Modeling ozone depletion in the marine boundary layer caused by natural iodine emissions

Greg Yarwood, Ou Nopmongcol, Jaegun Jung
ENVIRON International Corporation

Gary Z. Whitten
SmogReyes

Mark Estes, Jim Smith and Jocelyn Mellberg
Texas Commission on Environmental Quality

11th Annual CMAS Conference, Chapel Hill, NC, October 16, 2012
Acknowledgment

Sponsored by the Texas Commission on Environmental Quality
Background

• Ozone modeling for Texas with CAMx using 2-way nested 36, 12, 4 km grids
  – Houston/Galveston/Brazoria
  – Dallas/Fort-Worth
  – Near-nonattainment areas
    ▪ Austin
    ▪ Beaumont/Port-Arthur
    ▪ Corpus Christi
    ▪ El Paso
    ▪ Northeast Texas
    ▪ San Antonio
    ▪ Victoria
    ▪ Waco

• Several areas of interest located on the Gulf Coast
• Ozone over-predicted at monitors on the Gulf Coast
  – Example shows Galveston for June 2006
  – Observed ozone only 15-20 ppb during persistent onshore flow
  – CAMx regional model biased high by 10-15 ppb
• Many global models biased high for Gulf Coast (next slide)
Ozone Bias in Global Models for the Gulf

- 20 global models compared in HTAP 2007 interim assessment
  - Task Force on Hemispheric Transport of Air Pollution
- Models compared to Sumatra and Everglades CASTNET monitors in Florida
  - Observed summer minimum in MDA8 O₃ (June-September)
  - Most models over predict, including GEOS-Chem and MOZART
  - Fiore et al (2008) and Reidmiller et al. (2009; www.atmos-chem-phys.net/9/5027/2009/)
Several Potential Causes Investigated

• Ozone deposition velocity too low over water
  – Improved CAMx using $V_d(O_3)$ measurements from TexAQS 2006
  – Tended to increase ozone

• CAMx ozone boundary condition (from GEOS-Chem) too high over the Gulf
  – Most global models are biased high over the Gulf
  – Potential explanations: coarse resolution (~200 km) and lacking iodine chemistry

• Iodine chemistry destroys ozone over the Gulf
  – Chemistry proposed in early 1990s and well documented
  – CAMx shows potential ozone reductions of ~5 ppb over Gulf
  – Bromine also destroys ozone and is synergistic with iodine
Ozone Depletion by Iodine

• I-atoms destroy ozone catalytically
  – Single I-atom can destroy hundreds of $O_3$ molecules

• Proposed by Chameides and Davis (1980)
  – Confirmed by field studies in Ireland, tropical Atlantic (Cape Verde Islands), Tasmania, etc.
  – Very active research field driven by interest in particle nucleation by iodine oxides ($I_2O_4, I_2O_5$, etc.)

• Why do iodine and chlorine behave differently?
  – Cl-atoms react with VOCs, I-atoms don’t
  – I-atoms destroy $O_3$ unless stored in a temporary reservoir or converted to aerosol
  – Br-atoms more like I than Cl
Chemical Mechanisms

- Cycle 2 favored at low NOx e.g. in un-polluted marine boundary layers
- Cycle 3 can operate at high NOx
- All cycles begin with $I + O_3 \rightarrow IO + O_2$ and differ in how IO is converted back to I
- The sum of $I + IO$ indicates potential for ozone destruction; $I + IO$ observed at ppt concentrations during daylight
CAMx Iodine Mechanism

- Implemented for CB6
  - 33 reactions of 17 iodine-containing species
  - Easily implemented for other mechanisms
Oceanic Emissions of I-atom Precursors

- Volatile organo-iodine compounds (VOIs)
  - CH$_3$I, CH$_2$I$_2$, CH$_2$ClI, CH$_2$BrI (halo-methanes)
  - Photolysis liberates I-atoms in days to minutes
  - Photobiological source of VOIs
    - Macroalgae (seaweed)
  - Photochemical source of VOIs
    - Sunlight and dissolved organic carbon (DOC)

- Molecular iodine (I$_2$)
  - Photolysis to I-atoms occurs in minutes
  - Reaction with NO$_3$ at night produces I-atom
  - Emissions may result from reactions of deposited O$_3$
Oceanic VOI Emissions for CAMx

- Organic iodine emissions based on water content of chlorophyll-a
  - SeaWiFS satellite data provide global coverage, monthly averages
- Calibrated to global emission estimates

<table>
<thead>
<tr>
<th>VOI Species</th>
<th>Emission (Gg/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3I</td>
<td>213</td>
</tr>
<tr>
<td>CH2I2</td>
<td>234</td>
</tr>
<tr>
<td>CH2IBr</td>
<td>87</td>
</tr>
<tr>
<td>CH2I2</td>
<td>116</td>
</tr>
</tbody>
</table>

2006 Chlorophyll-a (ug/m³) from SeaWiFS
Iodine Speciation at Galveston, TX

Average diurnal profile of I-containing species at Galveston

Monthly average diurnal profile for species containing 1% or more of iodine
Ozone Depletion by Iodine Chemistry

- Change in MDA8 O$_3$ due to iodine emissions/reactions on days with persistent onshore flow
- ~5 ppb ozone reductions over wide areas of Gulf
- Reductions influence coastal monitors and cities
Iodine Chemistry Conclusions and Recommendation

• Iodine chemistry could cause up to ~5 ppb ozone depletion over the Gulf and at coastal monitors
  – Emissions are uncertain
  – Chemistry is uncertain, but constrained to match field studies

• Field studies find that Bromine and Iodine cause comparable ozone depletion, and acted synergistically
  – Also include bromine emissions/reactions

• Consider potential interaction between ozone deposition and I$_2$ emission from oceans
  – High ozone concentrations raise ozone deposition, raise I$_2$ emission, raise ozone destruction rate by iodine chemistry
End
GEOS-Chem and MOZART: June 16-18, 2006

GEOS-Chem  Ozone at noon CST

MOZART
Ozone Sensitivity to CAMx Boundary Conditions

Difference in MDA8 ozone on June 17 and 18, 2006 due to capping the Ozone BCs over the Gulf of Mexico and Atlantic Ocean to values from the tropical Atlantic.