Environmental Chamber Studies of Ozone And PM Impacts of VOCs

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Outline

• VOCs and air quality
• Need for mechanisms to predict atmospheric impacts of VOCs
• Role of environmental chamber data in mechanism development
• Recent mechanism evaluation data with new low-NOx chamber
• Recent chamber data on secondary PM from m-xylene
• Ongoing research
VOCs and Air Quality

- Volatile Organic Compounds (VOCs) enter the atmosphere from a variety of anthropogenic and biogenic sources

- Impacts of VOCs on air quality include:
  - Direct effects (for toxic VOCs very near large sources)
  - Formation of toxic or persistent oxidation products
  - Promotion of ground-level ozone formation
  - Contribution to secondary particle matter (PM) formation

- Contribution to ground-level ozone has been the major factor driving VOC regulations in the U.S.
  - Models calculate large VOC reductions are needed to achieve air quality standards in urban areas
  - $\text{NO}_x$ reduction is more important to reducing regional ozone

- But need to reduce PM has also become a priority. VOC control may also be necessary to reduce secondary PM.
Mechanism of VOCs Impact on O₃

- Ground level O₃ is actually formed from the photolysis of NO₂, with O₃ in a photostationary state relation with NO and NO₂:

\[
\text{NO}_2 + h\nu \rightarrow O(^3\text{P}) + NO
\]
\[
O(^3\text{P}) + O_2 \rightarrow O_3
\]
\[
O_3 + NO \rightarrow O_2 + NO_2
\]

**Overall:**

\[
h\nu
\]
\[
\text{NO}_2 + O_2 \Leftrightarrow O_3 + NO
\]

- VOCs promote O₃ by forming radicals that convert NO to NO₂ and shift the photostationary state towards O₃ formation, e.g.:

\[
\text{RH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{R}
\]
\[
\text{R} + O_2 \rightarrow \text{RO}_2·
\]
\[
\text{RO}_2· + \text{NO} \rightarrow \text{RO}· + \text{NO}_2
\]
\[
\text{RO}· \rightarrow \rightarrow \text{HO}_2 + \text{other products}
\]
\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2
\]

**Overall:**

\[
h\nu, \text{NO}_x, O_2
\]
\[
\text{VOC} + O_2 \rightarrow \rightarrow \rightarrow O_3 + \text{products}
\]
Factors Affecting Impacts of VOCs on $O_3$

- Ground level $O_3$ is formed from the reactions of NOx. But without VOCs $O_3$ levels are low because of its reaction with NO.

- VOCs differ significantly on their effects on $O_3$ formation

Mechanistic factors affecting ozone impacts are:
  - How fast the VOC reacts
  - NO to NO$_2$ conversions caused by VOC’s reactions
  - Effect of reactions of VOC or its products on radical levels
  - Effects of reactions of VOC or its products on NO$_x$ levels

- The effect of a VOC on $O_3$ also depends on where it reacts
  - The availability of NO$_x$. (NO$_x$ necessary for $O_3$ to form.)
  - The sensitivity to radical levels
  - The amount of time the VOCs have to react

- Models must take these factors into account to evaluate effective VOC control strategies to reduce $O_3$. 
Factors Affecting Impacts of VOCs on Secondary PM

- Many VOCs form low volatility oxidation products that can partition into the aerosol phase and contribute to secondary PM.
- Some higher volatility products may also partition into the aerosol phase due to heterogeneous reactions.
- The yields of condensable products varies from compound to compound and may also vary with atmospheric conditions.
- Identity, yields, formation mechanisms, and partitioning coefficients of condensable products are mostly unknown for most VOCs.
- Data and mechanistic knowledge are inadequate for models to predict secondary PM from VOCs with any degree of reliability.
- Inadequately tested and highly simplified parameterized models are used for predicting effects of emissions on secondary PM.
Importance of Environmental Chamber Data to Air Pollution Models

• **Chemical mechanisms** are needed for models to predict secondary pollutants such as $\text{O}_3$ and PM

• Mechanisms in current airshed models have many uncertain estimates, simplifications and approximations

