Evaluating the SAPRC and Carbon Bond chemical mechanisms for use in southeast Texas

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Distinct ozone formation chemistry in Houston-Galveston

- Industrial source region adjoining urban area.
- Elevated concentrations of reactive VOCs coemitted with NOx from industrial facilities.
- Substantial and rapid $O_3$ formation (> 50 ppb/hr) relative to slower formation and accumulation in most other urban areas.
- Significant variability of $O_3$ production over spatial scales of ~ 1km.
Domain-wide max $O_3$ concentrations in CAMx

**SAPRC-99**

- Min: 0.0 at (1,1)
- Max: 157.2 at (35,28)

**CB-IV**

- Min: 0.0 at (1,1)
- Max: 123.9 at (37,30)

**SAPRC minus CB-IV**

- Differences up to 45 ppb
- Aug. 30, 2000
Relative reductions in 8-hour O$_3$ after 75% NOx cut

\[
% \text{ relative reduction} = \left(1 - \frac{\text{basecase w/ 75\% NOx cut}}{\text{basecase}}\right) \times 100\%
\]

Episode: Aug 25-Sept 6, 2000

<table>
<thead>
<tr>
<th>Monitor</th>
<th>SAPRC-99</th>
<th>CB-IV</th>
<th>Difference from CB-IV</th>
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</thead>
<tbody>
<tr>
<td>Aldine</td>
<td>23.2 %</td>
<td>22.3 %</td>
<td>4.0 %</td>
</tr>
<tr>
<td>Chnnlview</td>
<td>17.7 %</td>
<td>12.9 %</td>
<td>37.2 %</td>
</tr>
<tr>
<td>DeerPk</td>
<td>15.6 %</td>
<td>8.9 %</td>
<td>75.3 %</td>
</tr>
<tr>
<td>Seabrook</td>
<td>16.9 %</td>
<td>7.1 %</td>
<td>138.0 %</td>
</tr>
<tr>
<td>BaylandPk</td>
<td>16.2 %</td>
<td>13.6 %</td>
<td>19.1 %</td>
</tr>
<tr>
<td>Westhollow</td>
<td>17.8 %</td>
<td>12.0 %</td>
<td>48.3 %</td>
</tr>
</tbody>
</table>
Policy implications: Required vs. predicted relative reductions in ozone with 75% NOx cut

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</thead>
<tbody>
<tr>
<td>BaylandPk</td>
<td>102 ppb</td>
<td>16.0 %</td>
<td>16.2 %</td>
<td>13.6 %</td>
</tr>
<tr>
<td>DeerPark</td>
<td>101 ppb</td>
<td>15.0 %</td>
<td>15.6 %</td>
<td>8.9 %</td>
</tr>
</tbody>
</table>
Conducted sensitivity studies in box model to identify specific hydrocarbons contributing to differences in the industrial source region.

- Sensitivity studies are not representative of actual atmospheric conditions
O$_3$ predictions in box model: VOC emissions assumed to be single explicitly-modeled species vs. mono-substituted aromatics

- **Ethylene**
  - O$_3$ Concentration (ppb) vs. Time (CDT)
  - SAPRC vs. CB-IV

- **Toluene**
  - O$_3$ Concentration (ppb) vs. Time (CDT)
  - SAPRC vs. CB-IV

- **Formaldehyde**
  - O$_3$ Concentration (ppb) vs. Time (CDT)
  - SAPRC vs. CB-IV

- **Ethylbenzene**
  - O$_3$ Concentration (ppb) vs. Time (CDT)
  - SAPRC vs. CB-IV
Different predictions of cresols for consistent mono-substituted aromatics inventories

SAPRC-99

ARO1

August 25, 2000 11:00:00
Min = 0.00 at (1.1), Max = 2.78 at (27.30)

CB-IV

TOL

August 25, 2000 11:00:00
Min = 0.00 at (1.1), Max = 2.68 at (27.30)

CRES

August 25, 2000 11:00:00
Min = 0.00 at (1.1), Max = 0.096 at (26.30)

CRES

August 25, 2000 11:00:00
Min = 0.00 at (1.1), Max = 0.245 at (21.30)
Eliminating aromatics:
Large differences in ozone persist

Hypothesis: If aromatics chemistry explains entire difference, eliminating aromatics should cause mechanisms to converge.

SAPRC-99 minus CB-IV
Predictions of HOx with SAPRC-99 and CB-IV in CAMx relative to measurements* in industrial source region

Aug. 30, 2000

*William Brune, PI, Penn. State University, Dept. of Meteorology.
Predictions of radicals in Houston-Galveston

• Overall underprediction of radicals in mechanisms relative to measurements
  – Group at UNC postulates additional radical generating emission sources
• Differences in radicals between SAPRC-99 and CB-IV
  – Our focus
Relative production of higher aldehydes in SAPRC-99 and CB-IV at location of max difference in O₃

Sources of higher aldehydes in SAPRC-99 but not in CB-IV

August 25, 2000; hour 13:00
Dominant sources of higher aldehydes in SAPRC-99 but not in CB-IV

• higher aldehydes + OH
• higher peroxyacyl radicals + NO
• higher reactivity non-aldehyde oxygenates + OH
• organic nitrates + OH
• methyl vinyl ketone + OH
• aromatic ring-opening products + OH
Summary

• Significant differences in predictions between SAPRC-99 and CB-IV under Houston-Galveston conditions
• Significant policy implications
• Differences due to complex and interacting phenomena
  – Aromatics chemistry
  – Free radical chemistry
• Mechanisms’ predictions will be evaluated against observables from TexAQSII*
• Similar differences reported for LA (Yarwood* et al., 2003)

*Texas Air Quality Study, II: [http://www.utexas.edu/research/ceer/texaqsII/](http://www.utexas.edu/research/ceer/texaqsII/)

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