The Reactivity Research Working Group: 
A Chronological Overview and Evaluation

**Report objectives:**
- provide a chronicle of RRWG activities and a repository of its products;
- provide a critical review of these products.

RRWG formed in 1998 with the objective of “providing an improved scientific basis for reactivity-related regulatory policies.”

**Structure:**
- public/private cooperative effort
- bilateral science/policy function

![Diagram of RRWG structure]

RRWG Overview Report

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RRWG Timeline and Products

Genesis

“Interim Breakpoint”

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RRWG VOC Reactivity Assessment

Policy White Paper

Science Assessment

1. Atmospheric Chemistry
2. Aerosol Forming Potential
3. Emissions Data
4. Volatility and Fate
5. Air Quality Models
6. Environmental Conditions
7. Reactivity Assessments

Recommended Research Projects
Priority RRWG Research Projects (Distilled List)

1,5,7,9. Assess effects of large-scale reactivity-based scales and substitutions on regional air quality using existing models.

2. Analyze available information relevant to how much of the environmental would be sensitive to VOC controls, and the distribution of conditions appropriate for reactivity assessments.

3. Improve information on atmospheric availability of low-volatility VOC and evaluate existing fugacity models.

4. Survey amounts of emissions that are suitable for reactivity-based controls.

6. Survey existing modeling assessments.

8. Improve emission processing modules in models.

10. Evaluate existing chamber data base.
Discussion Format

1. 15-minute jump start on reactivity concepts (important)
2. VOC vs. NO_x sensitivity (RP 2) (quickly)
3. Reactivity scales and substitutions (RP 1,5,7,9) (discussion focus)
4. Conclusions
Reactivity Concepts

**Major Questions:**

- How is “reactivity” defined?
- How are reactivities calculated?
Reactivity Concepts

**HO reactivity**

\[ \text{VOC}_i + \text{HO}^\cdot \rightarrow \text{HO}_2^\cdot, \text{RO}_2^\cdot \rightarrow \text{O}_3 \]

rate = \( k_{\text{HO}}^{\text{VOC}_i}[\text{VOC}_i][\text{HO}^\cdot] \)

HO reactivity = \( k_{\text{HO}}^{\text{VOC}_i} \)

**Sensitivity and incremental reactivity**

\[ s_{\text{O}_3}^\alpha = \frac{\partial [\text{O}_3]}{\partial \alpha} \Rightarrow \text{IR}_\alpha \]

\[ s_{\text{O}_3}^{\text{VOC}_i} = \frac{\partial [\text{O}_3]}{\partial \text{VOC}_i} \Rightarrow \text{IR}_{\text{VOC}_i} \]

\( \alpha, \text{VOC}_i = \text{“sensitivity parameters”} \)

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Reactivity Concepts

Reactivity Computation: Box-model approach

Chemical Parameterizations:
- CB4
- SAPRC##
- RADM2
- 
- 

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Reactivity Concepts • • •
Incremental Reactivity Characterization
Box-Model Output

![Graph showing the peak ozone and incremental reactivity.]

- **peak ozone**
- **incremental reactivity**
Reactivity Concepts

Maximum Ozone Incremental Reactivity

Box-Model Output

O3 Mixing Ratio (pphm) and Sensitivity to VOC Mix

- ozone(1.0)
- sens VOC(1.0)
- ozone(2.0)
- sens VOC(2.0)
- ozone(3.0)
- sens VOC(3.0)

maximum peak ozone

MOIR_{VOC}
Reactivity Concepts • • •

Maximum Incremental Reactivity

Box-Model Output

Maximum peak ozone
Reactivity Concepts

MIR/MOIR Comparison

Box-Model Output

MOIR

MIR
Reactivity Concepts • • •

“Amplification” by various reactivity scales

*From Carter, Tonnesen, and Yarwood
Reactivity Concepts • • •
Effects of NO\textsubscript{x} Addition

Computed results at time of ozone maximum

- Ozone Mixing Ratio, ppm X 10
- VOC Sensitivity, moles O3/mole VOC
- NO\textsubscript{x} Sensitivity, moles O3/mole NO\textsubscript{x}
Reactivity Concepts

