Modeling Ozone in the Eastern US: Using Observations to Guide CAMx and CMAQ

Presented at the

EPRI ENV-Vision

by

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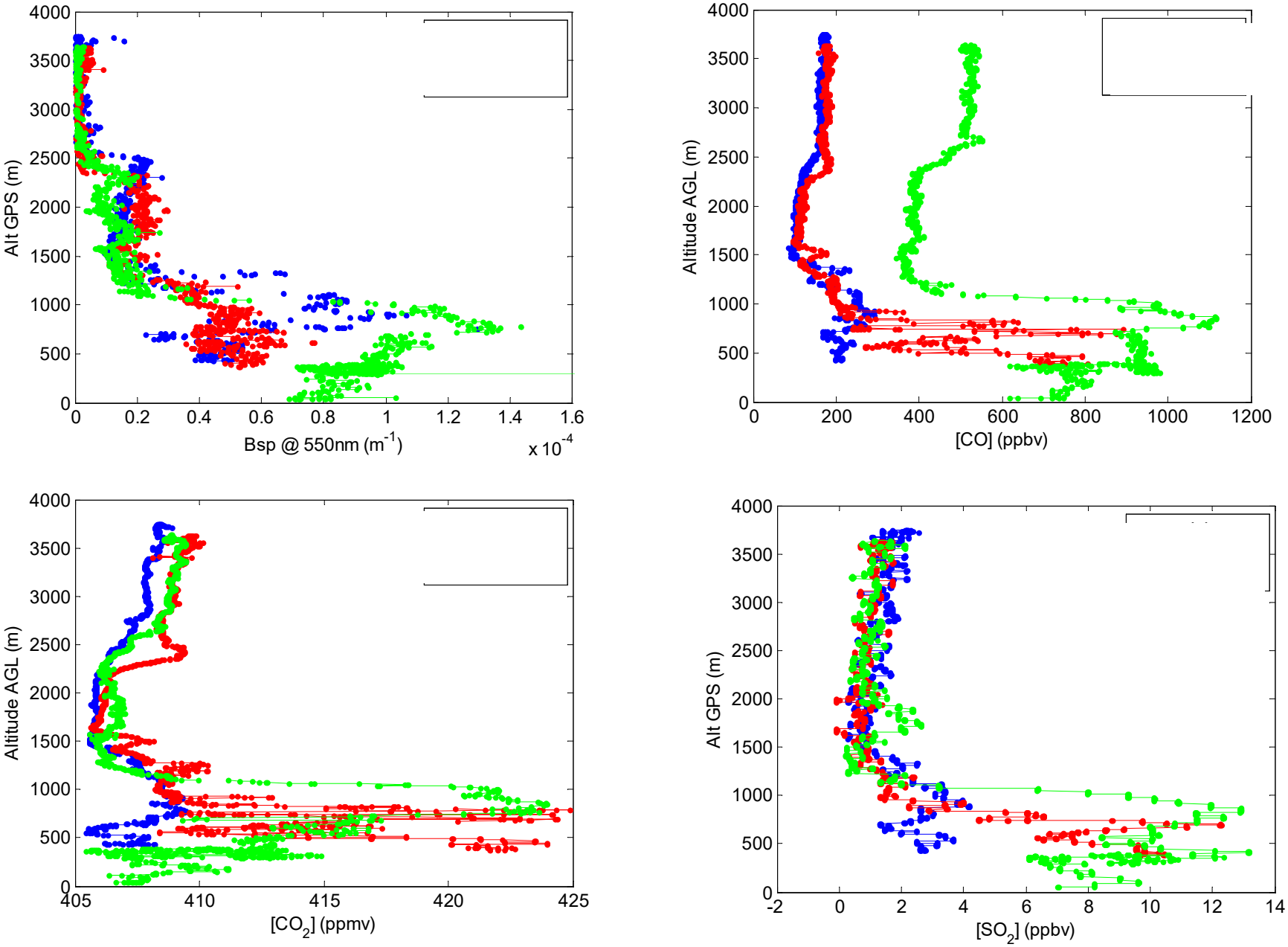
Supported by MDE

NIST, NASA, NOAA, and DNR

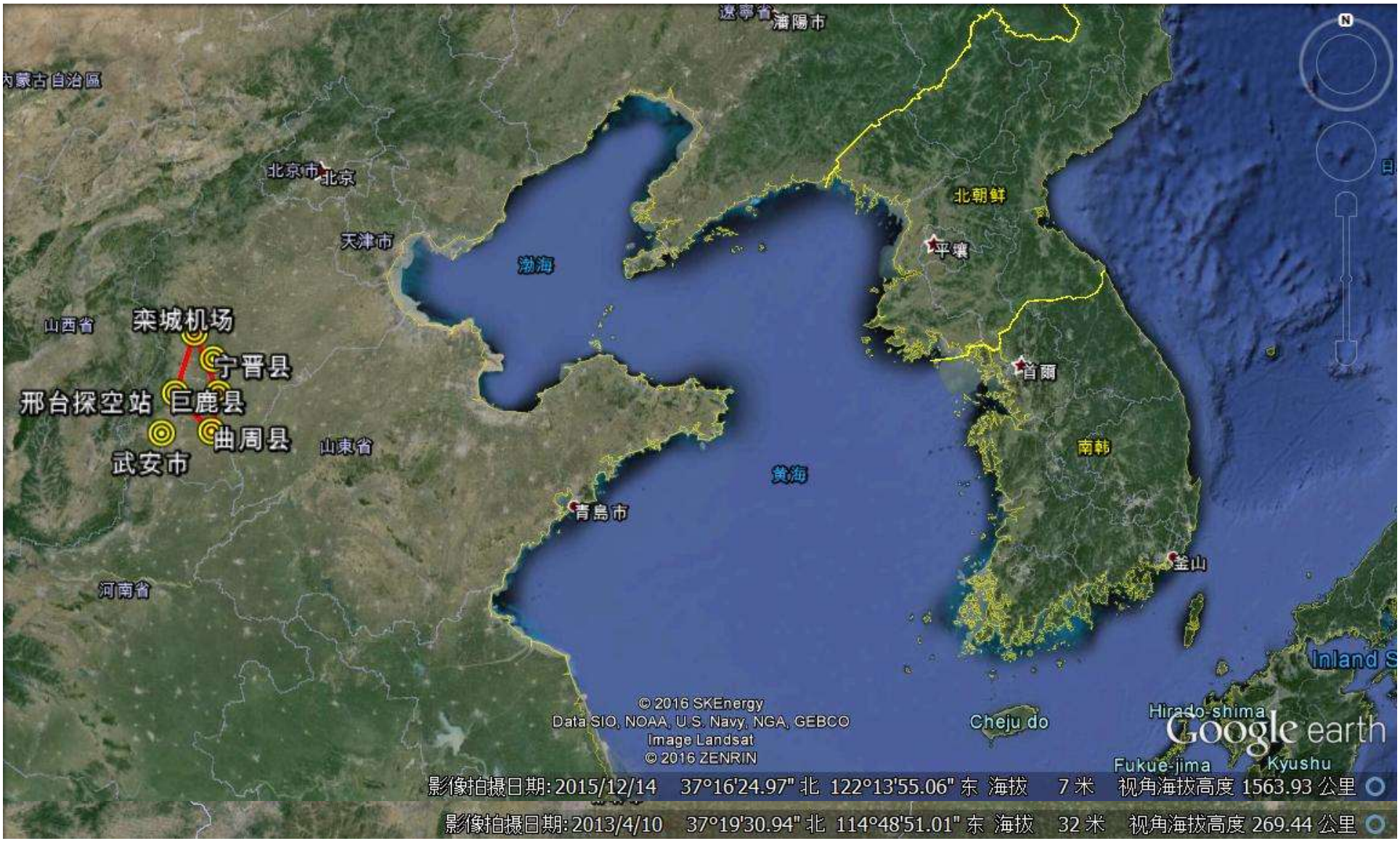
May 10-11, 2016

UMD/URF Cessna
Photo by J. Stehr

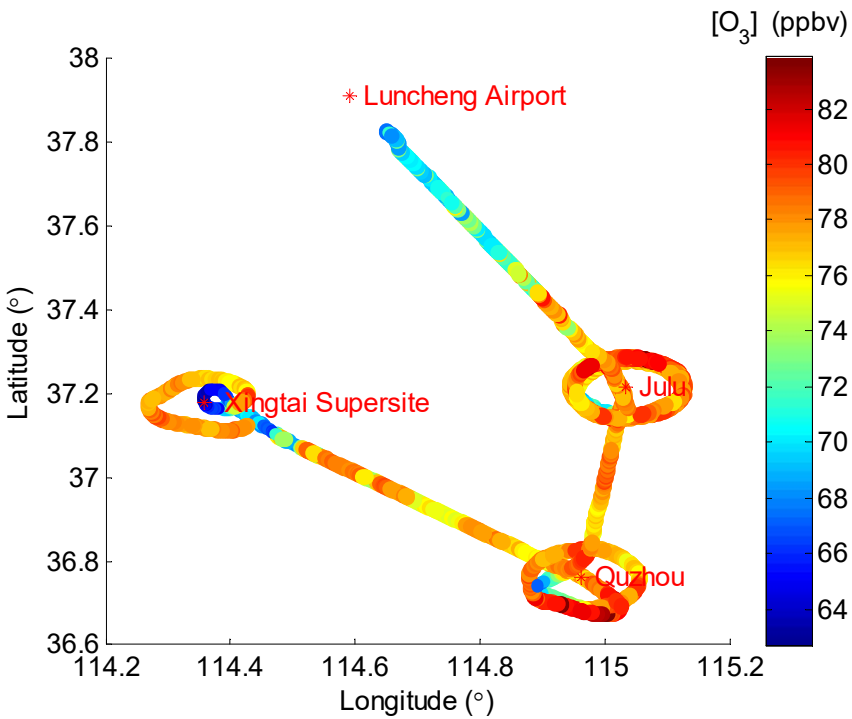
Three Vertical Profiles (Spirals) May 8, 2016

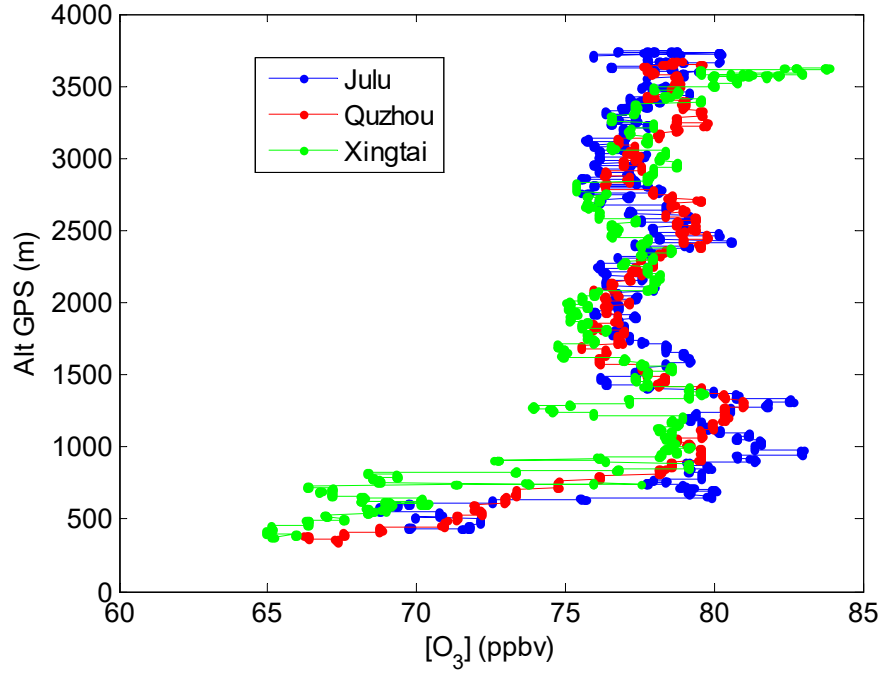


RF1 Flight Track



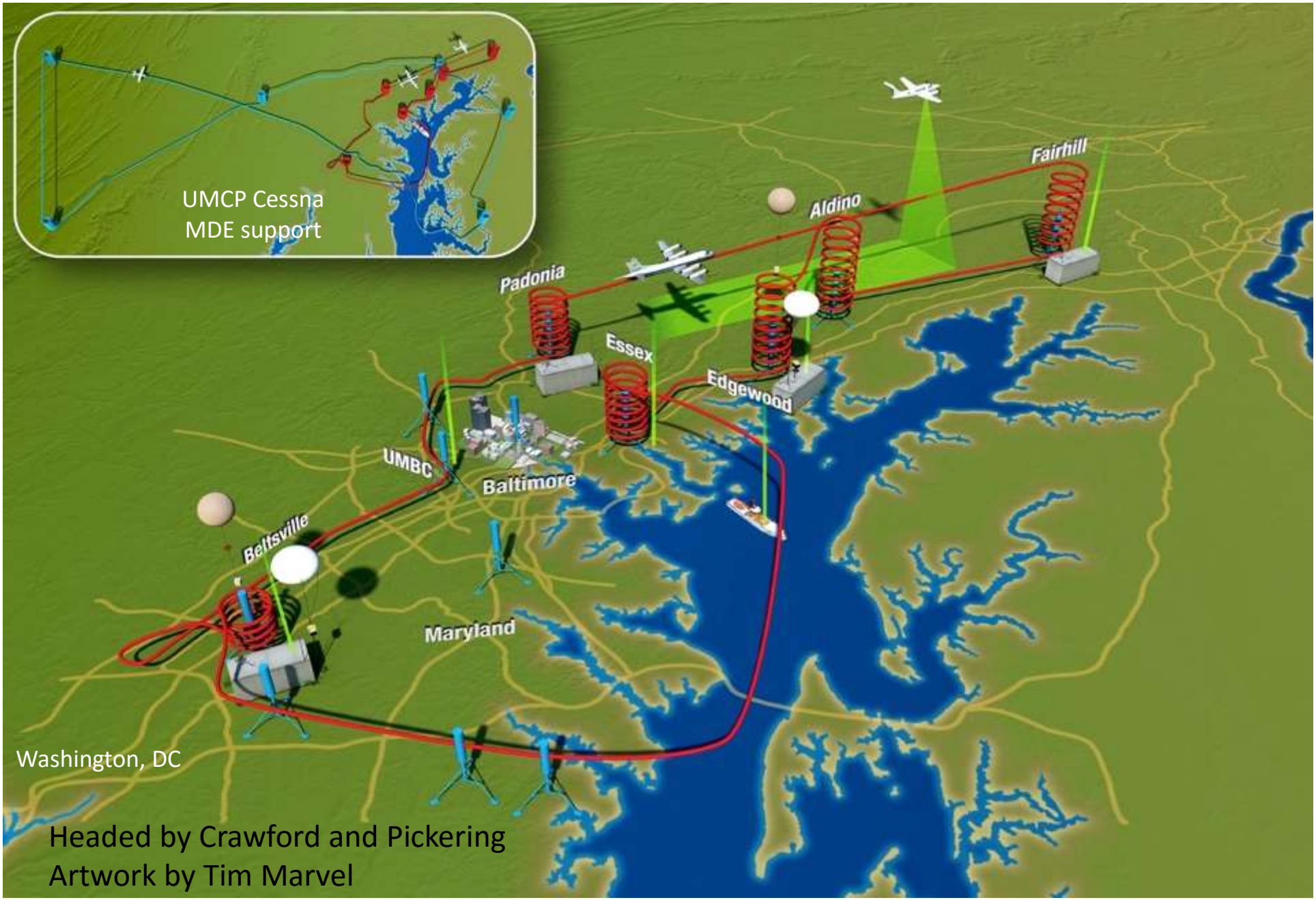
Ozone on flight track and vertical profiles





The Guilty Parties

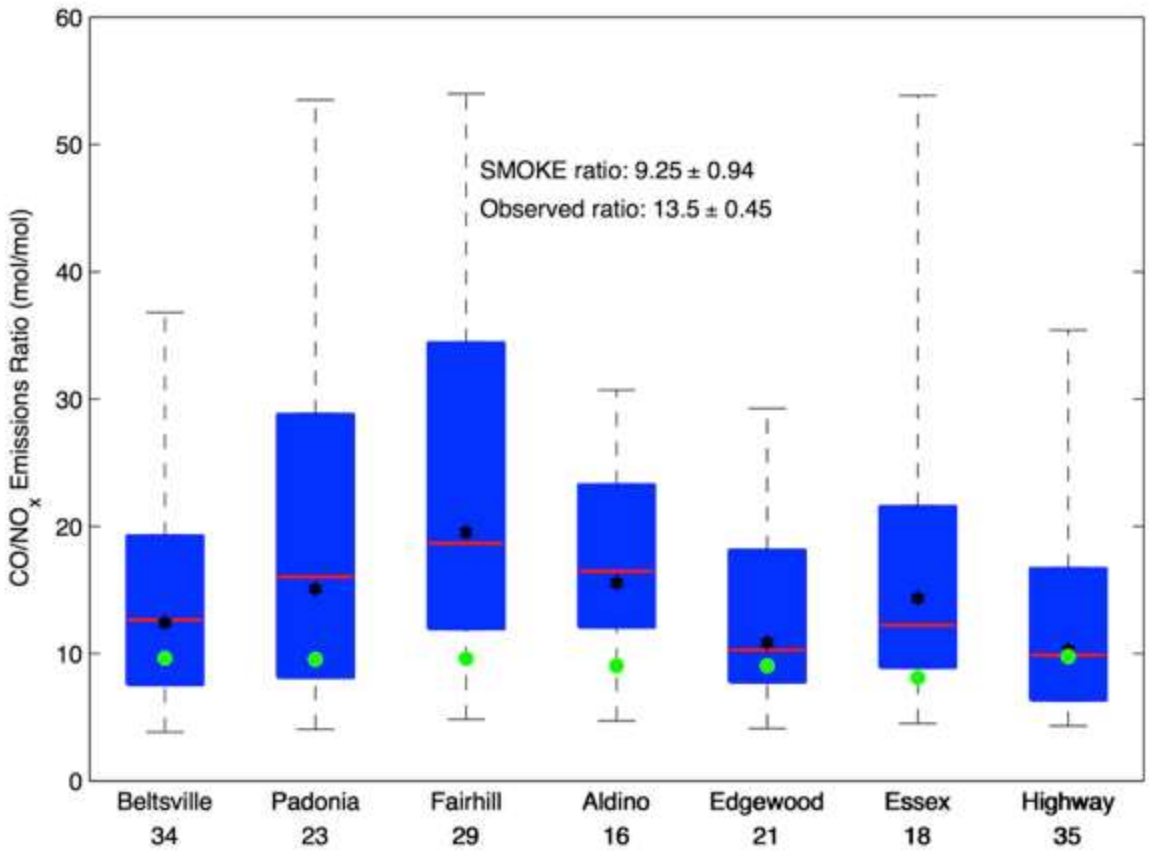
DISCOVER-AQ Maryland July 2011



Headed by Crawford and Pickering
Artwork by Tim Marvel

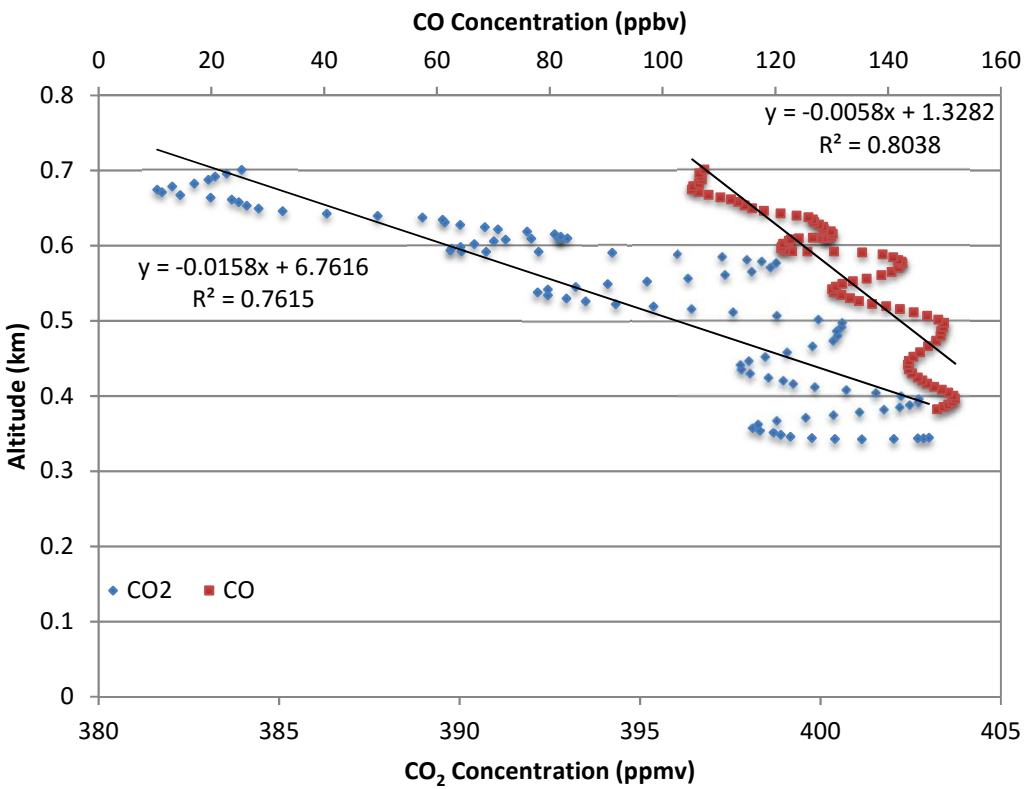
Summary of Results

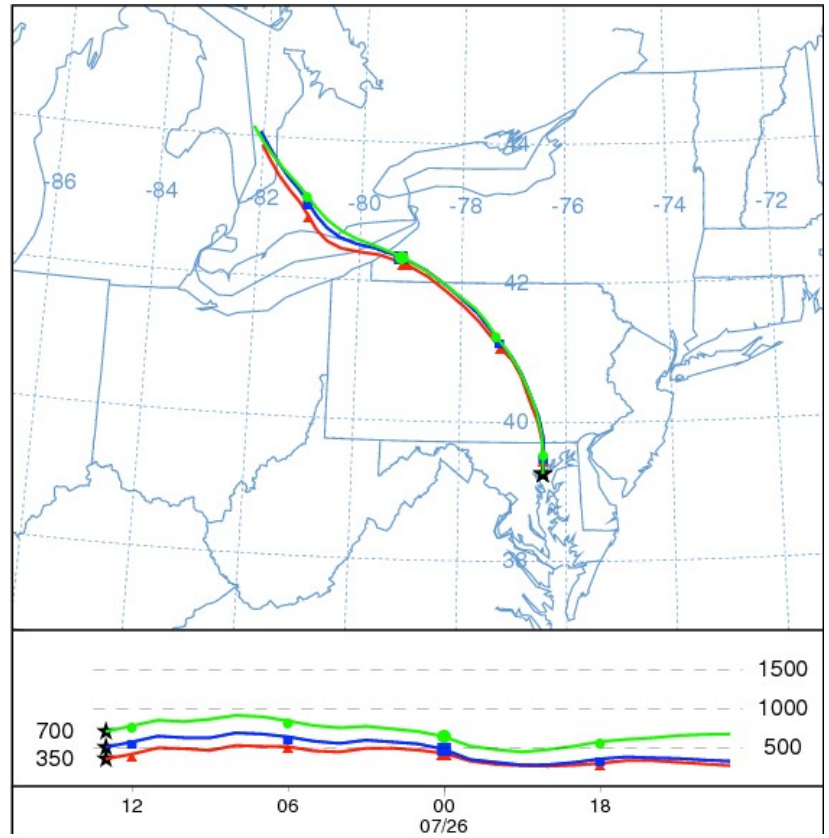
CMAQ/CB05 gets CO about right (15 ±11% high), but substantially overestimates NOy.



