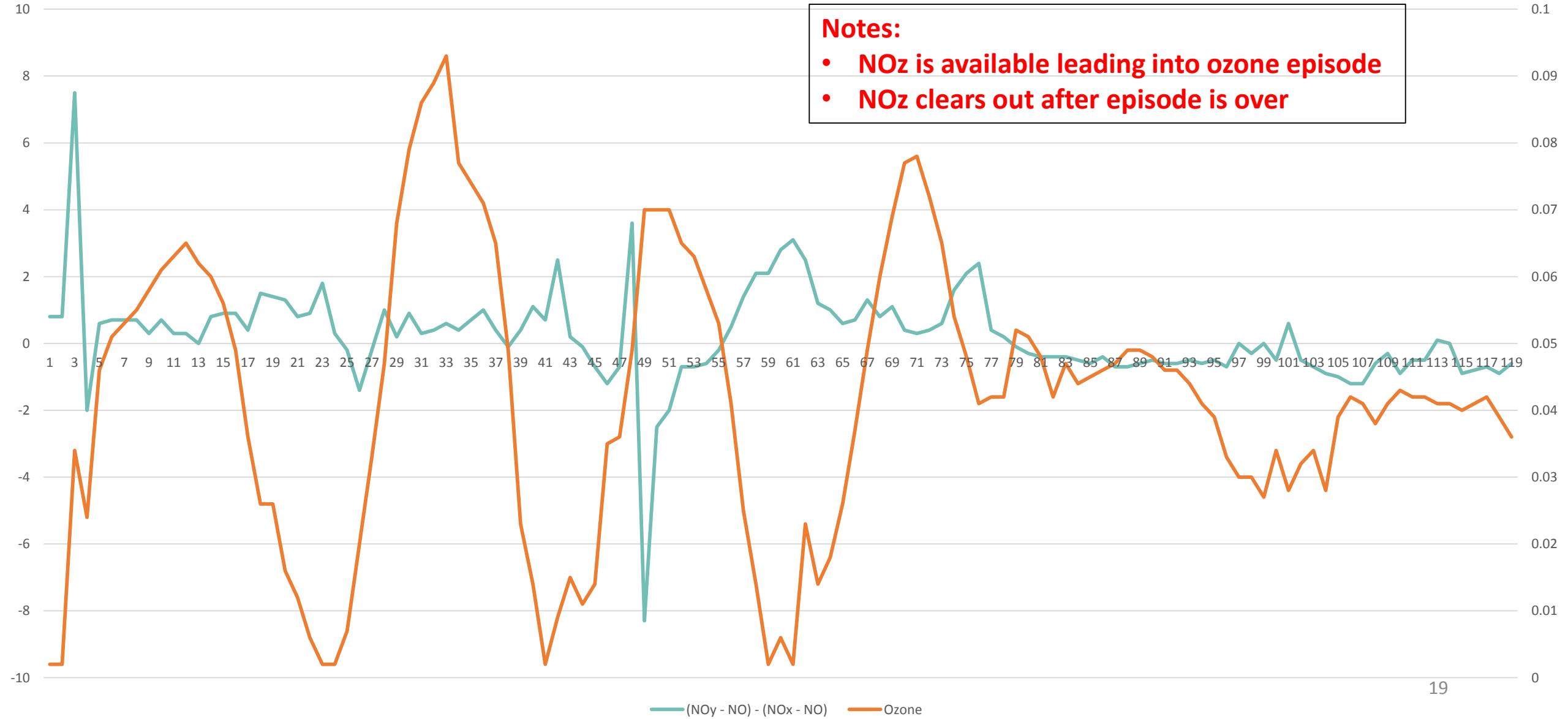


Comparing $(\text{NO}_y - \text{NO}) - (\text{NO}_x - \text{NO})$ with Ozone

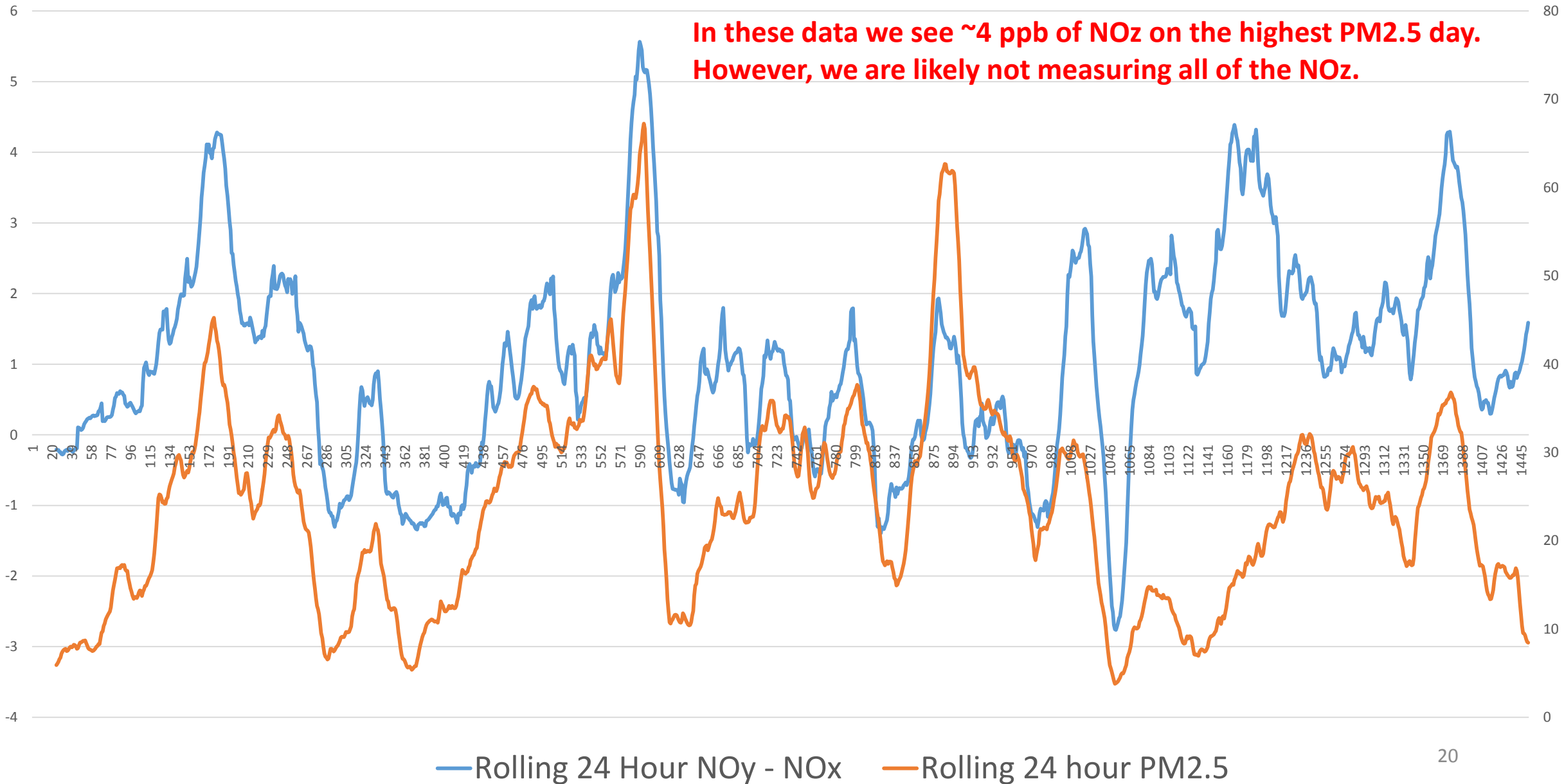
San Jose NCore station, May 2013

Notes:

- **NOz is available leading into ozone episode**
- **NOz clears out after episode is over**