• **Environmental chambers**, simulating atmospheric reactions under controlled conditions, are essential to:
  • Develop predictive mechanisms when basic mechanistic data insufficient.
  • Testing approximations and estimates in mechanisms for almost all VOCs under simulated atmospheric conditions
  • Testing entire mechanisms under the necessary range of conditions

• Results of experiments are influenced by chamber effects, so developing an appropriate chamber effects model is important
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 Characterization Data

Chamber Effects Model

Airshed Model

Airshed Scenario Conditions

Airshed Model Predictions
Examples of Chemical Mechanisms for Airshed Models

- Carbon Bond 4 Mechanism (~20 organic model species)
  - Highly condensed. Designed for computational efficiency
  - Developed in the late 80’s with some more recent updates
  - Limited testing against older chamber data
  - Widely used in regulatory modeling in the U.S.
  - Not suitable for secondary PM prediction

- European “Master Mechanism” (~4500 organic model species)
  - Highly explicit representation of major reaction routes for ~130 VOCs and their major oxidation products.
  - Development and testing against chamber data ongoing.
  - Used in trajectory models in Europe to estimate relative reactivity factors for VOCs. Too large for grid models
  - Being adapted for secondary PM prediction
Examples of Chemical Mechanisms for Airshed Models (cont’d)

• SAPRC-99 Mechanism (~60 to ~600 organic model species)
  • Can separately represent reactions of >550 types of VOCs. Condensed representation of oxidation products
  • Developed in late ‘90’s and comprehensively evaluated against then-available chamber data
  • “Lumped” version widely used for research and some regulatory modeling in the U.S.
• Versions with selected VOCs represented explicitly used for calculating VOC reactivity scales for $O_3$
• Not designed for secondary PM prediction, but some modeling groups have adapted it for this purpose
• Evaluation against newer chamber data ongoing.
• Updated version under development
## Chamber Data Base Used when Developing and Evaluating 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>76</td>
<td></td>
<td>0 - 660</td>
</tr>
<tr>
<td>Single VOC - NO$_x$</td>
<td>481</td>
<td>37</td>
<td>100 - 1000</td>
</tr>
<tr>
<td>VOC Mixture - NO$_x$</td>
<td>117</td>
<td></td>
<td>80 - 1000</td>
</tr>
<tr>
<td>Incremental Reactivity (effect of adding VOC to Surrogate - NO$_x$)</td>
<td>447</td>
<td>84</td>
<td>100 - 550</td>
</tr>
<tr>
<td>Base Case for Incremental Reactivity Reactivity</td>
<td>556</td>
<td></td>
<td>100 - 550</td>
</tr>
</tbody>
</table>
Measure of Model Performance for Ozone

Model performance for simulating both ozone formation and NO oxidation is measured by ability to predict $\Delta([\text{O}_3]-[\text{NO}])$:

$$\Delta([\text{O}_3]-[\text{NO}]) = ([\text{O}_3]-[\text{NO}])_{\text{FINAL}} - ([\text{O}_3]-[\text{NO}])_{\text{INITIAL}}$$

This gives a useful measure for both high NO and high $\text{O}_3$ conditions.

Measures $\text{O}_3$ formation once NO is consumed.

Measures initial NO oxidation rate.

Time

Concentration

Measures $\Delta([\text{O}_3]-[\text{NO}])$
Distribution of Model Errors for $\Delta([O_3]-[NO])$ in the Initial SAPRC-99 Evaluation

Radical Source Characterization

Single VOC - NOx

Various Mixture - NOx

Base Case Surrogate

$\Delta ([O_3]-[NO])$ Model Error: (Model - Experimental / Experimental)
Need for Improved Chamber Facility for Mechanism Evaluation

- Because of chamber effects and analytical limitations, most mechanism evaluation experiments conducted at higher pollutant levels than ambient.
- Large volume chambers are needed to reduce chamber effects and allow equipment with high sampling rates. But large outdoor chambers are difficult to control and characterize.
- Most chambers are not suitable to test predictions on how temperature affects O$_3$ and PM formation.
- Most U.S. chambers lack the analytical instrumentation needed to monitor many important trace species.
- The new UCR EPA Chamber was developed to address these needs.
Characteristics of New UCR EPA Chamber

- Indoor chamber design used for maximum control and characterization of conditions
- Dual reactor design for experimental productivity and to simplify reactivity assessment
- Largest practical volume for indoors (two ~100,000-L reactors)
- 200 KW filtered argon arc solar simulator
- Replaceable Teflon reactors in “clean room” to minimize background
- Positive pressure reactor volume control to minimize dilution and minimize contamination
- Temperature controlled to ±1°C in ~5°C to ~50°C range.
- Improved array of analytical instrumentation and provision for additional instrumentation in the future
Diagram of UCR EPA Chamber

This volume kept clear to maintain light uniformity

20 ft.

