Evidence for a Substantial Overestimate in NOx Emissions Guidance from Observations

Presented to

NOAA's Air Resources Lab

by

Russell R. Dickerson, Univ. Maryland

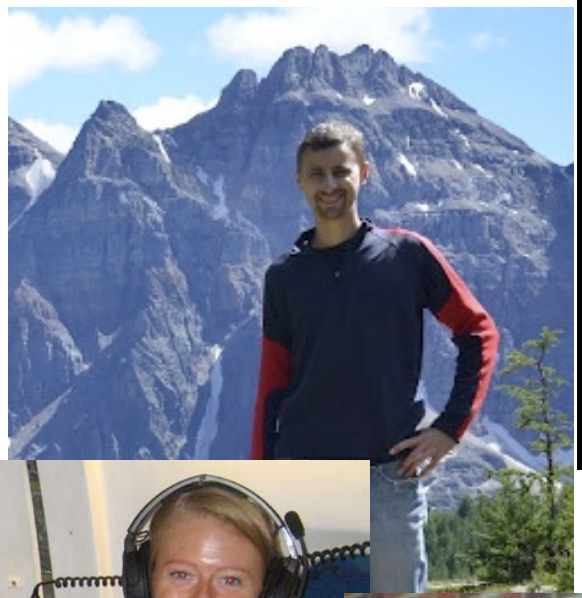
Supported by MDE

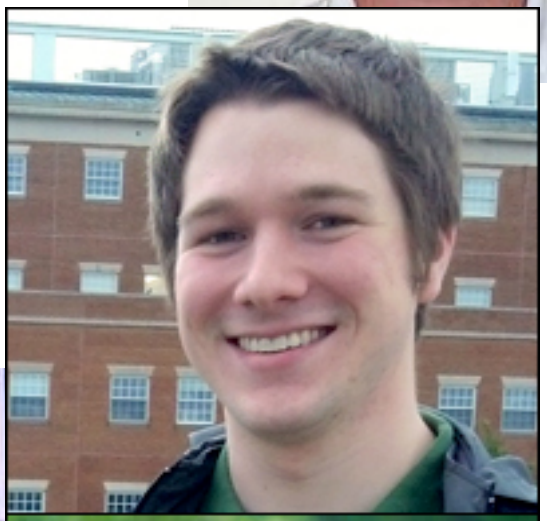
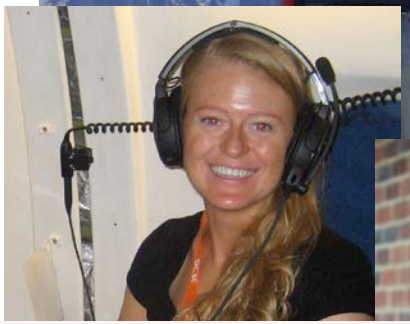
NASA, NOAA, NIST, and DNR

September 1, 2015

UMD/URF Cessna
Photo by J. Stehr

The Guilty Parties



When measurements and CTMs disagree:

- Dispersion could be wrong.
- Emissions could be wrong.
- Chemistry (formation, sequestering, or removal) could be wrong.
- Some combination of the above.

Let's look at ratios

- EPA inventories estimate a NO_y/CO ratio of ~136 mmol/mol (CO/NOx ~ 7-9).
- Previous research suggests inventory ratios of NO_y/CO are an overestimate:
  - Fujita (2012) – models overestimate concentrations by 25-40%
  - Parrish (2006) – Inventories are a factor of 2 larger than measurements
- Research questions:
  - What are the emissions ratios of pollutants NO_y & CO Maryland?
  - How well do emissions inventories represent these ratios?

* NOy = NOx + products HNO_3, PAN, $RONO_2$, NO_3^-

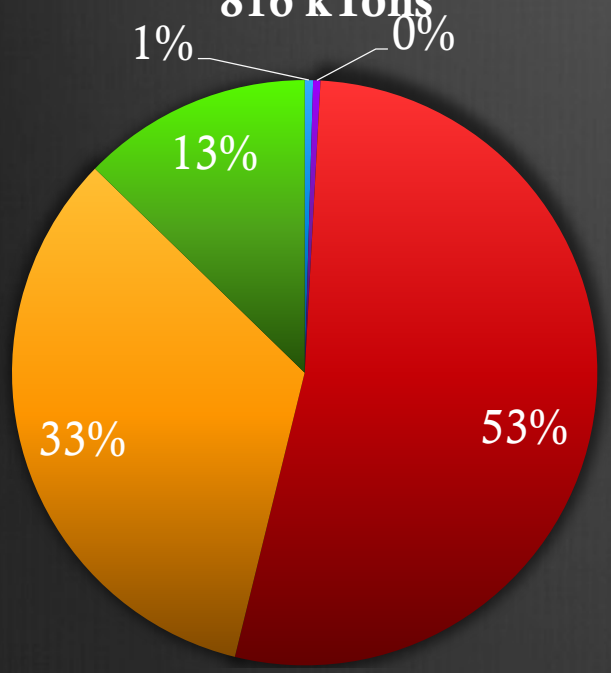
Methodology

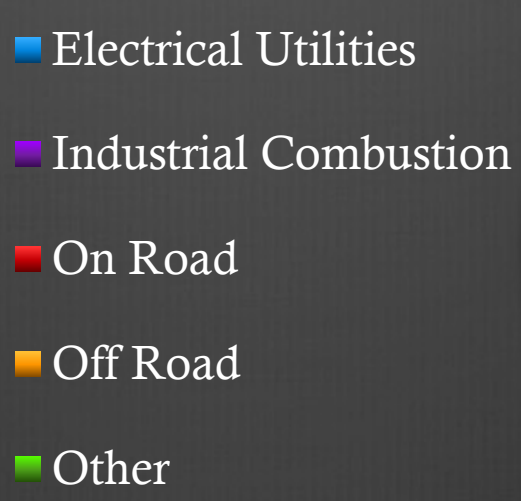
- Identified 70 spirals from DISCOVER-AQ P3B flights with simultaneous peaks and areas of correlated CO and NO_y concentration.
- Determined mixed layer from vertical profiles of relative humidity and equivalent potential temperature.
- Calculated, for measured compounds in the mixed layer, $\Delta NOy/\Delta CO_2$ and $\Delta NOy/\Delta CO$.
- Included only those correlations with $r^2 > 0.8$ and with > 10 data points.
- Average plume age ~ 3 hr.

Anderson et al., *Atmospheric Environment*, 2014.