Essex, 07/26, 9:13 EST

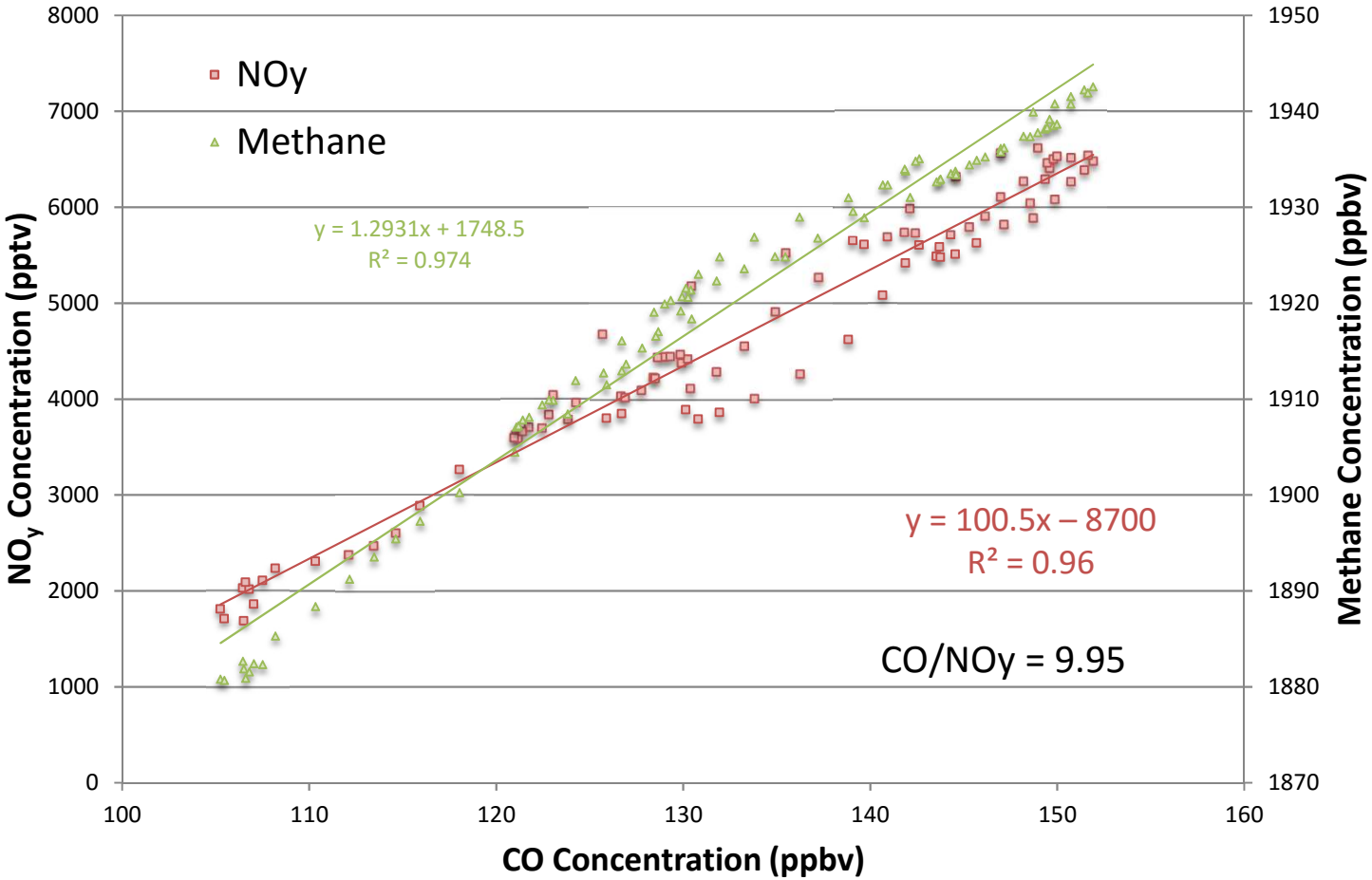
Portion of vertical profile in the mixed layer:





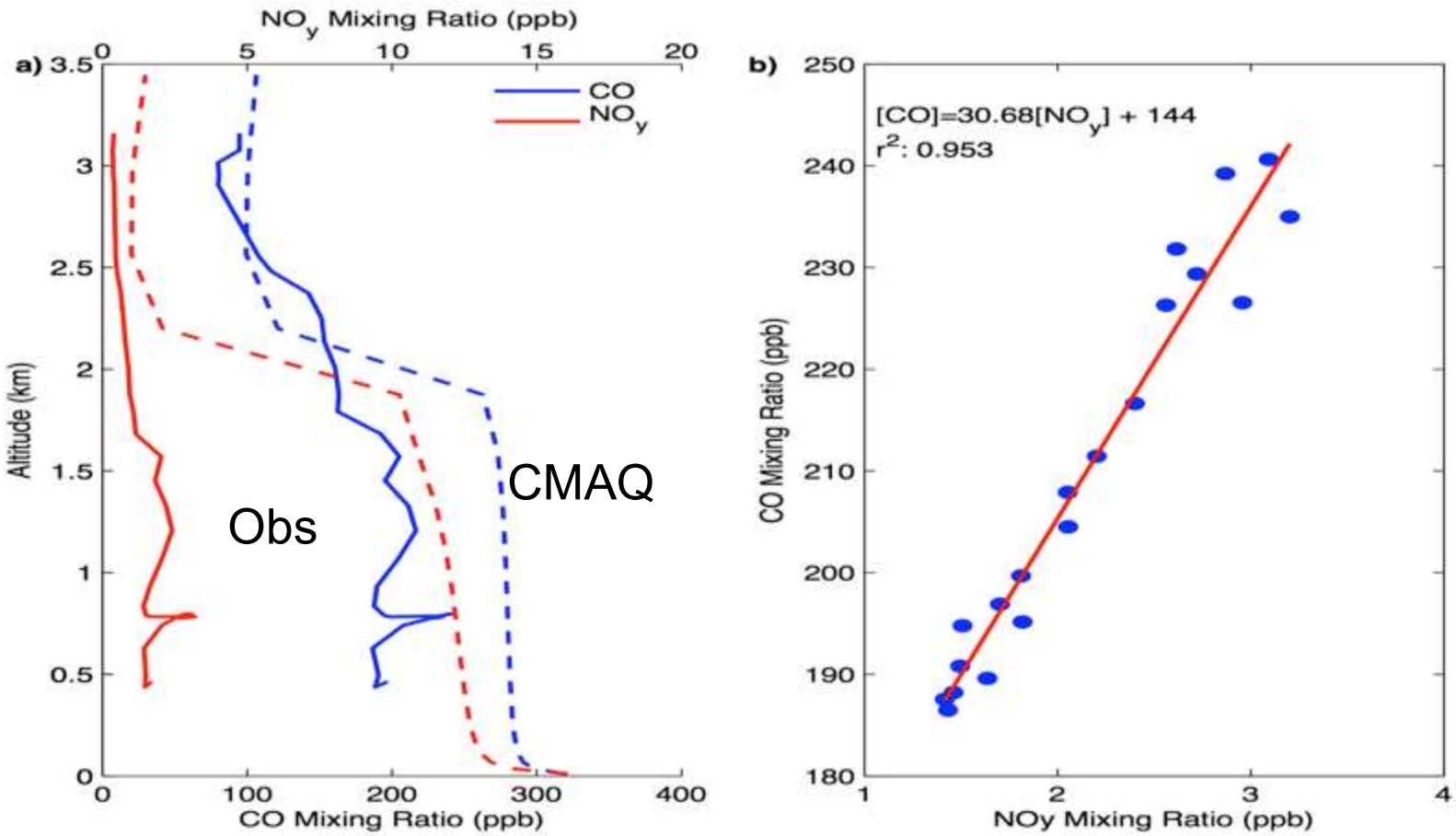
Air mass from "clean corridor" in PA. Pollution probably local.

Essex, MD 07/26, 9:13 EST



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

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



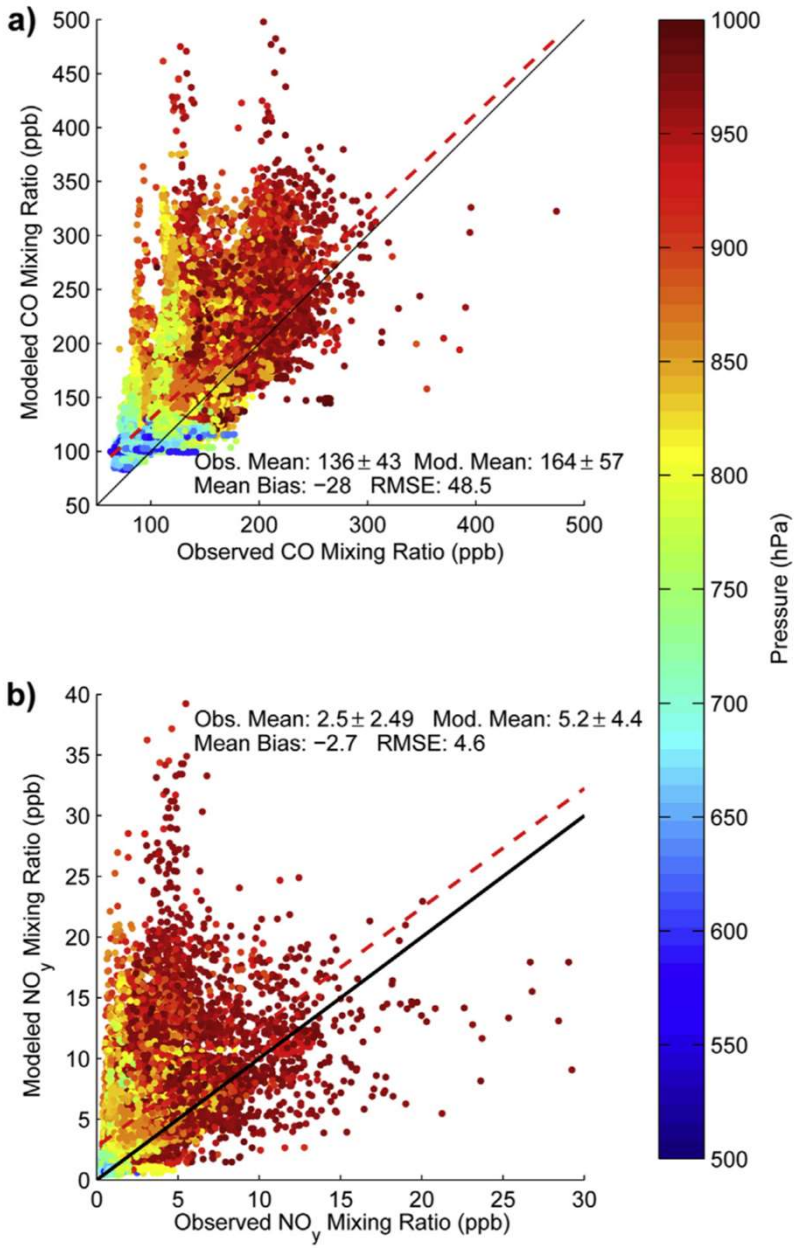


Fig. 7. a) Regression of measured and modeled CO for all flight days during DISCOVER-AQ. Values after means are 1σ. b) Same as a) but for NO_y. Solid line is the 1:1 line; dashed line, the line of best fit.

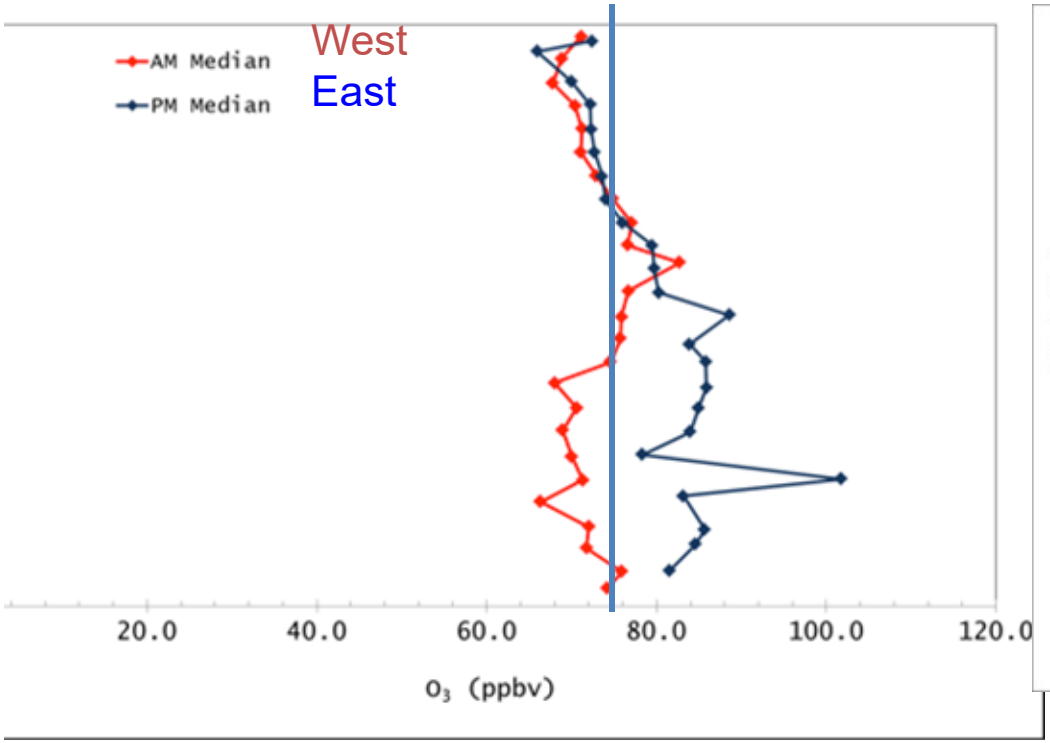
CMAQ gets CO a little high (bias = +28 out of 136 ppb) but NOy much too high (bias +2.7 out of 2.5 ppb).

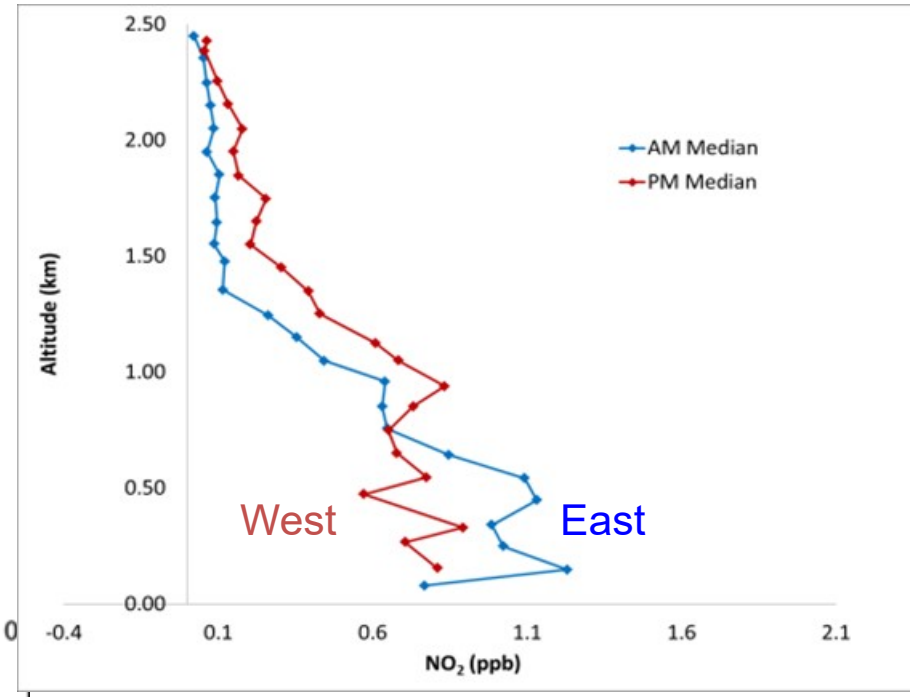
Outline

- Why?
  - Need to model for State Implementation Plan (SIP)
  - Off the shelf CMAQ produces ozone locally and removes NO_2 quickly – little interstate transport.
- How?
  - CMAQ(CB05) and CAMx (CB05 & CB6r2)
- What?
  - Examine chemistry and emissions.

NO_2 is pervasive in the eastern US

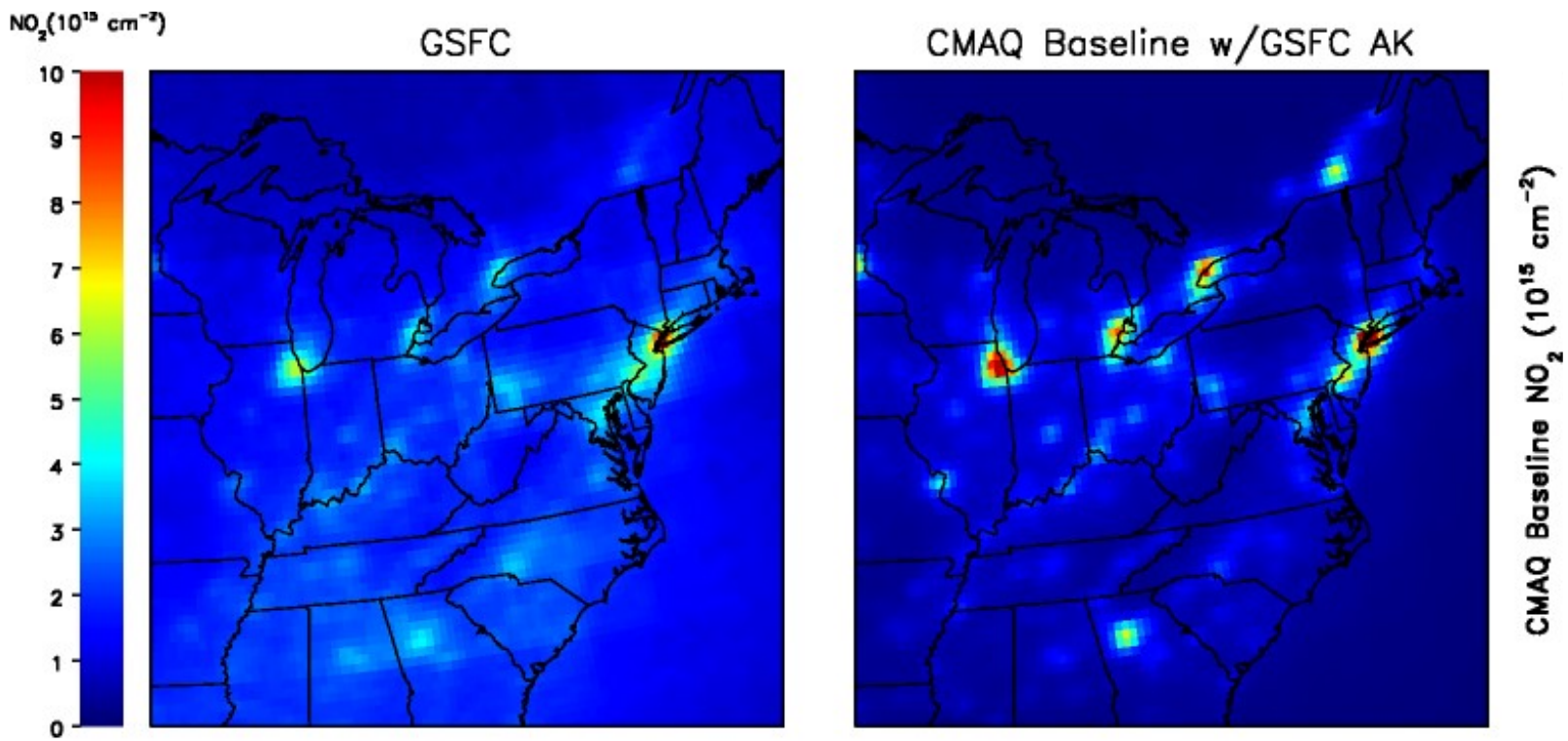
Ozone is a regional problem and reservoir species extend the lifetime of NOx. NO_2 is high enough to generate new ozone at ~3 ppb/hr at midday even upwind of Baltimore and Washington. Interstate transport matters. Brent et al., *Atmos. Chem.*, (2013).





Canty et al. *ACP*, 2015.

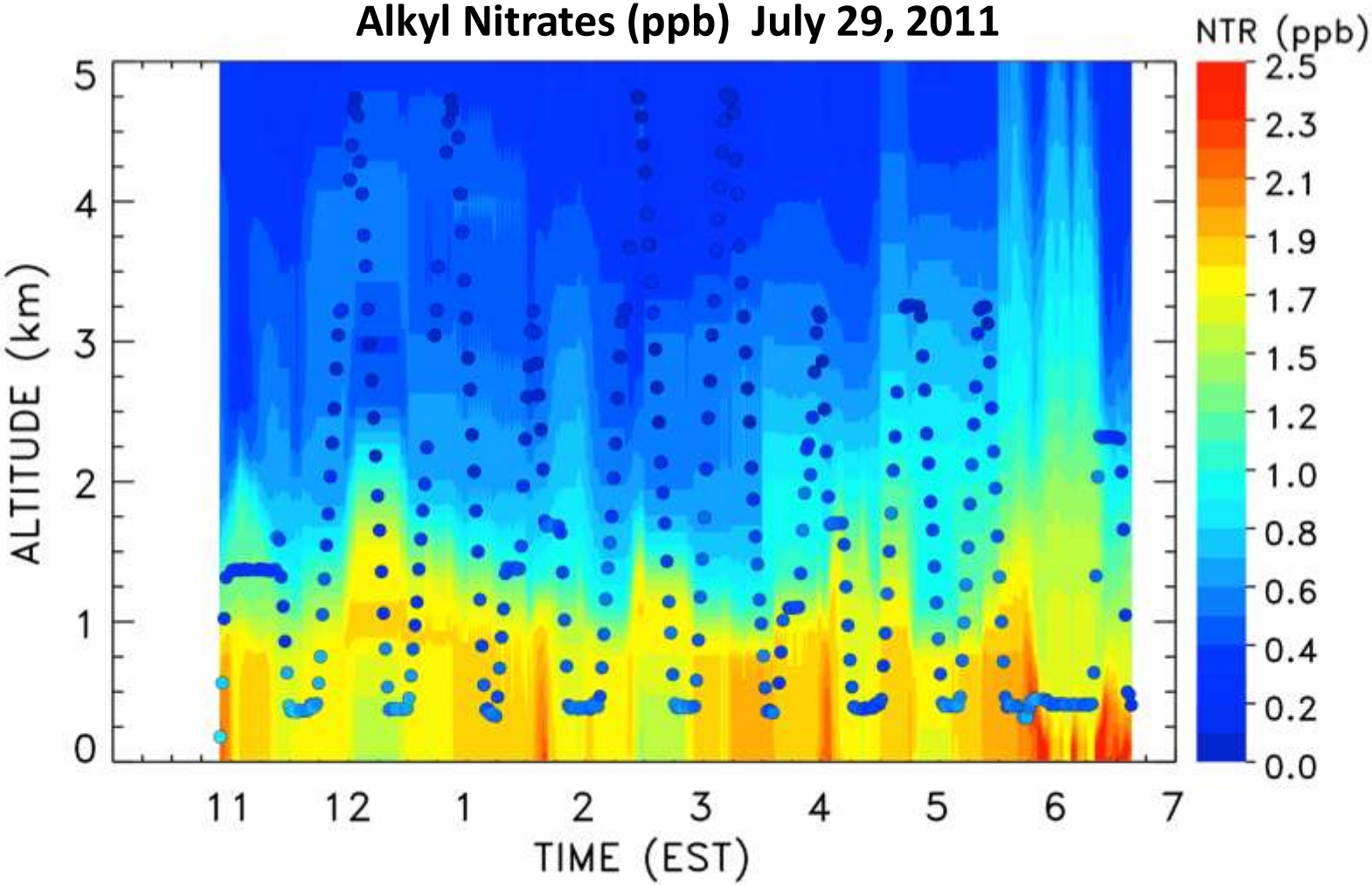
Satellite observations support aircraft data:
see also Streets et al., *Atmos. Environ*., 2013