20 ft.

20 ft.

Movable top frame allows reactors to collapse under pressure control

Mixing System Under floor of reactors

Floor Frame

Gas sample lines to laboratory below

2 Banks of Blacklights

200 KW Arc Light

Temperature controlled room flushed with purified air and with reflective material on all inner surfaces

Two air Handlers are located in the corners on each side of the light (not shown).

Access Door

SEMS (PM) Instrument

Dual Teflon Reactors

Mixing System Under floor of reactors

Floor Frame

Gas sample lines to laboratory below

Movable top frame allows reactors to collapse under pressure control

Diagram of UCR EPA Chamber
Diagram of Reactor and Framework
(One of Two)

- Ceiling
- Cable
- Takeup Drum
- Pulleys
- Shaft Supports
- Motor
- Shaft
- Teflon Film
- Access Hatch and Sampling Port Holder
- Enclosure Floor
- ~ 90,000 Liters Maximum Volume
- Wall
- Upper Frame
- Lower Frame
- Port for Mixing, Low Volatility Injection and Exchange System
- Light Source
Photographs of Chamber and Lights

Looking Towards Reactors (from light)

Reflective walls and Ceiling
Partially Filled Reactors

Looking Towards Lights and Air Inlet

Black Lights
Air Intake
Arc Light
Reflective walls
Light Source and Spectrum

![Image of environmental chamber]

The graph shows the normalized power of different light sources as a function of wavelength. The x-axis represents wavelength in nanometers (nm), ranging from 300 to 700 nm. The y-axis represents normalized power in arbitrary units. The graph includes data for Solar, Blacklights, and a New Chamber.

- **Solar** light shows a broad spectrum with peaks around 300 nm and 500 nm.
- **Blacklights** produce a more focused spectrum with peaks at 365 nm and 312 nm.
- **New Chamber** has a spectrum that is more concentrated in the ultraviolet range, with peaks at 300 nm and 320 nm.

The height of each line on the graph indicates the relative power of each light source at different wavelengths.
Summary of 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 in one of the two reactors before it was replaced, but reproducible results obtained when >10 µg/m$^3$ PM formed.
Radical or NO\textsubscript{x} Offgasing Rates Derived for Various Chambers

\begin{figure}
\centering
\includegraphics[width=\textwidth]{chart.png}
\end{figure}

\begin{itemize}
\item Previous UCR Indoor
\item Previous UCR Outdoor
\item Previous UCR Default Model
\item Used for Modeling UNC Outdoor
\item TVA Indoor (NOx offgasing)
\item UCR EPA Chamber
\item SAPHIR HONO offgasing (dry)
\end{itemize}
### Initial Evaluation Experiments in New Chamber

<table>
<thead>
<tr>
<th>Run Type</th>
<th>Runs</th>
<th>NO&lt;sub&gt;x&lt;/sub&gt; Range (ppb)</th>
<th>VOC Range (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characterization</td>
<td>32</td>
<td>0 - 200</td>
<td>Varied</td>
</tr>
<tr>
<td>Formaldehyde - NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>2</td>
<td>8 - 25</td>
<td>0.35 – 0.5</td>
</tr>
<tr>
<td>Formaldehyde - CO - NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>2</td>
<td>15-20</td>
<td>HCHO: 0.4 – 0.5</td>
</tr>
<tr>
<td>Ethene - NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>2</td>
<td>10 - 25</td>
<td>CO: 15 - 80</td>
</tr>
<tr>
<td>Propene - NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>2</td>
<td>5 - 25</td>
<td>0.4 – 0.5</td>
</tr>
<tr>
<td>Toluene or m-Xylene - NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>4</td>
<td>5 - 25</td>
<td>Toluene: 0.6 – 0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Xylene: 0.18</td>
</tr>
<tr>
<td>Aromatic - NO&lt;sub&gt;x&lt;/sub&gt; + CO</td>
<td>6</td>
<td>5 - 30</td>
<td>CO: 25 - 50</td>
</tr>
<tr>
<td>Ambient Surrogate - NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>61</td>
<td>2 - 315</td>
<td>0.2 – 4.2 ppmC</td>
</tr>
</tbody>
</table>
Model Errors in Simulating $\Delta([O_3]-[NO])$ in the Initial Evaluation Experiments