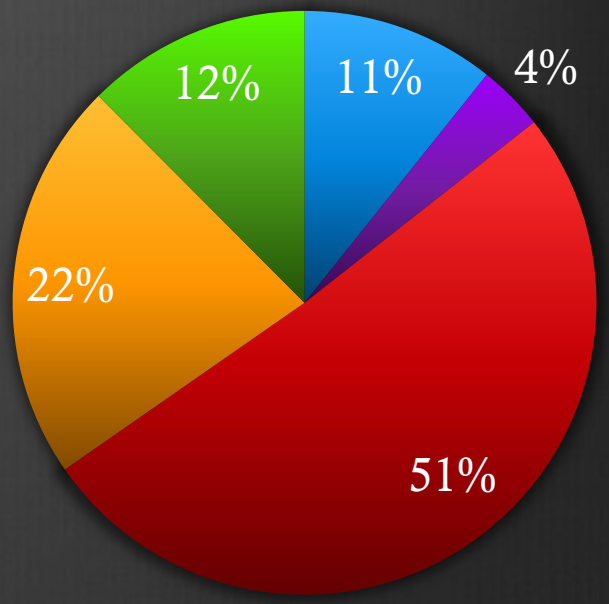
From NEI

2011 CO Emissions in Maryland
816 kTons

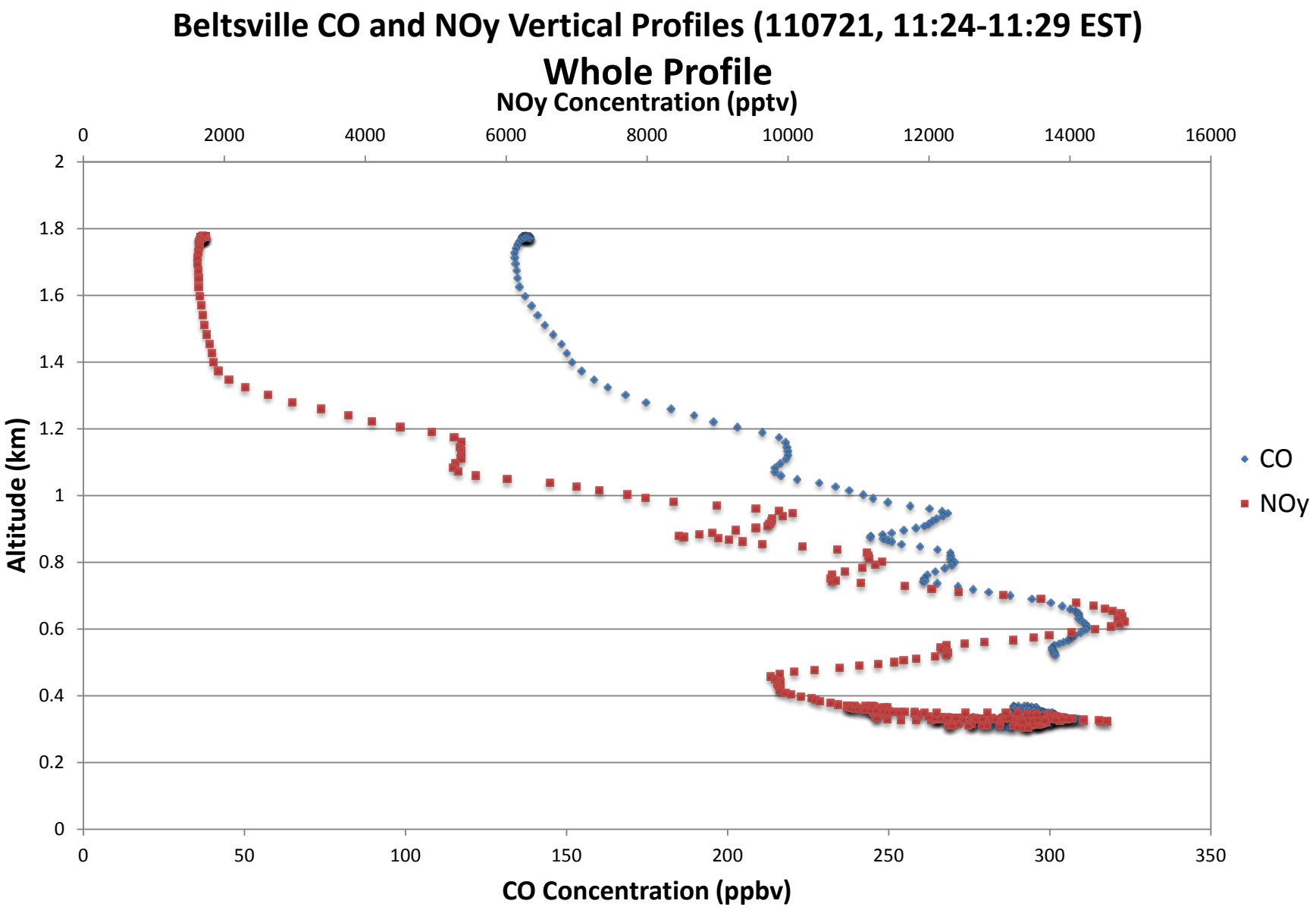


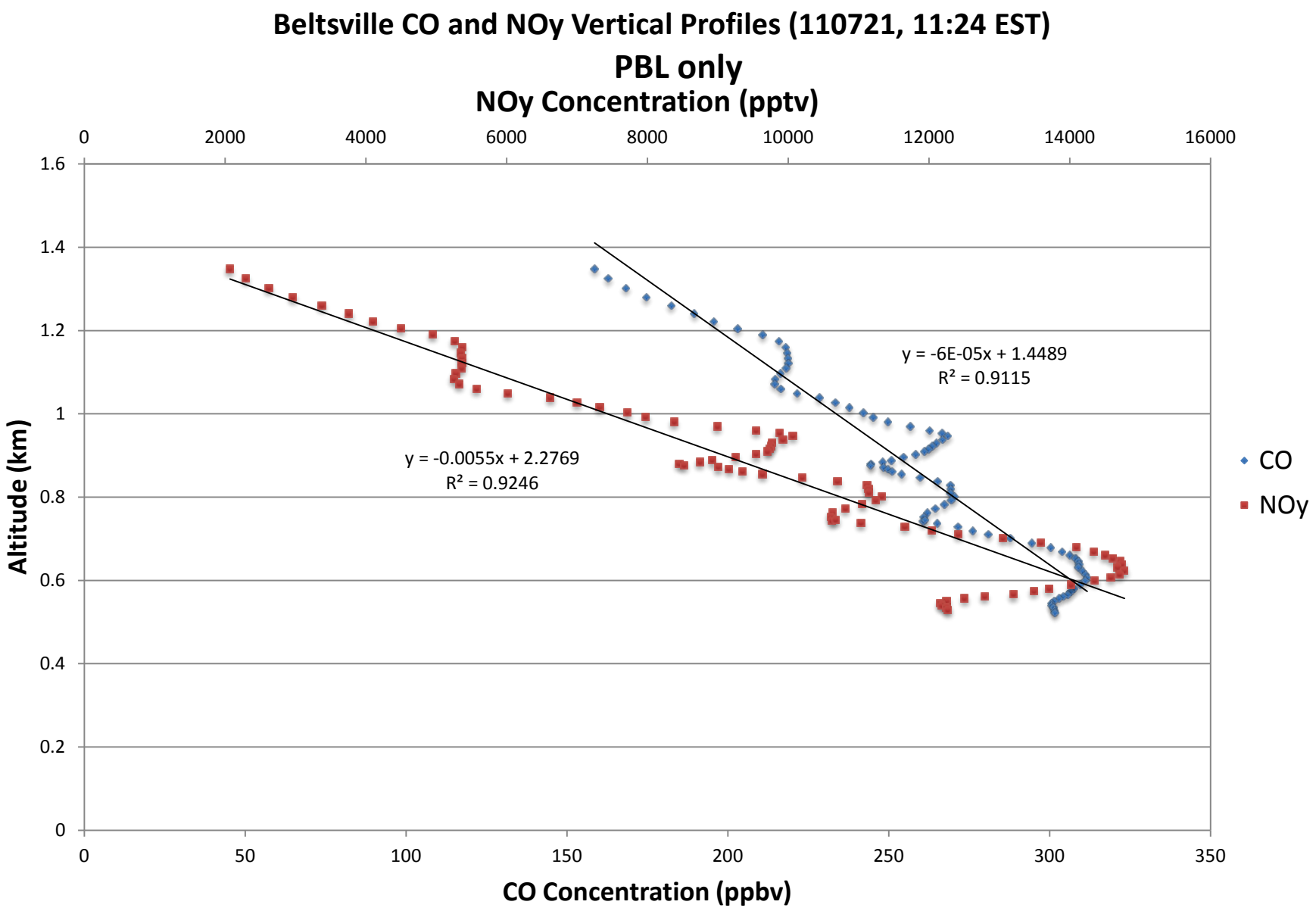


2011 NO_x Emissions in Maryland
172 kTons



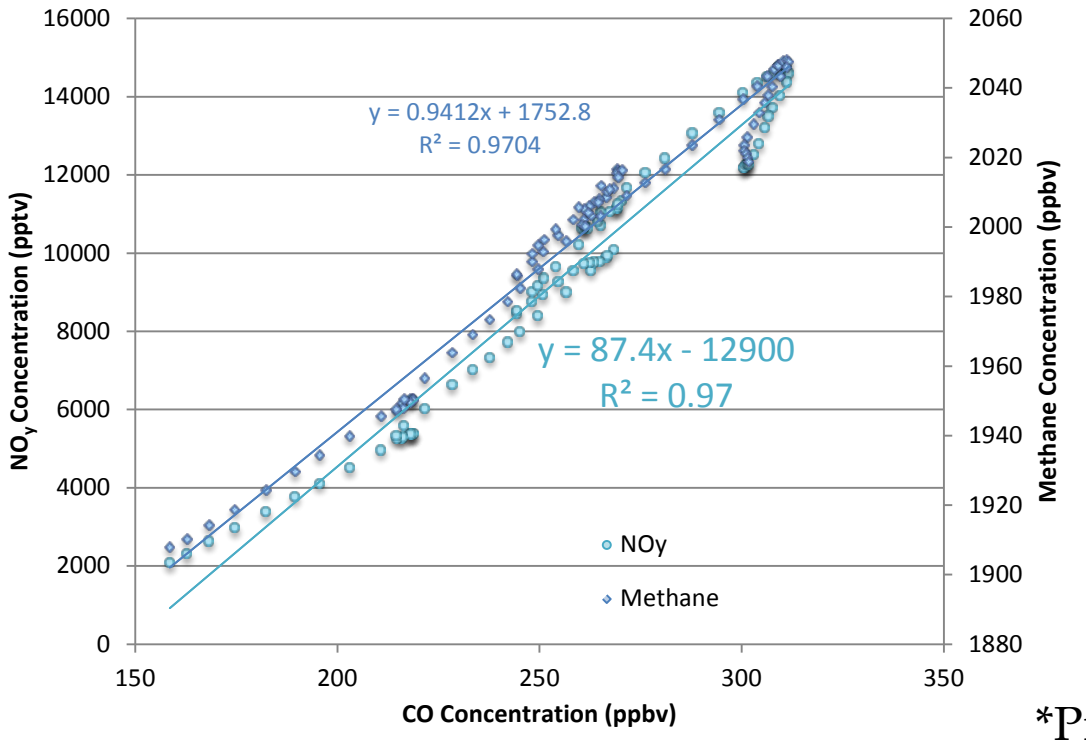
- CO and NO_x are important O_3 precursors.
- Significant disagreement among studies on NEI's accuracy.
- Can we use *in situ* observations to evaluate these numbers?

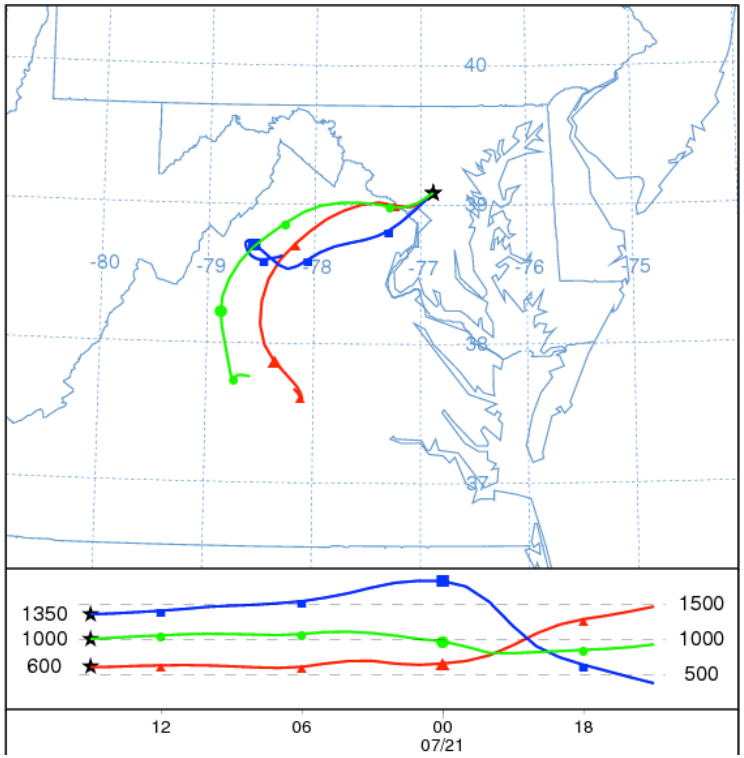

Beltsville CO and NOy Vertical Profiles (110721, 11:24-11:29 EST)
Whole Profile
NOy Concentration (pptv)
0
2000
4000
6000
8000
10000
12000
14000
16000
Altitude (km)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
CO Concentration (ppbv)
0
50
100
150
200
250
300
350
CO
NOy


Beltsville CO and NOy Vertical Profiles (110721, 11:24 EST)
PBL only
NOy Concentration (pptv)
0
2000
4000
6000
8000
10000
12000
14000
16000
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Altitude (km)
y = -6E-05x + 1.4489
R² = 0.9115
y = -0.0055x + 2.2769
R² = 0.9246
CO
NOy
0
50
100
150
200
250
300
350
CO Concentration (ppbv)

