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NO_y Speciation at the Queens College Air Quality Measurement Site

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With contributions from:

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Basic Definitions

- NO_x Source Gases (air pollution precursors) – byproduct of combustion activity
- **$NO_x = NO + NO_2$**
- These species play a **central role** in the ozone formation (air pollution) chemistry reactions
- NO_x is removed through chemical transformations that produce higher oxides of nitrogen, including nitric acid (HNO_3), nitrous acid (HONO), and organic nitrates (Alkyl Nitrates [ANs] and Peroxy Acetyl Nitrates [PANs])
- We can define the full set of oxides of nitrogen as **NO_y**

Definitions (cont.)

- $NO_y = NO + NO_2 + HNO_3 + HONO + ANs + PANs + others$
- We define just the higher oxides as **NO_z**
- **$NO_z = NO_y - NO_x$**
- NO_z is also referred to as the products of NO_x oxidation

Definitions (conclusion)

- There is very important interplay between O_3 and NO_x species, abbreviated as

$$\mathbf{NO + O_3 \rightleftharpoons NO_2}$$

- O_3 and NO_2 are both regulated atmospheric oxidants, and in high NO_x environments they must be considered together as
- **O_x = odd oxygen = O_3 + NO_2**
- This definition allows us to more correctly establish the oxidizing power of the atmosphere under conditions where NO_x and O_3 concentrations are both appreciable

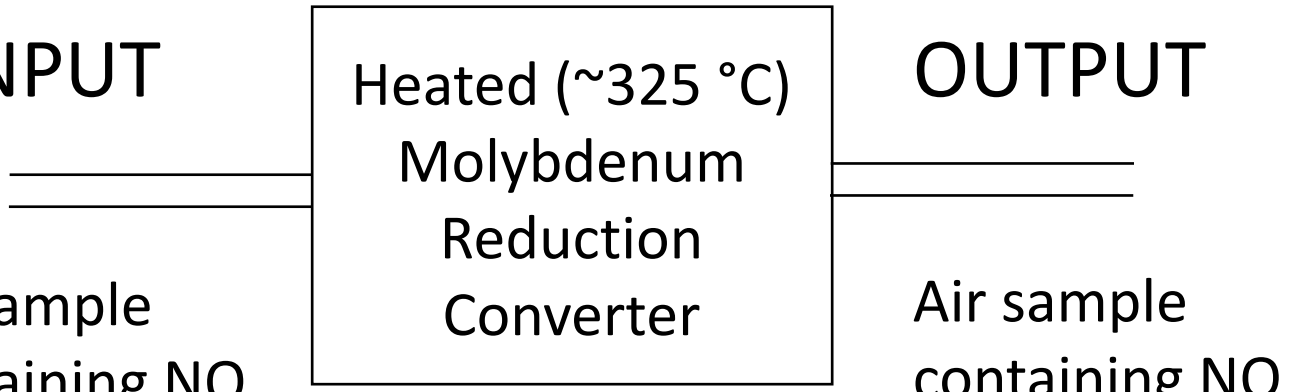
Measurement Details

- No measurement is perfect.
- Ozone measurement is pretty reliable. (And very minor known problems do not affect this work.)
- NO_x and NO_y measurements are much more challenging.
- We have a very good, long-standing method for measuring NO (chemiluminescence or CL).
- We can also measure NO_y pretty reliably if proper care is taken.
- While Ron Cohen's groups and quite a few others have sensitive and highly selective instruments for measuring NO_2, ***the instruments widely used in networks (and with EPA designations) are not selective for NO_2 (known since the 1980s!)***

Why is the EPA Method not selective for NO_2?

- Analyzers are based on the CL method for NO
- NO_2 must be converted to NO to be detected and measured.
- The commonly used, EPA designated method uses an NO_2 to NO converter that is **not selective for NO_2!**
- Illustrated on next slide

