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

Presented at the EPRI ENV-Vision by Russell R. Dickerson, Univ. Maryland

Supported by MDE NIST, NASA, NOAA, and DNR

May 10-11, 2016
Three Vertical Profiles (Spirals) May 8, 2016

- **Bsp @ 550nm (m⁻¹)**
- **Alt GPS (m)**
- **Altitude AGL (m)**
- **[CO₂] (ppmv)**
- **[SO₂] (ppbv)**
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
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:

\[ y = -0.0158x + 6.7616 \]
\[ R^2 = 0.7615 \]

\[ y = -0.0058x + 1.3282 \]
\[ R^2 = 0.8038 \]

Air mass from “clean corridor” in PA. Pollution probably probably local.
Essex, MD  07/26, 9:13 EST

\[ y = 100.5x - 8700 \]
\[ R^2 = 0.96 \]

\[ y = 1.2931x + 1748.5 \]
\[ R^2 = 0.974 \]

\[ \text{CO/NOy} = 9.95 \]

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

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 NOy. Solid line is the 1:1 line; dashed line, the line of best fit.
Outline

• Why?
  – Need to model for State Implementation Plan (SIP)
  – Off the shelf CMAQ produces ozone locally and removes NO₂ 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 $\sim$3 ppb/hr at midday even upwind of Baltimore and Washington. Interstate transport matters. Brent et al., *Atmos. Chem.*, (2013).
Satellite observations support aircraft data:
see also Streets et al., *Atmos. Environ.*, 2013
Model Modifications
Increase photolysis rate of RONO₂
(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
Background Contour → CMAQ decreased AN lifetime, 50% ↓ mobile NO\textsubscript{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 O₃ precursors: Using DISCOVER-AQ data

CAMx v6.10 vs. P3-B DISCOVER-AQ Maryland NOy

Baseline

Ratio of Means = 1.948
Slope = 2.009
R-squared = 0.400

Beta

Ratio of Means = 1.510
Slope = 1.222
R-squared = 0.384

CAMx v6.10 vs. P3-B DISCOVER-AQ Maryland FORM

Baseline

Ratio of Means = 0.689
Slope = 0.559
R-squared = 0.800

Beta

Ratio of Means = 1.021
Slope = 0.954
R-squared = 0.781
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\textsubscript{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

Ozone (ppbv)

Boundary Conditions Biogenic Mobile Nonroad Ship EGU Other Point Area Canada

Maryland Pennsylvania Ohio Virginia DC West Virginia Northeast Southeast Great Lakes Midwest Atlantic Ocean
Total ozone concentrations attributed to each source sector

<table>
<thead>
<tr>
<th>Ozone (ppb) attributed to each Source Sector</th>
<th>Biogenic</th>
<th>On-road Mobile</th>
<th>Non-road Mobile</th>
<th>Ships</th>
<th>EGUs</th>
<th>Other Point</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline Simulation</td>
<td>3.6</td>
<td>24.6</td>
<td>10.3</td>
<td>2.5</td>
<td>11.6</td>
<td>5.1</td>
<td>5.6</td>
</tr>
<tr>
<td>Beta Simulation</td>
<td>4.0</td>
<td>16.9</td>
<td>6.9</td>
<td>3.4</td>
<td>15.7</td>
<td>6.7</td>
<td>6.6</td>
</tr>
<tr>
<td>Percentage change</td>
<td>10.9%</td>
<td>-31.4%</td>
<td>-33.0%</td>
<td>39.6%</td>
<td>34.6%</td>
<td>31.0%</td>
<td>18.7%</td>
</tr>
</tbody>
</table>

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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

MD avg: 8.3 ppb/hr
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
Mean NO\textsubscript{x}: 3.4 ppb

Mean Net O\textsubscript{x} Production: 12.1 ppb/hr

Red dots indicate when HCHO > 5 ppbv

Net Ox Production vs NO\textsubscript{x} in Baltimore region

12PM during Sunny days

July 2002

Mean NO\textsubscript{x}: 3.4 ppb

Mean Net O\textsubscript{x} 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 NOx: 2.1 ppb
Mean Net Ox Production: 10.1 ppb/hr
Net Ox Production vs NOx in Baltimore region