Beltsville, 110721, 868-953 hPa, 11:27 EST

Air mass from DC and Virginia.
NO_y/CO ratio ~0.087 or CO/NOy = 11.5

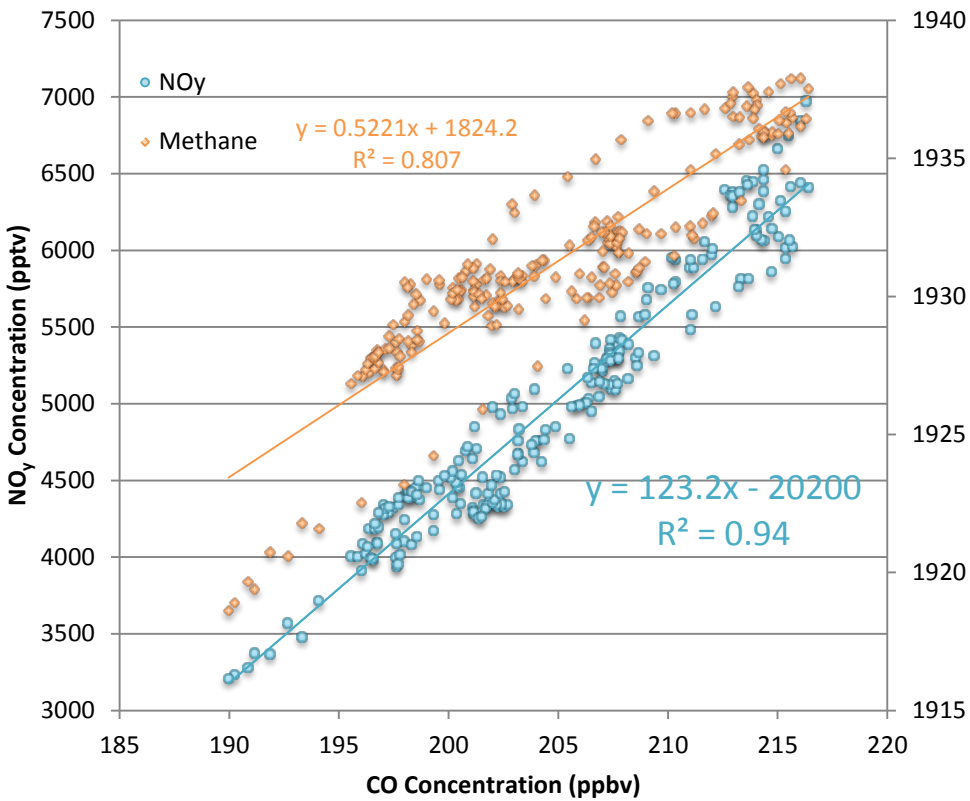


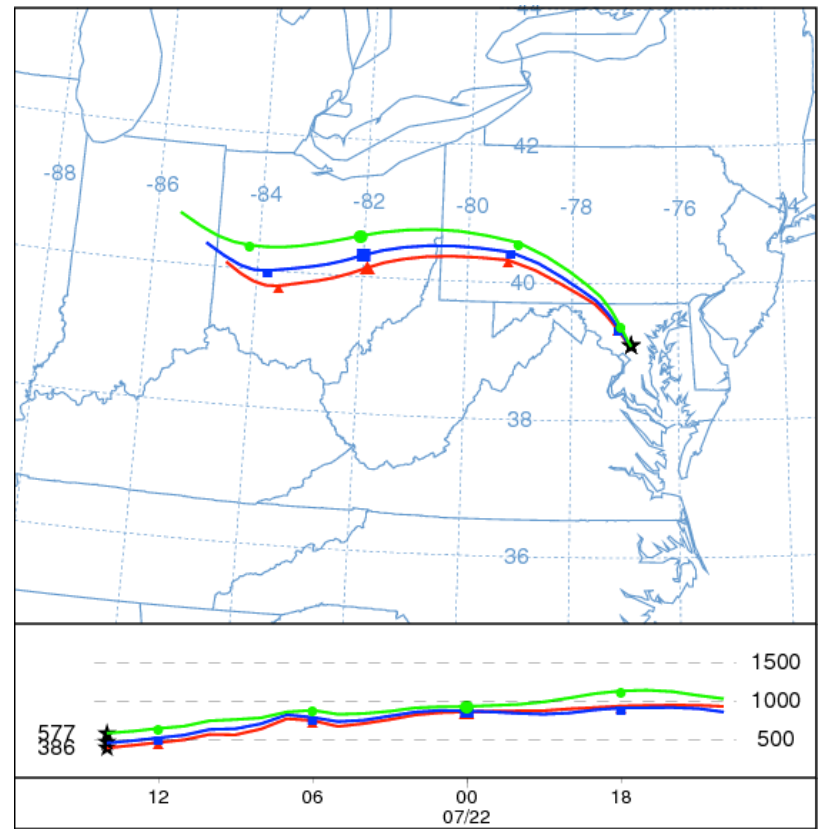


Preliminary Data. Do not cite.

Beltsville, 110722, 949-979 hPA, 10:05 EST

Air mass from Ohio River Valley.
NO_y/CO ratio slightly higher (123) or
CO/NOy lower (8.0) than previous profile.

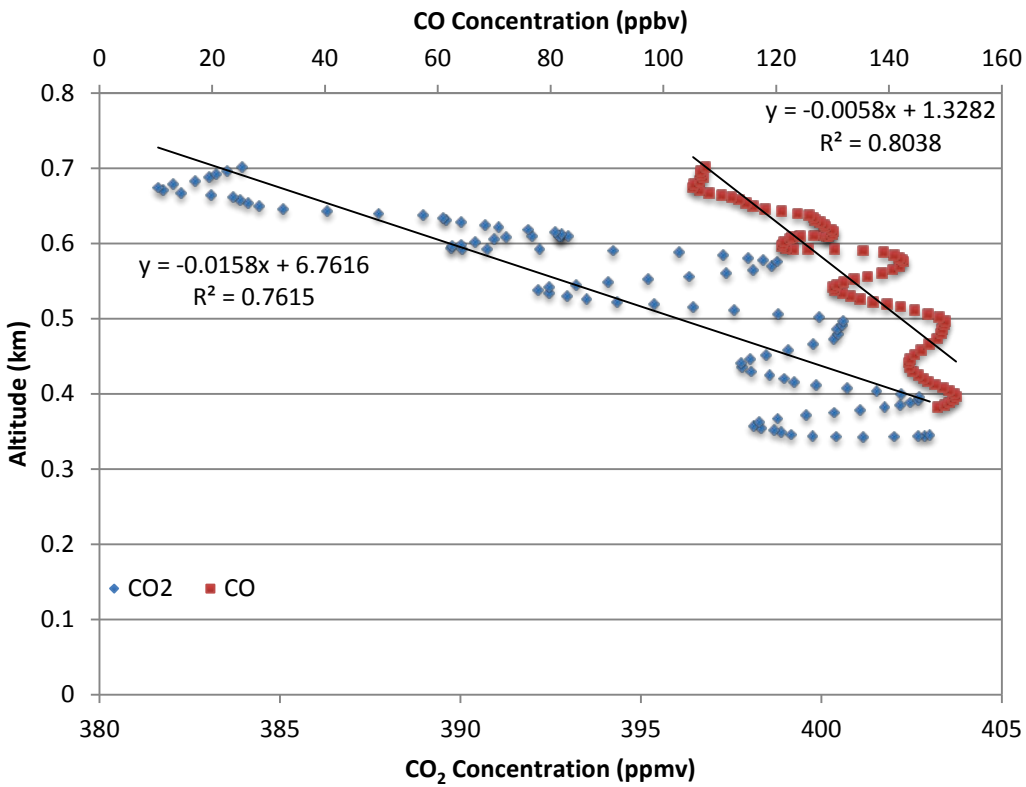


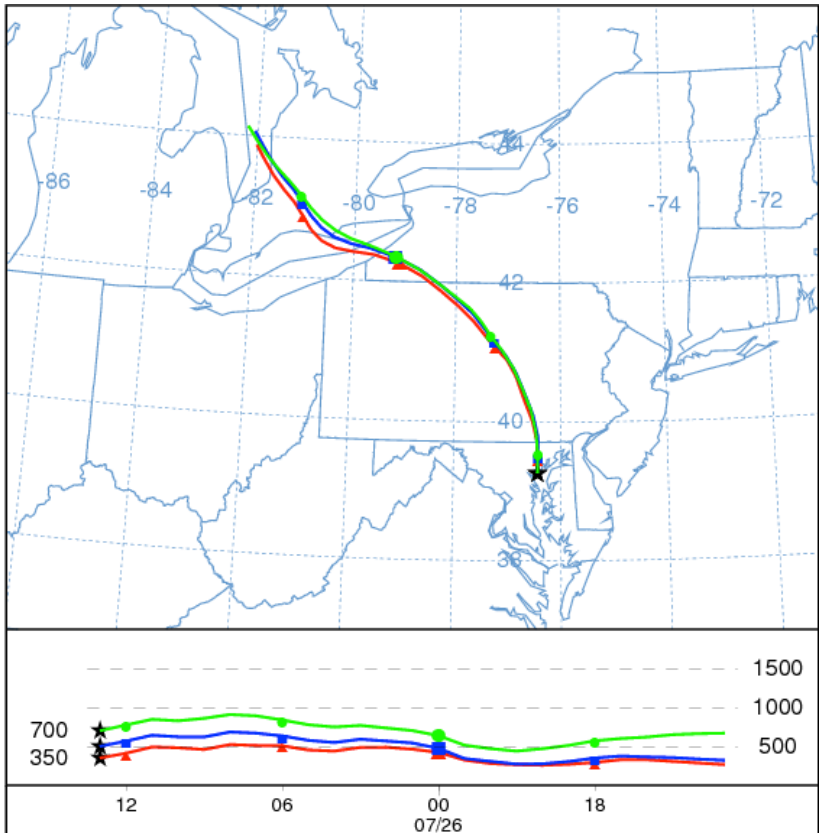


Preliminary Data. Do not cite.