Model Modifications

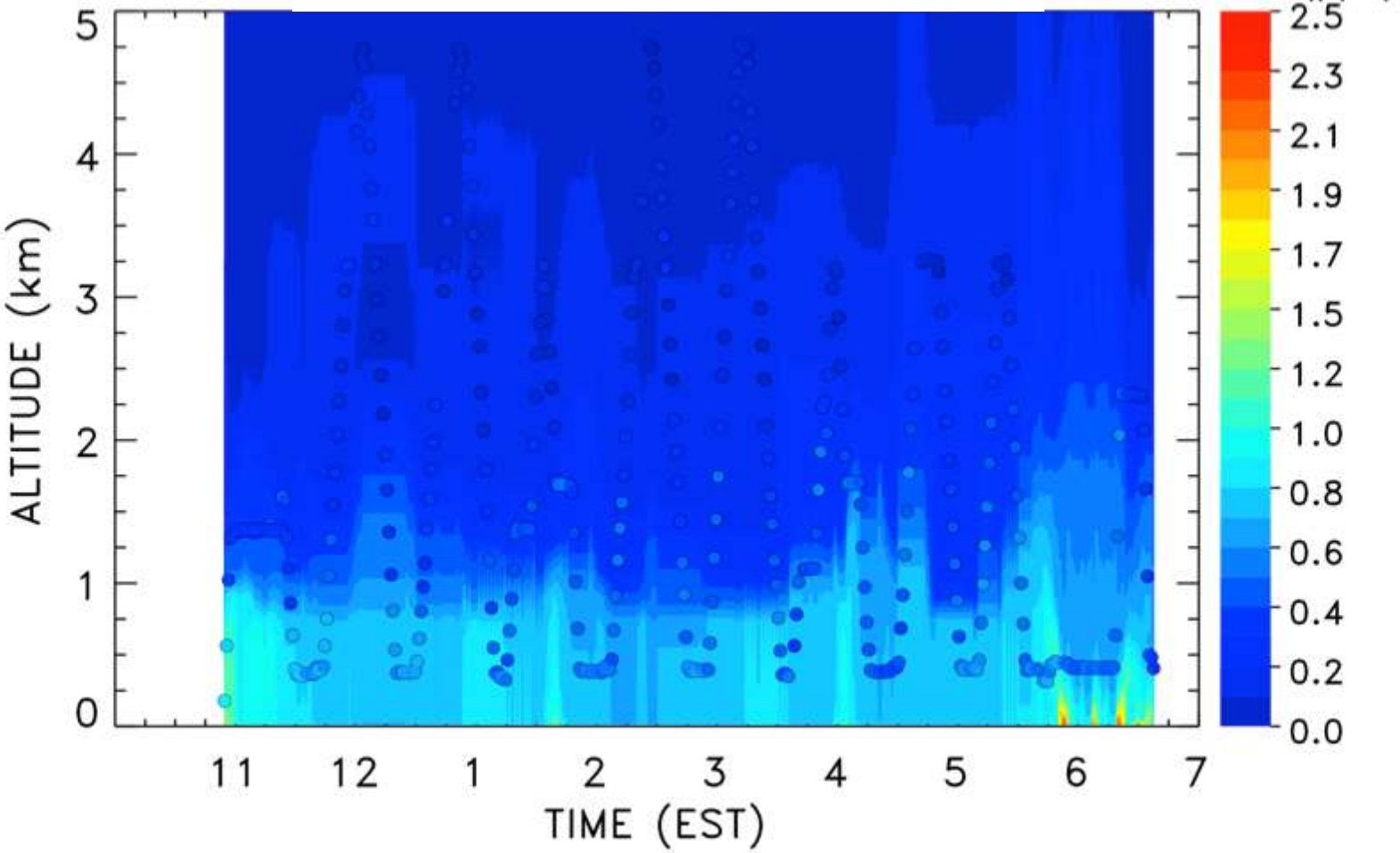
Increase photolysis rate of $RONO_2$
(alkly nitrates)
Decrease vehicular emissions of NOx by ~50%

Alkyl Nitrates (ppb) July 29, 2011



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

Alkyl Nitrates (ppb) July 29, 2011



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

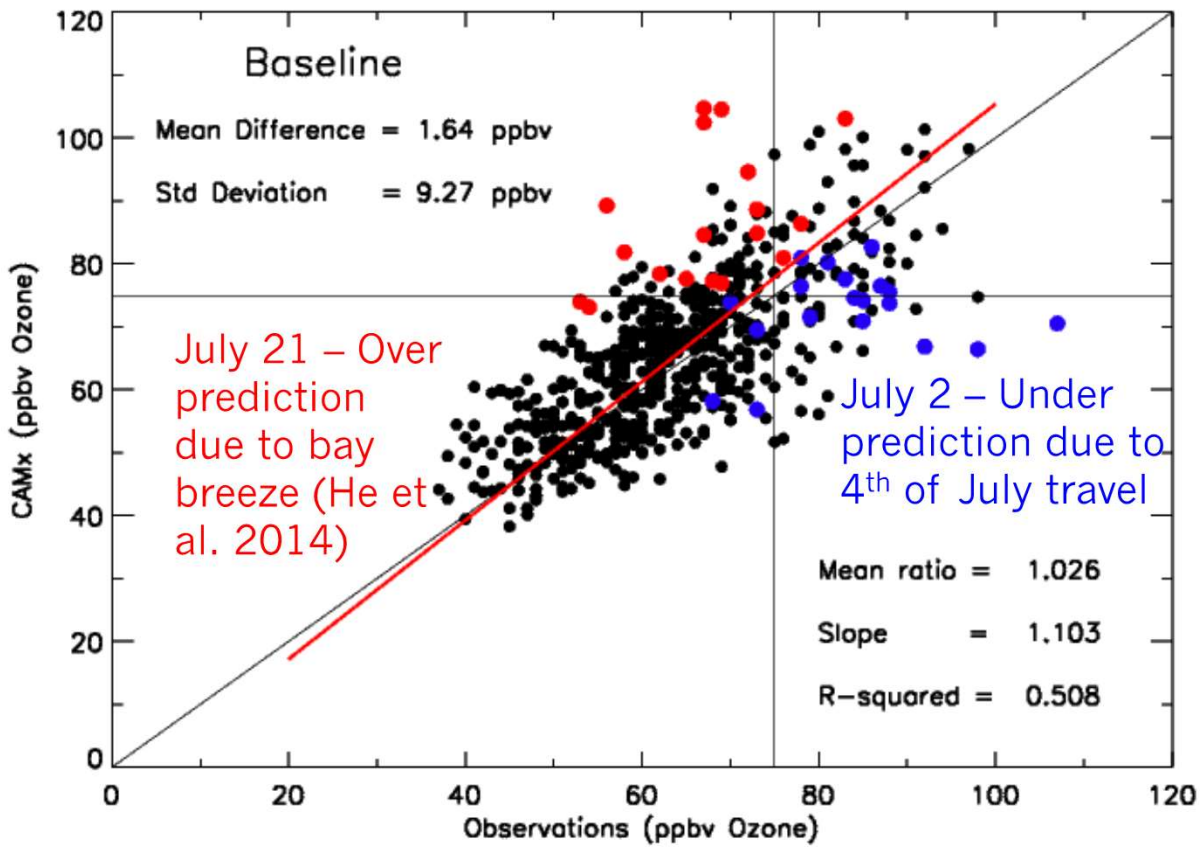
Model Emissions

NOx too high
VOC’s too low.

Description of model used:

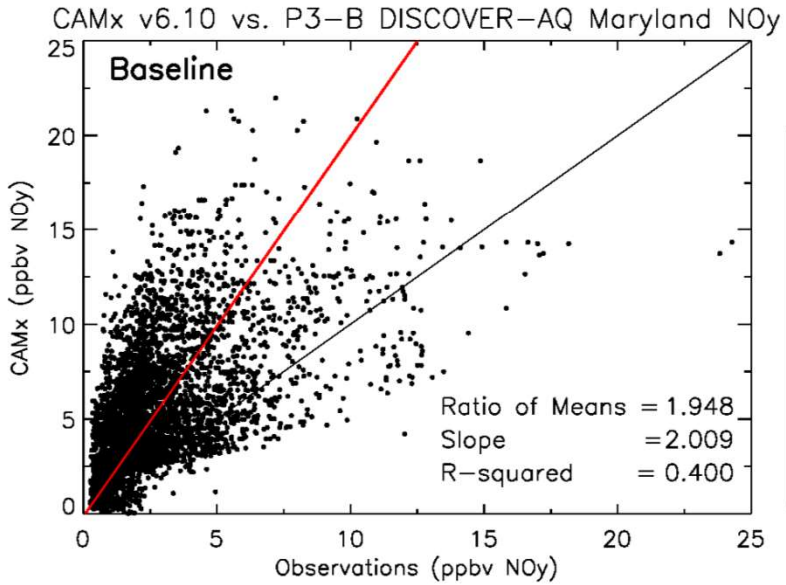
- CAMx v6.10 (12 km OTC model domain)
  - EPA-approved regulatory model
  - Can use the *CB6r2* gas-phase chemical mechanism (Ruiz & Yarwood, 2013)
    - Better alkyl nitrate chemistry
  - Ability to use ozone source apportionment technology (*OSAT*) to identify where the ozone "originated" by region & sector

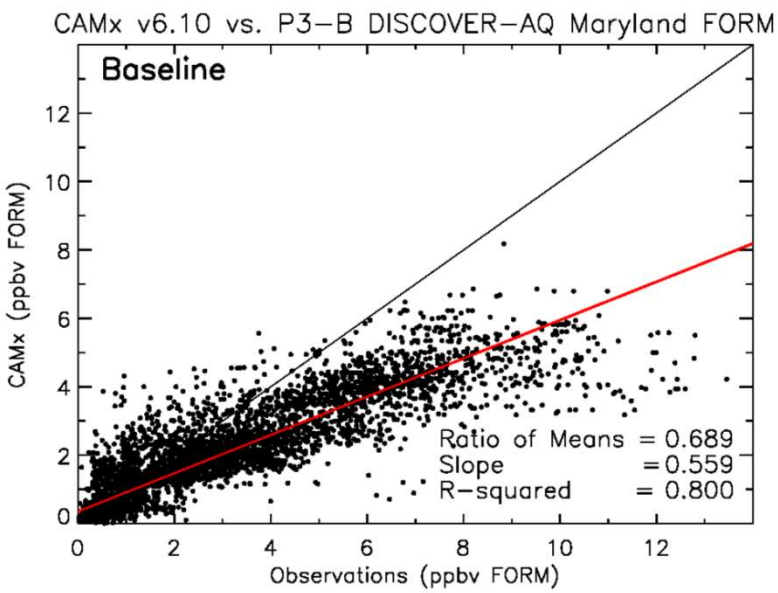
July 2011 8-hour maximum surface ozone: CAMx model vs. observations in Maryland



There is **excellent** model agreement in predicting *monthly surface* ozone when using the standard, "off-the-shelf" version of CAMx

Prediction of O_3 precursors: Using DISCOVER-AQ data

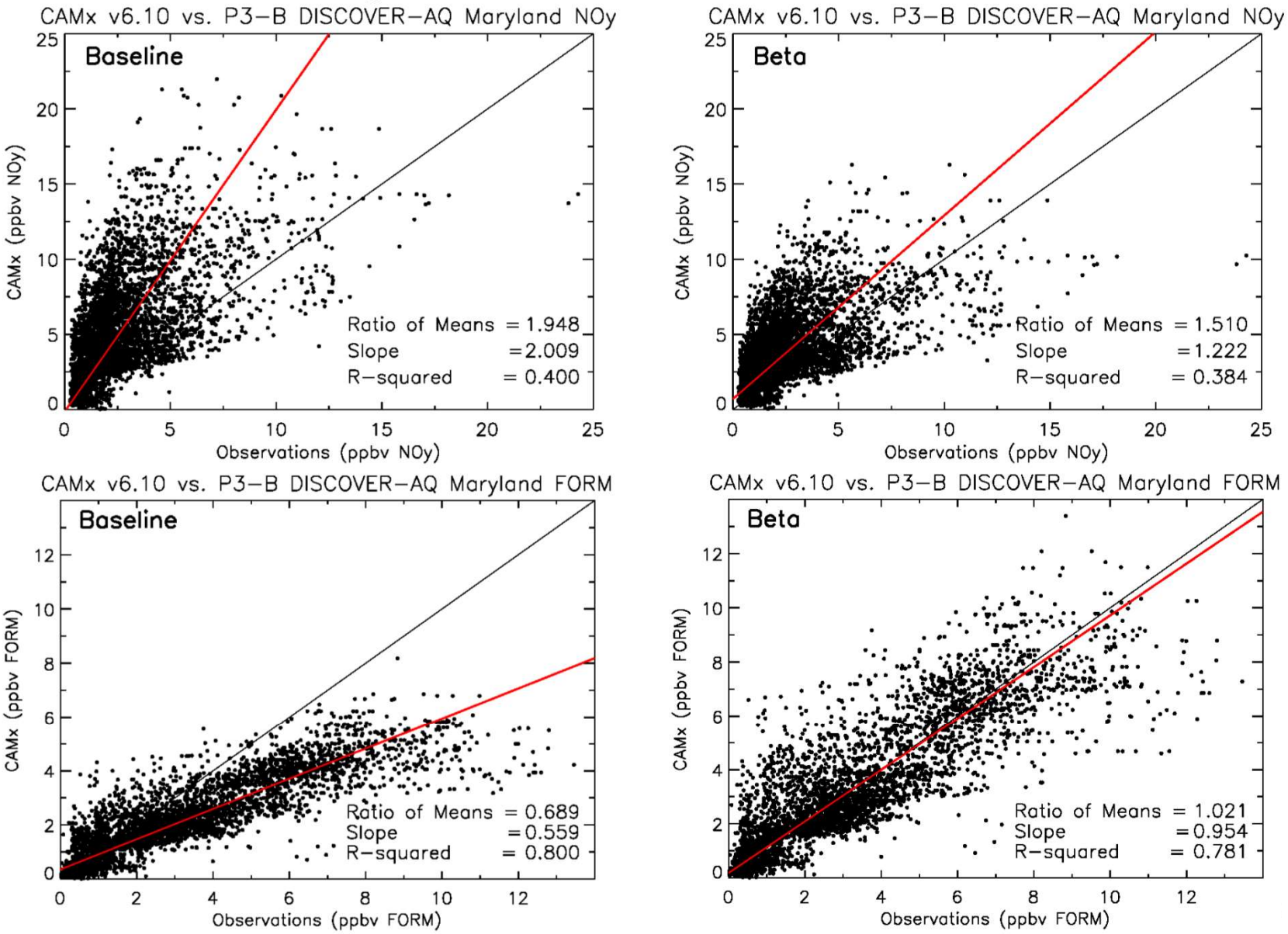




- The comparison with data from the P3-B aircraft during DISCOVER-AQ MD shows a significant over prediction of NO_y and a significant under prediction of HCHO.

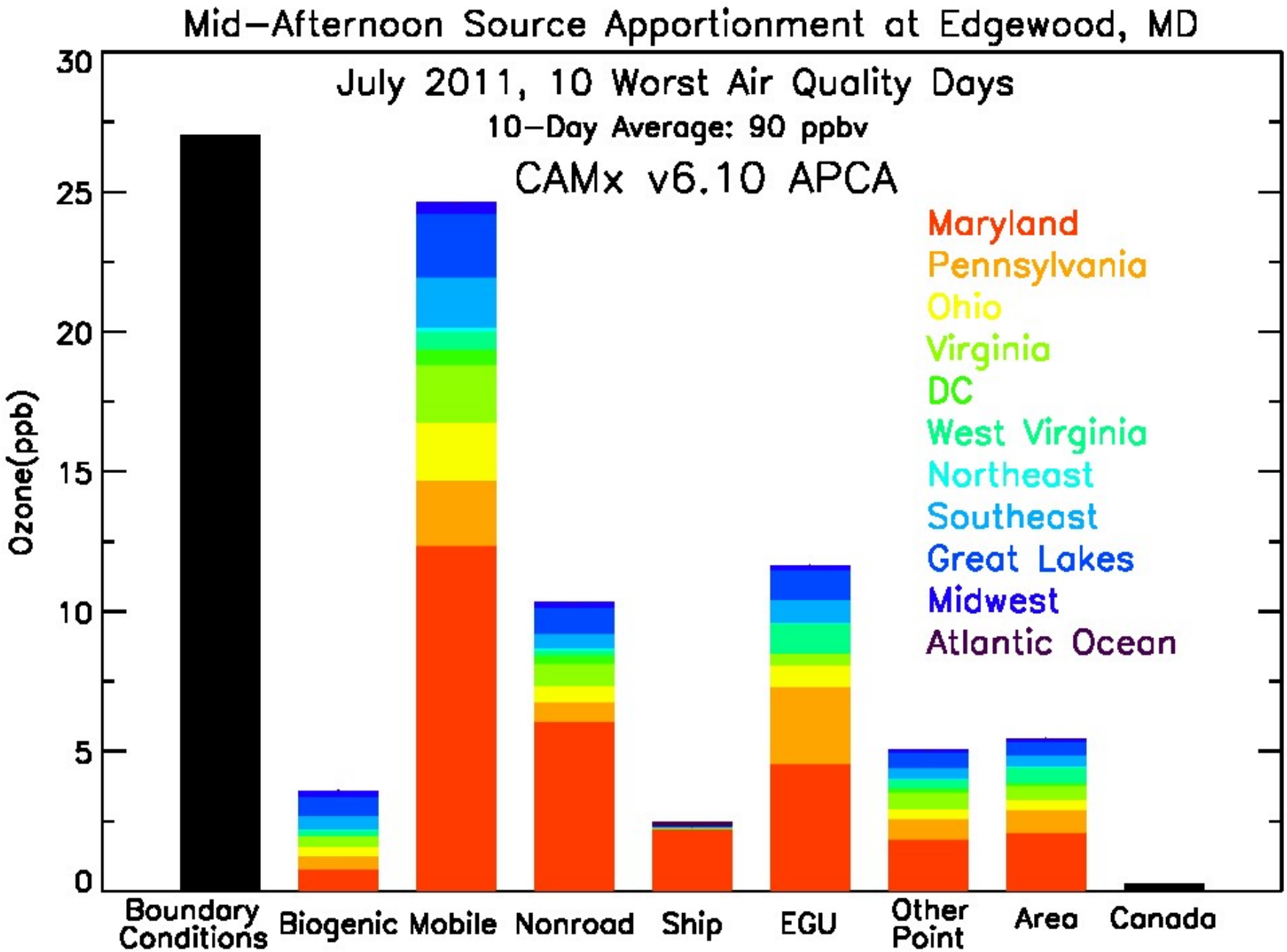
- We've made three changes to update the model, "Beta":
  - CB6r2 gas-phase chemistry (Old: CB05)
  - MEGAN v2.1 biogenic emissions (Old: BEISv3.14)
  - Reduce emissions from mobile sources by 50% (Anderson et al., 2014)

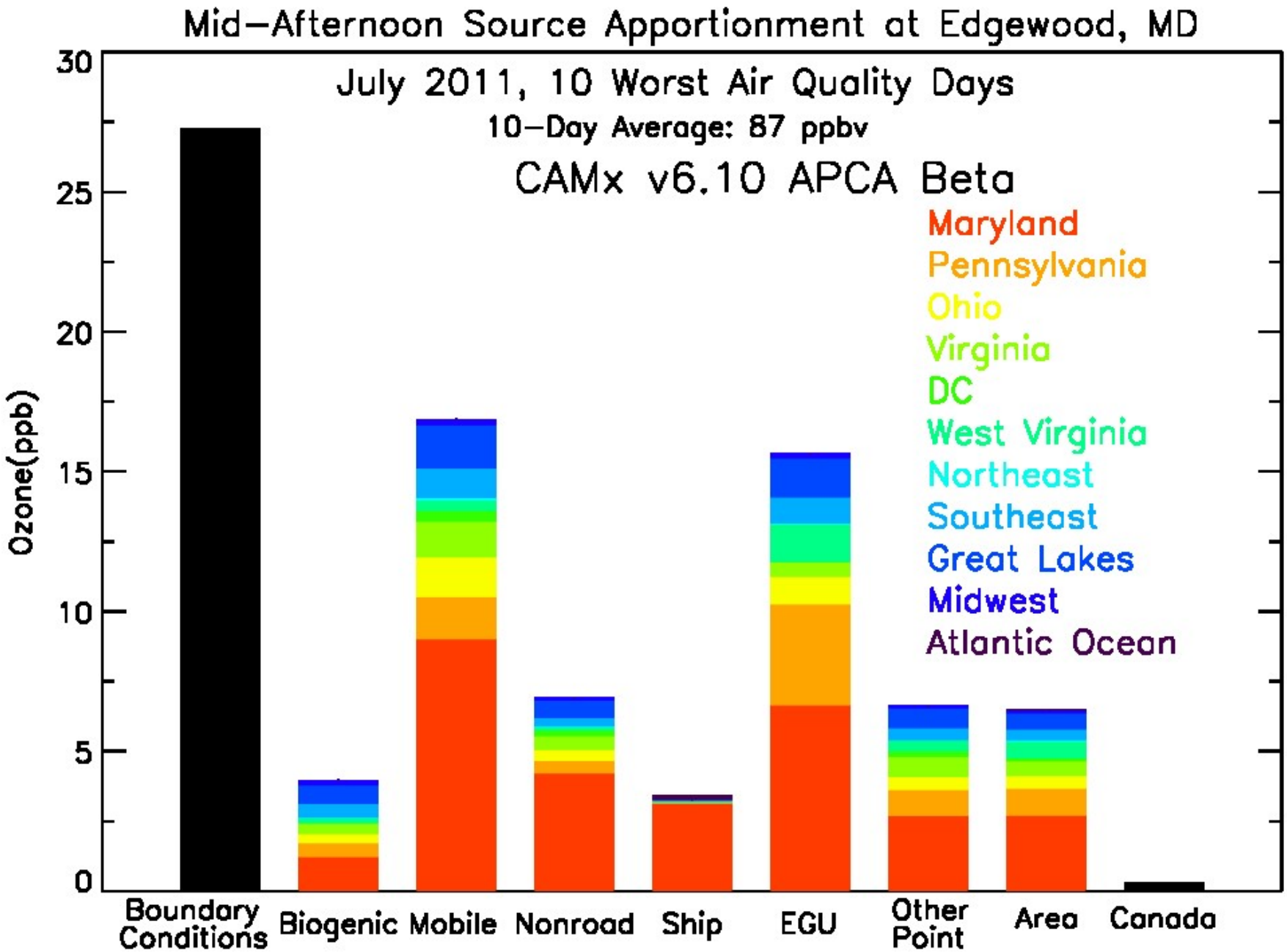
Prediction of O_3 precursors: Using DISCOVER-AQ data



Description of Slides: CAMx OSAT

- Two figures for surface ozone at Edgewood, Maryland during the 10 worst air quality days during July 2011.
  1. Baseline simulation
  2. Updated "Beta" simulation (on-road, off-road, AND non-road NO_x emissions reduced by 50%, in addition to changing to MEGAN v2.1 biogenics, CB6r2, and increased NTR deposition)
- A table indicating the total ozone concentrations attributed to each source sector.