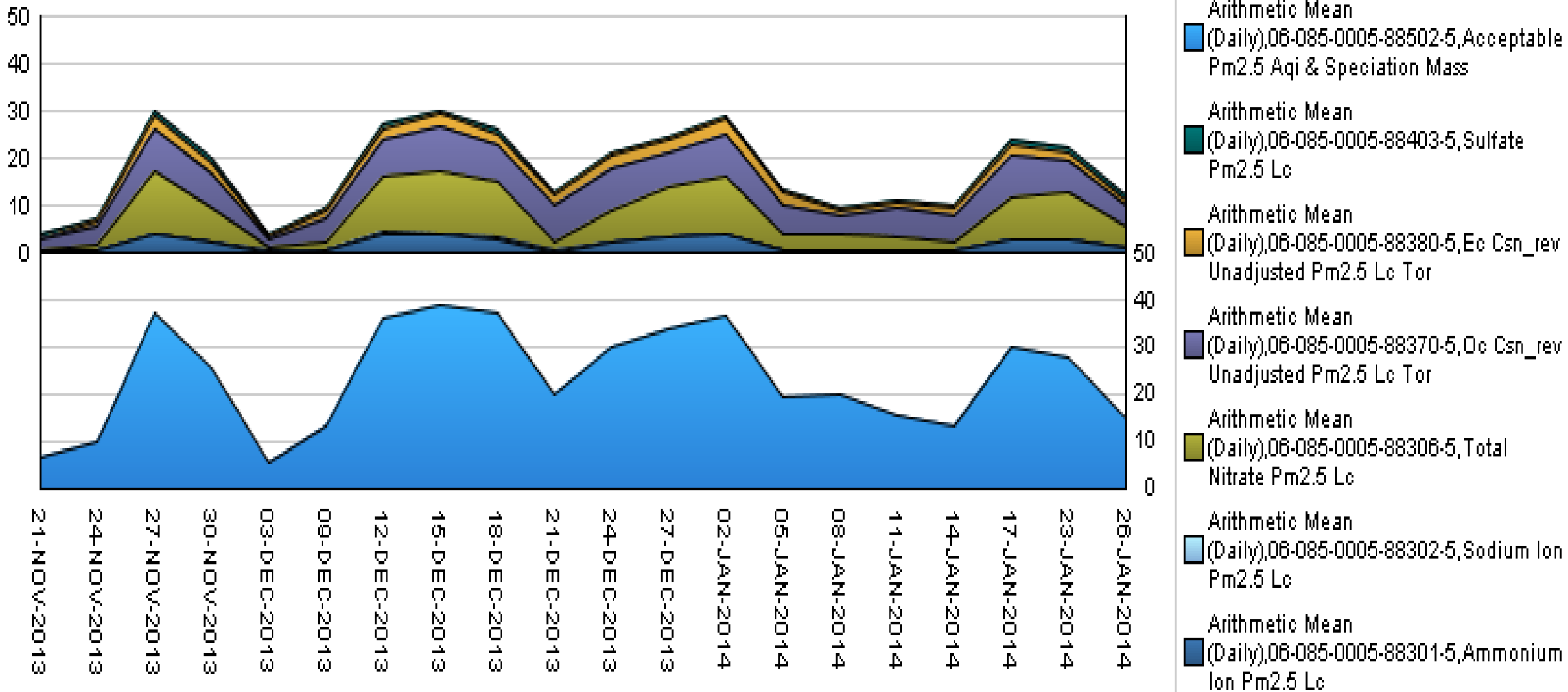


Trend of difference between NOy and NOx compared to PM_{2.5} (24 hour rolling averages) San Jose NCore Station 11/20/2013 to 1/28/2014