Essex, 07/26, 9:13 EST

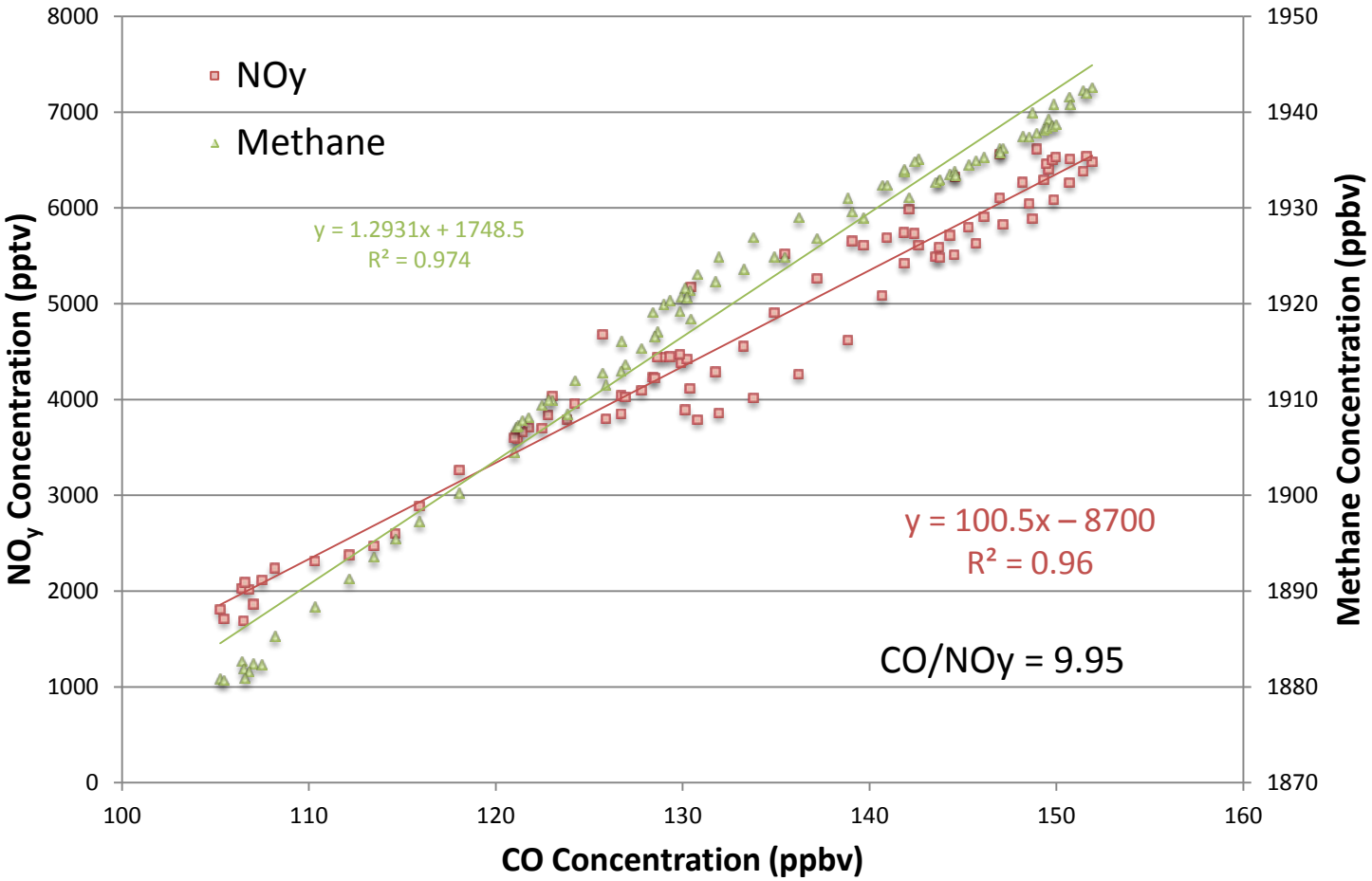
Portion of vertical profile in the mixed layer:





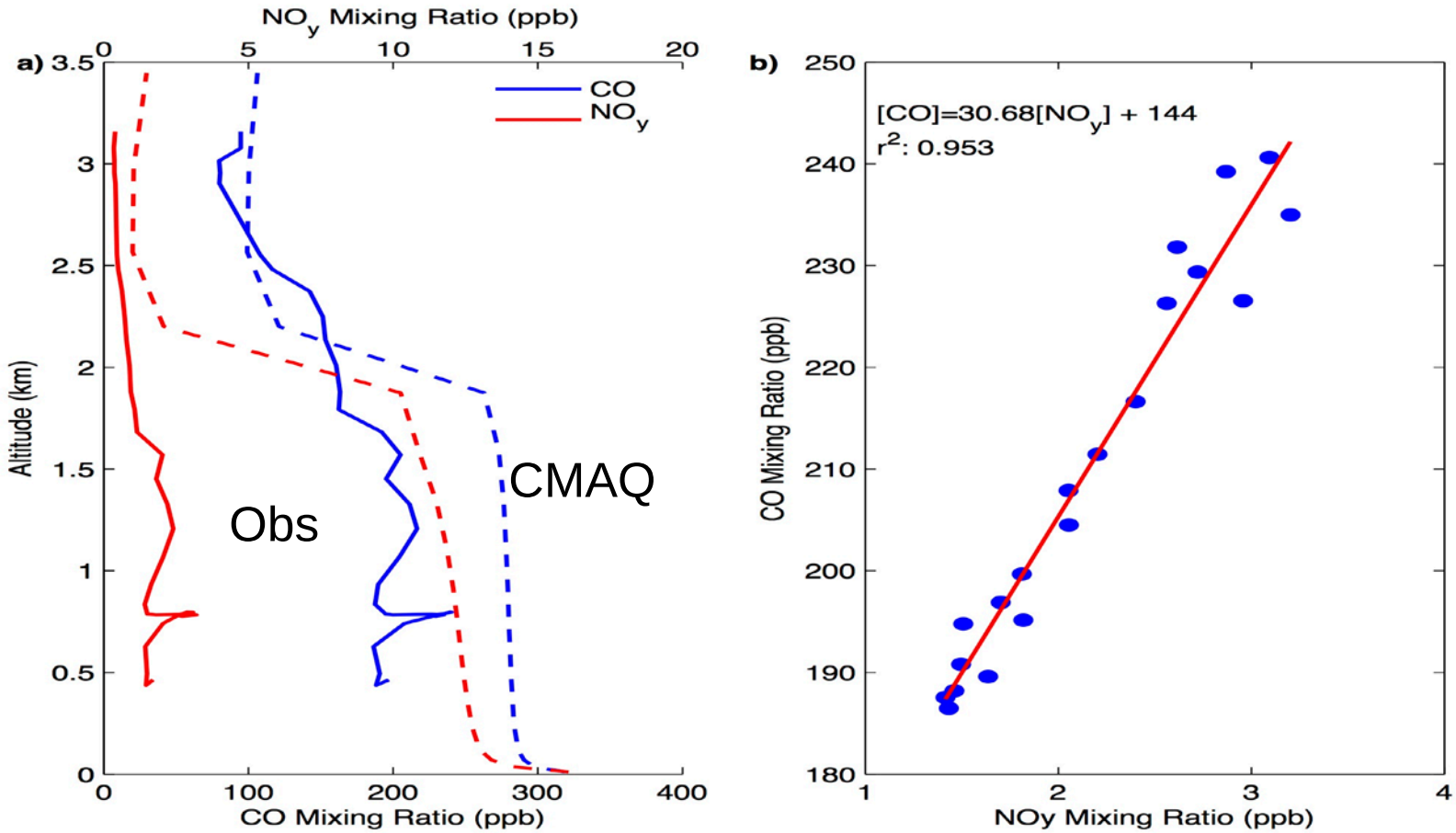
Air mass from "clean corridor" in PA. Pollution probably local.

Essex, **07/26, 9:13 EST**



Anderson et al. *Atmos. Environ.*, 2014.