Mid–Afternoon Source Apportionment at Edgewood, MD
July 2011, 10 Worst Air Quality Days
10–Day Average: 90 ppbv
CAMx v6.10 APCA
Maryland
Pennsylvania
Ohio
Virginia
DC
West Virginia
Northeast
Southeast
Great Lakes
Midwest
Atlantic Ocean
Ozone(ppb)
0
5
10
15
20
25
30
Boundary Conditions
Biogenic
Mobile
Nonroad
Ship
EGU
Other Point
Area
Canada


Mid–Afternoon Source Apportionment at Edgewood, MD
July 2011, 10 Worst Air Quality Days
10–Day Average: 87 ppbv
CAMx v6.10 APCA Beta
Maryland
Pennsylvania
Ohio
Virginia
DC
West Virginia
Northeast
Southeast
Great Lakes
Midwest
Atlantic Ocean
Ozone(ppb)
0
5
10
15
20
25
30
Boundary Conditions
Biogenic
Mobile
Nonroad
Ship
EGU
Other Point
Area
Canada

Total ozone concentrations attributed to each source sector

Ozone (ppb) attributed to each Source Sector

	Biogenic	On-road Mobile	Non-road Mobile	Ships	EGUs	Other Point	Area
Baseline Simulation	3.6	24.6	10.3	2.5	11.6	5.1	5.6
Beta Simulation	4.0	16.9	6.9	3.4	15.7	6.7	6.6
Percentage change	10.9%	-31.4%	-33.0%	39.6%	34.6%	31.0%	18.7%

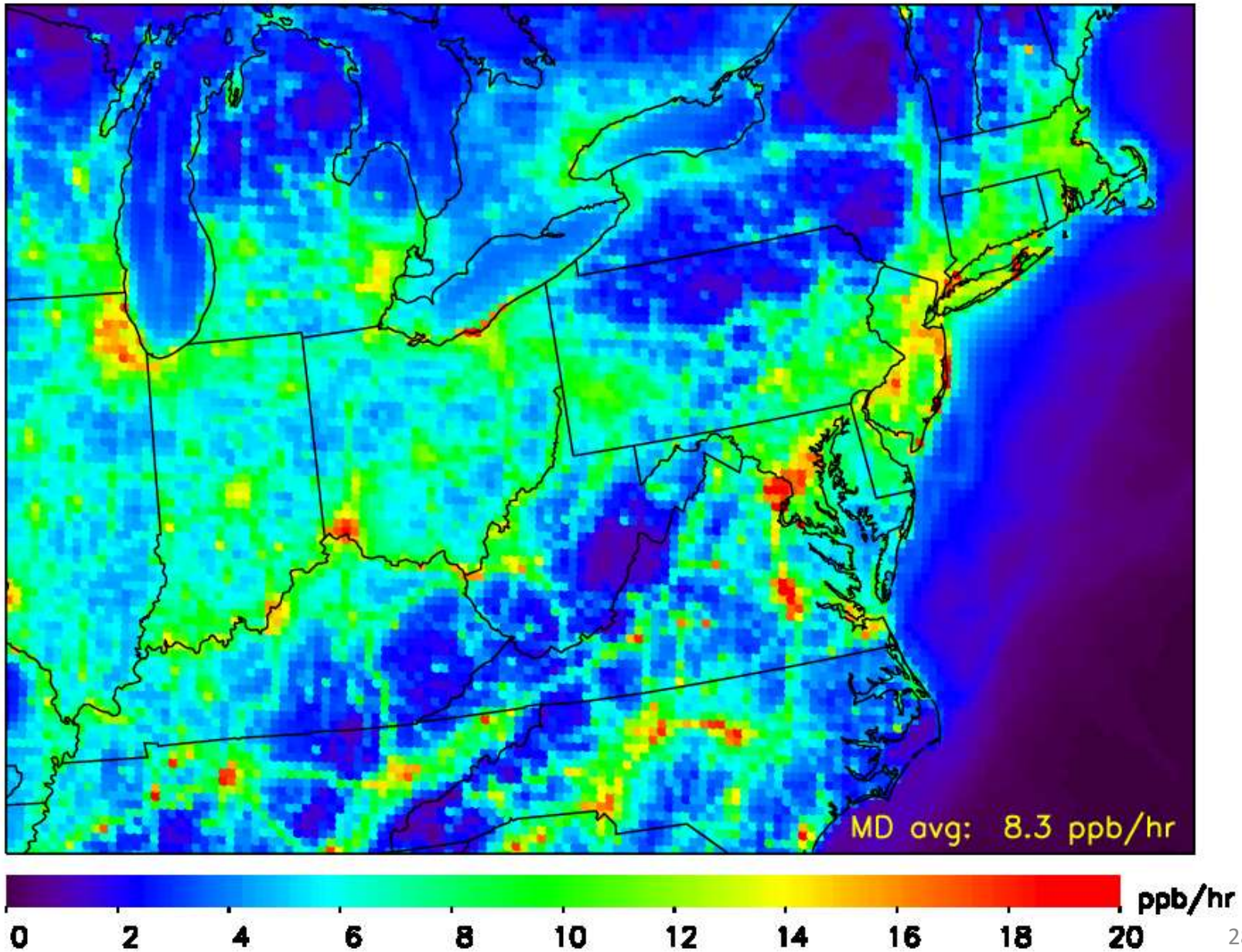
Changing Net O_3 Production Rates as NOx falls between 2002 and 2018

Thanks: Dan Goldberg

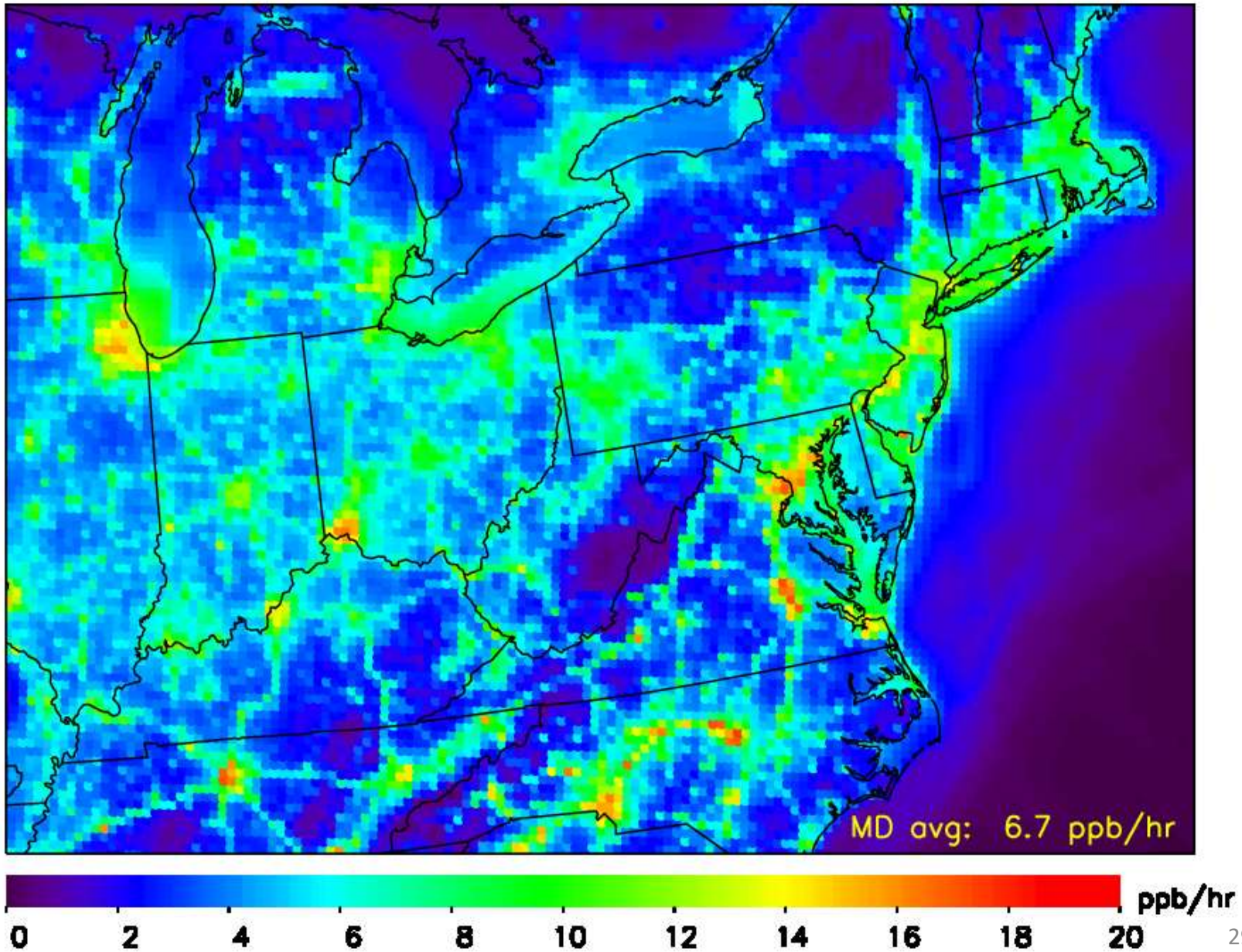
Description of Slides

- The first three slides show the mean daytime (8 AM – 8 PM) Net O_x (O_3+NO_y–NO) Production rates for July 2002, 2011, and 2018 at the surface.
  - This a standard output variable from the chemical process analysis (CPA) tool in CAMx.
- The second three slides show 12 PM Net O_x (O_3+NO_y–NO) Production rates for July 2002, 2011, and 2018 vs. NO_x during sunny days in the Baltimore region.
  - I define "sunny" days as days when j(NO_2) is greater than its median value.
  - The Baltimore region is a 72x96km grid box centered on Baltimore city.

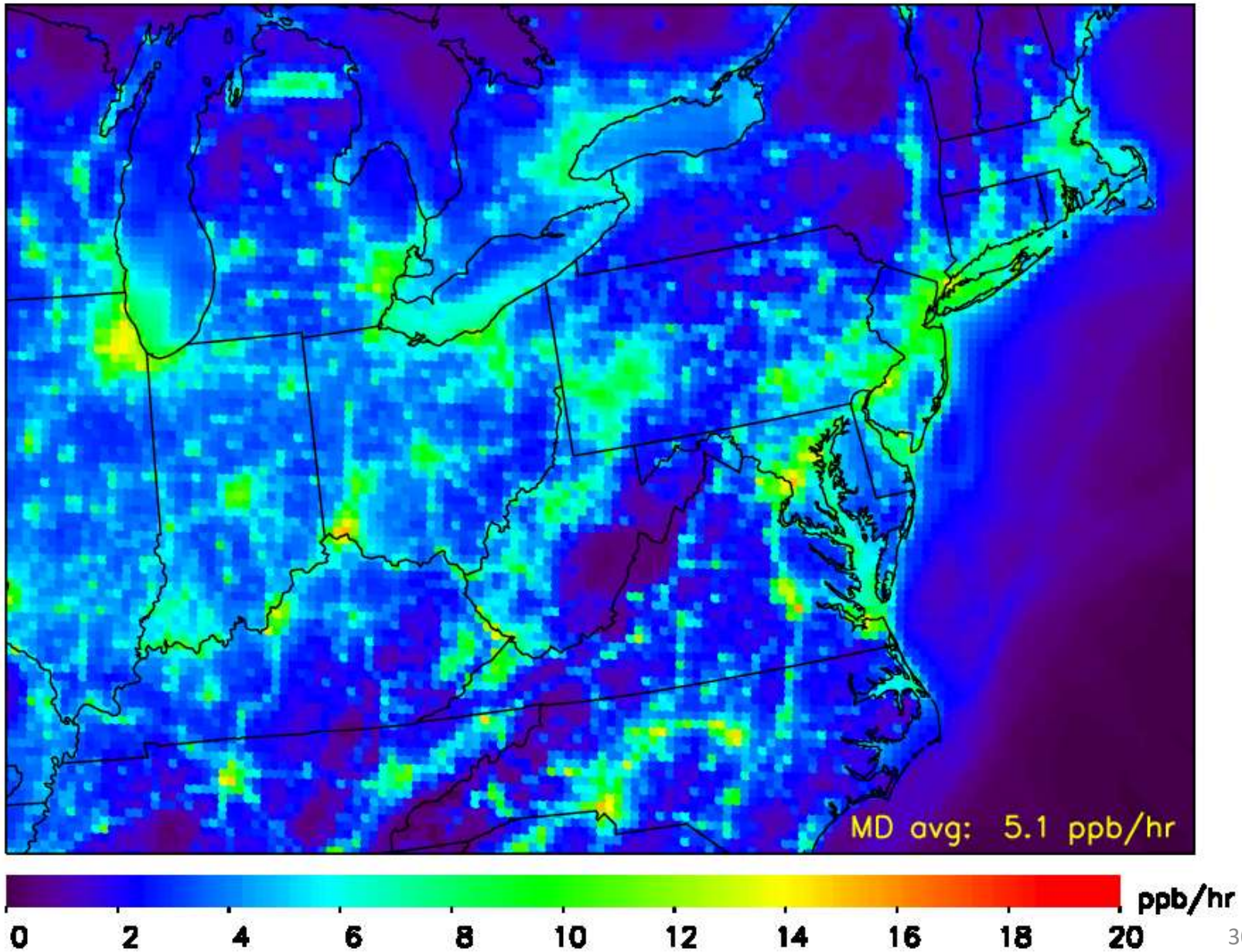
July 2002 Mean Daytime Net O_x (O_3+NO_y–NO) Production

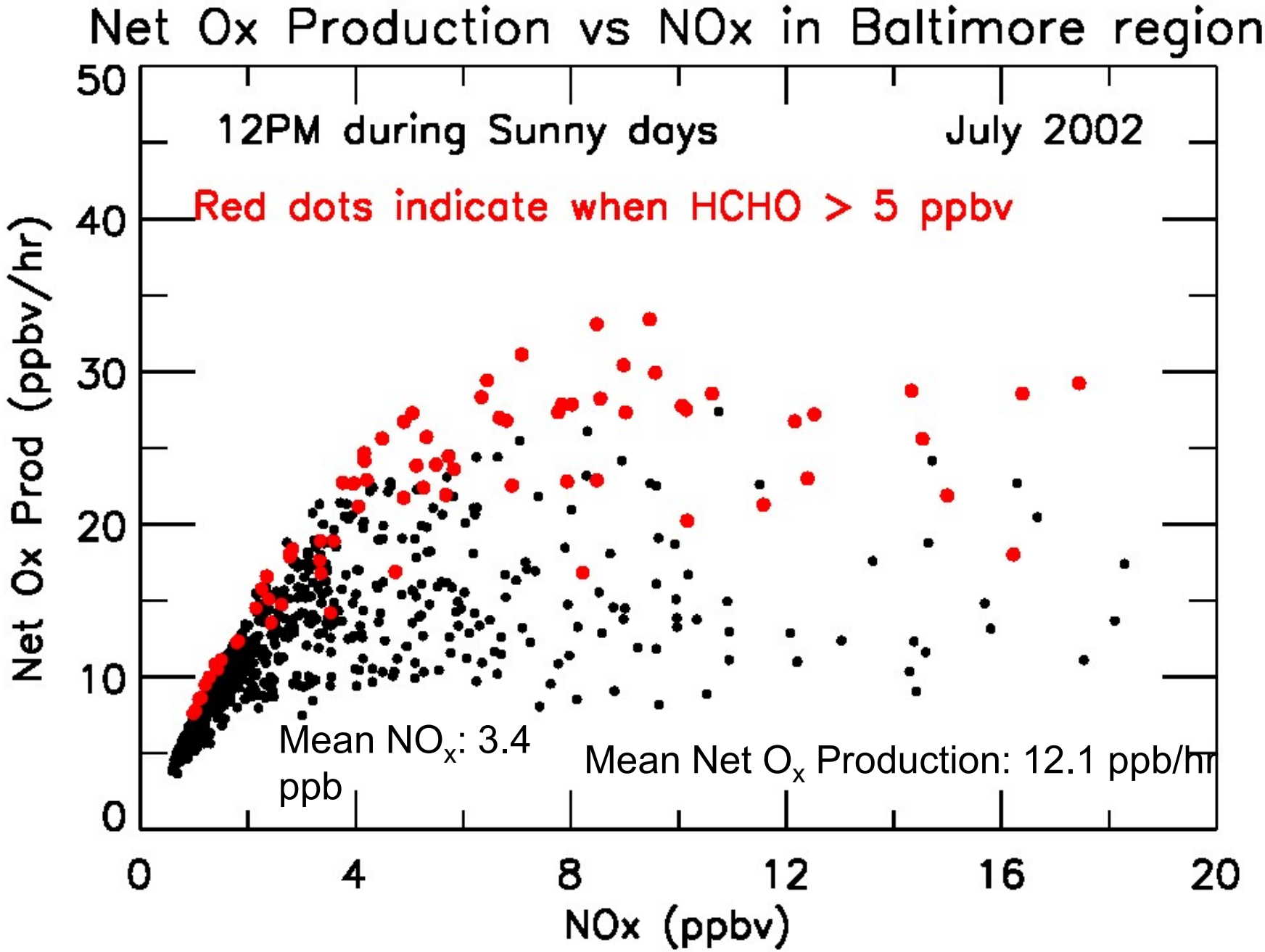


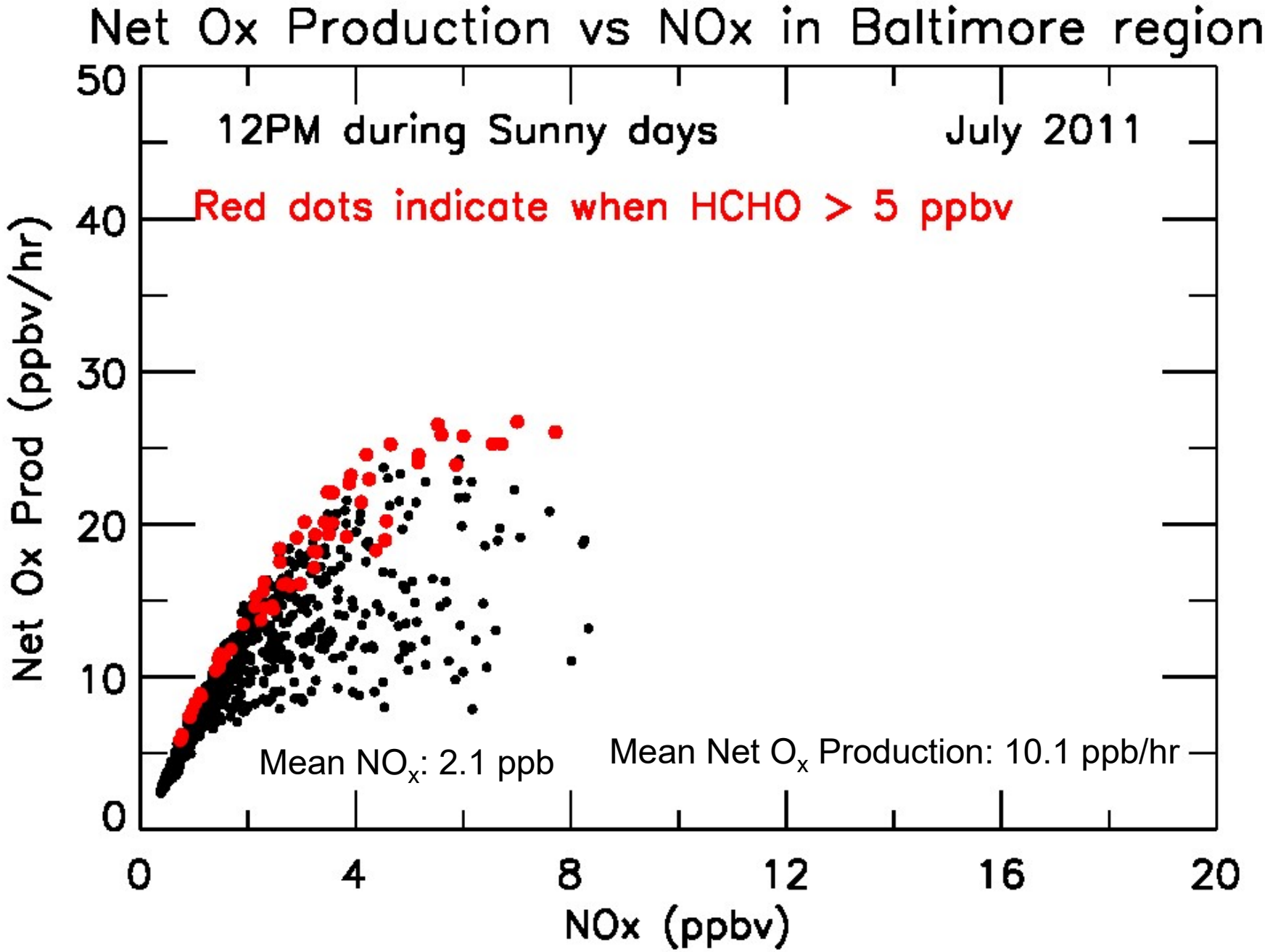
July 2011 Mean Daytime Net O_x (O_3+NO_y–NO) Production

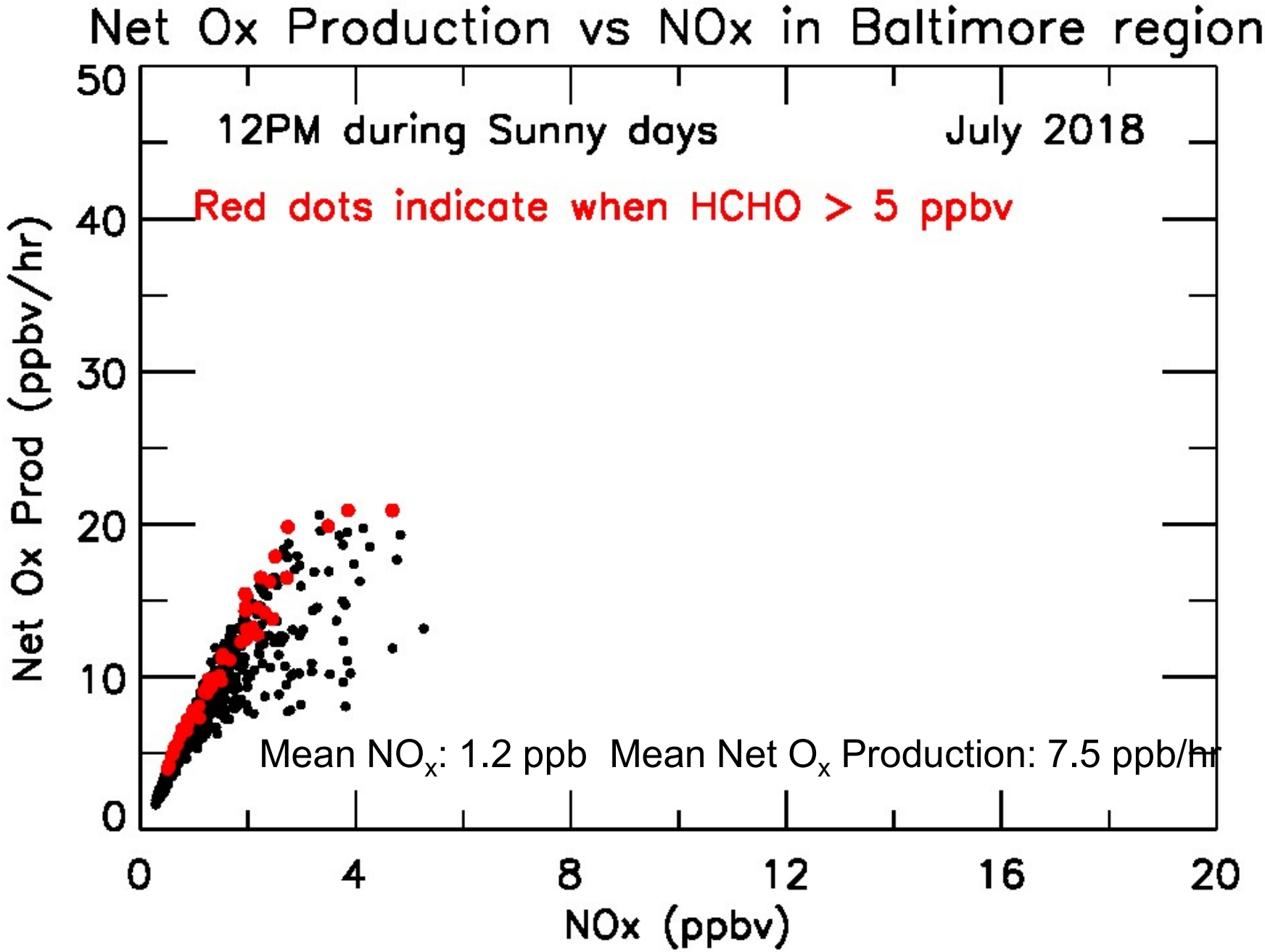


July 2018 Mean Daytime Net O_x (O_3+NO_y–NO) Production




Net Ox Production vs NOx in Baltimore region
12PM during Sunny days
July 2002
Red dots indicate when HCHO > 5 ppbv
Net Ox Prod (ppbv/hr)
NOx (ppbv)
0
10
20
30
40
50
0
4
8
12
16
20
Mean NOx: 3.4 ppb
Mean Net Ox Production: 12.1 ppb/hr

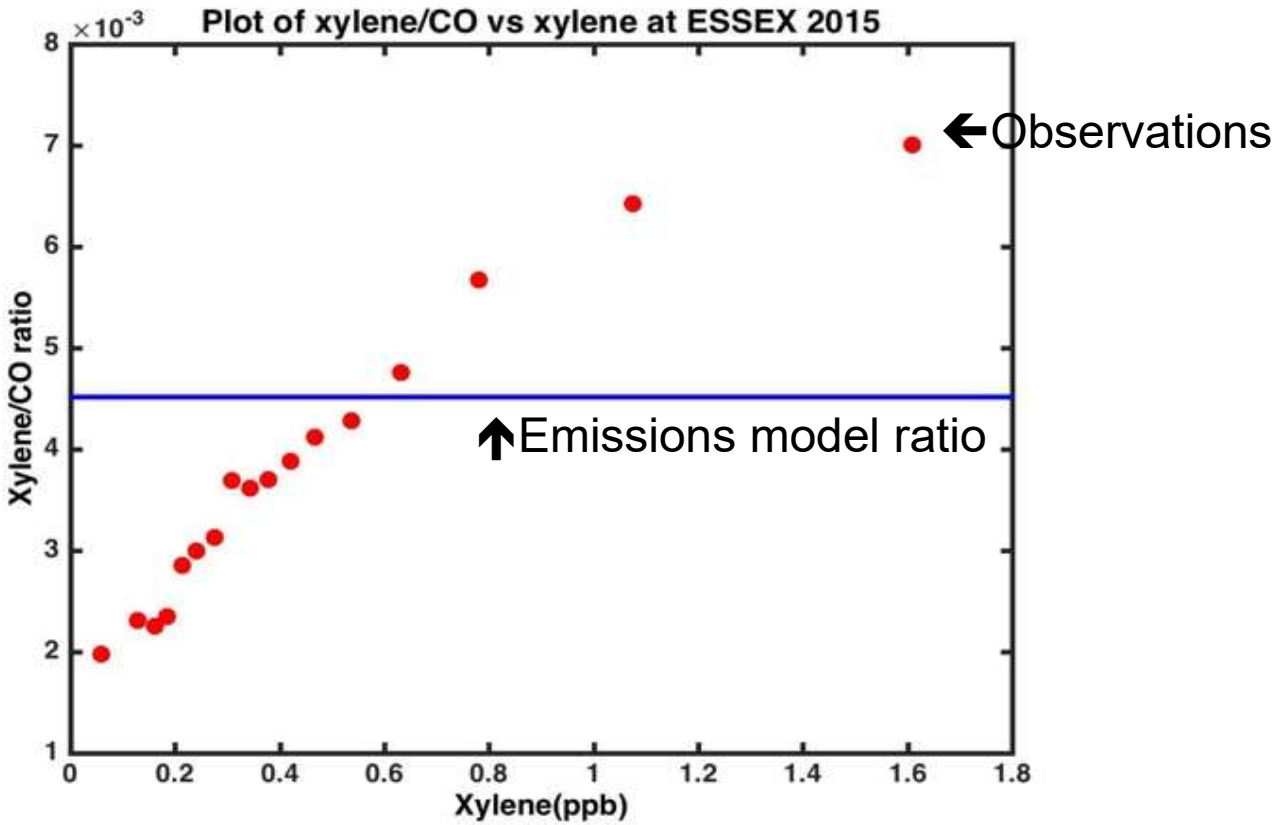

Net Ox Production vs NOx in Baltimore region
12PM during Sunny days
July 2011
Red dots indicate when HCHO > 5 ppbv
Mean NO_x: 2.1 ppb
Mean Net O_x Production: 10.1 ppb/hr
Net Ox Prod (ppbv/hr)
NOx (ppbv)
0
10
20
30
40
50
0
4
8
12
16
20


