The UCR Environmental Chamber Database for Mechanism Evaluation

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Outline

• Database used in SAPRC-99 evaluation and Current database
• New UCR-EPA chamber
• Examples of SAPRC and CB4 mechanism performance
• Issues regarding evaluating condensed mechanisms and mechanisms for secondary reactions of products
• Examples of PM measurements in the new UCR EPA chamber
• Summary and Recommendations
Relationship Between Mechanisms, Chamber Data and Airshed Models

Basic kinetic and mechanistic data and theory → Mechanism Under Development → Evaluated Mechanism → Environmental Chamber Experiments → Model Simulations of Chamber Experiments → Chamber Effects Model → Airshed Scenario Conditions → Airshed Model Predictions

Environmental Chamber Experiments → Chamber Characterization Data

Airshed Model
# UCR Chamber Data Base Used when Developing the SAPRC-99 Mechanism

<table>
<thead>
<tr>
<th>Type of Experiment</th>
<th>No. of Runs</th>
<th>No. of VOCs</th>
<th>NO$_x$ Range (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chamber Characterization</td>
<td>73$^1$</td>
<td></td>
<td>0 - 660</td>
</tr>
<tr>
<td>Simple VOC - NO$_x$ (a few with added CO or alkane)</td>
<td>490</td>
<td>39</td>
<td>90 - 1100</td>
</tr>
<tr>
<td>Incremental Reactivity (effect of adding VOC to Surrogate - NO$_x$)</td>
<td>435</td>
<td>81</td>
<td>180 - 610</td>
</tr>
<tr>
<td>Ambient Surrogate - NO$_x$</td>
<td>645</td>
<td></td>
<td>75 - 1200</td>
</tr>
<tr>
<td>Other Mixture - NO$_x$</td>
<td>29</td>
<td></td>
<td>50 - 2000</td>
</tr>
</tbody>
</table>

$^1$ Radical Source and NOx offgasing characterization experiments only
**UCR Chamber Data Base Available for Current Mechanism Evaluation**

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<tr>
<th>Type of Experiment</th>
<th>No. of Runs</th>
<th>No. of VOCs</th>
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</thead>
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<tr>
<td>Chamber Characterization</td>
<td>227\textsuperscript{1}</td>
<td></td>
<td>0 - 660</td>
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<tr>
<td>Simple VOC - NO\textsubscript{x} (a few with added CO or alkane)</td>
<td>611</td>
<td>40</td>
<td>4 - 1100</td>
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<tr>
<td>Incremental Reactivity (effect of adding VOC to Surrogate - NO\textsubscript{x})</td>
<td>479</td>
<td>88</td>
<td>5 - 610</td>
</tr>
<tr>
<td>Ambient Surrogate - NO\textsubscript{x}</td>
<td>834</td>
<td></td>
<td>2 - 1200</td>
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<tr>
<td>Other Mixture - NO\textsubscript{x}</td>
<td>29</td>
<td></td>
<td>50 - 2000</td>
</tr>
</tbody>
</table>

\textsuperscript{1} Radical Source and NOx offgasing characterization experiments only
UCR Chambers whose Data were Used for SAPRC-99 Mechanism Development

<table>
<thead>
<tr>
<th>Chamber</th>
<th>Walls</th>
<th>Lights</th>
<th>Vol (m(^3))</th>
<th>NO(_x) (ppb)</th>
<th>Runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITC</td>
<td>Teflon Film</td>
<td>Blacklights</td>
<td>6</td>
<td>75 - 1200</td>
<td>130</td>
</tr>
<tr>
<td>ETC, DTC</td>
<td>Teflon Film</td>
<td>Blacklights</td>
<td>3 - (2 x 6)*</td>
<td>80 - 990</td>
<td>1027</td>
</tr>
<tr>
<td>XTC, CTC</td>
<td>Teflon Film</td>
<td>Xenon Arc</td>
<td>2.5 - 5</td>
<td>90 - 650</td>
<td>292</td>
</tr>
<tr>
<td>EC</td>
<td>Teflon Coated Al., Quartz</td>
<td>Xenon Arc</td>
<td>6.4</td>
<td>90 - 2000</td>
<td>98</td>
</tr>
<tr>
<td>OTC</td>
<td>Teflon Film</td>
<td>Solar</td>
<td>2 x 20*</td>
<td>200 - 630</td>
<td>36</td>
</tr>
</tbody>
</table>