CO/NOy ratios in CMAQ are higher than observed.
Padonia 11 July 2011



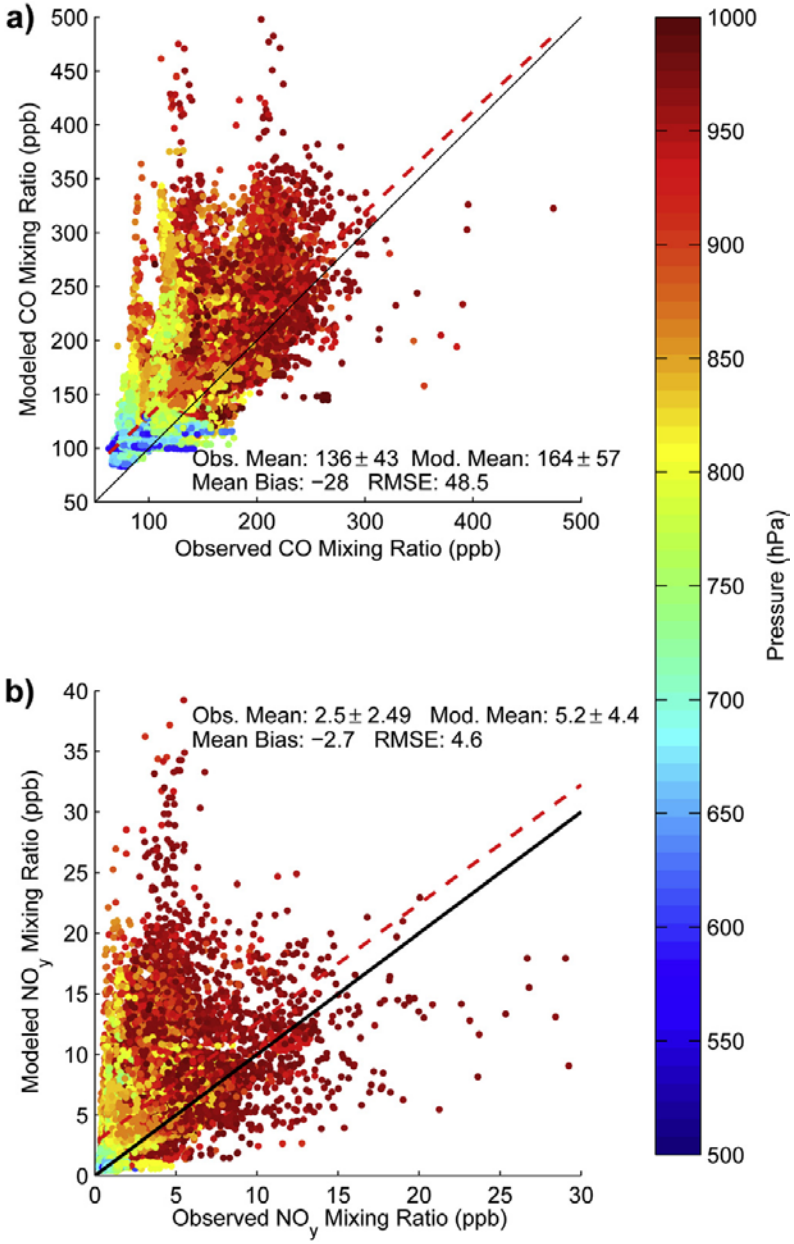
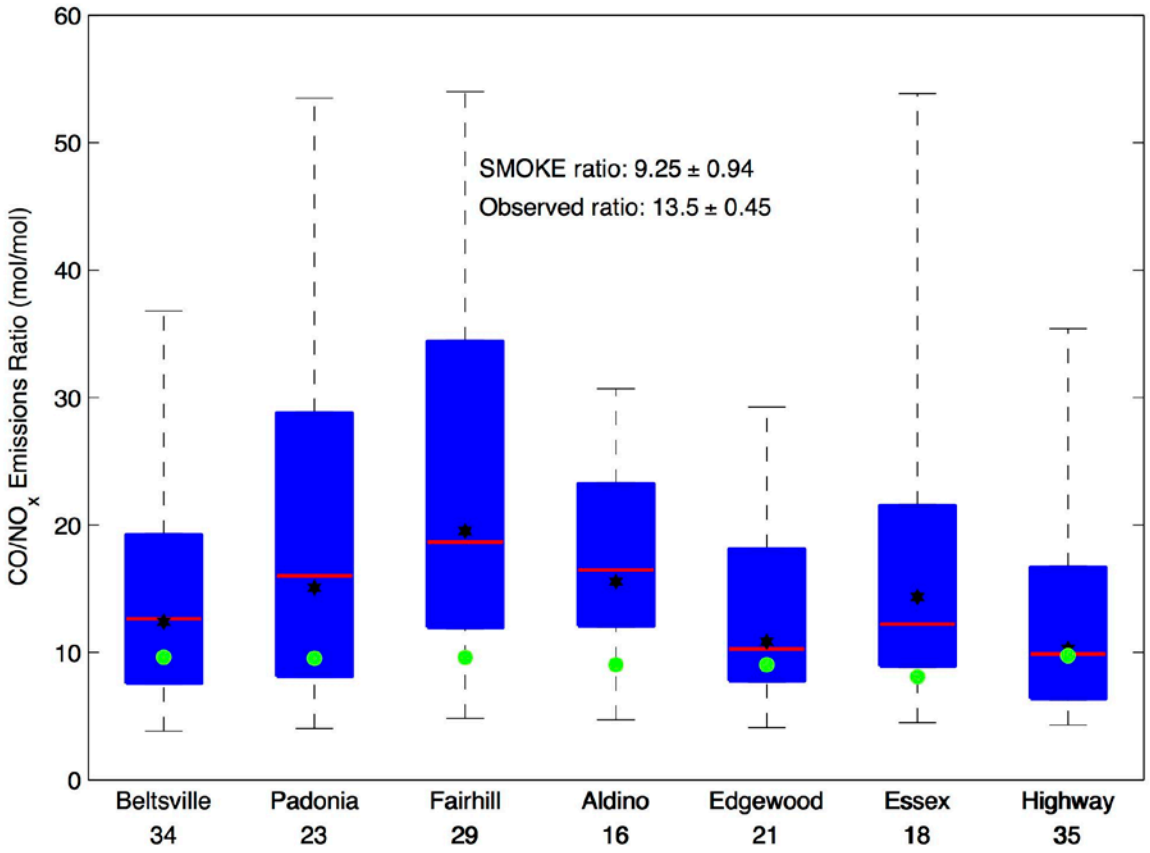


Fig. 7. a) Regression of measured and modeled CO for all flight days during DISCOVER-AQ. Values after means are 1σ. b) Same as a) but for NO_y. Solid line is the 1:1 line; dashed line, the line of best fit.

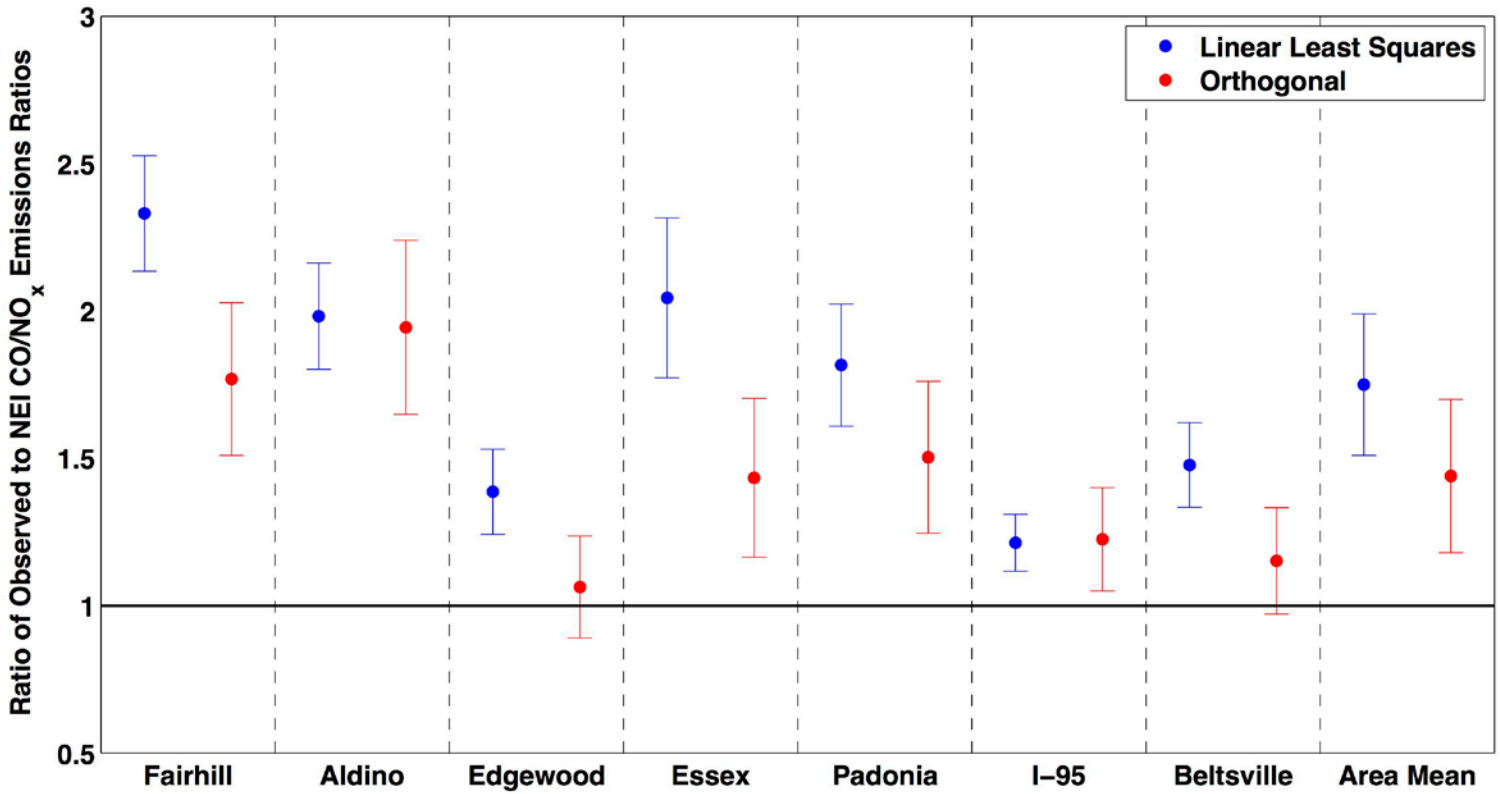
CMAQ gets CO a little high (bias = +28 out of 136 ppb) but NOy much too high (bias +2.7 out of 2.5 ppb).

Summary of Results

CMAQ/CB05 gets CO about right (15 ±11% high), but substantially overestimates NOy.



Evaluation of NEI NO_x Emissions



- NEI overestimates NO_x emissions by 40-75%.
- MOVES likely underestimates the lifetime & efficiency of catalytic converters.
- Is the driving cycle right?

Summary of Emissions Ratios

	DISCOVER-AQ Average (mol/mol) ± $\sigma/n^{0.5}$	Number of aircraft profiles	Fujita *et al* 2012 (mol/mol)	EPA (mol/mol)	EPA/DISCOVER-AQ
CO/NOy	**13.7 ± 1.4**	**60**	**9.3**	**7.4+**	**0.54**

*: Values for 2010 +: Values for 2011; CO & NO_y data from NEI.

NEI appears to overestimate NOx emissions by a factor of ~2.

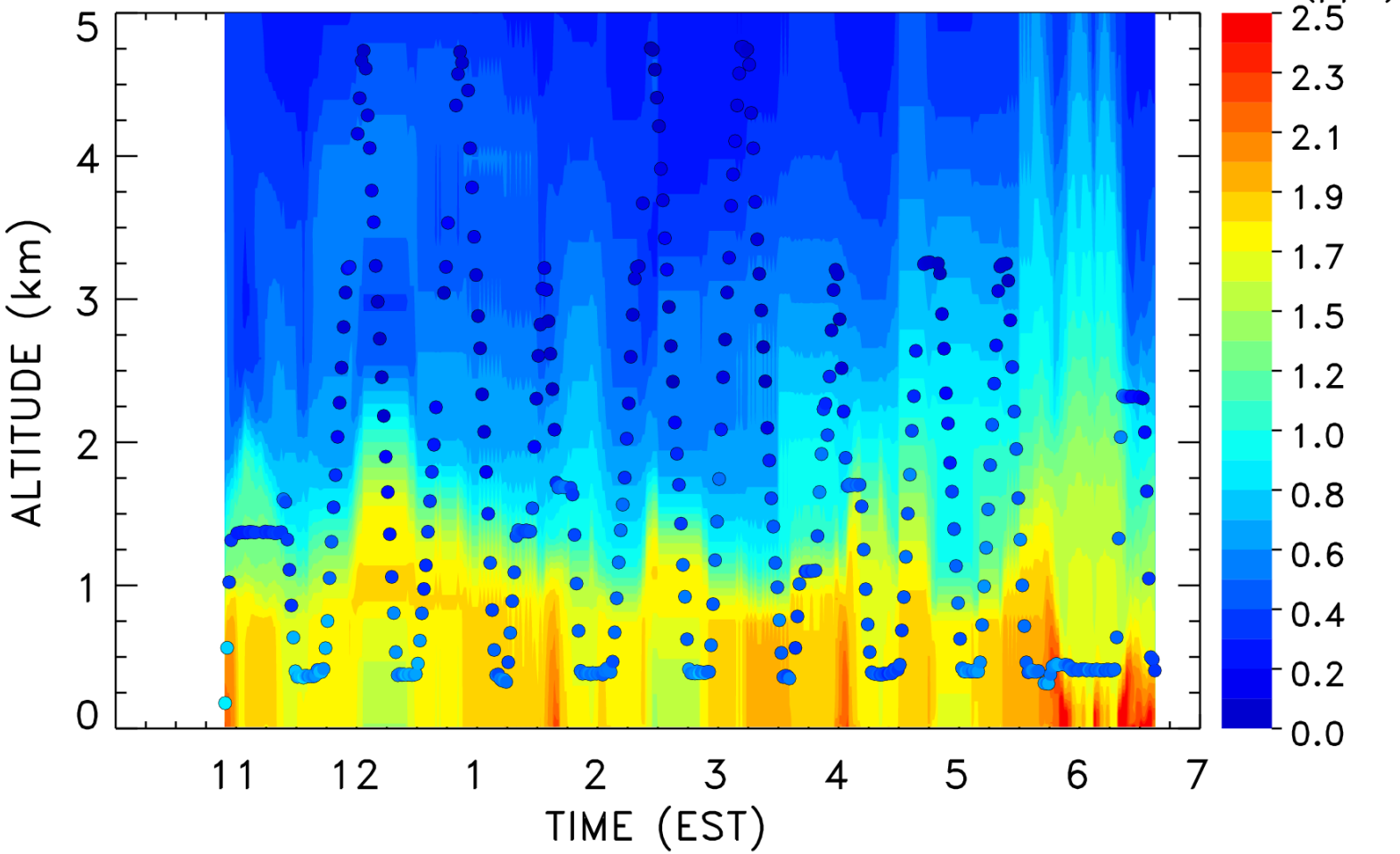
Anderson et al., Atmos. Environ., 2014.