Relative reactivities and reactivity scales

\[ \text{RMIR}_i = \frac{\text{MIR}_i}{\text{MIR}_{VOC_{mix}}} \]

\[ \text{RMOIR}_i = \frac{\text{MOIR}_i}{\text{MOIR}_{VOC_{mix}}} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>RMIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.034</td>
</tr>
<tr>
<td>methane</td>
<td>0.0052</td>
</tr>
<tr>
<td>ethane</td>
<td>0.033</td>
</tr>
<tr>
<td>propane</td>
<td>0.048</td>
</tr>
<tr>
<td>ethene</td>
<td>1.1</td>
</tr>
<tr>
<td>propene</td>
<td>1.4</td>
</tr>
<tr>
<td>benzene</td>
<td>0.054</td>
</tr>
<tr>
<td>toluene</td>
<td>0.35</td>
</tr>
</tbody>
</table>
Reactivity Concepts

Sensitivity calculation

Brute force:

\[ s_{O_3}^{VOC_i} = \frac{\partial O_3}{\partial VOC_i} \approx \frac{O_3(VOC_i + \delta) - O_3(VOC_i)}{\delta} \]

VOC_i = sensitivity parameter

DDM:

\[ \frac{\partial s_{1}^{VOC_i}}{\partial t} = f_1(s_{1}^{VOC_i}, ..., s_{n}^{VOC_i}, c_1, ..., c_n, VOC_i) \]
\[ \frac{\partial s_{2}^{VOC_i}}{\partial t} = f_2(s_{1}^{VOC_i}, ..., s_{n}^{VOC_i}, c_1, ..., c_n, VOC_i) \]
\[ ... \]
\[ \frac{\partial s_{n}^{VOC_i}}{\partial t} = f_n(s_{1}^{VOC_i}, ..., s_{n}^{VOC_i}, c_1, ..., c_n, VOC_i) \]

NOTES ON DDM:

- Must compute sensitivities for all species
- Must be initialized
- Must use consistent sensitivity parameter (esp. important for multidimensional modeling)
Reactivity Concepts

Box vs. Multidimensional Models

**Box Modeling**
- Convenient titration of NO\textsubscript{x}, allowing MOIR & MIR det’n
- Sensitivity parameters usually combinations of emissions and initial conditions
- Not particularly conducive to multiday or regional simulations
- Brute-force sensitivity determination tenable (but not particularly efficient)

**Multidimensional Modeling**
- Not conducive to NO\textsubscript{x} titration: direct MOIR & MIR det’n not practical
- Sensitivity parameters usually based on total grid emissions
- Require spin-up to purge initial conditions
- Conducive to multiday and regional simulations
- Brute-force sensitivity determination usually impractical
VOC/NO\textsubscript{x} Limitation

Blanchard and Tannembaum: *Spatial Mapping of VOC and NO\textsubscript{x} Limitation of Ozone Formation*

- Focuses on Observation Driven Models (ODMs), primarily the “Smog-Production” (SP) algorithm as implemented by the MAPPER (public domain) software package.
- Defines an observationally-based “extent of reaction,” \( E(t) \) as
  
  \[
  E(t) = \frac{O_3(t) - O_3(0) + NO(i) - NO(t)}{\sqrt{[NO_x(i)]^{1/2} + NO(i)}}
  \]

- Brackets limiting behavior according to the empirical relationship
  
  VOC – limited \( \leftarrow 0.6 > E(t) > 0.9 \rightarrow \) NO\textsubscript{x} - limited

- Mines North American datasets, produces plots and tables of limiting conditions

*Take-home message:* Substantial areas of NO\textsubscript{x} limitation exist, particularly in Eastern US regions
Regional Reactivity Modeling

Consolidated Tasks (1,5,7,9)

1. Assess effects of large-scale reactivity-based substitutions on regional air quality using existing models;
5. Develop appropriate scenarios for general reactivity assessment;
7. Develop model criteria for reactivity assessments; and
9. Use existing models to evaluate exemption standards

Subgoals:
• develop and assess reactivity metrics with respect to consistency, sensitivity, and directionality;
• compare various computational platforms for reactivity evaluation;
• investigate large geographical domains with multiday episodes;
• compare different chemical parameterization schemes for use in reactivity analyses; and
• test impact of chemical substitutions for selected VOC emissions.
Regional Reactivity Modeling

Initial three modeling projects:

1. Arunachalam, Mathur, Holland, Lee, Olerud, and Jeffries (AMHLOJ)
2. Carter, Tonnesen, and Yarwood (CTY)
3. Hakami, Bergin, and Russell (HBR)

Primary activities:

1. Substitution studies (AMHLOJ and CTY)
2. Reactivity calculations: incremental reactivities and scales (CTY and HBR)
# Regional Reactivity Modeling