* Two reactors
### UCR Chambers whose Data Are Available for Current Mechanism Evaluation

<table>
<thead>
<tr>
<th>Chamber</th>
<th>Walls</th>
<th>Lights</th>
<th>Vol (m³)</th>
<th>NOₓ (ppb)</th>
<th>Runs</th>
</tr>
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<tr>
<td>ITC</td>
<td>Teflon Film</td>
<td>Blacklights</td>
<td>6</td>
<td>75 - 1200</td>
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<tr>
<td>OTC</td>
<td>Teflon Film</td>
<td>Solar</td>
<td>2 x 20*</td>
<td>200 - 630</td>
<td>36</td>
</tr>
<tr>
<td>UCR EPA</td>
<td>Teflon Film</td>
<td>Argon Arc, Blacklights</td>
<td>2 x 100*</td>
<td>2 - 711</td>
<td>403</td>
</tr>
</tbody>
</table>

* Two reactors
UCR EPA Chamber

Major Objectives

• Reduce background effects to permit well-characterized mechanism evaluation experiments at lower pollutant levels
• Provide well-characterized data for PM mechanism evaluation

Characteristics

• Indoor chamber for maximum control and characterization
• Largest practical volume for indoors (two ~100,000-L reactors)
• 200 KW filtered argon arc solar simulator (also blacklights)
• “Clean room” design and positive pressure reactor volume control to minimize dilution and contamination
• Temperature controlled to ±1°C in ~5°C to ~50°C range.
• Improved array of instrumentation, including PM measurements
Diagram of UCR EPA Chamber

- 2 Banks of Blacklights
- 200 KW Arc Light
- Two air Handlers are located in the corners on each side of the light (not shown).
- Temperature controlled room flushed with purified air and with reflective material on all inner surfaces
- Access Door
- SEMS (PM) Instrument
- Gas sample lines to laboratory below
- Movable top frame allows reactors to collapse under pressure control
- Mixing System Under floor of reactors
- Floor Frame
Summary of UCR EPA Characterization Results

- Contamination or dilution by enclosure air is negligible when run on positive pressure control. (Volume decreases as sample is withdrawn)

- Light intensity with argon arc lamp at 80% recommended maximum power gives NO$_2$ photolysis rate of 0.26 min$^{-1}$

- Characterization results indicate chamber effects are comparable or lower than in other Teflon film chambers

- Good side equivalency in gas-phase results obtained when the same experiment is simultaneously run in the two reactors (except for some NO$_x$ offgasing-sensitive runs)

- Some background PM formation observed, but reproducible results obtained when >10 $\mu$g/m$^3$ PM formed.
Radical or NO$_x$ Offgasing Rates Derived for Various Chambers

![Graph showing the relationship between average temperature (K) and NO$_x$ offgasing or radical source rate/NO$_2$ photolysis rate ratio (ppt).]