Non-Selective Conversion

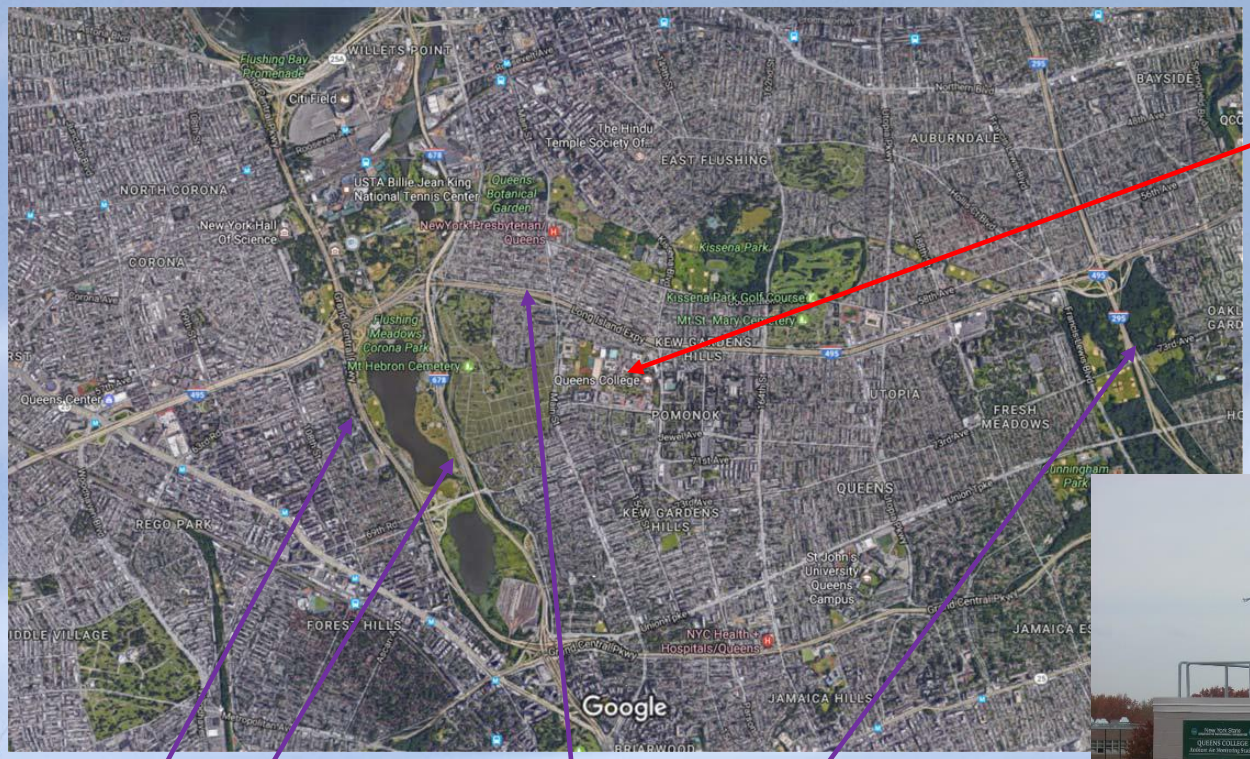


We define NO_2', NO_x' (and NO_z') as the parameters measured using this method.

Does This Matter?

- The answer to this question depends on how you want to use the data, i.e., the purpose of the measurements themselves.
- **NAAQS Compliance:** This complication is probably not very important for ascertaining NAAQS compliance. (The NO_2 standard is 100 ppb, which means NO_2 – and NO_x – are quite high. This can only happen near significant sources of NO_x. NO_z is always significantly less than 100 ppb (or even 10 ppb), and NO_x makes up most of NO_y. In these situations the compliance NO_2 reported by the EPA CL Method is a good approximation to the true NO_2.)
- **Understanding the NO_y Budget:** Yes, it matters!
- **Quantifying Ozone Production Efficiency (OPE):** Yes, it matters!