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Grid Structure</td>
<td>Nested</td>
<td>Nested</td>
<td>Nested</td>
</tr>
<tr>
<td>Chemistry</td>
<td>Modified CB4 including ethane</td>
<td>1. Modified RADM 2 including 2-butoxyethanol</td>
<td>SAFRC-99</td>
</tr>
<tr>
<td>Parameterization</td>
<td></td>
<td>2. Modified CB4, including 2-butane and 2-butoxyethanol</td>
<td></td>
</tr>
<tr>
<td>Sensitivity</td>
<td>1. O&lt;sub&gt;x&lt;/sub&gt; sensitivity to emissions of CB4 VOC species and groups plus ethane, NO, CO, and total VOC</td>
<td>O&lt;sub&gt;x&lt;/sub&gt; sensitivity to emissions of standard SAFRC-99 VOC species and groups</td>
<td></td>
</tr>
<tr>
<td>Specific</td>
<td>1. O&lt;sub&gt;x&lt;/sub&gt; sensitivity to biogenic + anthropogenic VOC + NO&lt;sub&gt;x&lt;/sub&gt; emissions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sensitivity Tests</td>
<td>2. O&lt;sub&gt;x&lt;/sub&gt; sensitivity to CO and anthropogenic CB4 species emissions</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. O&lt;sub&gt;x&lt;/sub&gt; sensitivity to 3 individual VOC source classes: mobile, area, point</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Averaging Times</td>
<td>1. 1-hour and 8-hour</td>
<td>1. 1-hour and 8-hour</td>
<td></td>
</tr>
<tr>
<td>and Data</td>
<td>2. 1-hour associated with highest O&lt;sub&gt;x&lt;/sub&gt; concentration for day</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stratification</td>
<td>3. 8-hour associated with highest 8-hour concentration for that day</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sensitivity</td>
<td>MIR, MOIR, EDIR, ZHIR, NIR, Least Squares</td>
<td>MIR, MOIR, Least Squares</td>
<td></td>
</tr>
<tr>
<td>Metrics</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Substitution</td>
<td>1. Eliminate anthropogenic VOCs replace with 100% ethane (carbon basis)</td>
<td>1. Reduce VOC emissions by 15% for all area and point sources</td>
<td></td>
</tr>
<tr>
<td>Tests</td>
<td>2. Eliminate anthropogenic VOCs replace with 50% ethane (carbon basis)</td>
<td>2. Substitute 2-butanone for 15% VOC emissions on a gram basis.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. Eliminate anthropogenic VOCs replace with 50% ethane (carbon basis)</td>
<td>3. Substitute styrene emissions from all non-mobile sources (area and point) with 2-butoxyethanol on a mole basis</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4. Eliminate anthropogenic VOCs replace with 50% ethane (carbon basis)</td>
<td>4. Repeat 2 on a mole basis</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5. Reduce anthropogenic VOCs 50%; replace with 255% ethane (carbon basis)</td>
<td>5. Repeat 2 on a mole basis</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6. Repeat 3 on a gram basis</td>
<td></td>
</tr>
</tbody>
</table>

*J. M. Hales, March 2007*
Regional Reactivity Modeling • • •

A common feature of all Eastern US modeling efforts:

→ Large (roughly 80%) contribution of natural VOCs.

Leads to:

• larger areas of NO$_x$-limitation
• controllable VOC limited
Substitution and indicator studies

CTY:
1. Reduce anthropogenic VOC’s 100%
2. Reduce anthropogenic VOC’s 100%, replace with ethane (various percentages)

AMHLOJ:
1. Reduce area and point-source emissions by 15%
2. Substitute 2-butanone (1.48) for the reduced VOC emissions
3. Substitute glycol ether (0.8) for xylene (10.6) for area and point sources

Take-home messages:
1. total anthropogenic VOC reduction has marginal influence (2 - 3 ppb) on average peak \( O_3 \) (larger in specific areas).
2. ethane substitution on a molar replacement basis has an effect similar to VOC reduction.
3. indicator studies (esp \( O_3/NO_x \) ratios) of AMHLOJ suggest that over 90% of grid cells are in the \( NO_x \)-limited regime.
Reactivity modeling:

CTY:
Incremental reactivities: Sensitivities @ peak $O_3$ to total-grid emissions of CB4 VOC groups plus ethane, total VOC, CO, and $NO_x$

Scales: regional MIR, regional MOIR, regionally averaged, regionally averaged above standard, least-squares, regional MOIR-MIR

HBR:
Incremental reactivities: Sensitivities @ peak $O_3$ to total-grid emissions of SAPRC-97 VOCs, VOC groups, and $NO_x$

Scales: regional MIR, regional MOIR, least-squares, regionally averaged, regionally averaged above standard, least-squares, regional MOIR-MIR
Regional Reactivity Modeling