- Previous UCR Indoor
- Previous UCR Outdoor
- Previous UCR Default Model
- Used for Modeling UNC Outdoor
- TVA Indoor (NO$_x$ offgasing)
- UCR EPA Chamber
- SAPHIR HONO offgasing (dry)

Modeled data derived using the SAPRC-99 mechanism
Lowest NO$_x$ Surrogate Experiment
(ROG surrogate = 300 ppbC, NO$_x$ = 2 ppb)

- Experimental
- - - No HONO Offgasing
- - - Maximum HONO Offgasing

Concentration (ppm) vs Time (minutes)
## Types of VOCs for which Data are Available

<table>
<thead>
<tr>
<th>Type of Compound or Mix</th>
<th>Number of Types</th>
<th>Number of Runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common organic products</td>
<td>5</td>
<td>49 41</td>
</tr>
<tr>
<td>Alkanes</td>
<td>16</td>
<td>- 94</td>
</tr>
<tr>
<td>Alkenes (incl. Styrene)</td>
<td>13</td>
<td>232 48</td>
</tr>
<tr>
<td>Aromatic Hydrocarbons</td>
<td>12</td>
<td>135 29</td>
</tr>
<tr>
<td>Alkynes (Acetylene)</td>
<td>1</td>
<td>5 7</td>
</tr>
<tr>
<td>Alcohols, ethers, esters, etc.</td>
<td>31</td>
<td>- 152</td>
</tr>
<tr>
<td>Aromatic oxygenates, furans</td>
<td>9</td>
<td>7 2</td>
</tr>
<tr>
<td>Other aldehydes, ketones</td>
<td>6</td>
<td>24 18</td>
</tr>
<tr>
<td>Misc. heteroatom-containing</td>
<td>12</td>
<td>- 41</td>
</tr>
<tr>
<td>Complex hydrocarbon mixes</td>
<td>11</td>
<td>- 12</td>
</tr>
</tbody>
</table>
Types of Measurement Data Available

- **All runs**: O$_3$, NO, NO$_y$, CO, added VOCs, temperature
- **All indoor chamber runs**: Sufficient light intensity and spectral distribution data to assign photolysis rates
- **All runs**: Sufficient characterization data to assign parameters for modeling radical source, NO$_x$ offgasing, dilution and humidity
- **Many but not all runs**: Data for formaldehyde, PAN, a few other oxygenated products in some cases (data quality varies)
- **Most EPA chamber runs**: PM number and size data from SEMS
- **Some EPA chamber runs**: NO$_2$ and HNO$_3$ data from TDLAS. H$_2$O$_2$, OH, and other radical data available for a few runs.

* Refers to experiments suitable for modeling

Note: Data on organic oxidation products are highly limited except for some earlier EC runs. Data are mainly suitable for evaluating predictions of O$_3$, overall oxidation rates, and (in some cases) PM number and volume.
Examples of Mechanism Evaluations

Mechanisms
- SAPRC-99 (Both detailed and “fixed parameter” condensed)
- Preliminary Updated SAPRC-99
- Carbon Bond 4 (CB4)
- Updated CB4 (CB 05) (May not be the final version)

Types of Experiments
- Propene - NO$_x$
- m-Xylene - NO$_x$
- Ambient Surrogate - NO$_x$ in UCR EPA chamber with arc light
  - Initial ROG surrogate and NO$_x$ varied over a wide range
  - Surrogate is mixture of n-butane, n-octane, ethene, propene, trans-2-butene, toluene, m-xylene and formaldehyde (one compound for each model species in lumped mechanisms)
Lumped Model Species Used for Propene and m-Xylene

### Propene and Other Terminal Alkenes

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Species</th>
<th>Mechanism Based On</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB4, CB05</td>
<td>OLE + PAR</td>
<td>Propene</td>
</tr>
<tr>
<td>Lumped</td>
<td>OLE1</td>
<td>29% Propene; 24% 1-Hexene; 12% 1-Butene; 35% Other 1-alkenes</td>
</tr>
<tr>
<td>SAPRC-99</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### m-Xylene and Other Higher Reactivity Aromatics

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Species</th>
<th>Mechanism Based On</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB4, CB05</td>
<td>XYL</td>
<td>Xylenes (probably primarily o-xylene)</td>
</tr>
<tr>
<td>Lumped</td>
<td>ARO2</td>
<td>23% p-Xylene; 20% o-Xylene; 20% m-Xylene; 37% Trimethylbenzenes</td>
</tr>
<tr>
<td>SAPRC-99</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Model Error for Propene Experiments