Measurement Location and Context



Queens College Location

Measurement Site

Grand Central Pkwy

Van Wyck

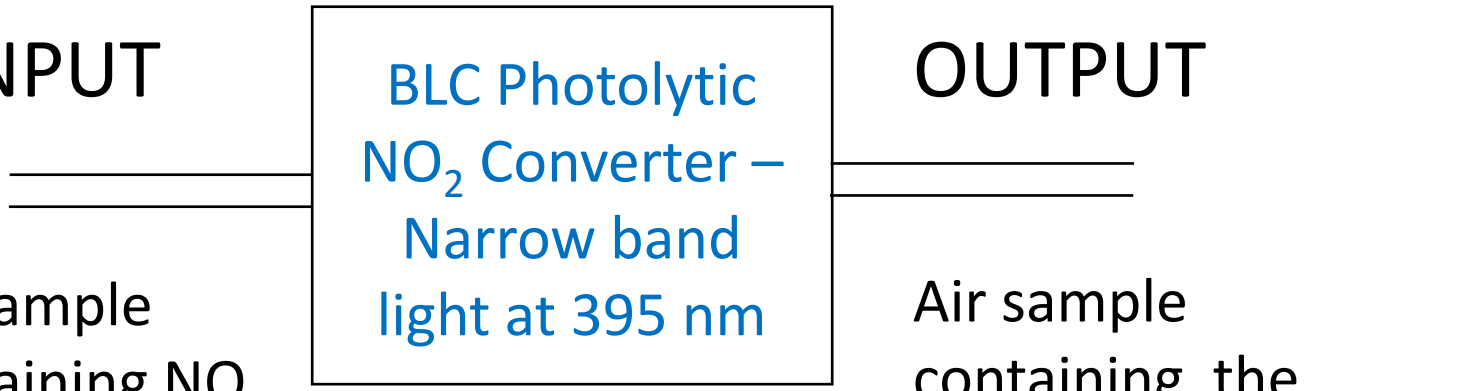
LIE

Clearview Expy

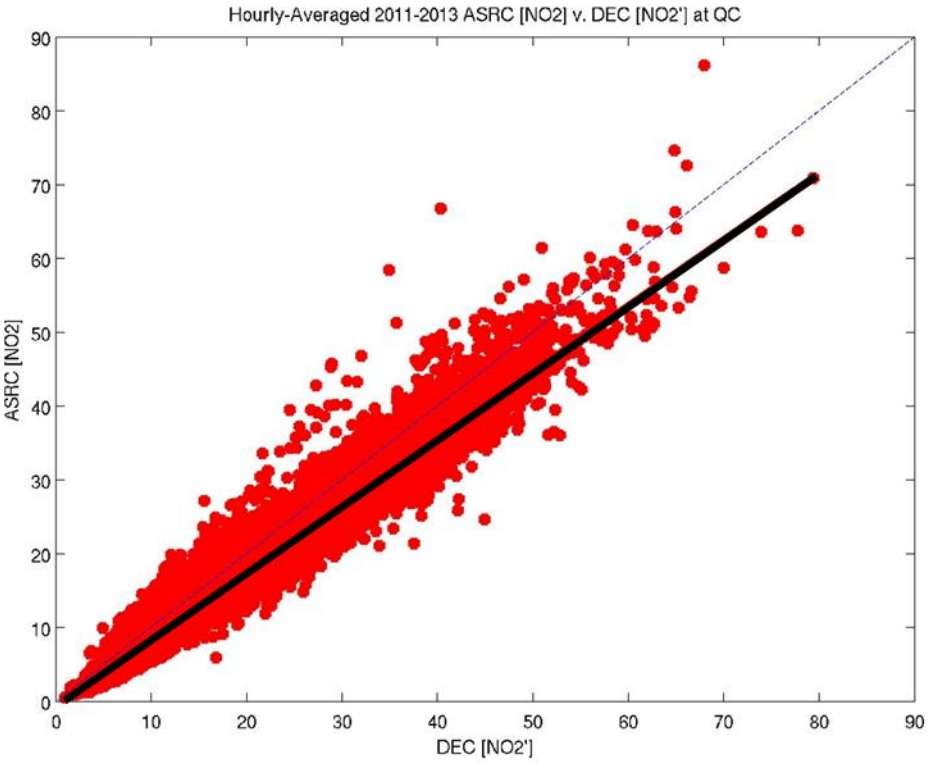
Observations of Speciated NO_y Components at QC

- Species specific NO_2 by ASRC from 2011 – 2013 using photolytic conversion
- In response to NCORE guidelines, DEC begins measurement of NO_y at QC in 2011
- ASRC joined with EPRI, ARA, and Envair to measure many "lesser" NO_z components at QC (and PSP) for a 15 month period in 2016-17.
- These species include HNO_3, particle nitrate (pNO_3), Alkyl Nitrates (ANs), and Peroxy Acetyl Nitrates (PANs)

Species Selective Photolytic Conversion for NO_2

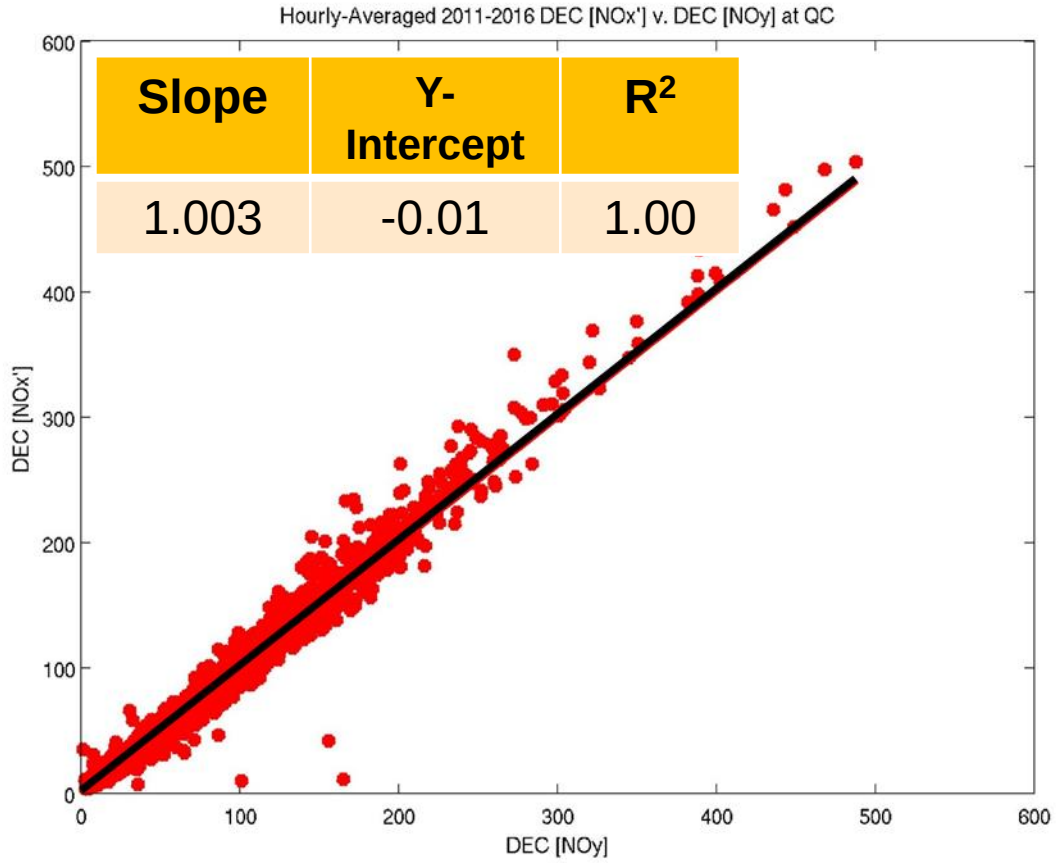


Photolytic NO_2 versus NO_2'