Previous Experiments
- HCHO - NO$_x$
- HCHO - CO - NO$_x$
- Ethene - NO$_x$
- Propene - NO$_x$
- Toluene - NO$_x$
- Toluene - CO - NO$_x$
- m-Xylene - NO$_x$
- m-Xylene - CO - NO$_x$
- Surrogate - NO$_x$

(Single Run) / Experimental

-50% -25% 0% 25% 50%

← Model Biased Low → Model Biased High

SAPRC-99 Mechanism used
Matrix of ROG Surrogate – NO\textsubscript{x} Experiments in the UCR EPA Chamber

- Initial Evaluation Runs
- Initial NO\textsubscript{x} (ppb)
- Initial ROG (ppmC)

VOC Sensitive Region

NO\textsubscript{x}-Limited Region

Calculated Maximum O3 Line

Calculated MIR Line

- OBM Runs without Radical Data
- OBM Runs with OH, HO\textsubscript{2} Data
- Used for Base Case for Reactivity Runs

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Lowest NO\textsubscript{x} Surrogate Experiment
(ROG surrogate = 300 ppbC, NO\textsubscript{x} = 2 ppb)

- Experimental
- Standard Model
- No HONO Offgasing
- Maximum HONO Offgasing

Concentration (ppm) vs Time (minutes)

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Environmental Chamber Studies of VOCs
Representative Data from a Radical Measurement Experiment

- **Experimental**
- **SAPRC-99 Calc.**

**EPA 189A**
- ROG = 1 ppmC
- NOx = 20 ppb

**LIF Data**
- Derived from m-Xylene

**Time (minutes)**: 0, 120, 240, 360

**O3 (ppb)**: 0, 50, 100, 150

**OH (ppt)**: 0, 0.1, 0.2, 0.3

**H2O2 (ppb)**: 0, 1, 2, 3, 4, 5

**HO2 (ppt)**: 0, 20, 40, 60, 80

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Model Errors in Simulating $\Delta([O_3]-[NO])$ in the Initial Evaluation Experiments

Variable fits with generally negative bias for surrogate experiments

Previous Experiments
- HCHO - NO$_x$
- HCHO - CO - NO$_x$
- Ethene - NO$_x$
- Propene - NO$_x$
- Toluene - NO$_x$
- Toluene - CO - NO$_x$
- m-Xylene - NO$_x$
- m-Xylene - CO - NO$_x$
- Surrogate - NO$_x$

(Calculated - Experimental) / Experimental

← Model Biased Low → Model Biased High
Model Underprediction Errors for Surrogate - NO\textsubscript{x} Experiments

- SAPRC-99 (Range gives low and high Walls->HONO)
Model Underprediction Errors for Surrogate - NO\textsubscript{x} Experiments

\[ \Delta (O_3 - NO) \text{ Model underprediction} \]

- SAPRC-99
- Reduced k(OH + NO2)

ROG/NO\textsubscript{x} Ratio relative to ratio giving maximum O\textsubscript{3}
Model Underprediction Errors for Surrogate - NO\(_x\) Experiments: SAPRC-99 vs Carbon Bond 4

\[
\Delta (O_3-NO) \quad \text{Model underprediction}
\]

\[
\text{ROG/NO}_x \quad \text{Ratio relative to ratio giving maximum O}_3
\]

- SAPRC-99
- Carbon Bond 4
SAPRC-99 Model Underprediction Errors for Mixture and Surrogate - NO$_x$ Experiments

- Full Surrogate (includes m-xylene and toluene)
- Non-Aromatic Surrogate (Range gives low, high Walls->HONO)

![Graph showing model underprediction errors for ROG/NO$_x$ ratio relative to ratio giving maximum O$_3$.]
Uncertainties in Aromatics Mechanisms

• Major atmospheric reactions of aromatics involve OH adding to the ring, followed by various ring fragmentation processes.