Explanation of scales:

- Regional MIR
- Regional MOIR
- Regional average reactivity
- Regional average reactivity above O₃ standard
- Regional MOIR - MIR
- Least squares

Relative Reactivity = \frac{\text{IR}(\text{VOC}_i)}{\text{IR}(\text{VOC}_{\text{mix}})} \text{, or}

\text{IR}(\text{VOC}_i) = (\text{Relative Reactivity}) \times \text{IR}(\text{VOC}_{\text{mix}})

J. M. Hales, March 2007
Satisfactory resolution of the regulatory application question must involve systematic examination of two major, (but largely unanswered) questions:

- What, precisely, are the objectives to be attained by the regulatory application?
- How, precisely, will the regulation be applied?
Regional Reactivity Modeling

Regulatory application of reactivity scales

Hakami, Arhami, and Russell criteria:

The scale should:

• exhibit minimal spatial and temporal variability;
• reflect relatively low uncertainty with regard to depicting the atmospheric physics and chemistry of the region in question;
• minimize the risk of error in intended $O_3$ reduction;
• benefit the maximum number of people as to the greatest extent possible;
• provide relatively uniform benefit to all individuals;
• integrate as much information across the region as possible, and not be overly dependent on conditions at a single point or a single species; and
• provide a straightforward and tractable means of calculation.
**Regional Reactivity Modeling**

**Bottom line on reactivity scales:**

<table>
<thead>
<tr>
<th>Reactivity Scale</th>
<th>Evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regional MIR</td>
<td>Consistent across model domains and days and protective of urban populations with high NOₓ levels</td>
</tr>
<tr>
<td>Regional MOIR</td>
<td>Based on the relative reactivity at one point and perhaps relatively rare conditions of most NOₓ-limited. Less typical of population centers. Least VOC-sensitive. High inter-domain and inter-episode variability</td>
</tr>
<tr>
<td>Least Squares</td>
<td>Consistent across model domains and episode days</td>
</tr>
<tr>
<td>Regionally Averaged Reactivity</td>
<td>Exhibits considerable inter-domain variability. Includes many VOC-insensitive, low-ozone cells.</td>
</tr>
<tr>
<td>Regional Average Over the O₃ Standard</td>
<td>Robust scale that shows little variability and gives the best estimates for regions in exceedance of standards.</td>
</tr>
<tr>
<td>Regional MIR - MOIR</td>
<td>Exhibits greatest inter-domain consistency, little variability between episode days. Focuses on areas where NOₓ control would be counterproductive.</td>
</tr>
</tbody>
</table>
Take-home message:

Several of the tested scales appear to be appropriate candidates for regulatory application, **BUT:**

1. **The issue of NO\textsubscript{x} limitation remains**

2. **Key questions are unresolved (something was missing here):**
   - What, precisely, are the objectives to be attained by the regulatory application?
   - How, precisely, will the regulation be applied?
Enhancing the science/policy interface: the Policy Testbed

1. What, precisely, are the objectives to be attained by the regulatory application?
2. How, precisely, will the regulation be applied?

Report Recommendation: Adopt a formalization for the science/policy interface, the “Policy Testbed.”

• The policy sector creates a testbed by describing a hypothetical, future regulatory system defining the answers to Question 1, but leaving most of the features of Question 2 open to further investigation. The testbed should be:
  • Reasonably forward-looking
  • Cognizant of current legislation, but not constrained to it.

• Once established, the testbed can be used for direct interaction with the science community to determine the best options for addressing Question 2.
Policy Testbed • • •

Advantages:

• Leads to well-posed statement of problem to be resolved;

• Identifies unambiguously the relative roles of policy makers and scientists;

• Provides a systematic and accountable means of identifying and focusing needed research;

• Provides an efficient mechanism for communicating information to policy-review committees, lawmakers, upper management, and the public.
Report Conclusions

The RRWG activity has been commendably productive for two major reasons:
• initiative of its participants
• productive interaction between its policy analysts and scientists.

The Interim Guidance approach adopted by the EPA seems appropriate at this development stage.

Future work by the RRWG or its successors should maintain and augment the strong science/policy structure and should broaden the scope to address more squarely Questions 1 and 2 above, with the policy sector taking a lead role in this process. Primary issues to be addressed are in this regard are:

• O₃ management by coordinated, optimized VOC and NOₓ control;
• definitive criteria for O₃ management; and
• multipollutant management.

These complex issues demand an effective interaction between scientists and policy analysts. To enhance and systematize this interaction, the report recommends that the “Policy Testbed” be applied in future programs of this type.

J. M. Hales, March 2007