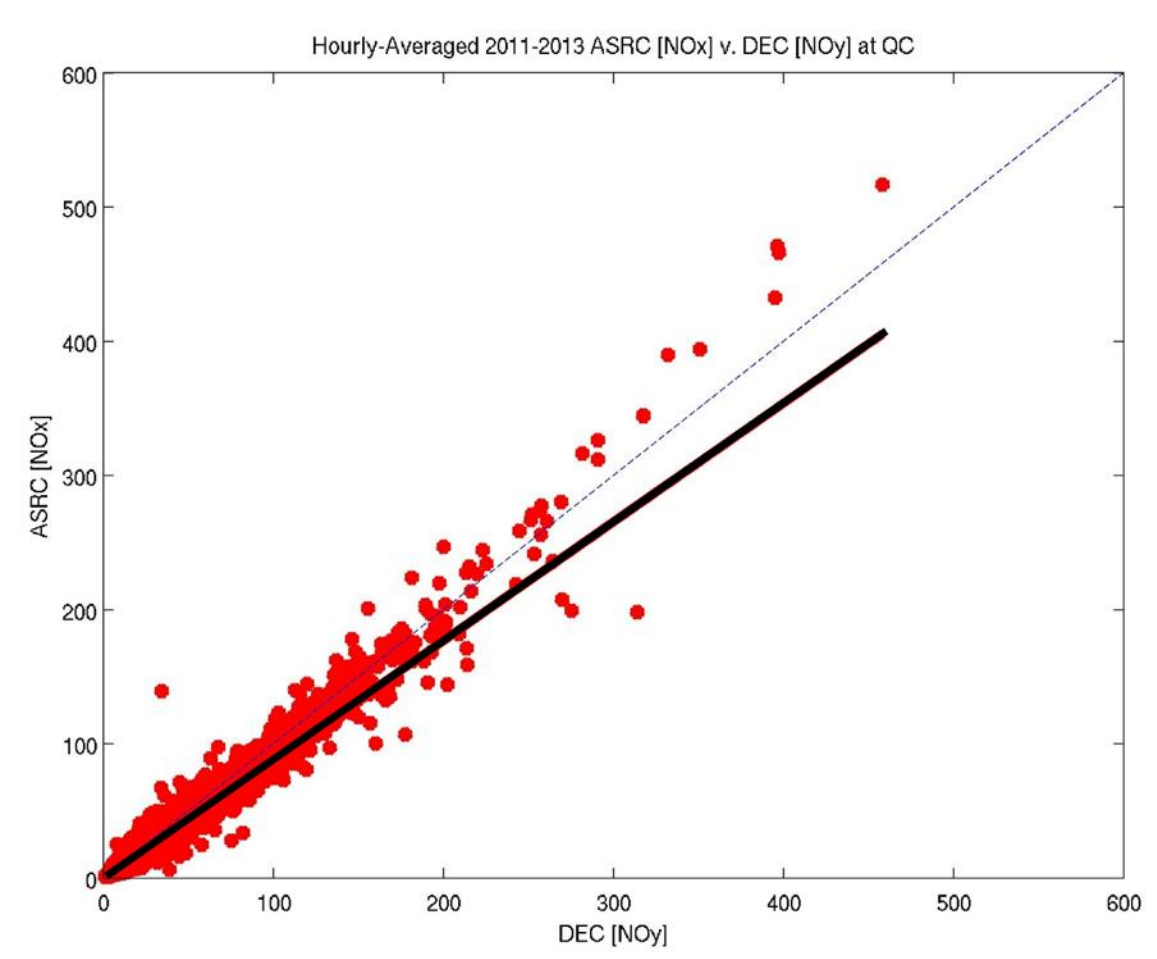
- Measurements are highly correlated.
- Slope of fit line (intercept set to 0) is 0.89, with an R^2 of 0.96.
- We infer that the DEC NO_2' measurement must include things like ANs and PANs

DEC NO_x' versus NO_y (2011-16)



- No discernable difference!
- Further evidence of AN and PAN inclusion in the NO_x' measurement

ASRC NO_x versus NO_y (2011-13)

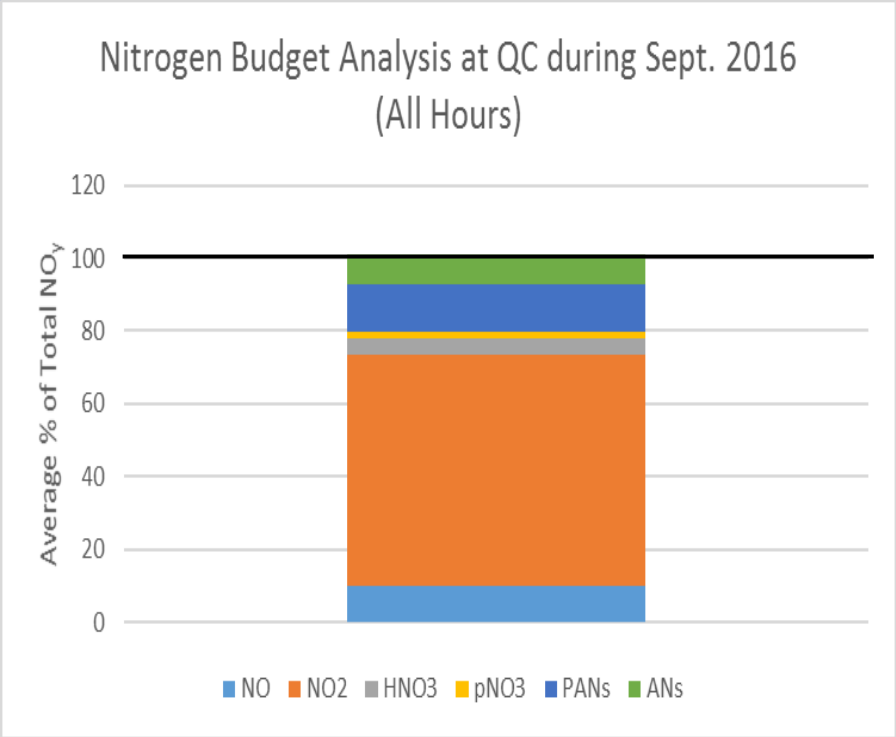


- Same story from a slightly different angle.
- Highly correlated (R^2 = 0.97)
- Slope of 0.88 (intercept set to zero), implies NO + NO_2 make up ~88% of NO_y
- (Note that many high concentration points even closer to 1:1.)
- Further implication is that ~12% of NO_y is made up of NO_z species

