Recent Ozone Modeling Results

Presentation by:
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Modified for AQAST, September 25, 2015
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
Model Verification
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.
Models compared to observations

- CAMx performs slightly better at predicting surface ozone using version 1 of the emissions
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- CAMx performs slightly better at predicting surface ozone using version 1 of the emissions
- CMAQ does better when using model version 5.02 and version 2 alpha of the emissions
Comparison: CAMx vs. CMAQ

- CAMx v6.10 vs MDE Observations July 2011, 8 hour Max Ozone
  - Baseline
  - Mean Difference = 1.64 ppbv
  - Std Deviation = 9.27 ppbv

- CMAQ v5.01 vs MDE Observations July 2011, 8 hour Max Ozone
  - Baseline version 1
  - Mean Difference = 4.17 ppbv
  - Std Deviation = 9.66 ppbv

Red indicates observations > 75 ppbv
Ozone Source Apportionment
Ozone Source Apportionment Examples

- The CAMx software can attribute ozone to different source regions.
- Ozone can be transported long distances downwind of the original source.
Summer 2011 & 2018: Ozone Source Attribution

- The attribution of ozone in all states decreases 10 – 25% over 7 years.
- The only portion to increase is the ozone attributed to the model boundary.

BC = boundary conditions
Mid-Afternoon Source Apportionment at Gloucester Co, NJ

Summer 2011, Days where O3 > 75 ppb
CAMx v6.10 OSAT

Preliminary work by Dan Goldberg, University of Maryland, please contact prior to use
Mid-Afternoon Source Apportionment at Monmouth Co, NJ

Summer 2011, Days where O₃ > 75 ppb

CAMx v6.10 OSAT

Preliminary work by Dan Goldberg, University of Maryland, please contact prior to use
Mid-Afternoon Source Apportionment at Suffolk Co, NY

Summer 2011, Days where O3 > 75 ppb

CAMx v6.10 OSAT

Preliminary work by Dan Goldberg, University of Maryland, please contact prior to use
Mid—Afternoon Source Apportionment at Fairfield Co, CT

Summer 2011, Days where O3 > 75 ppb

CAMx v6.10 OSAT

Ozone(ppb)

Preliminary work by Dan Goldberg, University of Maryland, please contact prior to use
Boundary Ozone
Ozone from the model boundary

Ozone attributed to areas beyond the model domain, i.e., Texas, Cal, Asia

- Ozone from the boundary is uniformly greater than 15 ppbv.
- Some locations, especially close to the boundaries, are higher.
July 2011: Ozone attributed to the Model Domain Boundaries

~2/3rds of Boundary ozone in Maryland came from the Western Boundary.
Curtain plots of Ozone at the Boundary during July 2011

- MOZART is marginally higher in the lower layers at all boundaries, except the Southeast.
- GEOS–Chem has higher ozone in the mid–troposphere, especially at the western boundary (which is the boundary that most often influences ozone in the eastern United States).
Sensitivity study: **MOZART** vs. GEOS-Chem Boundary Conditions

Ozone aloft is poorly represented in the model.
More ozone aloft when using GEOS-Chem, which better agrees with observations!

... but still underestimated especially between 1 – 3 km agl
Evidence for an Increase in the Photochemical Lifetime of Ozone
Trends in the Apportionment of Surface Ozone

- Boundary and meteorology are initialized *identically* in each simulation.
- Total surface ozone has decreased and is projected to further decrease.
  - Sources inside the model domain will decrease.
  - **If the sources outside the model domain remain the same, ozone attributed to these sources will increase.**

Goldberg et al., Submitted, *JGR*
## Trends in the Apportionment of Surface Ozone