Net Ox Production vs NOx in Baltimore region
12PM during Sunny days
July 2018
Red dots indicate when HCHO > 5 ppbv
Net Ox Prod (ppbv/hr)
NOx (ppbv)
0
10
20
30
40
50
0
4
8
12
16
20
Mean NOx: 1.2 ppb Mean Net Ox Production: 7.5 ppb/hr

Summary

- Between 2002 and 2011, NO_x falls by 1.3 ppb; net O_3 production rate decreases by 2.0 ppb/hr.
- Between 2011 and 2018, NO_x falls by 0.9 ppb; net O_3 production rate decreases by 2.6 ppb/hr.
- Bigger bang for our buck as we continue to reduce NOx emissions

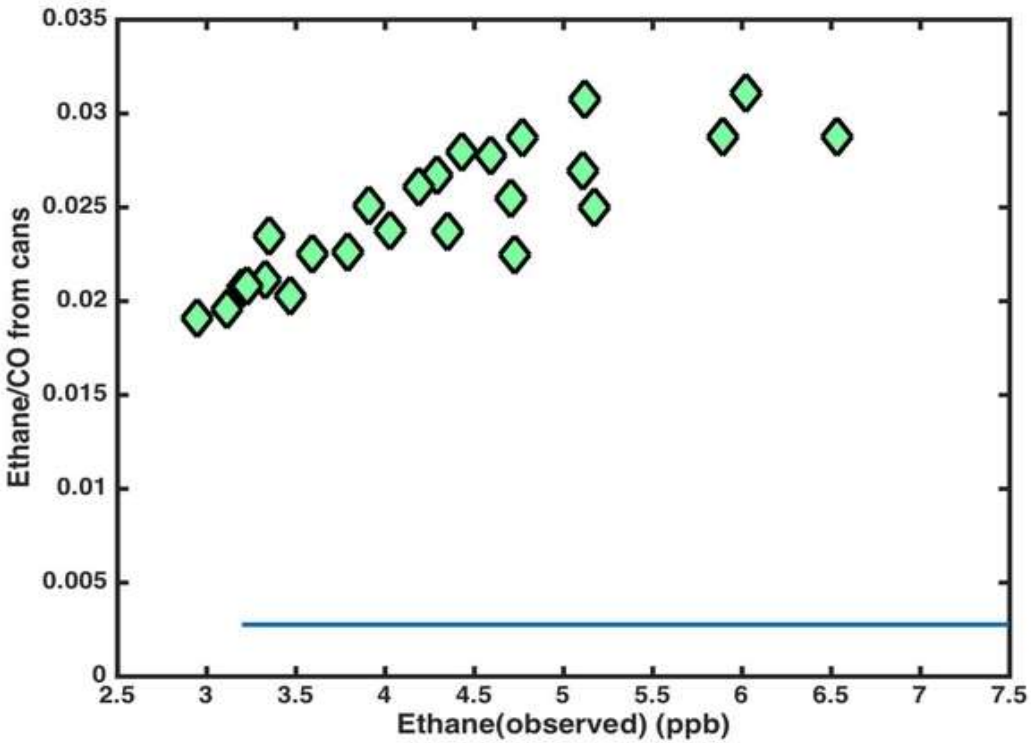
New Work:
Evaluation of emissions of "Xylenes"
Using VOC's and CO observed at Essex, MD
X/CO ratio should approach emissions ratio at high X/CO.
Emissions apparently underestimated.



Same Analysis for ethane.

Using obs from Cessna in Balt/Wash PBL.

Concentrations (Emissions) underestimated by factor of ten.



Calculated ozone is right, but in

$NO + HO_2 (RO_2) \rightarrow NO_2 + OH (OR)$

In CAMx and CMAQ, apparently NO too high and RO_2 too low.

Next step PAN.

Conclusions

- NOx reservoirs needed to be better simulated – the CB6r2 mechanisms is a big improvement over CB05.
- NOx emissions are apparently overestimated.
- VOC emissions may have been (be) underestimated MEGAN and BEIS 3.61 are a big improvement.
- Looking to observations to help model get ozone right for the right reasons.

The End

Fear the Turtle!

Reprints can be found at http://www.atmos.umd.edu/~russ/recent_pubs.html

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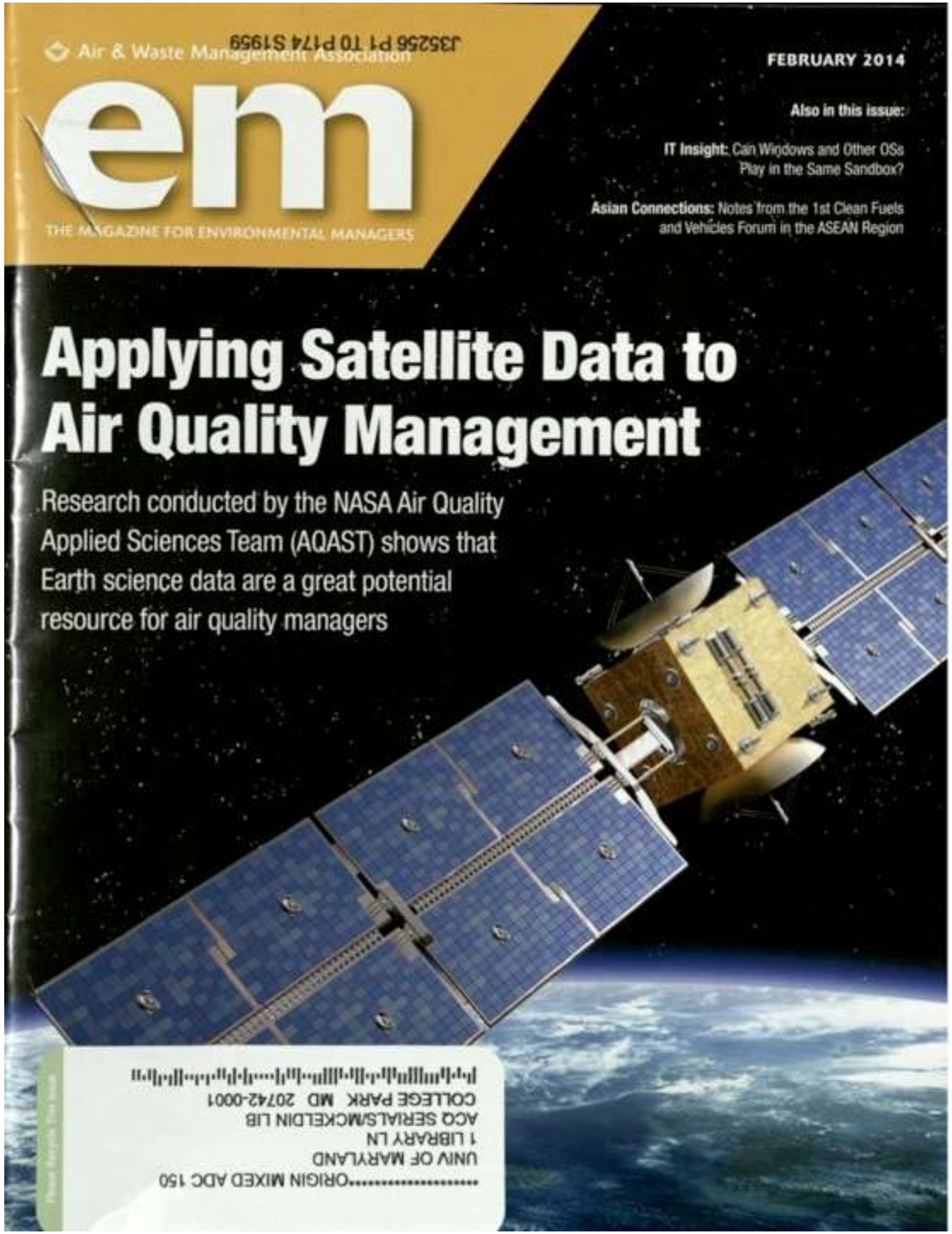
Slides for backup



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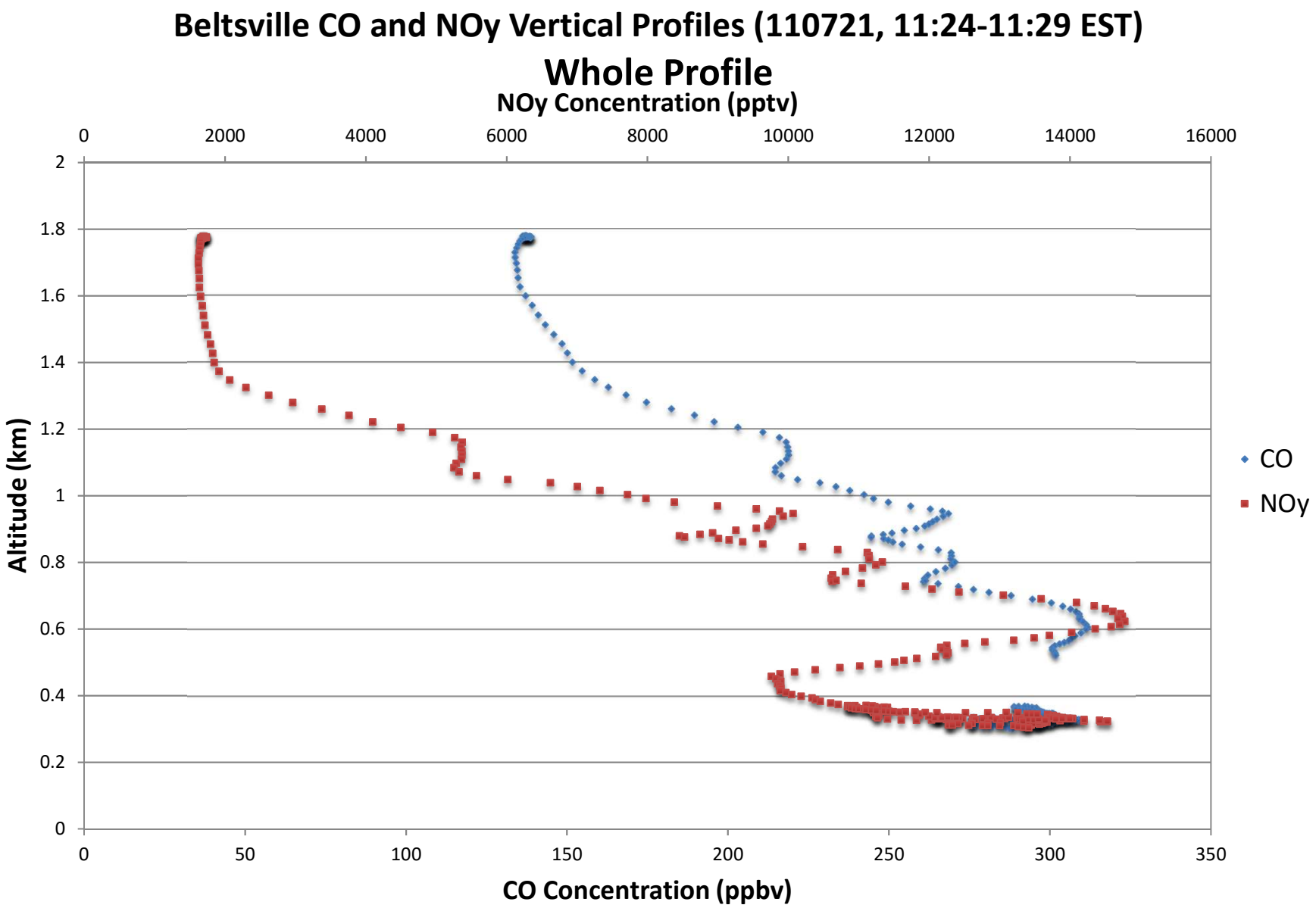
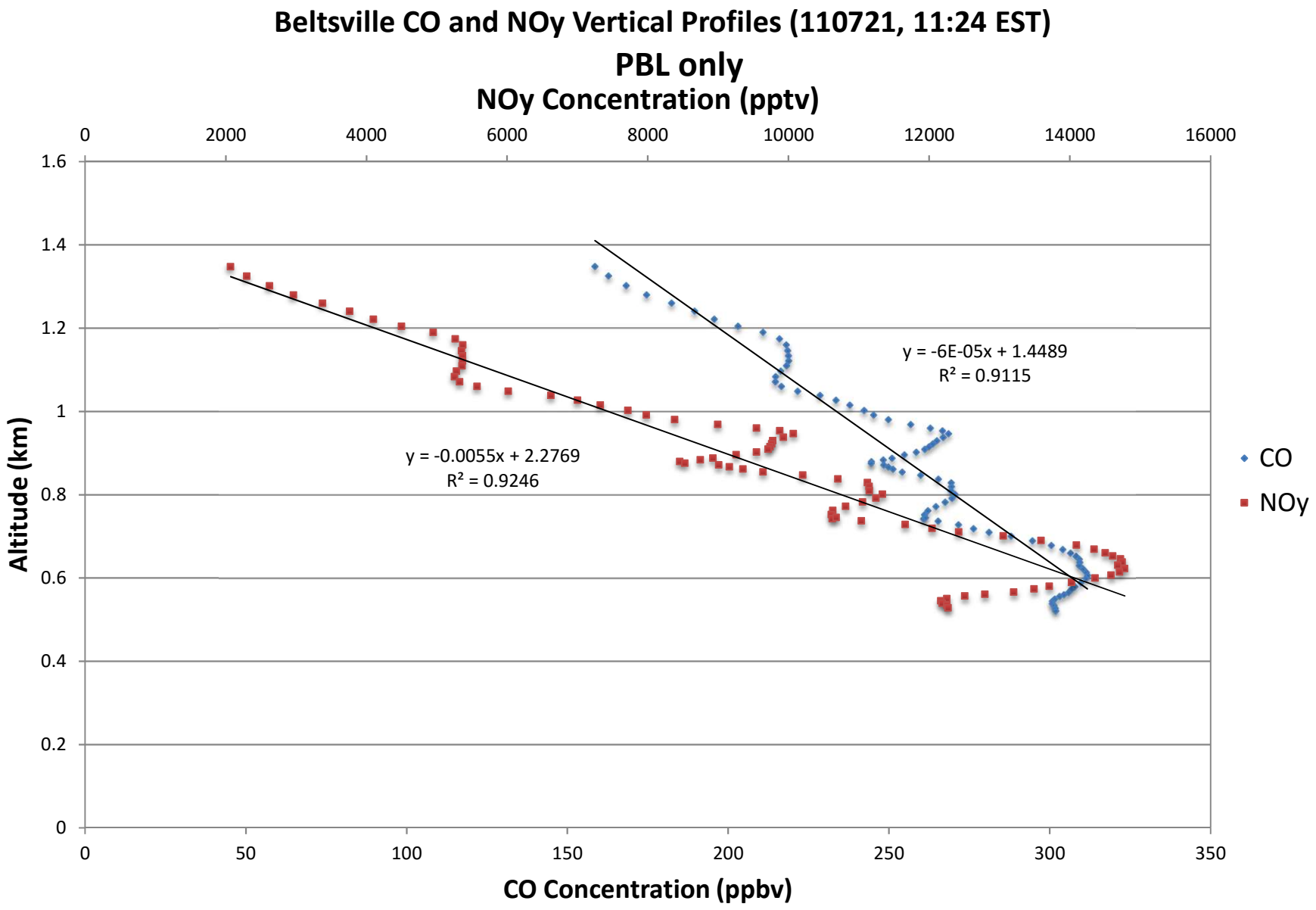
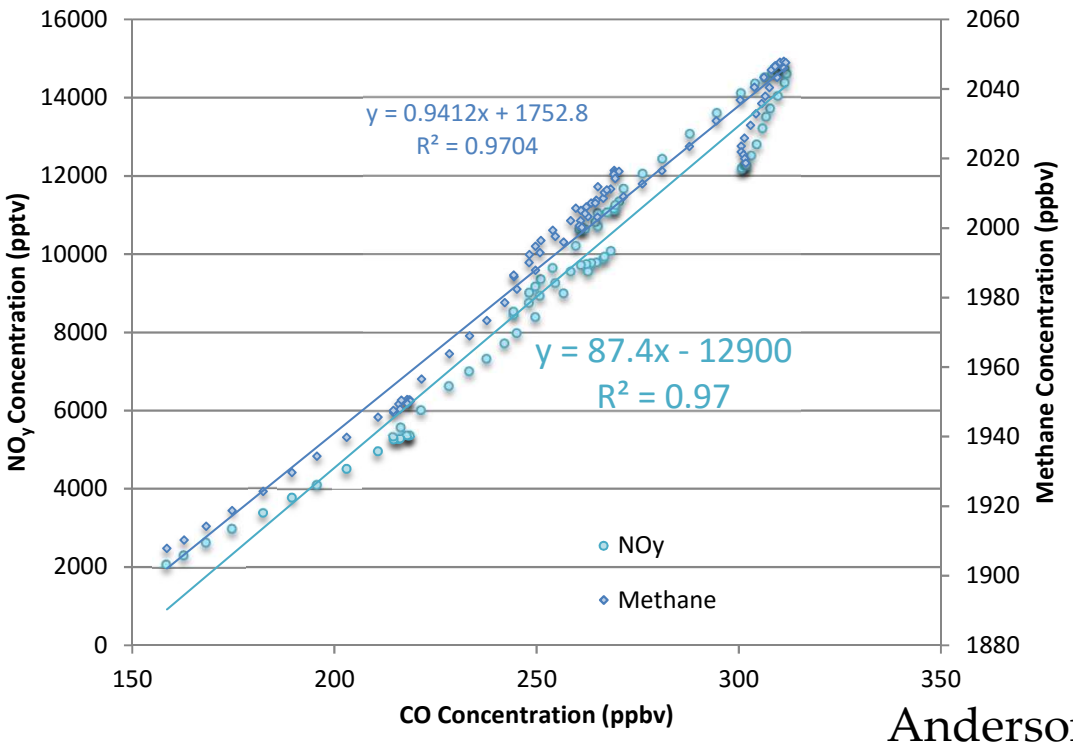
September issue of EM dedicated to DISCOVER-AQ.
Six articles

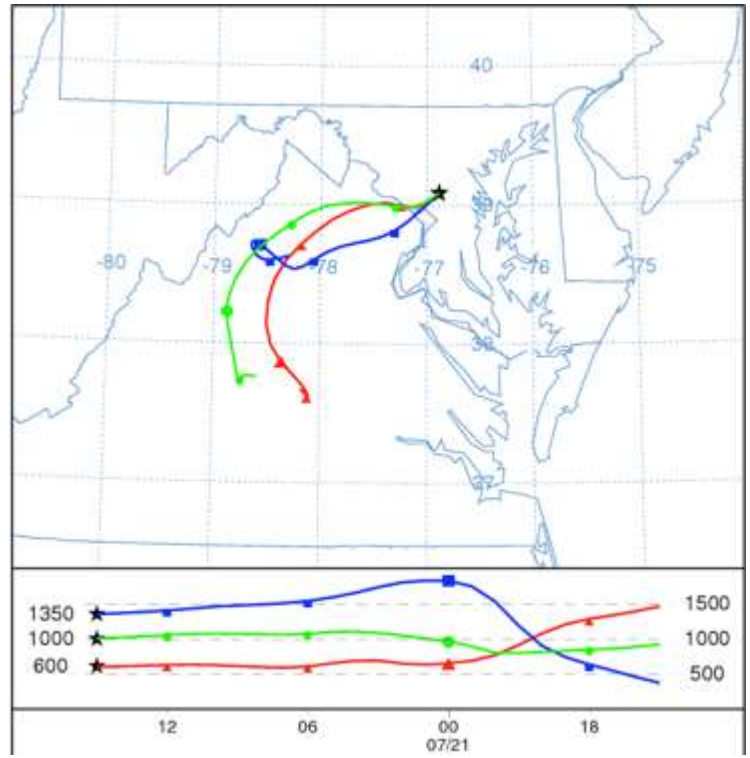

Beltsville CO and NOy Vertical Profiles (110721, 11:24-11:29 EST)
Whole Profile
NOy Concentration (pptv)
0
2000
4000
6000
8000
10000
12000
14000
16000
Altitude (km)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
50
100
150
200
250
300
350
CO Concentration (ppbv)
CO
NOy


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

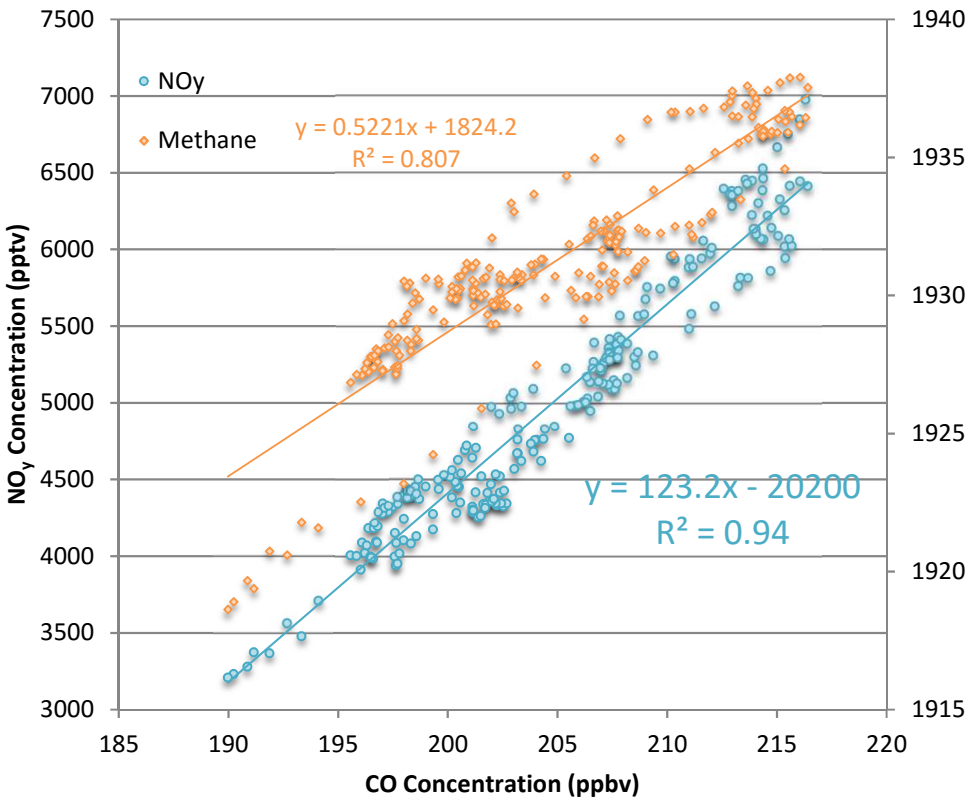


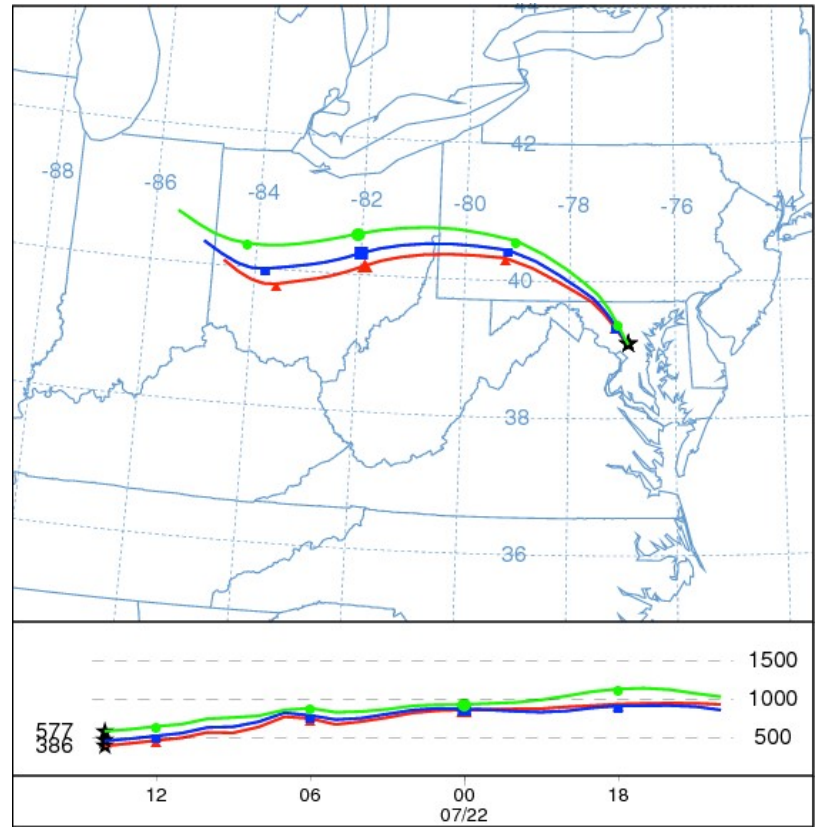


Anderson et al., Atmos. Environ., 2014.