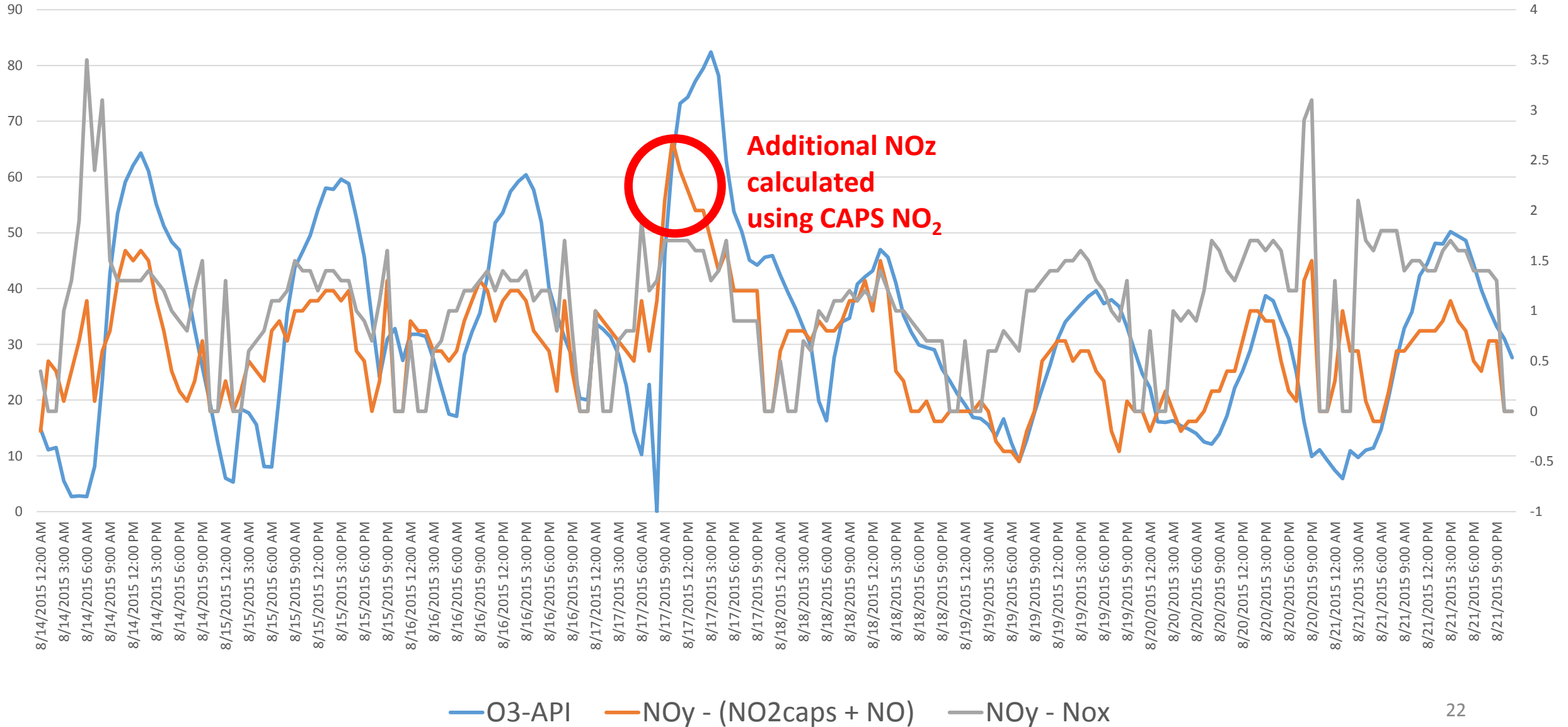
Comparing ions and Carbon to Mass in CSN

San Jose - November 2013 to January 2014



What do we see in the NOy and NOx data during high ozone in RTP?