### Mean July percentage of ozone (%) attributed to the boundary

<table>
<thead>
<tr>
<th>Metropolitan Area</th>
<th>2002</th>
<th>2011</th>
<th>2018</th>
</tr>
</thead>
<tbody>
<tr>
<td>New York, NY</td>
<td>37.0%</td>
<td>41.6%</td>
<td>45.3%</td>
</tr>
<tr>
<td>Philadelphia, PA</td>
<td>38.1%</td>
<td>42.7%</td>
<td>47.6%</td>
</tr>
<tr>
<td>Baltimore, MD</td>
<td>34.5%</td>
<td>38.8%</td>
<td>43.6%</td>
</tr>
<tr>
<td>Washington, DC</td>
<td>35.9%</td>
<td>41.0%</td>
<td>46.5%</td>
</tr>
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### Mean July concentration of ozone (ppbv) attributed to the boundary

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<tr>
<td>New York, NY</td>
<td>23.9</td>
<td>24.6</td>
<td>25.9</td>
</tr>
<tr>
<td>Philadelphia, PA</td>
<td>26.8</td>
<td>27.4</td>
<td>27.7</td>
</tr>
<tr>
<td>Baltimore, MD</td>
<td>26.0</td>
<td>26.8</td>
<td>27.2</td>
</tr>
<tr>
<td>Washington, DC</td>
<td>27.1</td>
<td>27.6</td>
<td>28.0</td>
</tr>
</tbody>
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- An increasing role of the boundary is seen in all metropolitan areas in the eastern United States.
Trends in the Apportionment of Surface Ozone

Mean July percentage of ozone (%) attributed to the boundary

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<tr>
<td>New York, NY</td>
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<td>41.6</td>
<td>45.3</td>
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<td>Philadelphia, PA</td>
<td>38.1</td>
<td>42.7</td>
<td>47.6</td>
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• An increasing role of the boundary is seen in all metropolitan areas in the eastern United States.

What is causing this increase???

Ironically, we think it’s related to reductions in NO\textsubscript{x} and VOCs

Reductions in NO\textsubscript{x} and VOCs are causing the ozone lifetime to increase!

*See supplementary material for more detail

Goldberg et al., Submitted, JGR
Updates to the Modeling Platform that better predict Ozone Precursors
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.
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

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
Prediction of O$_3$: Using DISCOVER-AQ data

- Prediction of ozone is similar in each case, but **how** the ozone produced is much different

*Using the updated O3 data adjusted for the water vapor interference (this data is not in the D-AQ data archive).*
Policy Implications of the model updates

Percentage of $O_3$ formed in a VOC-limited environment during the daytime of July 7, 2011

Baseline

Beta

• The model will be more responsive to $NO_x$ emission changes.
Application of Source Apportionment Modeling
OSAT and APCA

*OSAT= Ozone Source Apportionment Tool
*APCA=Anthropogenic Precursor Culpability Assessment
Example: OSAT vs. APCA: OSAT

Diurnal Profile of Surface Ozone at Edgewood, MD on July 05

CAMx v6.10 OSAT CB6r2

<table>
<thead>
<tr>
<th>Area</th>
<th>Biogenic NOx</th>
<th>Anthropogenic NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Other Pt</td>
<td>Biogenic</td>
<td>Anthro &amp; Biogenic</td>
</tr>
<tr>
<td>Ship</td>
<td>Biogenic</td>
<td>Anthro &amp; Biogenic</td>
</tr>
<tr>
<td>Nonroad</td>
<td>Biogenic</td>
<td>Anthro &amp; Biogenic</td>
</tr>
<tr>
<td>Canada</td>
<td>Biogenic</td>
<td>Anthro &amp; Biogenic</td>
</tr>
<tr>
<td>Small EGUs</td>
<td>Biogenic</td>
<td>Anthro &amp; Biogenic</td>
</tr>
<tr>
<td>EGUs</td>
<td>Biogenic</td>
<td>Anthro &amp; Biogenic</td>
</tr>
<tr>
<td>Mobile</td>
<td>Biogenic</td>
<td>Anthro &amp; Biogenic</td>
</tr>
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</tr>
<tr>
<td>Boundary Conditions</td>
<td></td>
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</tr>
</tbody>
</table>