What impact does reduced NOx emissions have on model performance?

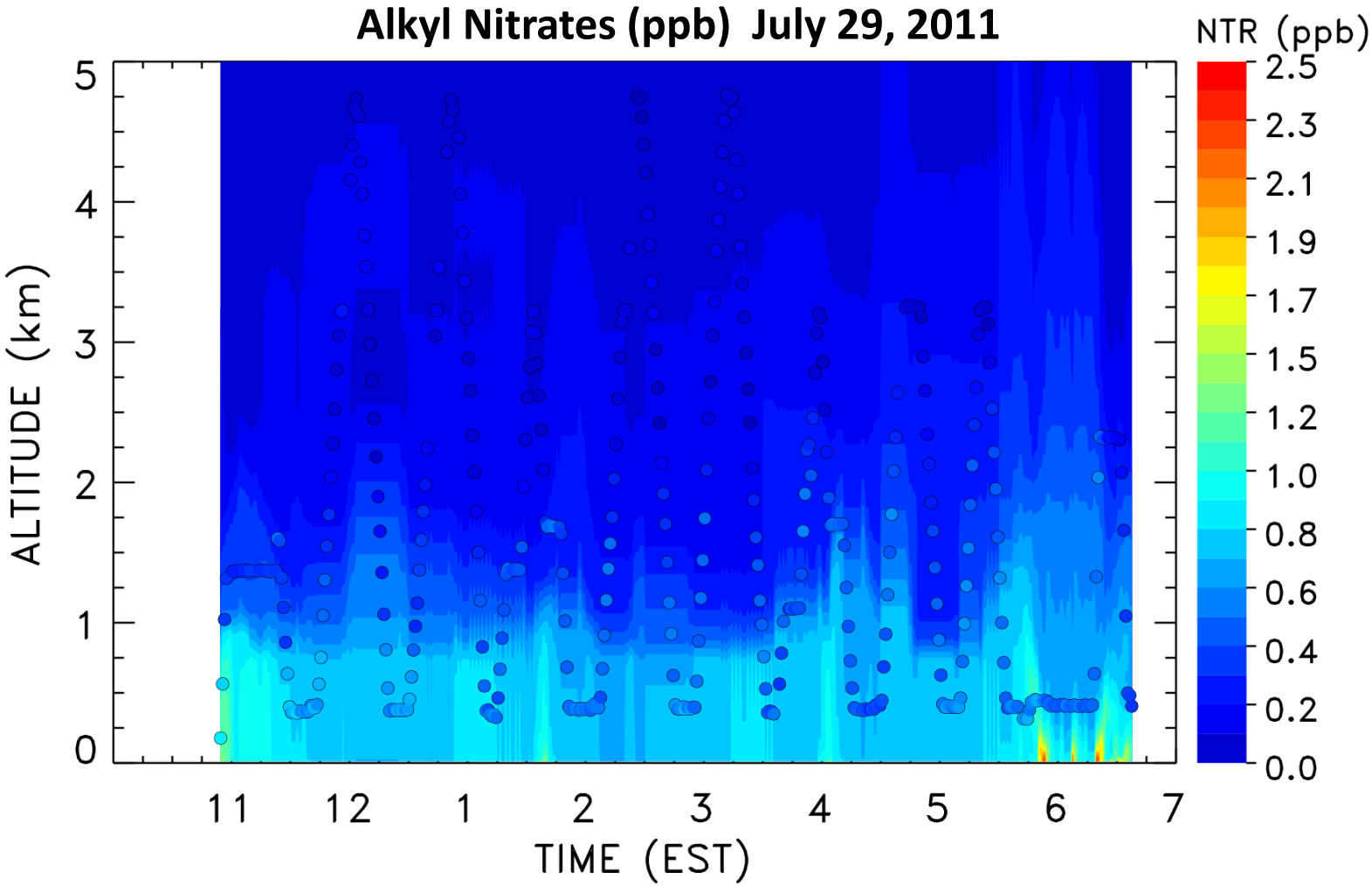
- Do we get O_3 right for the wrong reasons?
- Alkyl nitrates (AN), including isoprene nitrates, represented as single species (NTR).
- We can compare aircraft observations during DISCOVER-AQ to CMAQ model run for 2011.
- With CMAQ "off the shelf" NTR overestimated.

From Canty et al., *ACP*, 2015.

Alkyl Nitrates (ppb) July 29, 2011



Background Contour → CMAQ Baseline
Colored points → DISCOVER-AQ Flight #14



Background Contour → CMAQ decreased AN lifetime, 50% ↓ mobile NO_x
Colored points → DISCOVER-AQ Flight #14

Has this been seen before?

Houston - EPA RTP guys [*Yu et al.*, 2012]

Compares CMAQ (WRF; CB4.2; Mobile 6 and BEIS) to the TEXaqs 2006 observations. They conclude:

Compared to P3 obs in the lowest 200m, the model:

- Does well for CO (124 observed vs. 117 ppb modeled)
- Does well for O_3.
- **Overestimates NOy (9.2 vs. 4.6 ppb) and all NOy constituents.**
- Shows the OPE substantially less than observed from O_3 vs. NOz (8 vs. 3).

Yu, S. C., et al. (2012), Comparative evaluation of the impact of WRF-NMM and WRF-ARW meteorology on CMAQ simulations for O_3 and related species during the 2006 TexAQS/GoMACCS campaign, *Atmospheric Pollution Research, 3*(2), 149-162.

The following slides on loan from DJJ

Factors Controlling PM and Ozone Over the Southeast US as Emissions Decrease: Insights from the NASA SEAC^{4}RS Campaign

Daniel J. Jacob

with J.A. Fisher, P.S. Kim, E.A. Marais, K.R. Travis, K. Yu, L. Zhu

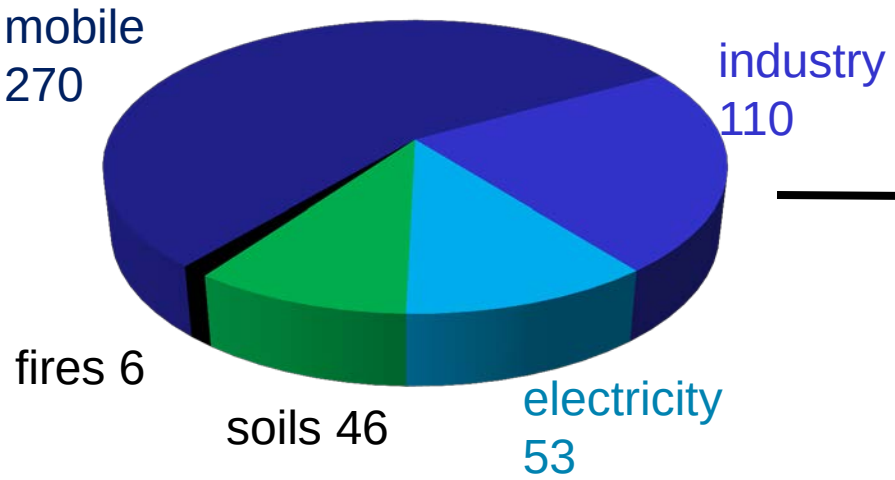
UNIVERSITY OF WOLLONGONG AUSTRALIA

HARVARD UNIVERSITY ATMOSPHERIC CHEMISTRY MODELING GROUP

and SEAC^{4}RS PIs R. Cohen, J. Dibb, A. Fried, T. Hanisco, G. Huey, J. Jimenez, T. Ryerson, A. Thompson, P. Wennberg, A. Wisthaler

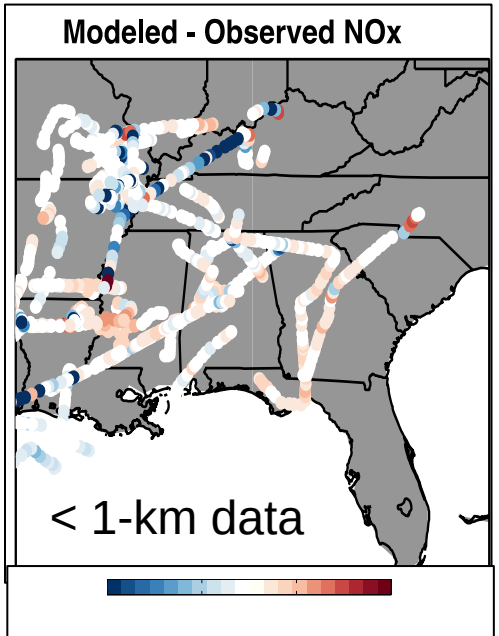
SEAC^{4}RS data imply that NEI NO_x emissions are too high

Aug 2013 Southeast US NO_x emissions including 2013 EPA NEI [Mg]