12PM during Sunny days

July 2018

Red dots indicate when HCHO > 5 ppbv

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

\[ \text{NO} + \text{HO}_2 (\text{RO}_2) \rightarrow \text{NO}_2 + \text{OH} \ (\text{OR}) \]

In CAMx and CMAQ, apparently NO too high and RO\textsubscript{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
Slides for backup
Applying Satellite Data to Air Quality Management

Research conducted by the NASA Air Quality Applied Sciences Team (AQAST) shows that Earth science data are a great potential resource for air quality managers.
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)

CO Concentration (ppbv)

Altitude (km)

CO

NOy
Beltsville CO and NOy Vertical Profiles (110721, 11:24 EST)
PBL only

NOy Concentration (pptv)

CO Concentration (ppbv)

y = -0.0055x + 2.2769
R² = 0.9246

y = -6E-05x + 1.4489
R² = 0.9115

NOy Concentration (pptv)

CO

NOy

Altitude (km)

0 2000 4000 6000 8000 10000 12000 14000 16000

0 50 100 150 200 250 300 350

0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6

0 50 100 150 200 250 300 350

y = -0.0055x + 2.2769
R² = 0.9246

y = -6E-05x + 1.4489
R² = 0.9115
Beltsville, 110721, 868-953 hPa, 11:27 EST

Air mass from DC and Virginia.
$\text{NO}_y/\text{CO}$ ratio ~0.087 or $\text{CO}/\text{NO}_y = 11.5$

Anderson et al., Atmos. Environ., 2014.
Beltsville, 110722, 949-979 hPA, 10:05 EST

Air mass from Ohio River Valley. NO<sub>y</sub>/CO ratio slightly higher (123) or CO/NO<sub>y</sub> lower (8.0) than previous profile.

\[ y = 123.2x - 20200 \]
\[ R^2 = 0.94 \]

\[ y = 0.5221x + 1824.2 \]
\[ R^2 = 0.807 \]

*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 probably local.
Essex, 07/26, 9:13 EST

\[ y = 100.5x - 8700 \]
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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 NOy. Solid line is the 1:1 line; dashed line, the line of best fit.
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

<table>
<thead>
<tr>
<th></th>
<th>DISCOVER-AQ Average (mol/mol) ± σ/n^{0.5}</th>
<th>Number of aircraft profiles</th>
<th>Fujita et al. 2012 (mol/mol)</th>
<th>EPA (mol/mol)</th>
<th>EPA/DISCOPER-AQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO/NOy</td>
<td>13.7 ± 1.4</td>
<td>60</td>
<td>9.3</td>
<td>7.4^</td>
<td>0.54</td>
</tr>
</tbody>
</table>

*: Values for 2010  +: Values for 2011;  CO & NO\textsubscript{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).

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 must 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?
Major NOx controls
Implemented after 2000.
From EPA NEI trends.
In 2010, Maryland implemented the “Healthy Air Act”
Power Plant Emissions in Maryland and surrounding states.

The Healthy Air Act
How has ambient SO\textsubscript{2} responded to this reduction in emissions?  

Do satellite observations agree?

Ambient SO\textsubscript{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\textsubscript{2} reflects emissions reductions.
Observed changes (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 $\text{NO}_X$ 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\textsubscript{x} levels have gone down ...

... *So have ambient ozone levels*

Observations show:

NO\textsubscript{x} 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: $b_{scat} (@450, 550, 700 \text{ nm})$, Nephelometer
- Absorption: $b_{ap} (565 \text{ nm})$, 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 O₃ 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 SO₂ (Krotkov et al., ACPD, 2015)

Total S deposition (EPA - NADP)
Emissions, ambient concentrations, and deposition all tell a consistent story. Control measures are working.