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.

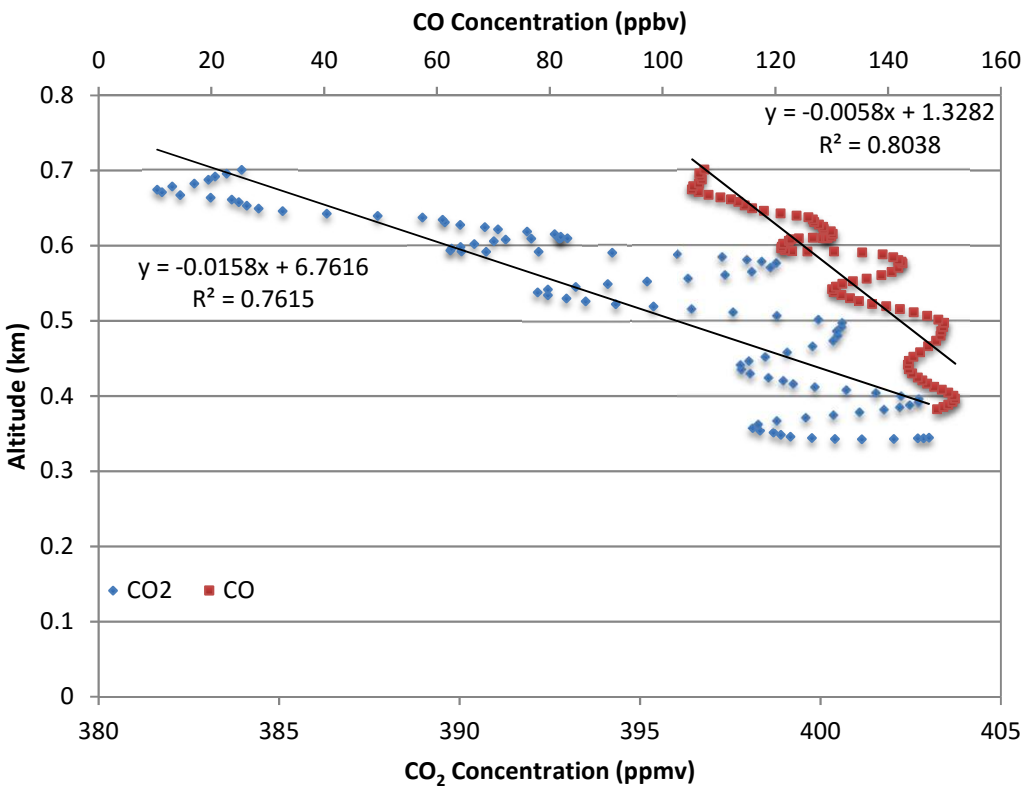


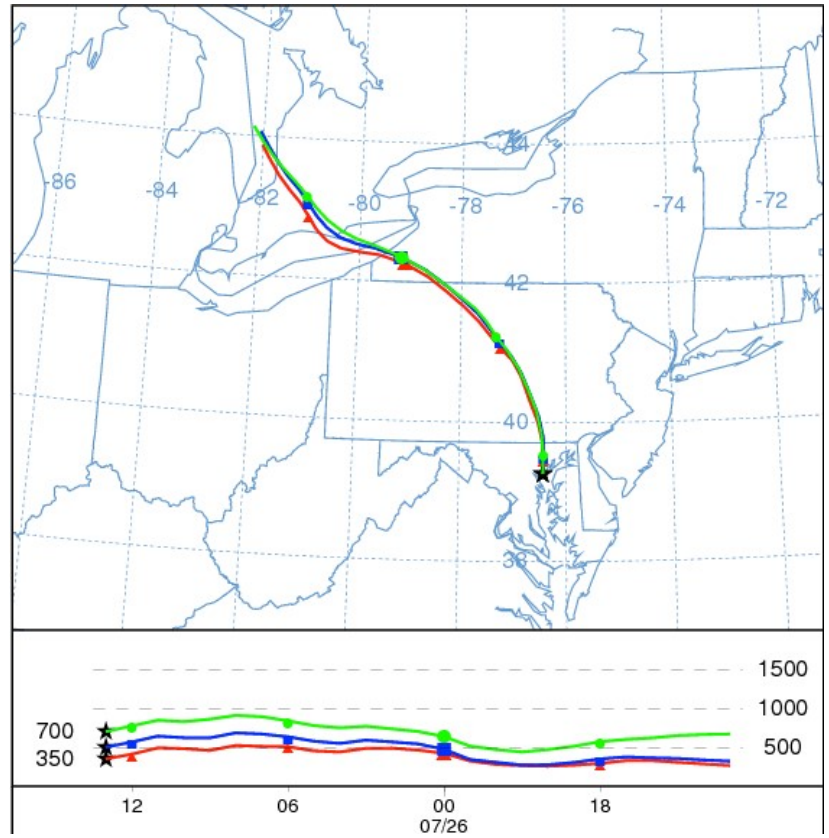


Preliminary Data. Do not cite.

Essex, 07/26, 9:13 EST

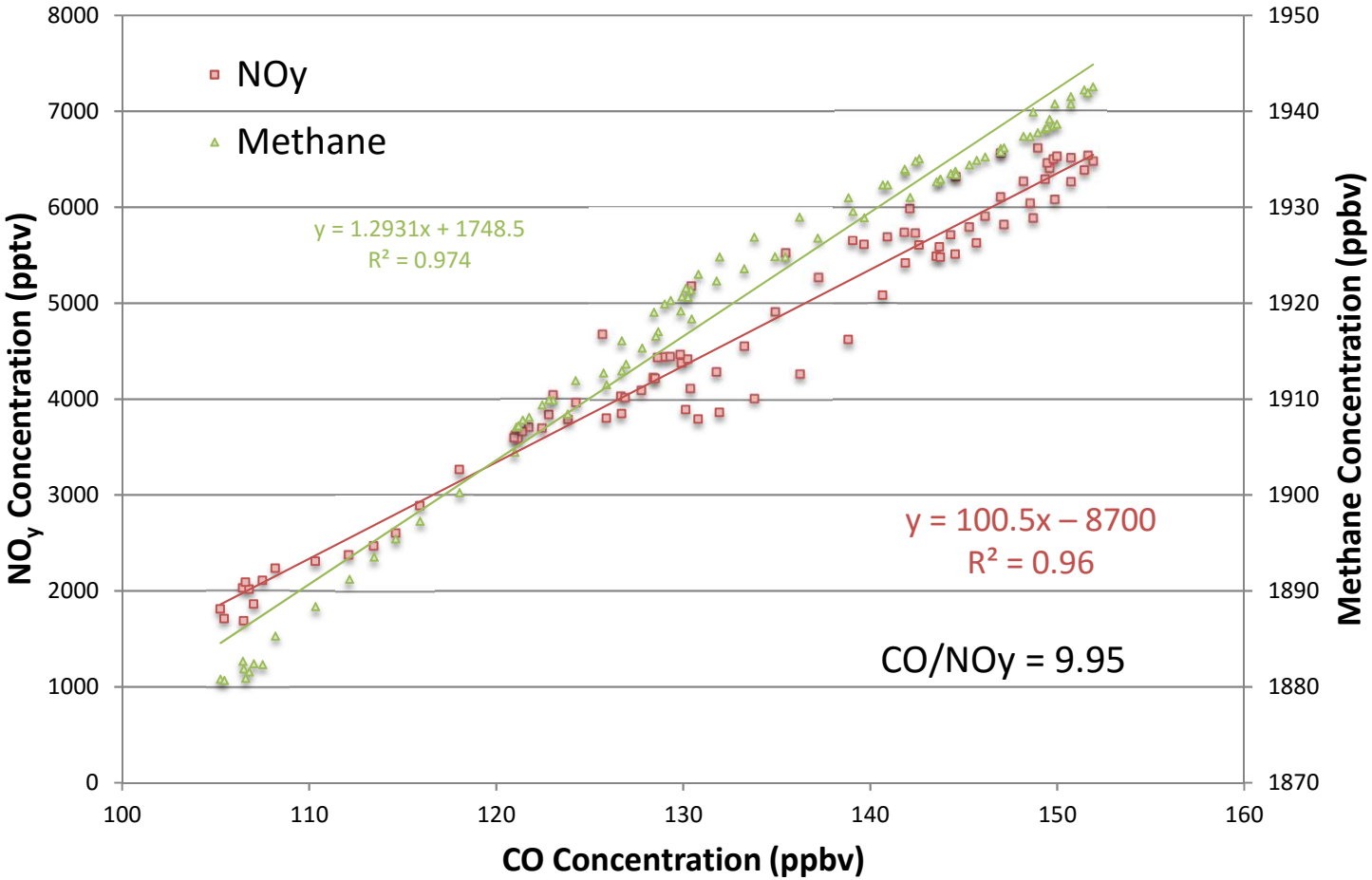
Portion of vertical profile in the mixed layer:





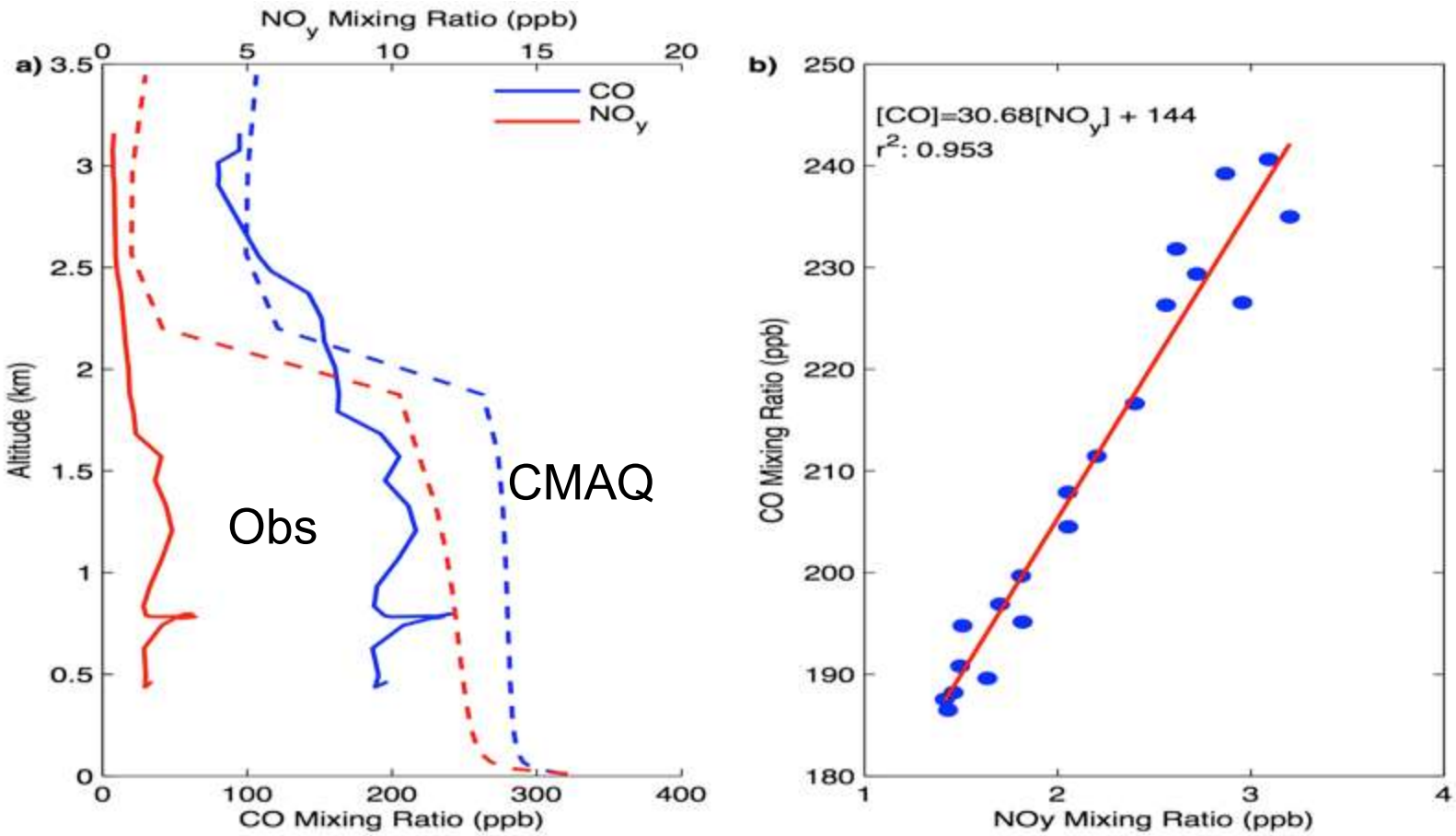
Air mass from "clean corridor" in PA. Pollution probably local.

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



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

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



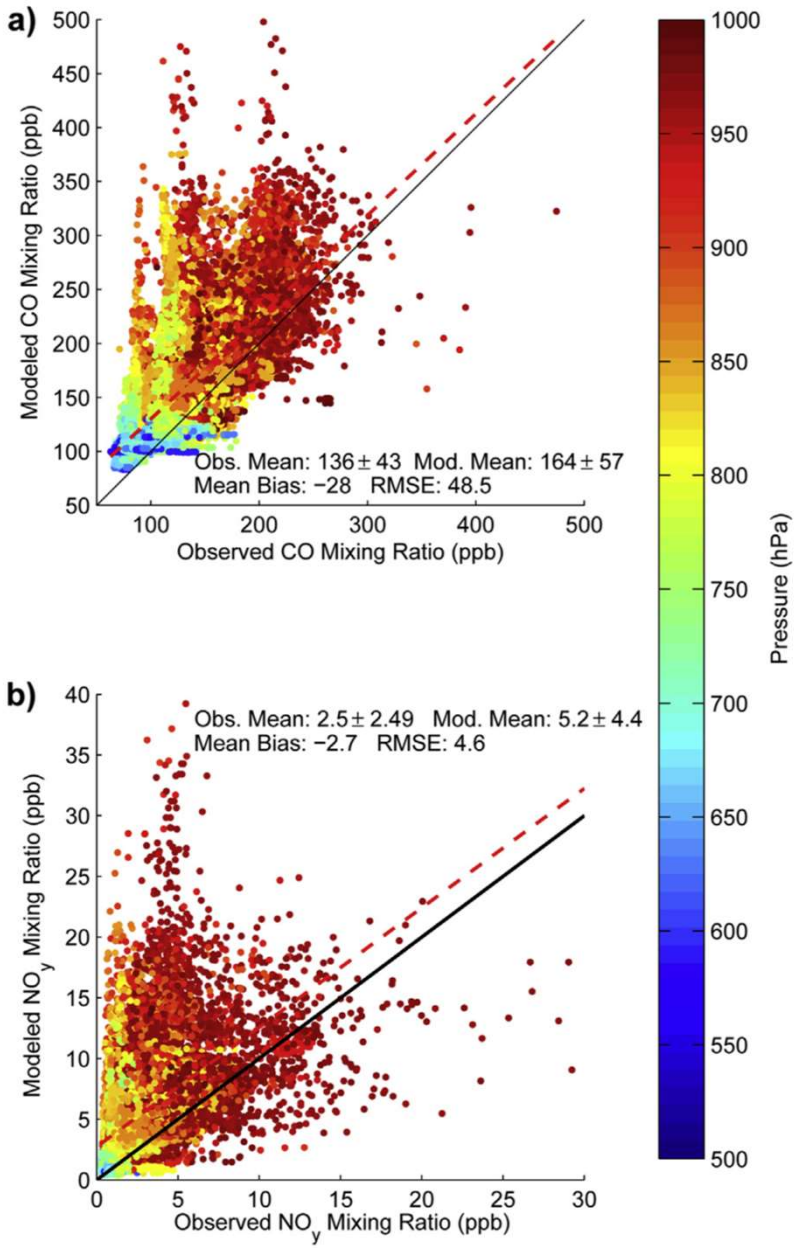
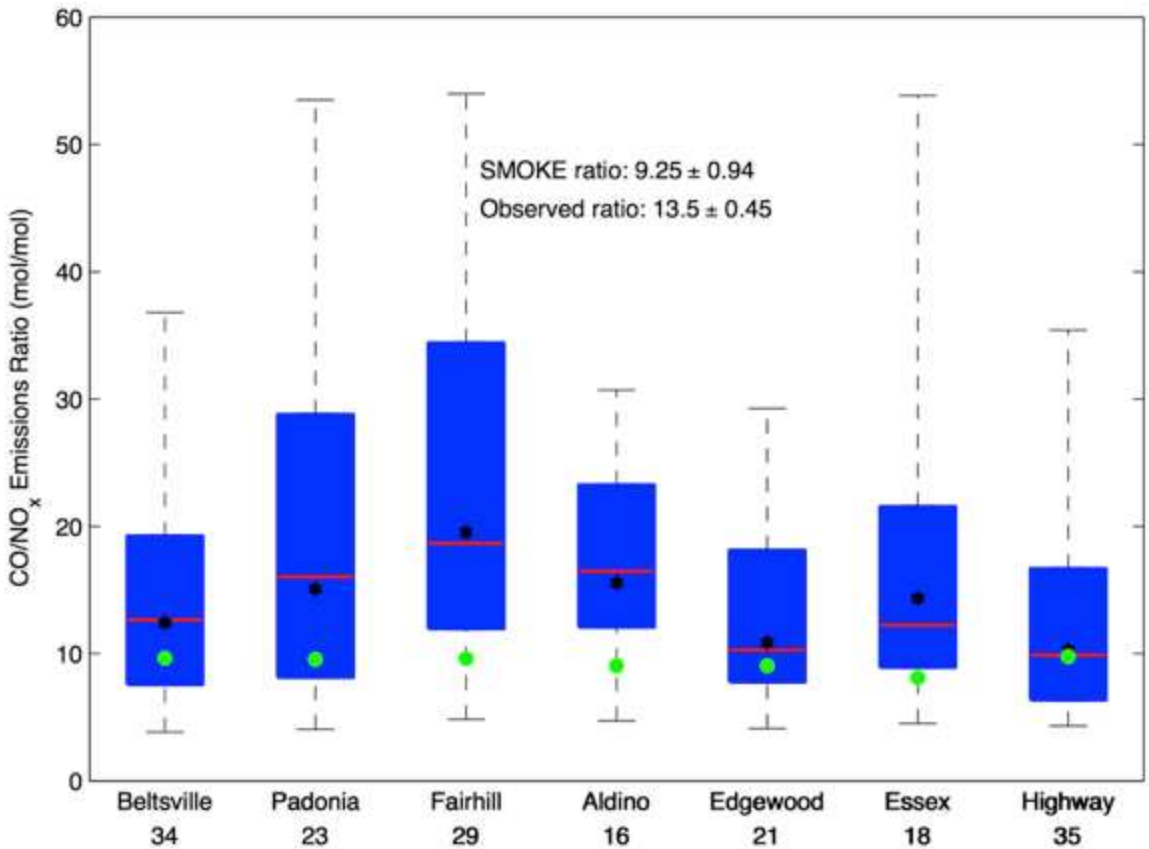


Fig. 7. a) Regression of measured and modeled CO for all flight days during DISCOVER-AQ. Values after means are 1σ. b) Same as a) but for NO_y. Solid line is the 1:1 line; dashed line, the line of best fit.

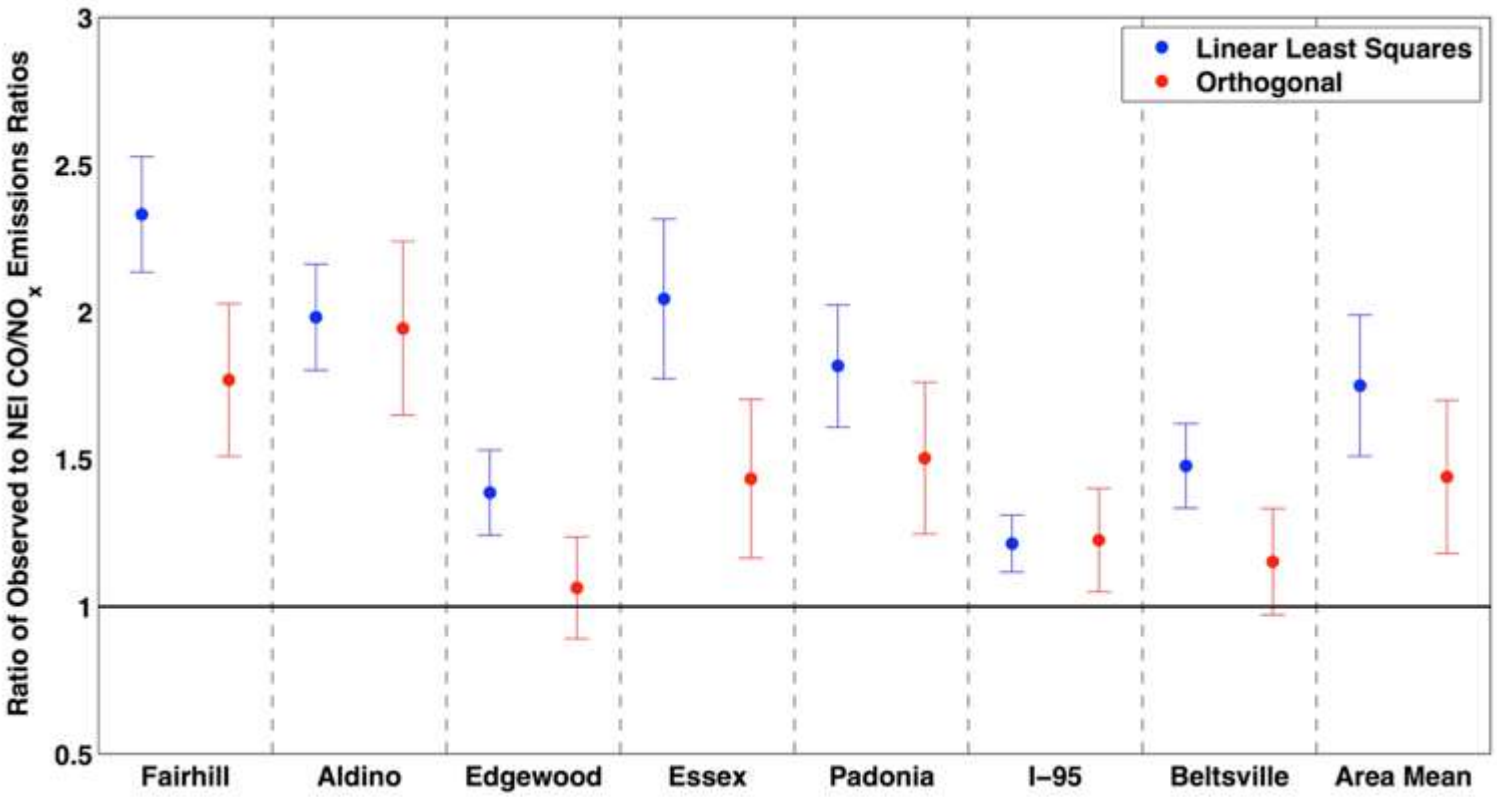
CMAQ gets CO a little high (bias = +28 out of 136 ppb) but NOy much too high (bias +2.7 out of 2.5 ppb).

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.

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).

