Development of Reactivity Scales via 3-D Grid Modeling of California Ozone Episodes

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Reactivity Research Advisory Committee
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Outline

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• Methodology
• VOC Reactivity in SoCAB
• Uncertainty and Variability
• VOC Reactivity in Central California
• Conclusions
Introduction

Concerns:
- Physical detail of box model
- Multi-day vs one-day scenarios
- Uncertainties

Objectives:
- Use state-of-science grid-based photochemical air quality models to assess VOC reactivity in the SoCAB and central California;
- Compare 3-D reactivity with box model reactivity; and
- Conduct sensitivity and uncertainty analysis.
Methodology

- CIT model (SoCAB) and MAPSIP (Central California)
- Extended version of the SAPRC99 chemical mechanism
- 31 chemical species (7 alkanes, 7 alkenes, 5 aromatics, 6 carbonyls, and 6 others)
- Incremental reactivity scales: AIR and RIR
- Metrics: MIR-3D, MOIR-3D, MOIR-3D-8hr, exposure, average
VOC reactivity in the SoCAB

Alkanes

Hawthorne
Long Beach
Central Los Angeles
Anaheim
Burbank
Azusa
Claremont
Rubidoux
Carter (2000b) R_MIR

relative incremental reactivity

methane, ethane, n-butane, n-pentane, isopentane, methylcyclopentane, 2,2,4trimethylpentane
VOC reactivity in the SoCAB

Alkenes

- Ethene
- Propene
- 2-methyl-2-butenes
- 1,3-butadiene
- Isoprene
- α-Pinene
- OLE1

Relative incremental reactivity

Locations:
- Hawthorne
- Long Beach
- Central Los Angeles
- Anaheim
- Burbank
- Azusa
- Claremont
- Rubidoux
- Carter (2000b) R_MIR
VOC reactivity in the SoCAB

Aromatics

- benzene
- toluene
- m-xylene
- p-xylene
- 1,2,4-trimethylbenzene

Relative incremental reactivity

- Hawthorne
- Long Beach
- Central Los Angeles
- Anaheim
- Burbank
- Azusa
- Claremont
- Rubidoux
- Carter (2000b) R_MIR
Uncertainty and Variability

Absolute Incremental Reactivities and associated Uncertainties

- Anaheim
- Azusa
- Claremont
- Riverside

Chemicals: CO x 10, ETOH, HCHO, MEK, N-C4, PRPE, 224P, XYL, BASE
Uncertainty and Variability

Relative Incremental Reactivities and Associated Uncertainties

Anaheim
Azusa
Claremont
Riverside
### Uncertainty and Variability

#### RIR and Contributing Parameters

<table>
<thead>
<tr>
<th></th>
<th>Anaheim</th>
<th>Azusa</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HCHO</strong> (RIR = 8.45 (0.20); $R^2 = 0.97$)</td>
<td><strong>HCHO</strong> (RIR = 11.54 (0.14); $R^2 = 0.95$)</td>
<td></td>
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<tr>
<td>HCHO + hv</td>
<td>0.34</td>
<td>0.27</td>
</tr>
<tr>
<td>O3 + hv</td>
<td>0.27</td>
<td>0.34</td>
</tr>
<tr>
<td>EMCO</td>
<td>0.25</td>
<td>0.18</td>
</tr>
<tr>
<td>O1D2 + M</td>
<td>0.18</td>
<td>0.42</td>
</tr>
<tr>
<td>NO2 + hv</td>
<td>0.18</td>
<td>CCO-O2 + NO</td>
</tr>
<tr>
<td>HO + NO2</td>
<td>0.27</td>
<td>O3 + hv</td>
</tr>
<tr>
<td>CCO-O2 + NO</td>
<td>0.34</td>
<td>0.34</td>
</tr>
<tr>
<td>PAN</td>
<td>0.40</td>
<td>0.10</td>
</tr>
</tbody>
</table>

**Contributing Parameters**:
- $0.34 \pm 0.52$ for 27.5
- $0.27 \pm 0.45$ for 20.5
- $0.25 \pm 0.33$ for 11.0
- $0.18 \pm 0.30$ for 8.8
- $0.18 \pm 0.29$ for 8.3
- $0.27 \pm 0.28$ for 8.0
- $0.34 \pm 0.24$ for 5.6
- $0.40 \pm 0.23$ for 5.3

**Values**:
- $0.27 \pm 0.52$ for 26.8
- $0.34 \pm 0.46$ for 20.9
- $0.18 \pm 0.36$ for 12.8
- $0.42 \pm 0.27$ for 7.5
- $0.34 \pm 0.23$ for 5.3
- $0.27 \pm 0.21$ for 4.2
- $0.18 \pm 0.20$ for 4.2
- $0.10 \pm 0.20$ for 4.1
VOC Reactivity in Central California

Relative Reactivity Metrics, MIR-3D

- Relative Reactivity (g O3 / g VOC)

- 2MBT, BUTD, PRPE, ISOP, XYL, ETHE, HCHO, RCHO, OLE1, 124B, CCHO, APIN, XLYP, TOLU, MCPT, ETOH, IPNT, N_C5, MEK, 224P, N_C4, C2H2, BACT, C2H2, MTBE, MEOH, ACET, C2H6, CO, CH4, BALD

- MIR-3D
- MIR

- X (10)
- X (100)
- X (-1)
VOC Reactivity in Central California

Relative Reactivity Metrics, Comparison

- Exposure
- MIR-3D
- MOIR-3D
- MOIR-3D-8hr

Relative Reactivity (g O3 / g VOC)

Chemicals:
- 2MBT
- BUTD
- PRPE
- ISOP
- XLYM
- ETHE
- HCHO
- RCHO
- OLE1
- 124B
- CCHO
- APIN
- XLYP
- TOLU
- MCPT
- ETOH
- IPNT
- N_C5
- MEK
- 224P
- N_C4
- C2H2
- BAC
- C6H4
- MTBE
- MEOH
- ACET
- C2H6
- CO
- CH4
- BALD
SoCAB vs. Central California

Relative Incremental Reactivity
SoCAB vs. Central California

![Graph showing relative incremental reactivity between SoCAB and Central California](graph.png)
Conclusions

- Reactivity scales developed using 3-D modeling resulted in similar ranking of individual VOC when compared to Carter’s Box model MIR.
- The variation in reactivity across the basin is less on a relative rather than absolute scale.
- The results from central California are similar to those for the South Coast Air Basin. Most VOCs behaved similarly in all metrics studied.
- The uncertainties range from 0.3 to 0.4 in the absolute scale and 0.2 to 0.35 in the relative scale.
Eastern US vs. California

MIR-3D

California

Eastern US