EPRI/ASRC/ARA/Envair Project

- Four CL NO detection systems, three measuring oxidized nitrogen species
- One system measures NO_y and HNO_3
- One measures pNO_3 (and pNH_4)
- One measures ANs and PANs using thermal dissociation and NO_2 photolytic detection
- While ARA has worked to “routinize” these methods, these are **not easy measurements!** A lot of work is required to tease out the full accounting for this level of detail.

First Results – NO_y Speciation at QC



Species	Average % of Total NO_y	Average Concentration (ppb, All Hours)
NO	9.8	1.8
NO_2	63.9	7.9
HNO_3	4.3	0.6
pNO_3	1.7	0.2
PANs	12.9	1.4
ANs	8.1	0.8
$\sum NO_{yi}$	100.7	12.7

First results for September 2016 – the first month all four systems (ARA + ASRC) operational. Much more to come!

Implications for Ozone Production

- Please see Matt Ninneman's poster later today for the full story.
- Ozone Production Efficiency (OPE) is defined as the number of ozone molecules produced in the VOC-NO_x reaction system until the NO_x molecules are removed (deactivated)
- Empirically this is written as

$$\mathbf{OPE = \Delta O_x / \Delta NO_z}$$

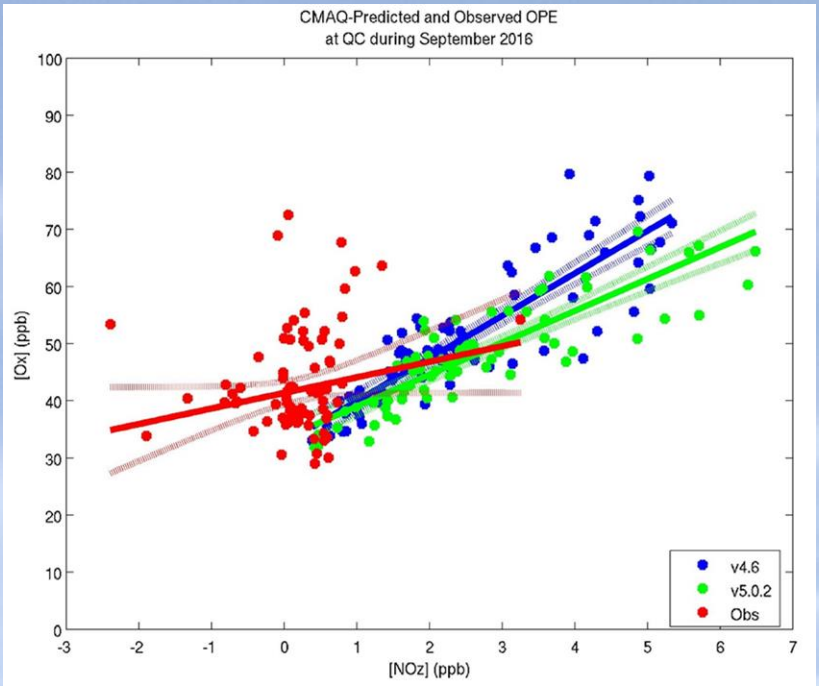
- That is, forming NO_z species interrupts the chain reaction producing ozone.

Observed and Model Derived OPEs

- OPEs are the slopes of the plots of odd oxygen (think ozone) vs. NO_z
- Many ways to determine NO_z observationally, but all require at least two analyzers!
- Method 1: $NO_z' = NO_y - NO_x'$ (DEC data)
- Method 2: $NO_z \approx HNO_3 + pNO_3 + ANs + PANs$ (ARA data – August & September only)
- Method 3: $NO_z = NO_y - NO_x$ (photolytic NO_x – September only)
- Model OPEs are straightforward

QC OPE Analysis Results – Observations and Model Output

Method 1 (Sept. 2016):