SAPRC-99

New SAPRC

Updated CB4 (CB 05)

Lumped SAPRC-99

Model Error Range (Calculated - Experimental) / Experimental

Shows model fits to $\Delta([O3]-[NO])$

Each curve gives distribution of fits for an hour in the experiment
Model Error for m-Xylene Experiments

SAPRC-99

CB4

Lumped SAPRC-99

New SAPRC

Updated CB4 (CB 05)

Run Matrix

Model Error Range (Calculated - Experimental) / Experimental

W. P. L. Carter  12/14/2006  Environmental Chamber Database
Model Error for UCR EPA Standard Surrogate Experiments (Arc Light)

Final D(O3-NO) fit

Surrogate C / NOx

NOx (ppb)

Surrogate (ppmC)

-90%
-60%
-30%
0%
30%

SAPRC-99
New SAPRC
Model Error for UCR EPA Standard Surrogate Experiments (Arc Light)
Model Error for UCR EPA Standard Surrogate Experiments (Arc Light)

![Graph showing model error for surrogate experiments compared to real data.

- **Y-axis:** Final D(O3-NO) fit percentage
- **X-axis:** Surrogate C / NOx

Legend:
- **SAPRC-99**
- **New SAPRC**
- **Lumped SAPRC-99**
- **CB4**

The graph illustrates the model error for different surrogate experiments compared to the EPA standard, with data points distributed across various concentrations.
Model Error for UCR EPA Standard Surrogate Experiments (Arc Light)

![Graph showing model error for different surrogate experiments]

- SAPRC-99
- New SAPRC
- Lumped SAPRC-99
- CB4
- Updated CB4 (CB 05)
Differences in Incremental Reactivities Between Environmental Chamber and Simulated Atmospheric Conditions

Incremental Reactivity Chamber Simulation (MIR Conditions)

Ambient Simulation ("Averaged Conditions" MIR Box Model Scenario)

- Change in O3 (ppb)
- Irradiation time (hours)
- Hour of day

Alkane Petroleum Distillate
(Added = 25%)

Water based coatings solvent (Texanol)
(Added = 5%)

Amounts added are % of moles carbon of base ROG. Same % for chamber and ambient
### Approximate Contributions of Aspects of Mechanisms to n-Decane Reactivity in Chamber and Atmospheric Simulations

Contributions relative to effect of NO to NO₂ Conversions.

<table>
<thead>
<tr>
<th>Aspect of Mechanism</th>
<th>Chamber Experiment</th>
<th>Atmospheric Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO to NO₂ Conversions due to Peroxy + NO</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Nitrate formation from RO₂ + NO</td>
<td>-0.6</td>
<td>-0.8</td>
</tr>
<tr>
<td>Contribution of Product Reactions</td>
<td>0.08</td>
<td>1.0</td>
</tr>
</tbody>
</table>

- Note much lower contributions of product reactions under chamber simulations

Calculated using “pure mechanism” model species mechanistic reactivities for kOH = 3 x 10⁴ ppm⁻¹ min⁻¹.
Relative Importance of Product Formation on Reactivity as a Function of Integrated Radical Levels

- Atmospheric Simulation (MIR) (High NOx)
- Atmospheric Simulation (MOIR) (Max O3)
- Atmospheric Simulation (EBIR) (Low NOx)
- Simulations of Standard Chamber Experiments
- Simulations of Modified Chamber Experiments

Graph showing the relationship between Integrated OH (ppt-min) and Product formation / NO to NO2 Conversion Mechanism Species Reactivity Ratio.
PM Measurements in the UCR EPA Chamber