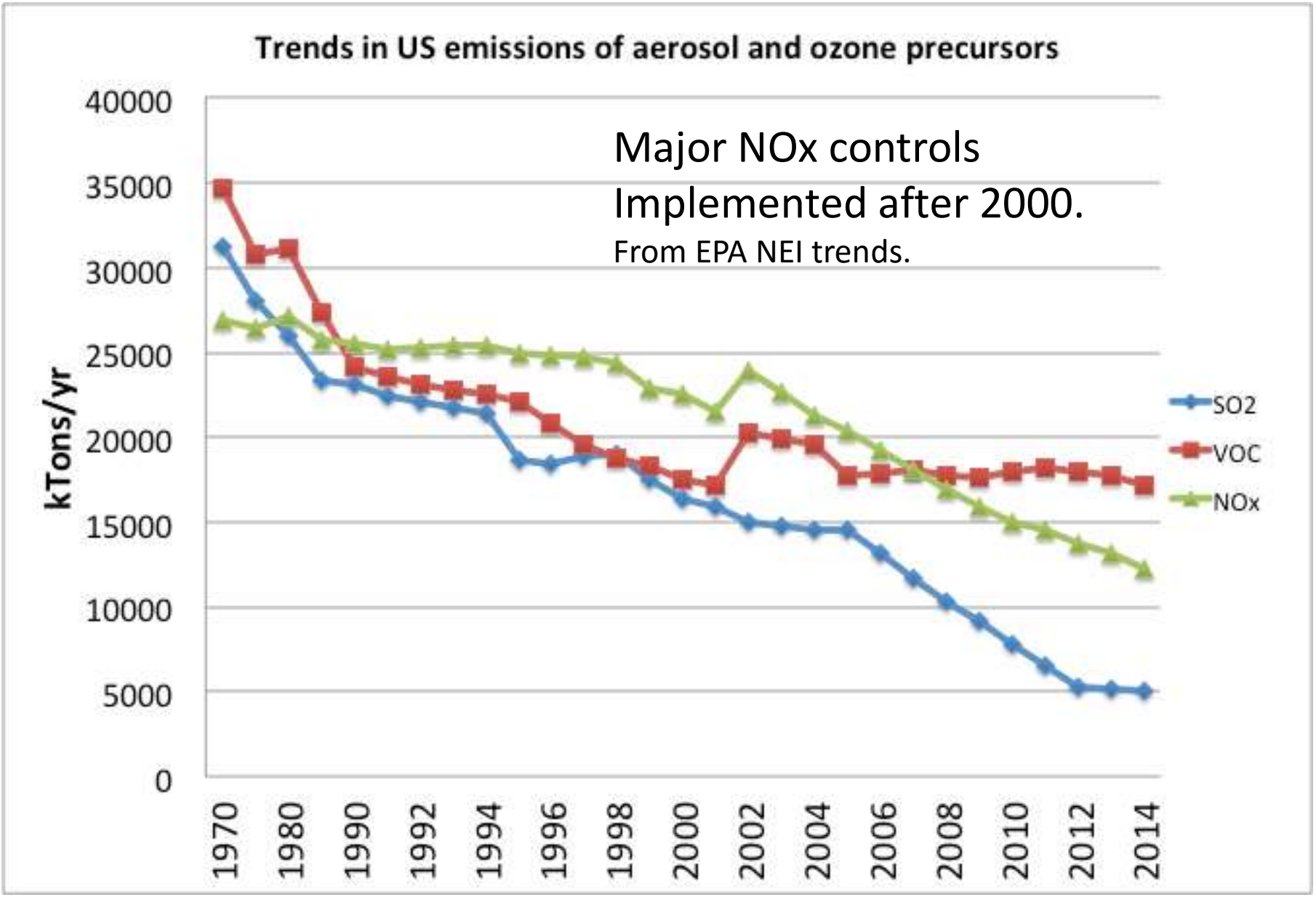
Yu, S. C., et al. (2012), Comparative evaluation of the impact of WRF-NMM and WRF-ARW meteorology on CMAQ simulations for O_3 and related species during the 2006 TexAQS/GoMACCS campaign, *Atmospheric Pollution Research, 3*(2), 149-162.

Interim 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!

Science-Policy questions.

- Did reported emissions go down?
- Did atmospheric concentrations respond?
- Did surface deposition respond?


Trends in US emissions of aerosol and ozone precursors
Major NOx controls
Implemented after 2000.
From EPA NEI trends.
kTons/yr
40000
35000
30000
25000
20000
15000
10000
5000
0
1970
1980
1990
1992
1994
1996
1998
2000
2002
2004
2006
2008
2010
2012
2014
SO2
VOC
NOx

Work in progress:
An experiment of opportunity: SO_2

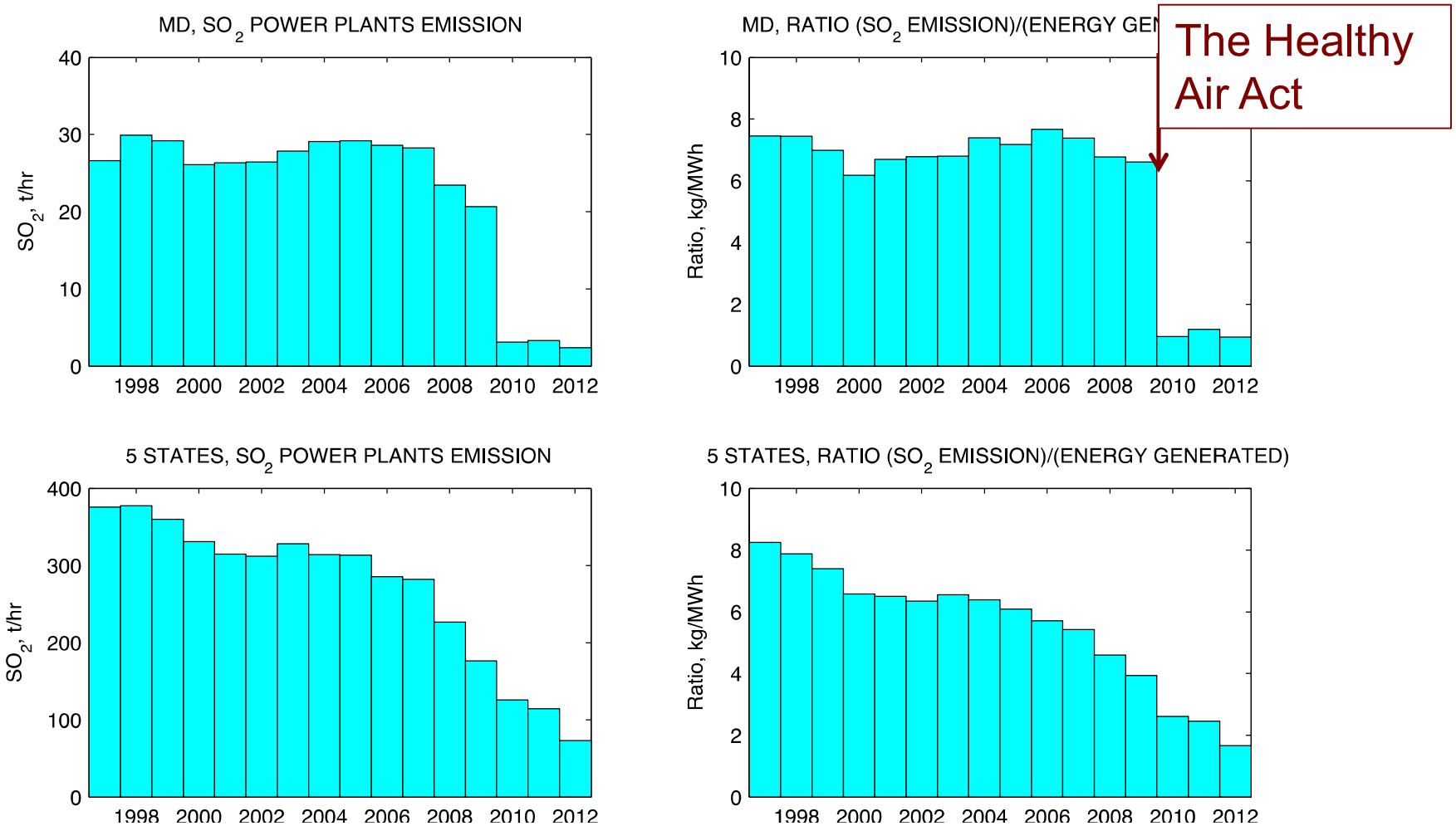
In 2010, Maryland implemented the

"Healthy Air Act"

The Morgantown Generating Station in Newburg, MD

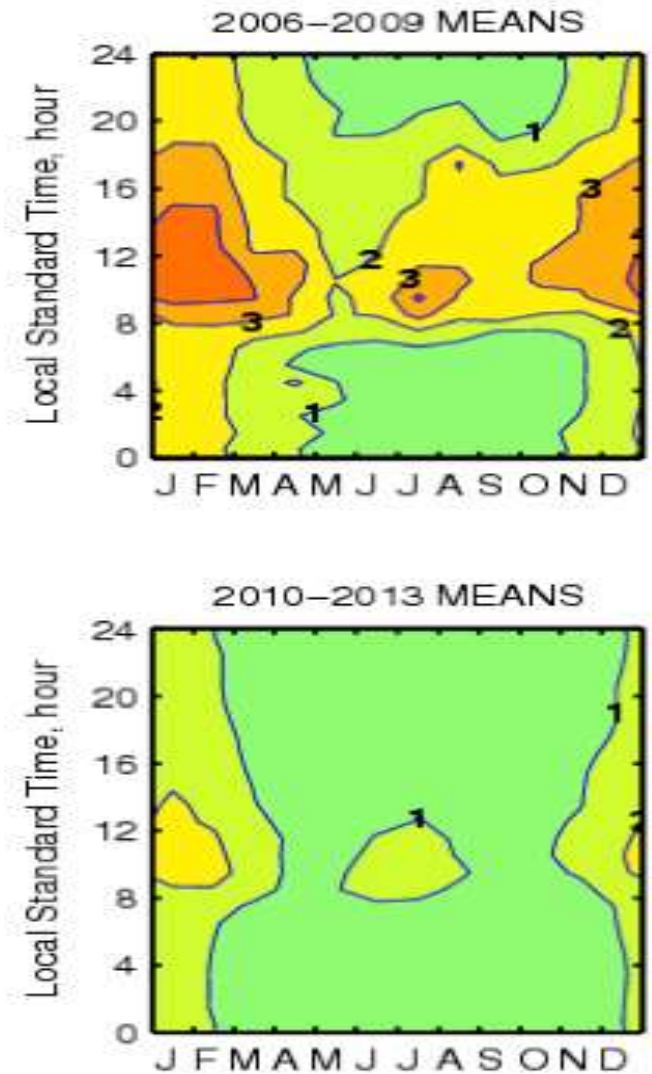
Image from NYT Oct. 1, 2015.

Power Plant Emissions in Maryland and surrounding states.



How has ambient SO_2 responded to this reduction in emissions?

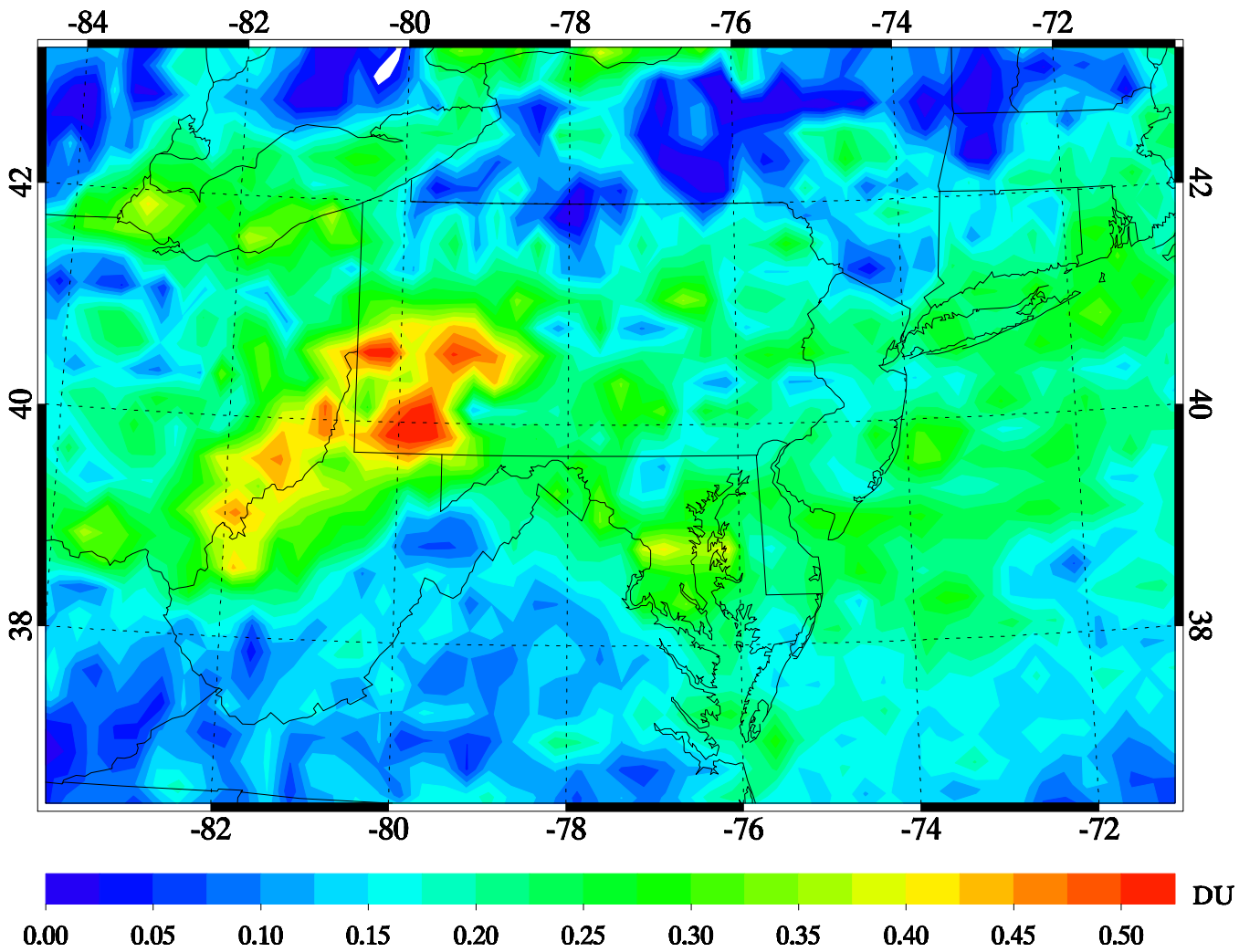
Do satellite observations agree?



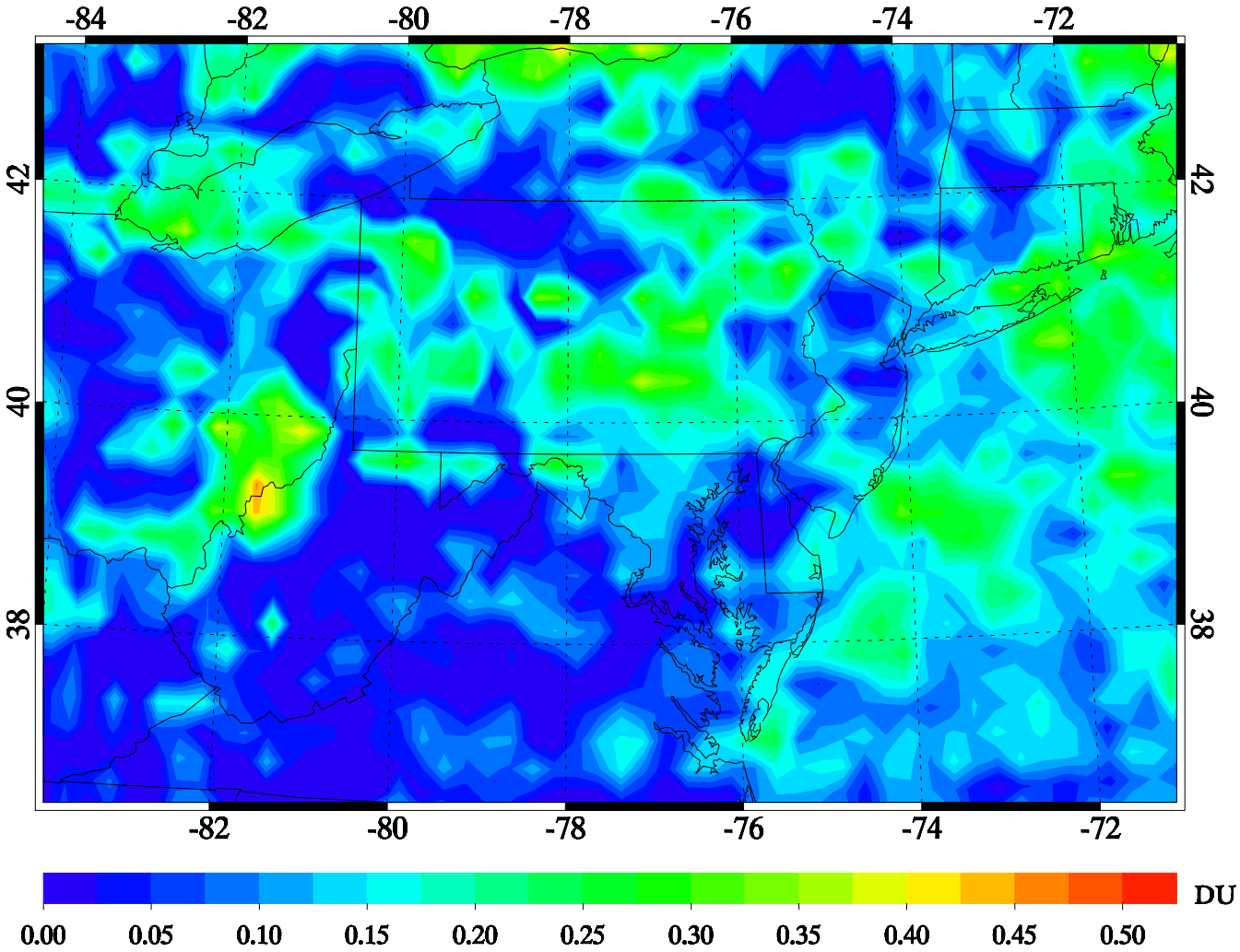
Ambient SO_2 (ppb) at Beltsville, MD

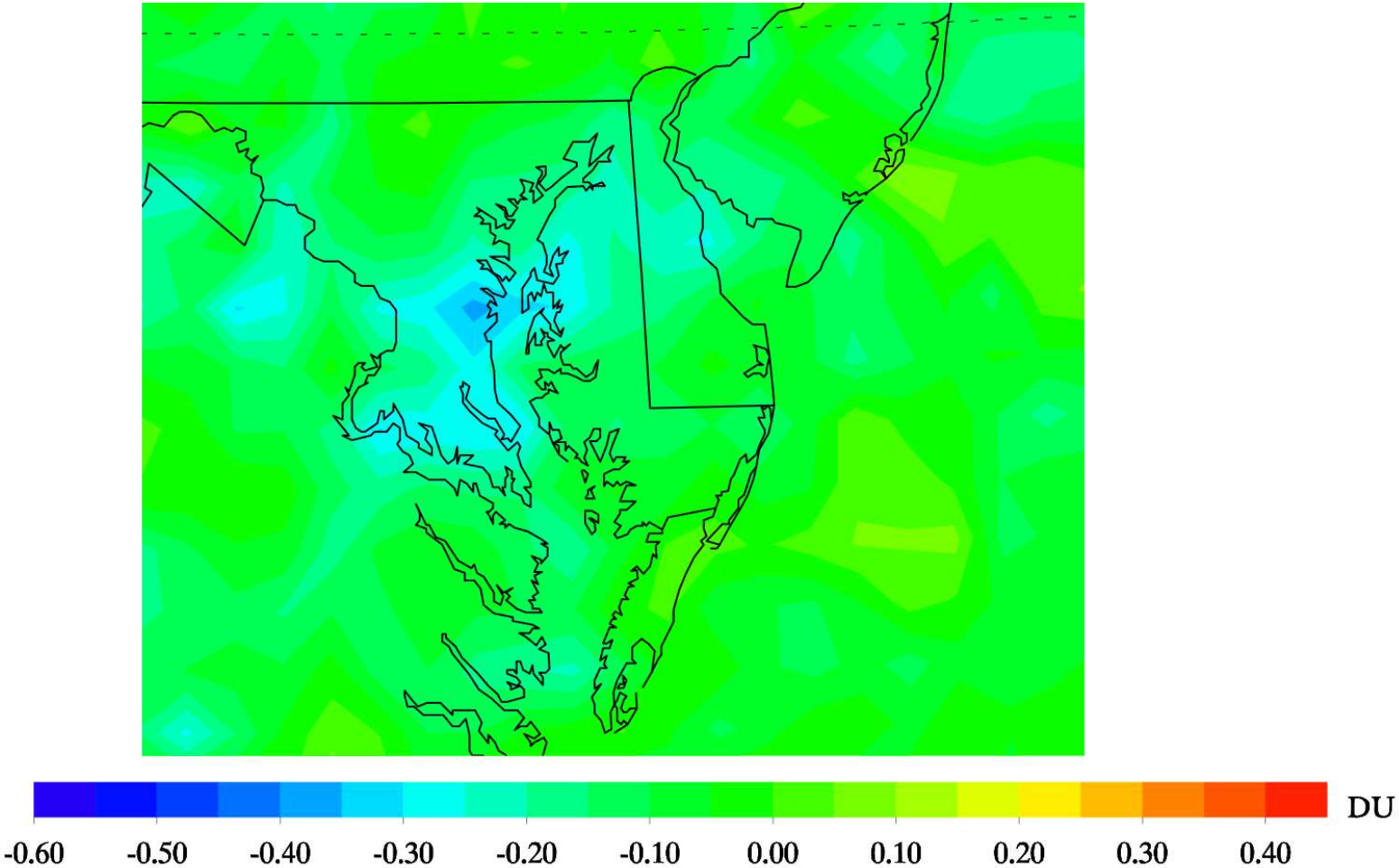
- Daily cycle ~factor of two.
- Seasonal cycle ~factor of two.
- Dramatic decreases after Healthy Air Act.
- Maxima in mid day when PBL entrains plumes from aloft.
- Surface SO_2 reflects emissions reductions.

OMI SO_2 2005-09



OMI SO_2 2010-12

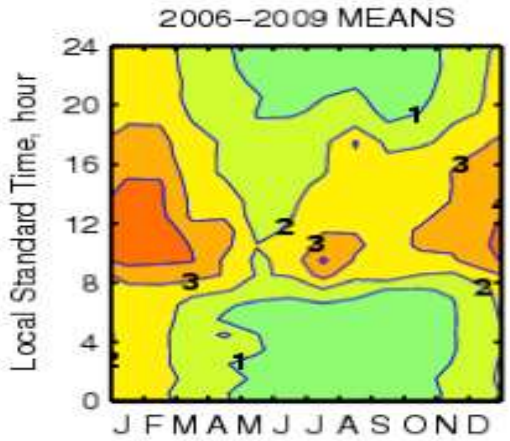


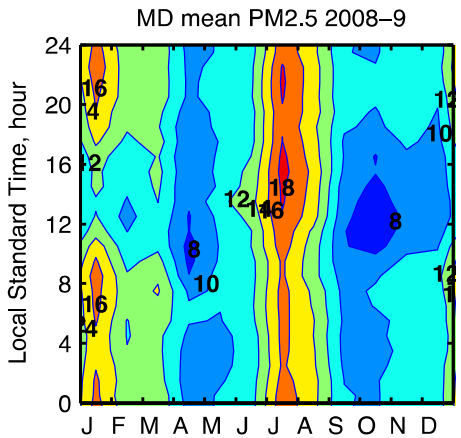


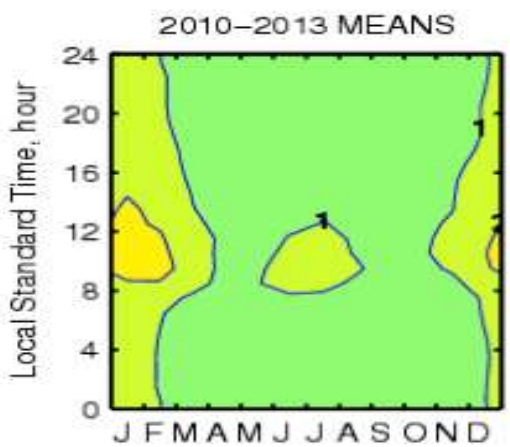
Observed <u>changes</u> (2005-09 minus 2010-12) in column SO_2 from NASA's OMI instrument on the AURA satellite. Thanks to Nick Krotkov and Can Li NASA/GSFC.

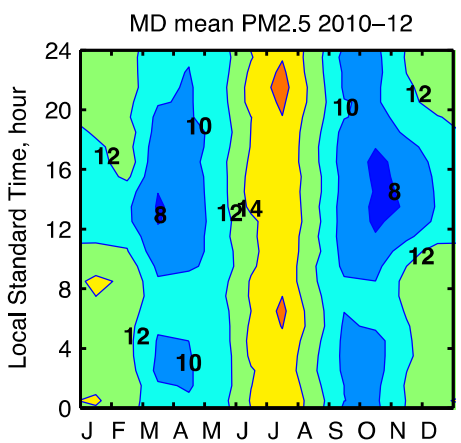
Ambient SO_2 responded to this reduction in emissions.