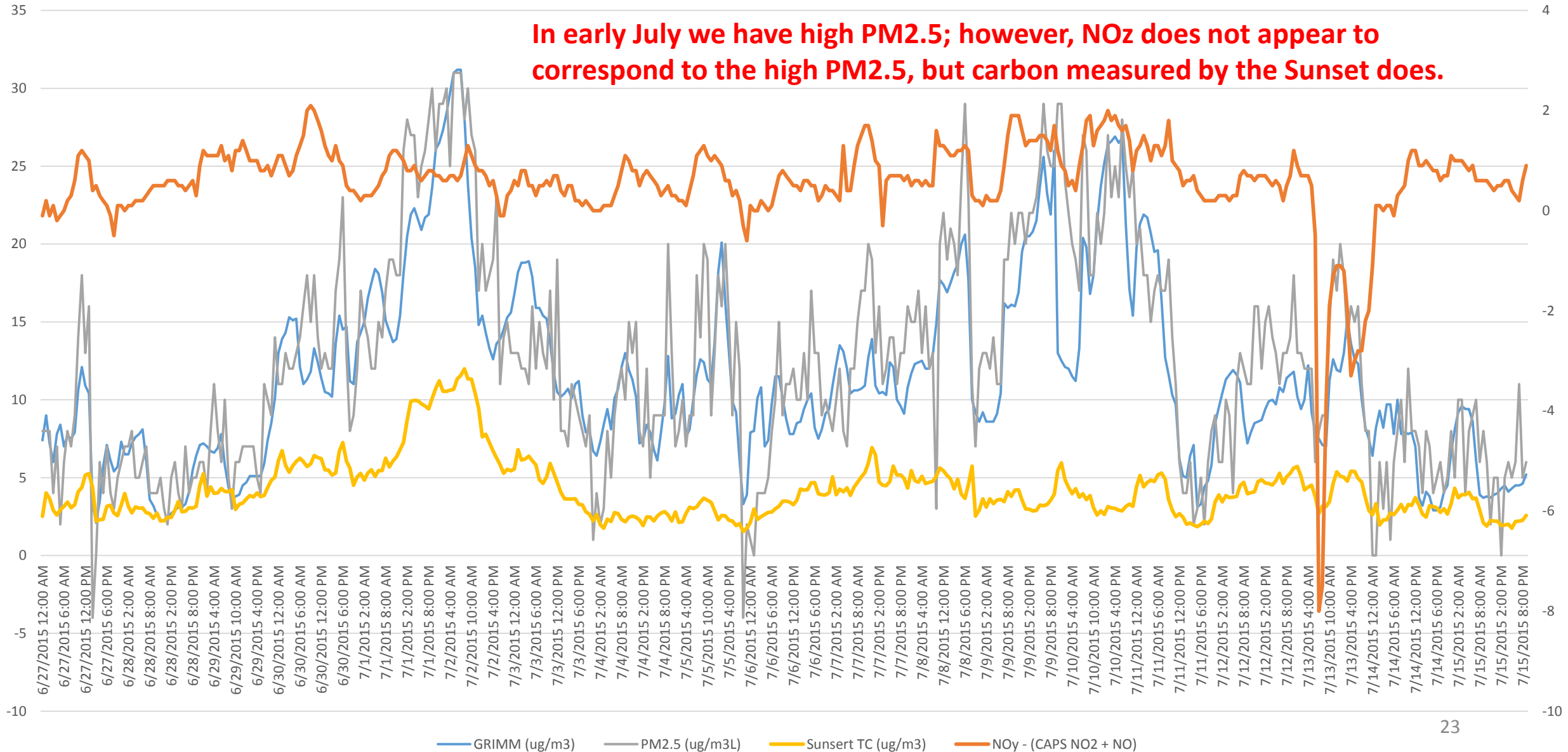
AIRS RTP, NC



What do we see in the NOy and NOx data during high PM2.5 in RTP?

AIRS RTP NC - PM2.5, Sunset Carbon, and NOz

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 NO_y and CAPS (direct method) NO₂.
- Difference between NO_y and NO_x (NO + NO₂) is identified as NO_z
- Denver NO_z compares very well on high ozone and high PM_{2.5} days.
- The peak of NO_z appears to compare very favorably with the peak of ozone and PM_{2.5}
- **These data appear to support the value of true NO₂ collocated with NO_y.**
- Data in San Jose and RTP are similar; except:
 - San Jose NO_z data is out of phase with ozone, while in Denver it is nearly in phase.
 - RTP summer PM_{2.5} appear to be impacted by OC and not NO_z. September Ozone data is impacted by NO_z.

Related Notes and Next Steps:

- EPA ORD has been investigating optimizing the NO_y 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 NO_y on an NO_y analyzer
 - “true” NO₂ on photolytic or CAPS NO₂ analyzer