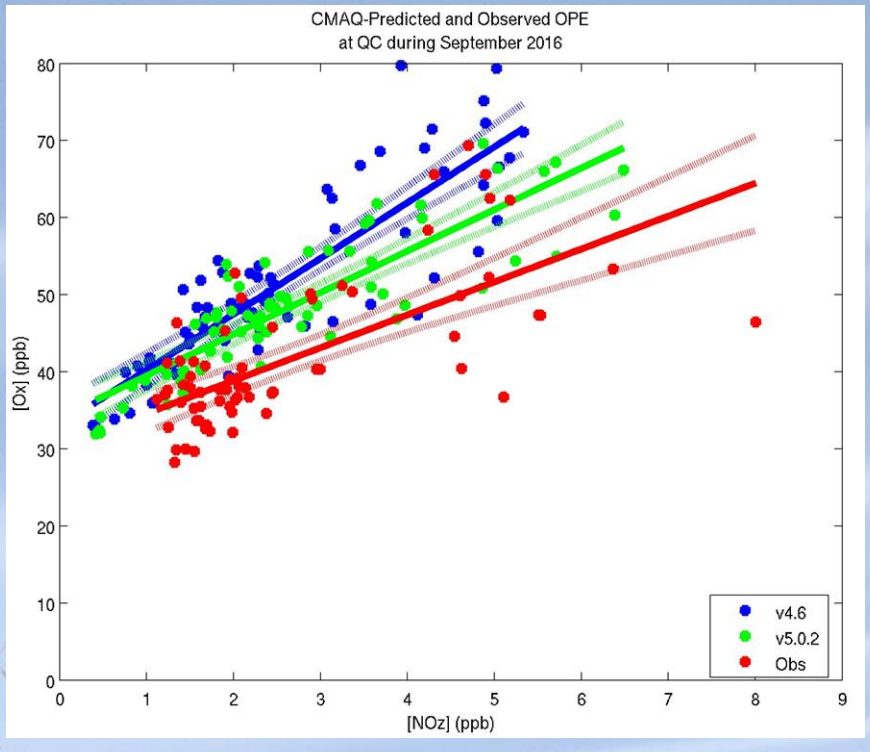
Month	Data Type	OPE	Y-Intercept	R^2
September	v4.6	7.44	32.53	0.78
	v5.0.2	5.57	33.46	0.73
	OBS	2.73	41.39	**0.06**

V4.6 and v5.0.2 are CMAQ model versions

The observed NO_z' data using this method are obviously a problem – note the many negative values and very low R^2!

QC OPE Analysis Results

Method 2 (Sept. 2016):



Month	Data Type	OPE	Y-Intercept	R^2
September	V4.6	7.23	33.03	0.75
	V5.0.2	5.39	34.11	0.72
	OBS	4.27	30.32	0.48

- Correlation using observed data much better (if not great).
- OPE agreement with models is decent as well.

Method 3 produces a higher R^2 (0.66) and OPE (7.28).

Conclusions

1. Commonly used NO_2 measurement methods using Mo converter and CL are flawed *(Known for decades, but we have pointed out why this is important.)*
2. Routine speciated measurements of NO_y components into chemically related groups is feasible (but demanding)
3. These speciated measurements are necessary to better reflect atmospheric reactivity and ozone production chemistry

Thank You!

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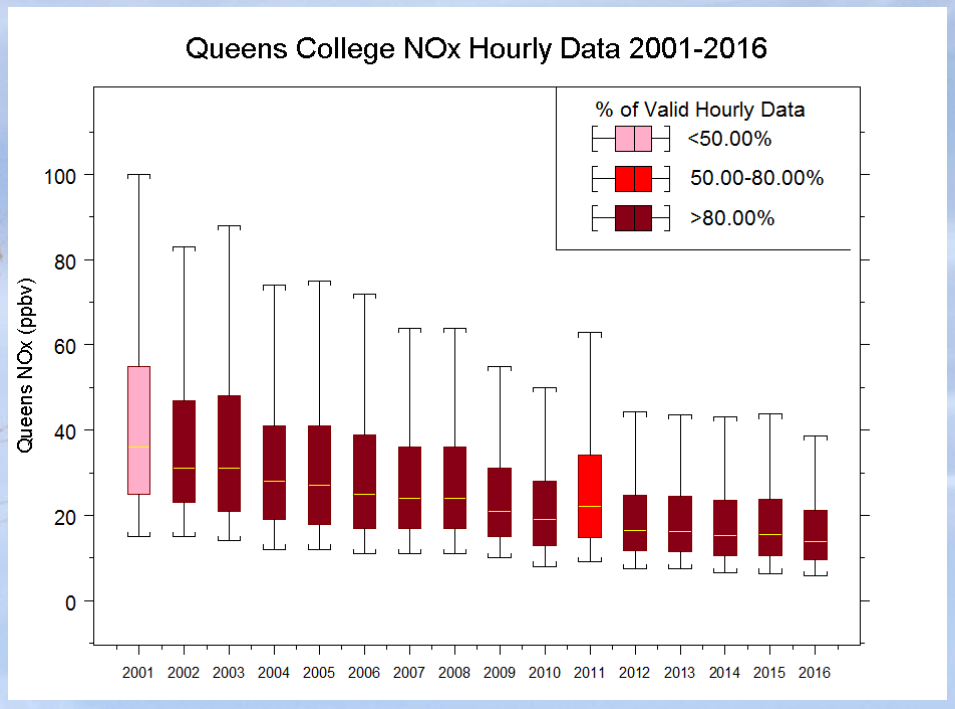
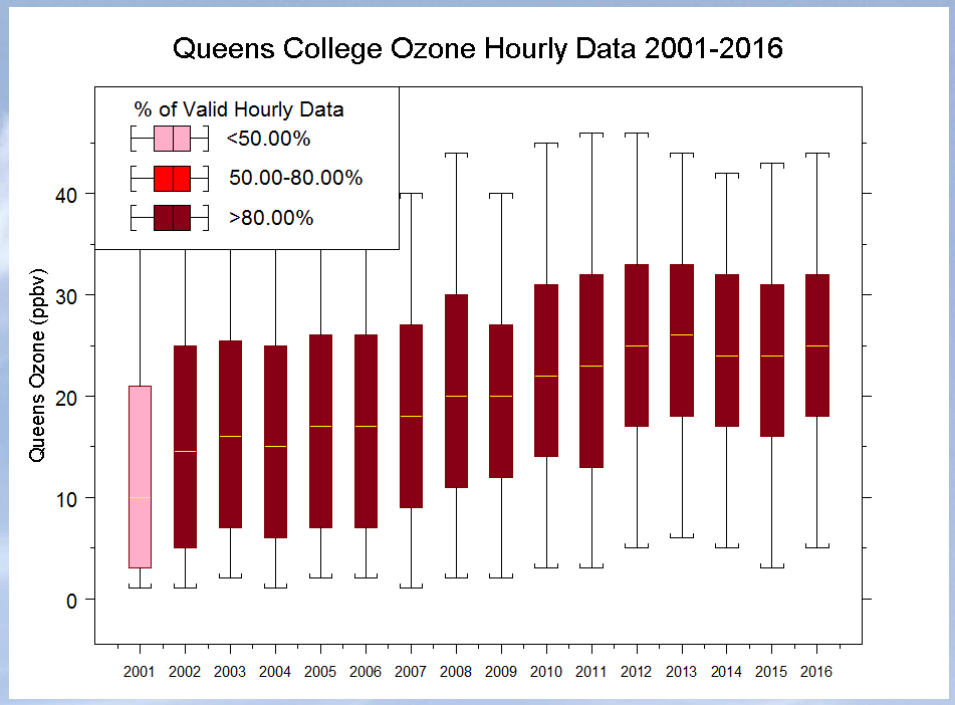
Thanks to NYSERDA (CNs 48971 and 59807) and EPRI (10004919) for support.