• Despite considerable study, details of ring fragmentation process is unknown. Less than half of the product mass has been identified and quantified.

• In order for model to simulate chamber data, it is necessary to derive parameterized mechanisms with following characteristics:
  • Some uncharacterized products are highly photoreactive.
  • Photoreactive product yields and photolysis rates adjusted for model to predict O₃ in aromatics - NOₓ experiments.

• Evidence for compensating errors between numbers of NO to NO₂ conversions and radical input rates.
Measurement of Direct Reactivity

- Direct reactivity is the number of NO to NO2 conversions caused by a VOC’s reactions.
- A HONO + VOC photolysis flow system was developed to give a measurement sensitive to direct reactivity.
- Initial experiments indicate SAPRC-99 overpredicts direct reactivities of aromatics by up to a factor of 2.
Effect of CO in Aromatic - NO\textsubscript{x} Runs

Toluene

- Ozone
- Ozone Change (effect of CO)

EPA077 (~25 ppb NO\textsubscript{x})

- Concentration (ppm)
- Time (minutes)

- Aromatic - NO\textsubscript{x} experiment
- Aromatic - CO - NO\textsubscript{x} experiment
- Aromatic - NO\textsubscript{x} model
- Aromatic - CO - NO\textsubscript{x} model

m-Xylene

- Ozone
- Ozone Change (effect of CO)

EPA067 (~20 ppb NO\textsubscript{x})

- Concentration (ppm)
- Time (minutes)

- Concentration (ppm)
- Time (minutes)

EPA066 (~5 ppb NO\textsubscript{x})

- Concentration (ppm)
- Time (minutes)
Effects Of Adjustments to Parameterized Toluene Mechanism

Effect of CO (EPA074)

Toluene - NOx Runs

CTC079

EPA074A
Ongoing Mechanism Development Work

- SAPRC mechanism is being updated as part of a contract for the California ARB. Due to be completed by the end of 2006
- Significant work on the European Master Mechanism is underway. Current version does not perform well for aromatics
- Improving the aromatics mechanism is a high priority.
  - New chamber experiments conducted to evaluate models for aromatics products
  - New laboratory data are available
  - A more explicit aromatics mechanisms is being developed, but simulations of data no better than SAPRC-99.
- The California ARB is sponsoring an international conference on the future of mechanism development in December, 2006. See http://www.cert.ucr.edu/~carter/Mechanism_Conference
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 µg/m$^3$. (Was up to 2 µg/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**

- PM Volume ($\mu g/m^3$)
  - y-axis: 0.0 to 0.4
  - x-axis: 0 to 8 hours

**m-Xylene - NOx**

- PM Volume ($\mu g/m^3$)
  - y-axis: 0 to 8
  - x-axis: 0 to 10 hours

**CO - Air Irradiation**

- PM Number (1000/cm$^3$)
  - y-axis: 0 to 0.02
  - x-axis: 0 to 8 hours

**Surrogate - NOx**

- PM Number (1000/cm$^3$)
  - y-axis: 0 to 1.2
  - x-axis: 0 to 6 hours

**Side B Data**

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Matrix of m-Xylene - NOx Experiments to Study Effect of Reactant Levels on PM

<table>
<thead>
<tr>
<th>Ozone formed in 6 hours</th>
<th>&lt;70 ppb</th>
<th>70 - 158 ppb</th>
<th>158 - 200 ppb</th>
<th>&gt;200 ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial m-Xylene (ppb)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial NOx (ppb)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Final Aerosol Volume (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;10</td>
</tr>
<tr>
<td>10 - 21</td>
</tr>
<tr>
<td>21 - 60</td>
</tr>
<tr>
<td>&gt; 60</td>
</tr>
</tbody>
</table>

Graph showing the relationship between initial m-Xylene and initial NOx concentrations with respect to ozone formation and aerosol volume.
Equilibrium Model for PM in Experiments

- Measured PM yield is the ratio of aerosol mass formed (corrected for wall loss) to mass of VOC reacted