- PM Measurements are being made in conjunction with most UCR EPA chamber experiments. PM alternately sampled from each of the two reactors, switching every 10 minutes.
- Number densities of particles in 71 size ranges (28 - 730 nm) measured using a Scanning Electrical Mobility Spectrometer. Data used to compute particle number and volume densities.
- Background PM formation now less than 0.5 $\mu$g/m$^3$. (Was up to 2 $\mu$g/m$^3$ in Reactor A before it was replaced).
- PM measurements made during incremental reactivity experiments with representative architectural coatings VOCs.
- A number of experiments were conducted to determine effects of varying initial concentrations on secondary PM from m-xylene.
- Most experiments to date are unhumidified with no seed aerosol.
Representative PM Data

- Volume
- Corrected Volume
- Number
- Corrected Number

Pure Air Irradiation

<table>
<thead>
<tr>
<th>Hours of Irradiation</th>
<th>PM Volume (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
</tr>
<tr>
<td>6</td>
<td>0.6</td>
</tr>
<tr>
<td>8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

CO - Air Irradiation

<table>
<thead>
<tr>
<th>Hours of Irradiation</th>
<th>PM Number (1000/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
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<tr>
<td>2</td>
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</table>

m-Xylene - NOx

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<thead>
<tr>
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<th>PM Volume (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>0.6</td>
</tr>
<tr>
<td>8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Surrogate - NOx

<table>
<thead>
<tr>
<th>Hours of Irradiation</th>
<th>PM Number (1000/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Side B Data
PM Formation in Incremental Reactivity Experiments with Coatings VOCs

- Benzyl Alcohol
- Butyl Carbitol
- Aromatic 100
- Regular Mineral Spirits (MS)
- Reduced Aromatics MS
- Dearomatized MS
- Synthetic Isoparrifin Mix
- Texanol®
- Ethylene Glycol
- Propylene Glycol
- Base Case Experiments

Average 5 Hour PM Volume $\mu g/m^3$

Side B data only
Error Bars are 1-$\sigma$ standard deviations.
No error bar means only one experiment.
Summary and Recommendations

• The ability to simulate suitable environmental chamber data is necessary (but not sufficient) to assure mechanism accuracy

• A large database of environmental chamber experiments exists for O₃ mechanism evaluation for a wide variety of VOCs

• The new UCR EPA chamber is providing low NOₓ mechanism evaluations and is beginning to provide data for PM impacts

• Current mechanisms differ significantly in their ability to simulate the available chamber database

• Care must be taken when evaluating condensed mechanisms against chamber data. The lumped species may not be designed to represent the compounds in the experiments.

• The present chamber database is not adequate for evaluating contributions of oxidation products to ozone reactivity. Need experiments with higher integrated radical levels.
Availability of Data

• Data for experiments up to 1995 and associated documentation are available at
  http://www.cert.ucr.edu/~carter/absts.htm#databa

• Partially documented data for more recent experiments are available upon request. Contact
  
  William P. L. Carter
  CE-CERT, University of California, Riverside, CA 92521
  Phone: (951) 781-5797
  Email: carter@cert.ucr.edu
  Url: http://www.cert.ucr.edu/~carter

• Additional funding is required to fully compile and document available UCR chamber experiments carried out after 1995
Acknowledgements

- James N. Pitts, Jr. Arthur Winer, Karen Darnall
  - Leadership in early UCR chamber programs

- William Long, Frank Burleson, Glen Vogelaar, Sara Aschmann, John Pierce, Dongmin Luo, Irina Malkina, Kurt Bumiller (incomplete list)
  - Major contributors to conducting the mechanism evaluation chamber experiments during various periods.

- Dennis Fitz, Kurt Bumiller, Claudia Sauer, John Pisano, Charles Bufalino, Matthew Smith
  - Assistance in design and construction of UCR EPA chamber

- David Cocker and Chen Song
  - PM experiments and measurements in UCR EPA chamber

- United States EPA, California Air Resources Board, Coordinating Research Council, California SCAQMD
  - Major funding sources