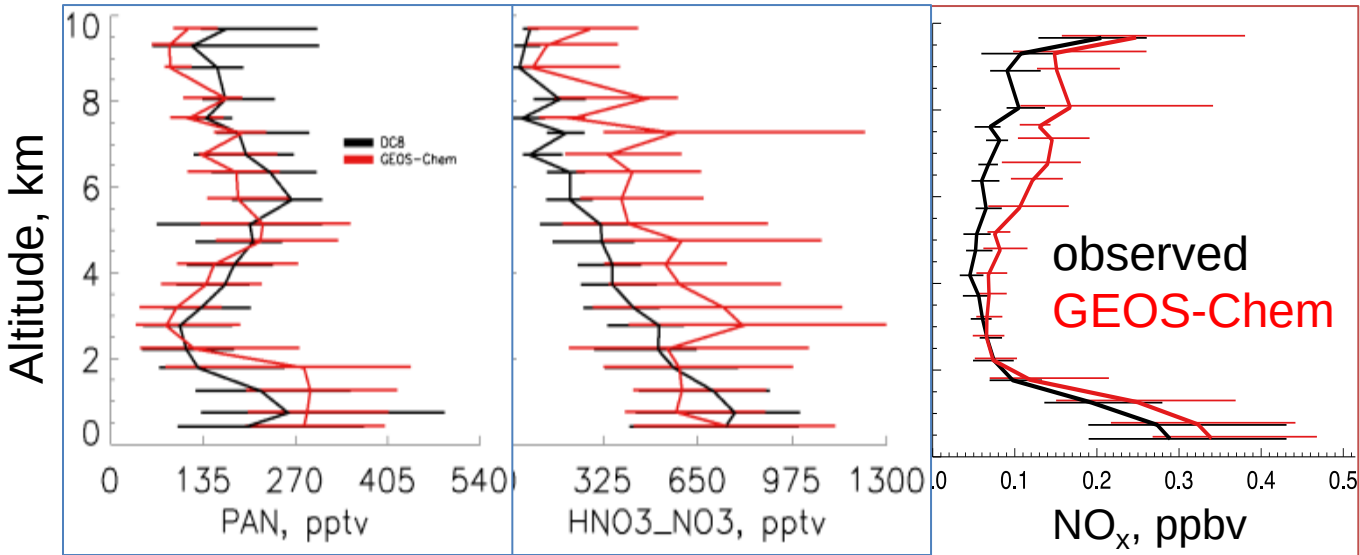
Reduce emissions by 50%

Observations by G. Huey, J. Dibb, T. Ryerson



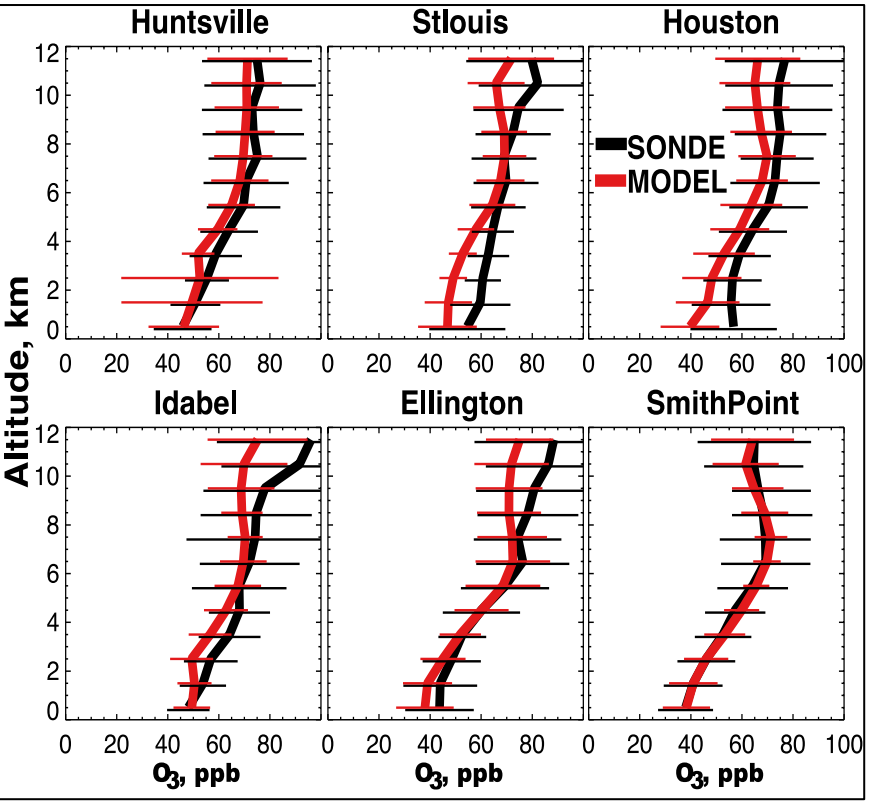
Median vertical profiles

K. Travis, in prep.

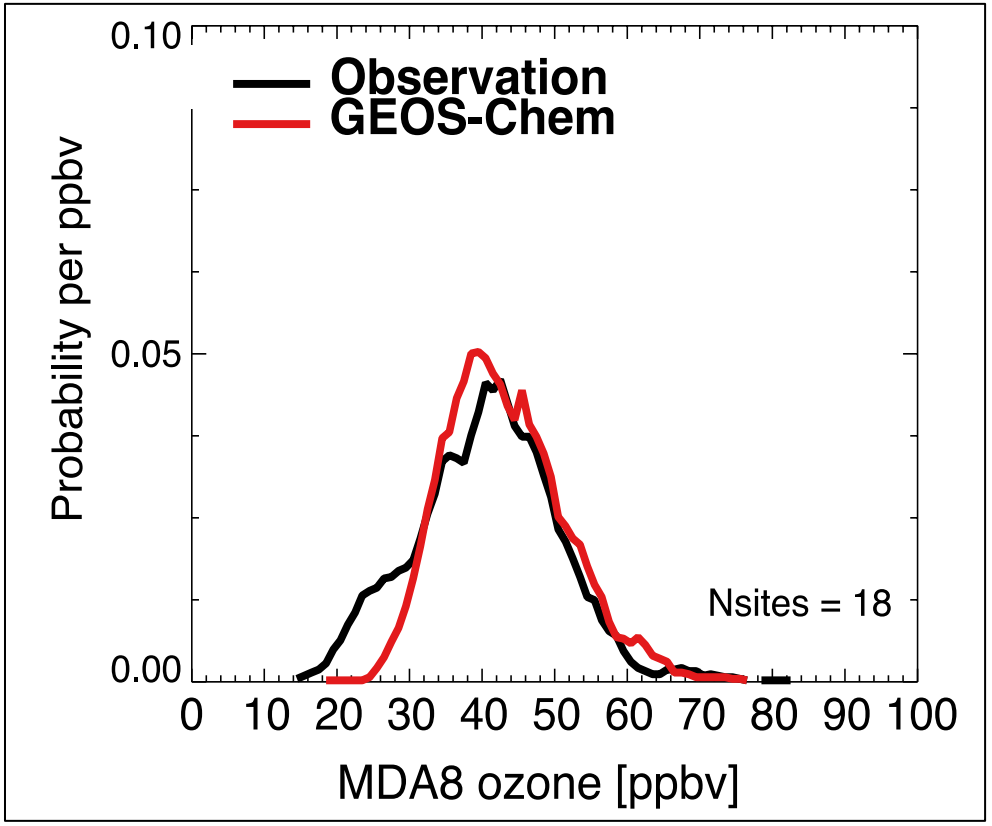


Reducing NO_x emissions by 50% yields unbiased simulation of Southeast ozone during SEAC^{4}RS

Ozonesondes (*A. Thompson*)



CASTNet sites, Aug-Sep 2013

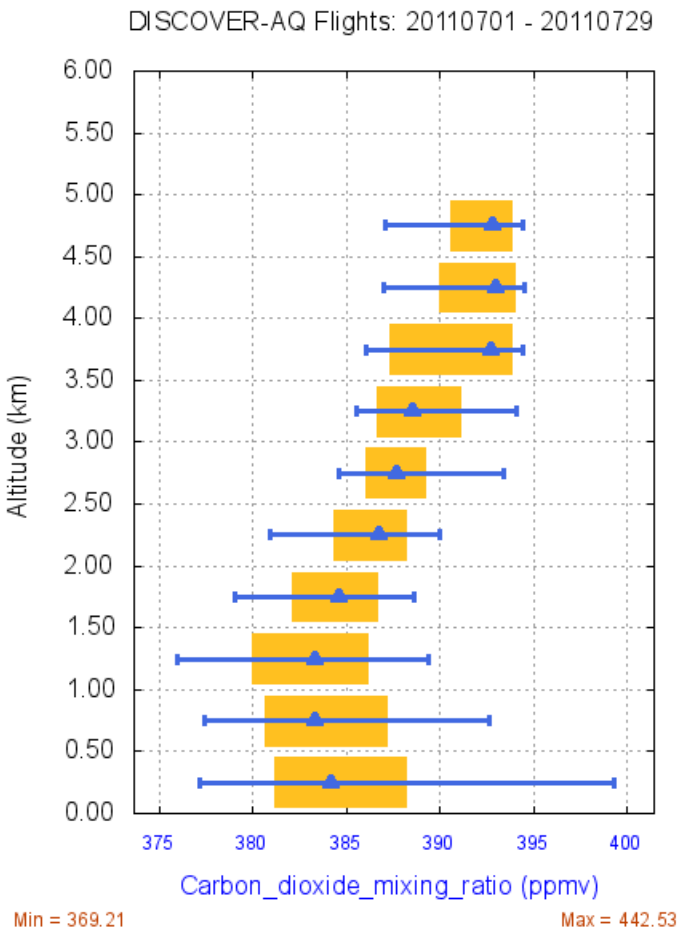


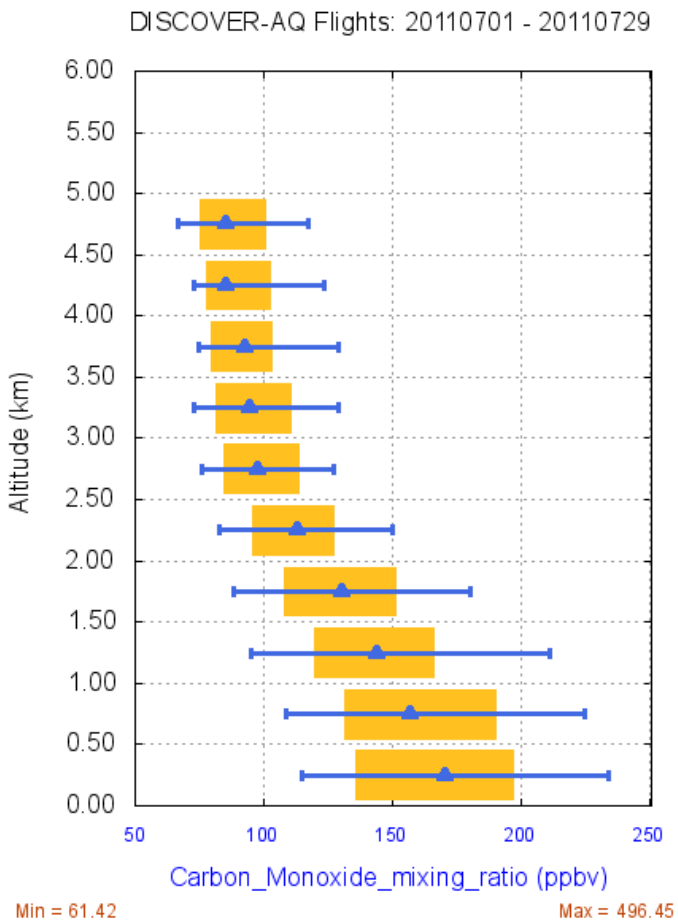
K. Travis, in prep.