Did PM2.5 respond?







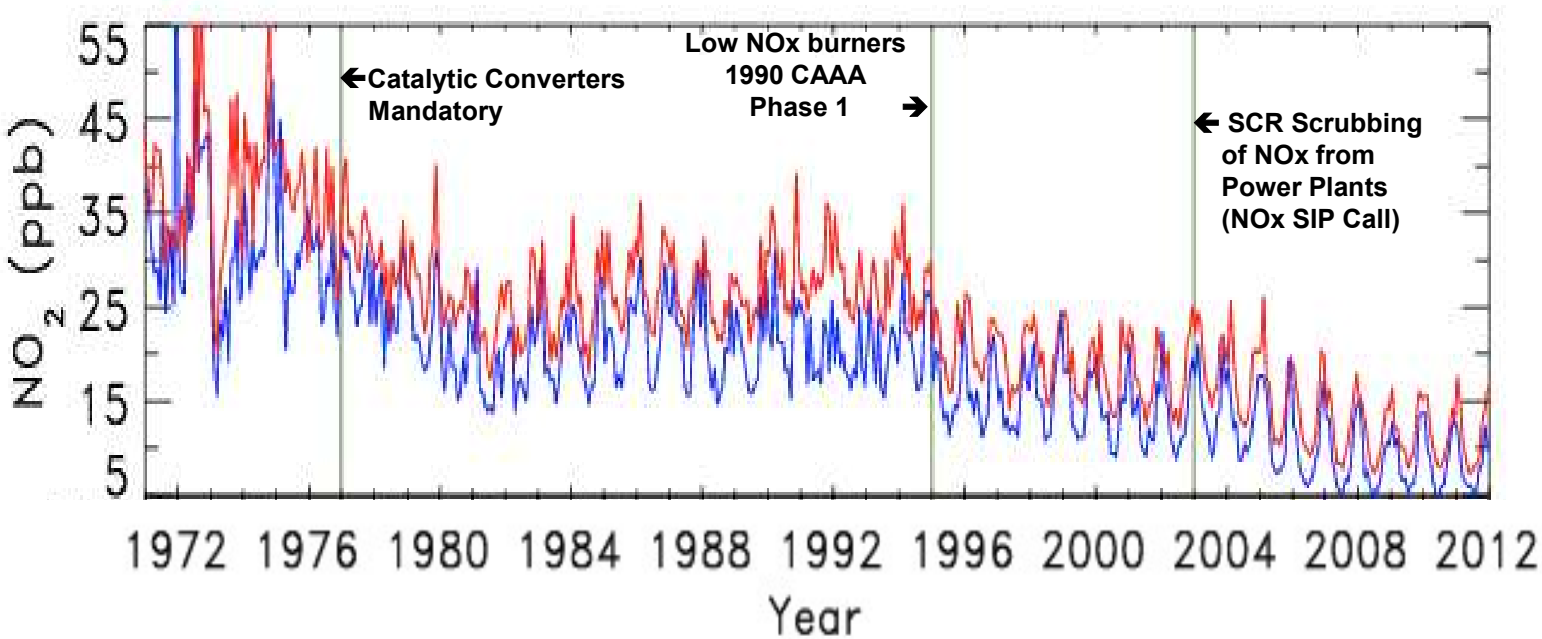


Local actions have less impact on longer-lived species

Trend Analysis

Tracking NO_X Reductions and Ozone Improvements

Ambient NO_2 concentration trends: DC, MD, VA



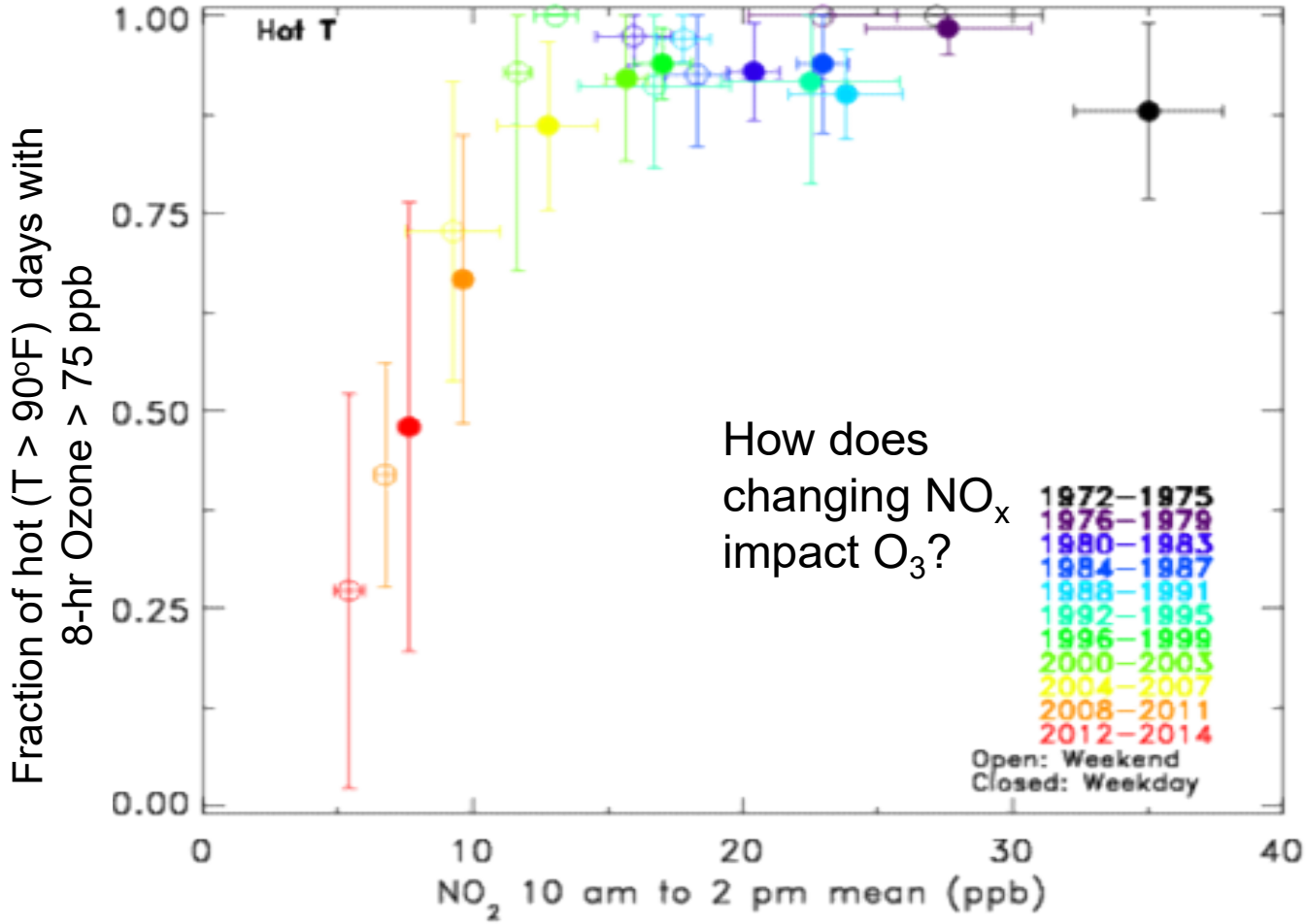
Red - Weekdays

Blue - Weekends

From Hosley, Salawitch, Canty, et al. in preparation, 2012; Preliminary Data. Do not cite!

As measured NO_x levels have gone down …

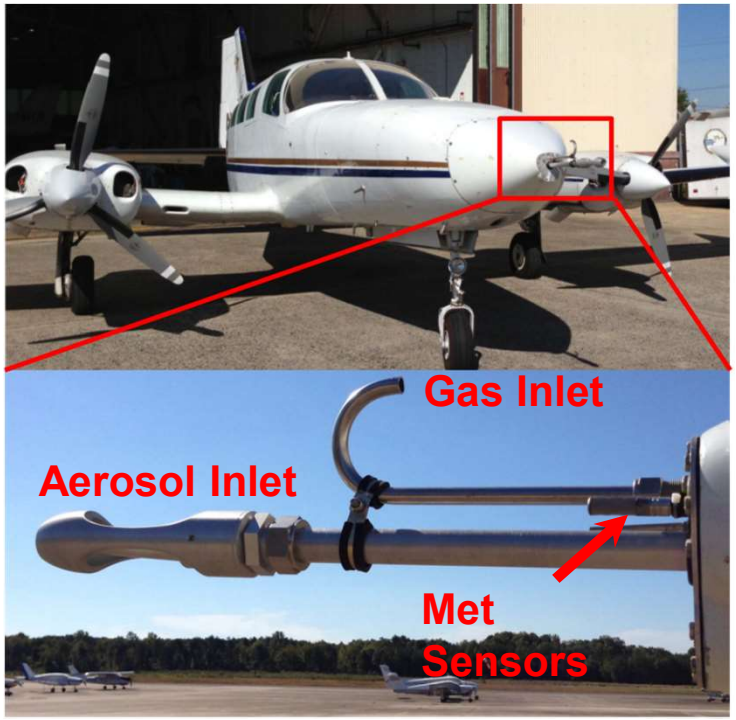
… *So have ambient ozone levels*



Observations show:
NOx reductions worked, but response is nonlinear;
we had to get over the hump.

From Goldberg, et al. submitted, 2015; Preliminary Data. Do not cite!

UMD Cessna 402B Research Aircraft



GPS Position (Lat, Long, Altitude)

Met (T, RH, P, wind speed/direction)

Trace gases:

- O_3: UV Absorption, modified TECO
- SO_2: Pulsed Fluorescence, modified TECO
- $CH_4/CO_2/CO/H_2O$: Cavity Ringdown, Picarro
- NO_2: Cavity Ring Down, Los Gatos
- NO: Chemiluminescence, modified TECO
- VOCs: whole air samples

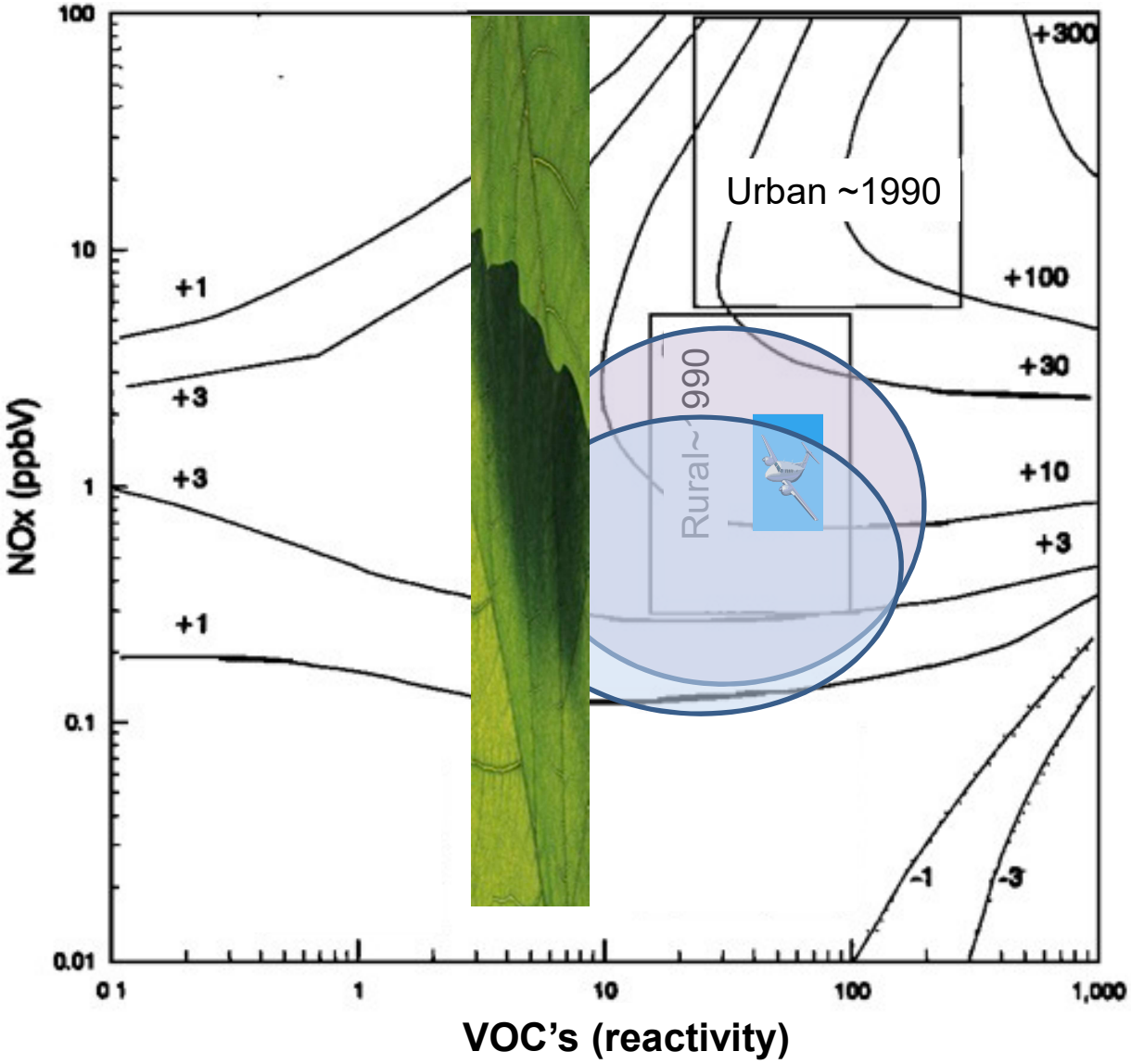
Aerosol Optical Properties:

- Scattering: b_{scat} (@450, 550, 700 nm), Nephelometer
- Absorption: b_{ap} (565 nm), PSAP

Aerosol Chemistry:

- Black Carbon: Aethalometer
- Major ions and SOA: filter samples

How fast do precursor pollutants make ozone (ppb/hr)?



Where is the Balt/Wash area? (boundary layer)

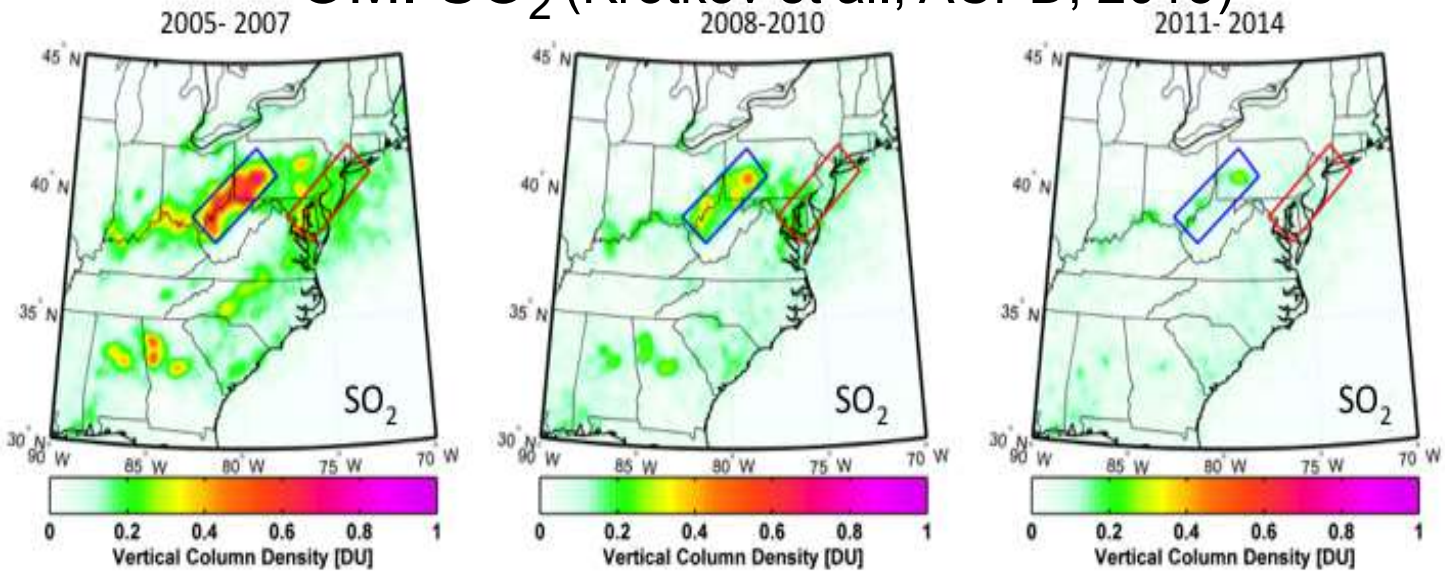
Where is Western MD?

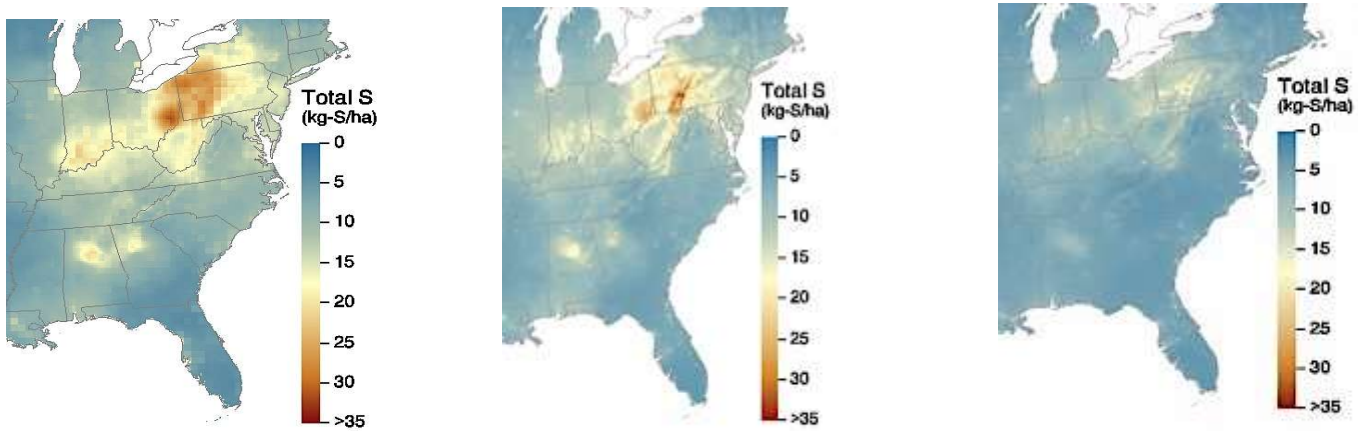
Smog chamber and modeling results on O_3 formation rates.

Is the decrease in concentration reflected in a decrease in deposition?

Let's compare to EPA's CASTNET site data to NASA's satellite observations.
Examine longer time scales larger area.

OMI SO_2 (Krotkov et al., ACPD, 2015)





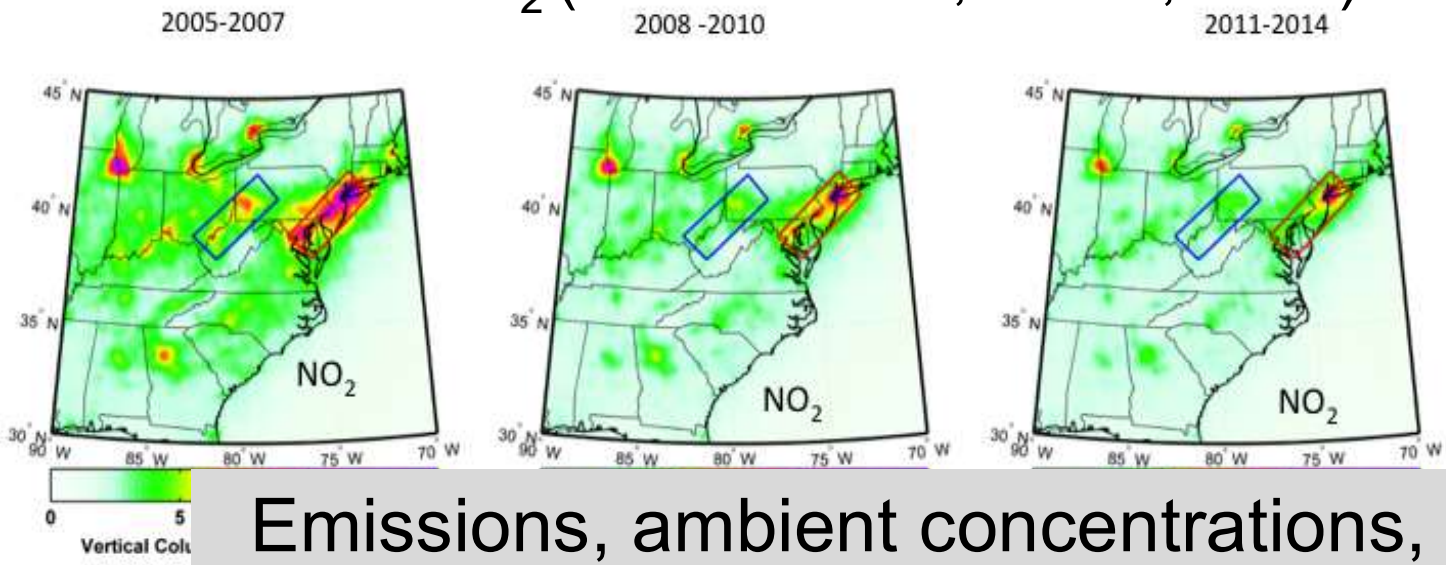
Total deposition of sulfur 2006
USEPA 10/16/14

Total deposition of sulfur 2009
USEPA 10/16/14

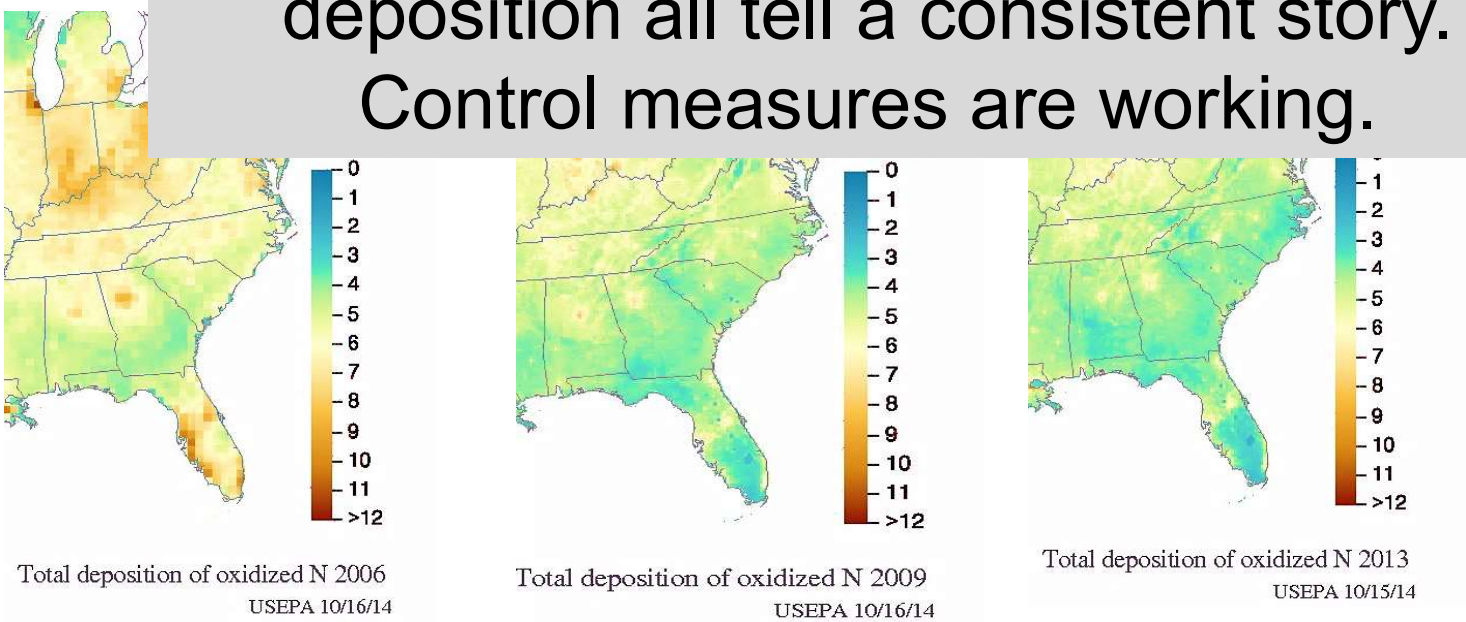
Total deposition of sulfur 2013
USEPA 10/15/14

Total S deposition (EPA - NADP)

OMI NO_2 (Krotkov et al., ACPD, 2015)



Emissions, ambient concentrations, and deposition all tell a consistent story. Control measures are working.



Total NOy deposition (EPA-NADP)