Ozone (ppb)

1AM  3AM  5AM  7AM  9AM  11AM  1PM  3PM  5PM  7PM  9PM  11PM
Example: OSAT vs. APCA: APCA

Diurnal Profile of Surface Ozone at Edgewood, MD on July 05

CAMx v6.10 APCA CB6r2

<table>
<thead>
<tr>
<th>APCA</th>
<th>Biogenic NOx</th>
<th>Anthropogenic NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogenic VOC</td>
<td>Biogenic</td>
<td>Anthropogenic</td>
</tr>
<tr>
<td>Anthropogenic VOC</td>
<td>Anthropogenic</td>
<td>Anthropogenic</td>
</tr>
</tbody>
</table>

Boundary Conditions

Ozone (ppb)
2011 APCA: Version 2 Emissions

July 2011 Mean Surface O3 from On- & Off-road

July 2011 Mean Surface O3 from Nonroad

July 2011 Mean Surface O3 from EGUs

July 2011 Mean Surface O3 from Area Sources
HOWEVER... We have shown a “Beta” version of the model (slides 25 – 29) that better matches observations of ozone precursors.

What happens when we implement those changes???
2011 APCA Beta: Version 2 Emissions

July 2011 Mean Surface O3 from On− & Off−road

July 2011 Mean Surface O3 from Nonroad

July 2011 Mean Surface O3 from EGUs

July 2011 Mean Surface O3 from Area Sources
• Ozone attributed to on-road and non-road mobile sources decreases
• Ozone attributed to EGUs and area sources increases
• In the original simulation, mobile sources dominated the attribution, but now mobile sources and EGUs have the same order of magnitude in Maryland.
Miscellaneous
Notice over the Chesapeake Bay and off the coast of New Jersey, there is a very sharp gradient in ozone attributed to ships that is not advected inland. A 12-km horizontal resolution model setup can not resolve this.
Midwestern & Ohio River valley states have larger role during westerly transport days
Virginia & North Carolina have double the role during southerly transport days

With help from Joel Dreessen, MDE
Conclusions

• Baseline version of CAMx shows good agreement with surface ozone observations

• Nonlinearities associated with NO\textsubscript{x} and VOC emission reductions are responsible for an increase in the ozone lifetime
  – This is an unintended consequence of the policies to reduce these emissions.

• Updates to the model to give a better prediction of NO\textsubscript{y} and HCHO.
  – The model will respond better to reductions in NO\textsubscript{x} emissions, which is a better representation of what is happening in reality.
Change in $O_3$ lifetime due to less NO$_x$

Assuming 1 mol of $O_3$ is removed for every 1 mol of HNO$_3$ deposited.

- As HNO$_3$ deposition decreases, the lifetime of ozone will increase

$\tau_{O_3} = 19.2$ days

$\tau_{O_3} = 28.6$ days
HO\textsubscript{2} Chemistry in the eastern United States

Mean July 2011 daytime (7 AM – 7 PM EDT) HO\textsubscript{2} concentrations

- The HO\textsubscript{2} + O\textsubscript{3} reaction can be an important sink of \(O_x\) (O\textsubscript{3}+NO\textsubscript{2}+...) when HO\textsubscript{2} > 15 pptv.
Change in daytime HO$_2$ concentrations between July 2002 and 2018

- Daytime HO$_2$ concentrations are decreasing in most areas.
- This is increasing the lifetime of ozone when reaction with HO$_2$ is important.
- Ozone lifetime with respect to reaction with HO$_2$ increases from 9.0 to 9.5 days.
Tagging Ozone Aloft

- Between 500 – 2000 m above surface, over 50% of ozone is from the boundary.
- Large portion from Ohio.
Between 2 – 4.5 km above the surface, over 75% of ozone is from the boundary.

Above 4.5 km above the surface (not shown), over 99% of ozone is from the boundary.