Conclusions: What can observations tell us about emissions?

- **CMAQ with CB05 and the NEI overestimate [NOy] and NOy/CO (factor of ~2) in urban areas, probably due to overestimated NOx emissions.**
- **If total emissions of NOx are overestimated then any source could be overestimated, but mobile sources <u>must</u> be overestimated.**
- **Lower NOx puts the Mid Atlantic States on the steeper part of the ozone production curve: NOx controls more effective!**

DISCOVER-AQ Average CO_2 and CO Profiles

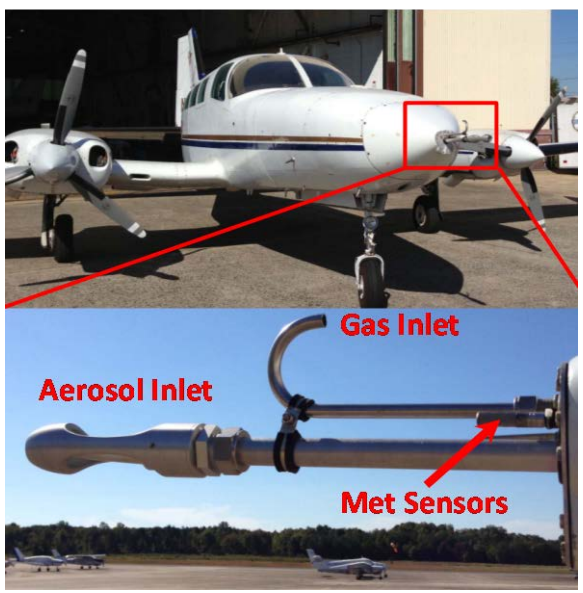


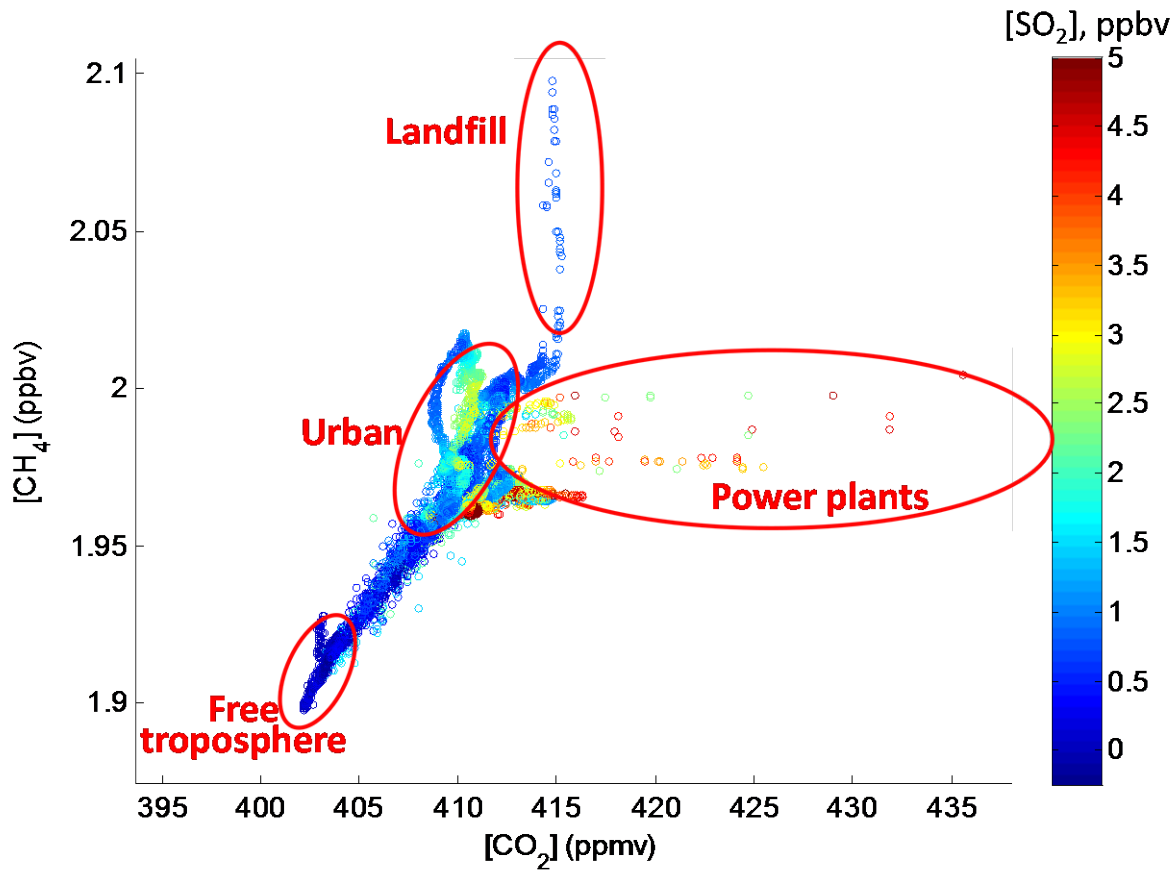


Observations of greenhouse gas fluxes in the Baltimore/Washington area

What are the emissions of trace gases from urban areas and what are the major sources?

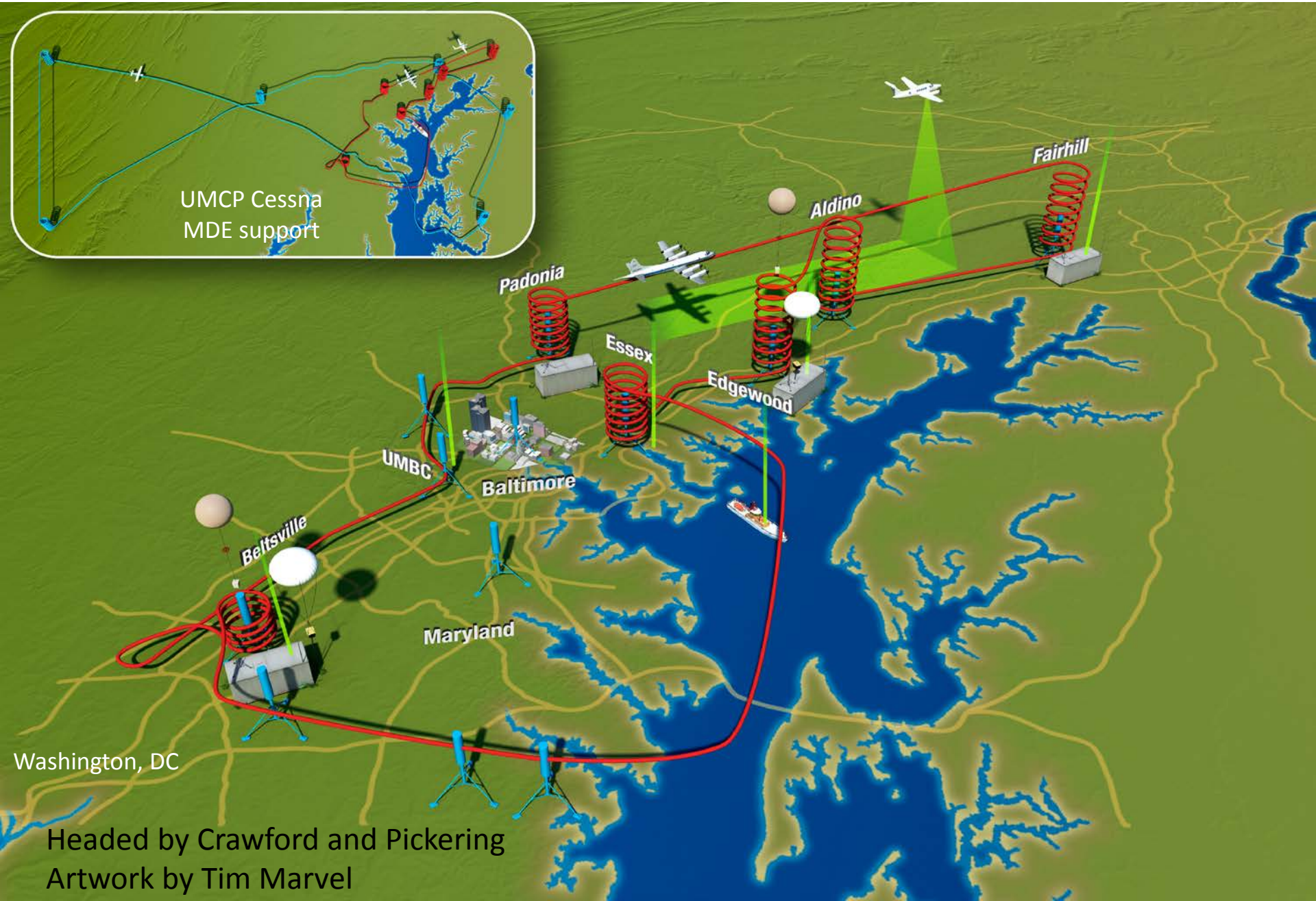
Does Fracking impact the air quality?





Dickerson, Ren, Shepson, et al. UMD, Purdue, NIST

DISCOVER-AQ Maryland July 2011



Headed by Crawford and Pickering
Artwork by Tim Marvel