- From equilibrium gas-particle absorptive partitioning theory, assuming no initial PM and all PM is secondary organic aerosol:

\[
\text{PM Yield} = \frac{\text{PM}_{\text{tot}}}{\Delta\text{VOC}} \approx \text{PM}_{\text{tot}} \sum_i \frac{\alpha_i K_{\text{part}_i}}{1 + K_{\text{part}_i} \text{PM}_{\text{tot}}}
\]

Where:
- \(\alpha_i\) = Yield of condensable product \(i\) in VOC reactions
- \(K_{\text{part}_i}\) = Gas-particle partitioning constant for product \(i\)
- \(\text{PM}_{\text{tot}}\) = Total organic PM mass formed in experiment
- \(\Delta\text{VOC}\) = Mass of VOC reacting in experiment

- Standard parameterization for chamber experiments assumes:
  - Stoichiometric yields, \(\alpha_i\), are constant for a given VOC
  - Maximum of 2 products \((i = 1,2)\) sufficient to fit data
Standard Equilibrium Model Yield Curves for the m-Xylene Experiments

PM Yield (mass basis) vs. PM Formed ($\mu$g/m$^3$)

- Low ROG/NOx Experiments
- High ROG/NOx Experiments
- Fit for high ROG/NOx
- Fit for low ROG/NOx
NO\textsubscript{x}-Dependent Yield Model

- Assume that of formation yield of PM precursor, $\alpha_i$, is NO\textsubscript{x} dependent, as suggested by:

\[
\begin{align*}
\text{Xylene + OH} & \rightarrow \text{Intermediate} \\
\text{Intermediate} & \xrightarrow{k_1} \alpha' \text{ PM Precursor} \\
\text{Intermediate} + \text{NO}_x & \xrightarrow{k_2} \text{other products}
\end{align*}
\]

- Adjust $\alpha'$, $K_{\text{part}}$, and $k_1/k_2$ to fit data
- Single product model ($i=1$) is sufficient to fit data
- Fits better using NO\textsubscript{x} to xylene ratio rather than total NO\textsubscript{x}.
- Model and best-fit $K_{\text{part}}$, and $k_1/k_2$ values can be used to derive precursor yields, $\alpha$, for individual experiments
Dependence of Derived PM Precursor Yields on NO$_x$/ROG, O$_3$, and Extent of Reaction

- PM precursor yields (molar) derived from data for a run
- Predicted dependence on NO$_x$/xylene ratio by NO$_x$-dependent yield model

![Graphs showing relationship between initial NO$_x$ / m-xylene ratio, 6-hour ozone (ppb), and fraction xylene reacted.](image)
PM Yields from Zero NOx (m-Xylene – H$_2$O$_2$) Experiments

As predicted by fit to m-Xylene - NOx experiments extrapolated to zero NOx

- m-Xylene - H$_2$O$_2$ Experiments
Partial Mechanism for m-Xylene Reactions

These hydroperoxides are the probable zero-NOx PM precursors.
Comparison of Hydroperoxide and Derived PM Precursors Yields vs NO$_x$/Xylene Ratio
Comparison of Hydroperoxide and Derived PM Precursors Yields vs NOₓ/Xylene Ratio

PM Precursor Yield (mass basis)

Predicted hydroperoxide yield (molar basis)

ROG/NOₓ - independent PM Precursor?

Hydroperoxide formation?

- Predicted by best-fit parameters
- Derived from data for a Run
- SAPRC-99 prediction of hydroperoxide yield
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 $\mu g/m^3$

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

Error Bars are 1-$\sigma$ standard deviations. No error bar means only one experiment. Side B data only.
FUTURE RESEARCH DIRECTIONS

• Continue $O_3$ reactivity and mechanism evaluation experiments as currently underway

• Utilize the capabilities of chamber for well-characterized SOA studies needed for SOA model development and evaluation

• Investigate temperature and humidity effects on $O_3$ and SOA

• Obtain instrumentation needed for $NO_3$, $N_2O_5$, $HO_x$, and other trace species to improve capabilities and utility of this facility

• Serve as a resource for collaborative studies where environmental chamber measurements under highly controlled and characterized conditions would be useful

• Serve as test bed for instrumentation for ambient monitoring
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