Back Up Slides

NO_x' and Ozone Trends

NO_x' levels (mostly NO_2) have come down since 2001 from ~ 32 ppbv to ~ 15 ppbv

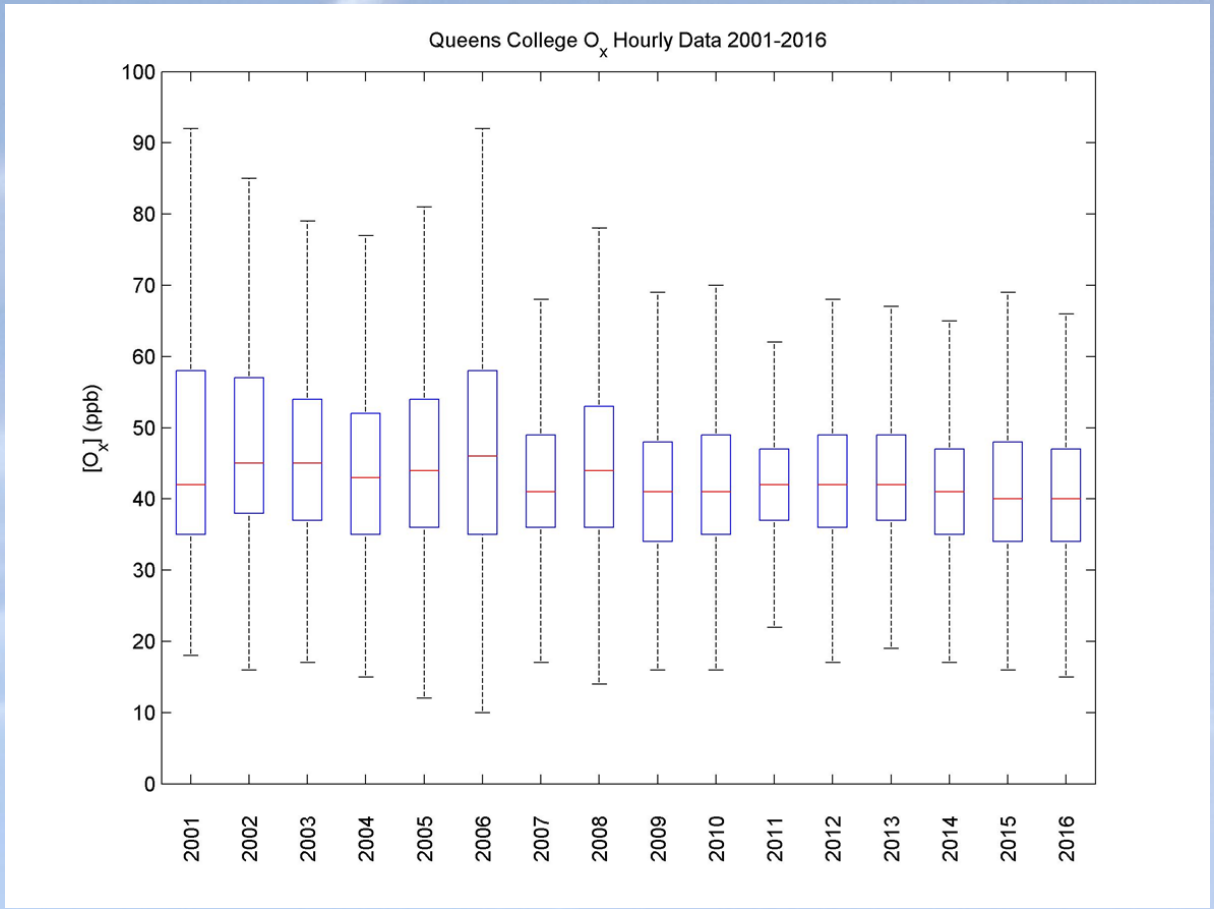


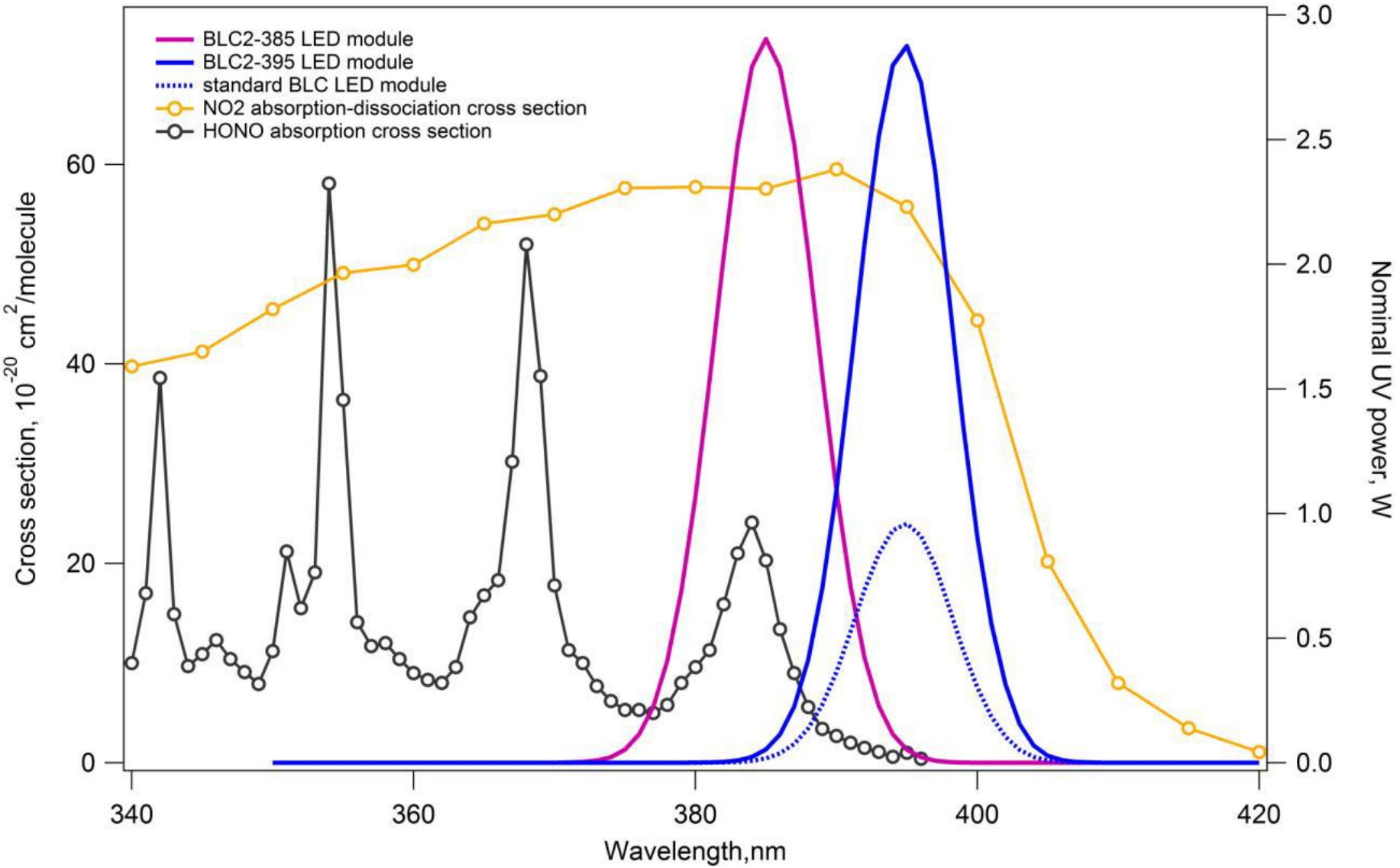


Over the same period, annual median ozone has **increased** from less than 15 ppbv to near 25 ppbv

The oxidant level is best described by odd oxygen

Recall that O_x is the sum of O_3 and NO_2' - This parameter combines the two trends from the previous slide and shows, if anything, a slight decrease.




BLC2-385 LED module
BLC2-395 LED module
standard BLC LED module
NO2 absorption-dissociation cross section
HONO absorption cross section
Cross section, 10^-20 cm^2/molecule
Nominal UV power, W
Wavelength,nm
0
20
40
60
0.0
0.5
1.0
1.5
2.0
2.5
3.0
340
360
380
400
420

TON Analyzer for Peroxyacetylnitrates (PANs) and Alkylnitrates (ANs)

- Continuous 3-Channel Thermal-Photolytic Difference
- CH1 (baseline) measures NOx
- CH2 (160°C thermo-converter) measures NOx + NO_2 produced from PANs
- CH3 (380°C converter) measures NOx + NO_2 produced from PANs and ANs
- Assumes PANs and ANs are only compounds to produce NO_2 at 160°C and 380°C **AND** that back reactions (recombination of NO_2 + $RO^{\cdot}$ or $RO_2^{\cdot}$) are negligible

TON System Overview Rev 1