

Issues and Recent Research on Ozone Reactivities of VOCs

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Outline

- Factors affecting ozone reactivity and ozone reactivity scales
- Methods for deriving ozone reactivity scales: models, scenarios, metrics and other issues
- Recent SAPRC chemical mechanism and MIR scale updates
- Recommendations for improving ozone reactivity scales

Factors Affecting Impacts of VOCs on O₃

- Ground level O₃ is formed from the reactions of NO_x. But without VOCs O₃ levels are low because of its reaction with NO.
- VOCs differ significantly on their effects on O₃ formation
Mechanistic factors affecting ozone impacts are:
 - How fast the VOC reacts
 - NO to NO₂ 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 O₃ also depends on where it reacts
 - The availability of NO_x. (NO_x necessary for O₃ 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 O₃.

Quantification of O₃ Reactivity

- A useful measure of the ozone impact of a VOC is its **Incremental Reactivity**

$$\text{Incremental reactivity of a VOC in an episode or experiment (scenario)} = \lim_{[\text{Added VOC}] \rightarrow 0} \frac{\text{O}_3 \text{ formed after VOC added} - \text{O}_3 \text{ formed in scenario ("Base Case")}}{\text{Amount of VOC added}}$$

- This depends on the condition of the episode as well as the chemistry of the VOC

Measurement or Calculation of Atmospheric Reactivity

- Reactivity can be measured in chamber experiments, but the **results are not the same as reactivity in the atmosphere.**
 - Impractical to duplicate all relevant conditions
 - Chamber experiments have wall effects, static conditions, higher levels of test VOCs, etc.
 - Atmosphere has dilution, variable emissions schedule, entrained and initial pollutants, variable mixing, etc.
- Atmospheric reactivity must be calculated using **computer airshed models**, given:
 - Chemical mechanism for VOC's Atmospheric Reactions
 - Models for airshed conditions
 - Choice of airshed condition(s) and ozone impact quantification metric if a single reactivity scale is needed

Methods for Derivation of Reactivity Scales: Summary of Choices Required

- Type of **airshed model**
- Types of **atmospheric conditions** (airshed scenarios or episodes) to model
- Method to **quantify ozone impact** from model results
- Method to **derive a single scale** from distribution of impacts in scenarios modeled (if more than one scenario used)
- **Chemical mechanism** used to represent ozone formation reactions of VOCs and NO_x in model

Methods for Derivation of Reactivity Scales: Type of Airshed Models

Single Cell Box, Trajectory, or “EKMA” models

- Most practical way to use mechanisms for hundreds of VOCs
- Highly simplified representation of actual airsheds, but *may* represent range of chemical conditions relevant to reactivity
- Used for existing comprehensive scales (e.g., MIR and POCP)

Multi-Cell, 3-D Regional Models

- Only way to model how O₃ varies with time and space in *actual* airsheds. Only type of model acceptable for SIP demonstrations
- Has been used for selected compounds but not yet used to for comprehensive scales
- Feasible but expensive. **Requires work on scenario selection and methodology and improved model software**

Methods for Derivation of Reactivity Scales: Type of Scenario Conditions

Maximum Incremental Reactivity (used for MIR scale)

- Represents high NO_x conditions where O_3 most sensitive to VOCs. Currently used in California Regulations
- Regional model analogue: Average of MIR to MOIR cells: cells where reducing NO_x increases ozone. Generally urban areas

Worse Case or Maximum Ozone (used for MOIR scale)

- Represents conditions where the highest ozone concentrations or exposures occur. Generally used for SIP modeling
- Could include regions where O_3 is not sensitive to VOC controls

Representative or Regional Conditions (Base Case Scales)

- Represents typical conditions or wide regions
- Includes wide regions where O_3 is not sensitive to VOC controls

Methods for Derivation of Reactivity Scales: Ozone Impact Quantification

Effect of VOCs on Daily Maximum Ozone

- Used for existing MIR scale used in California Regulations
- Representative of 1-hour ozone standards

Effect of VOCs on 8-Hour Average Ozone

- Representative of 8-hour standards

Effect on Ozone Exposure

- Requires specifying a method to quantify ozone exposure
- Options include: integrated O_3 , hours O_3 over the standard, integrated O_3 over the standard, etc.

Methods for Derivation of Reactivity Scales: Methods for Deriving a Single Scale

Average incremental reactivities in chosen cells or scenarios

- Depends on criteria used to chose cells or scenarios (e.g., MIR)
- *Not valid if low O₃ or highly NO_x-limited areas are included*

Use effects of VOCs on total O₃ in multiple cells or scenarios

- Permits derivations of valid scales over wide regions, including low NO_x or VOC sensitive areas
- Gives greatest weight to cells with highest O₃

Quantify impact using total population-weighted exposure

- High population areas tend tend to be more VOC sensitive

Minimum Substitution Error

- Minimizes ozone differences in reactivity-weighted substitutions.
- Gives greater weight to VOC-sensitive areas

Methods for Derivation of Reactivity Scales: Chemical Mechanism

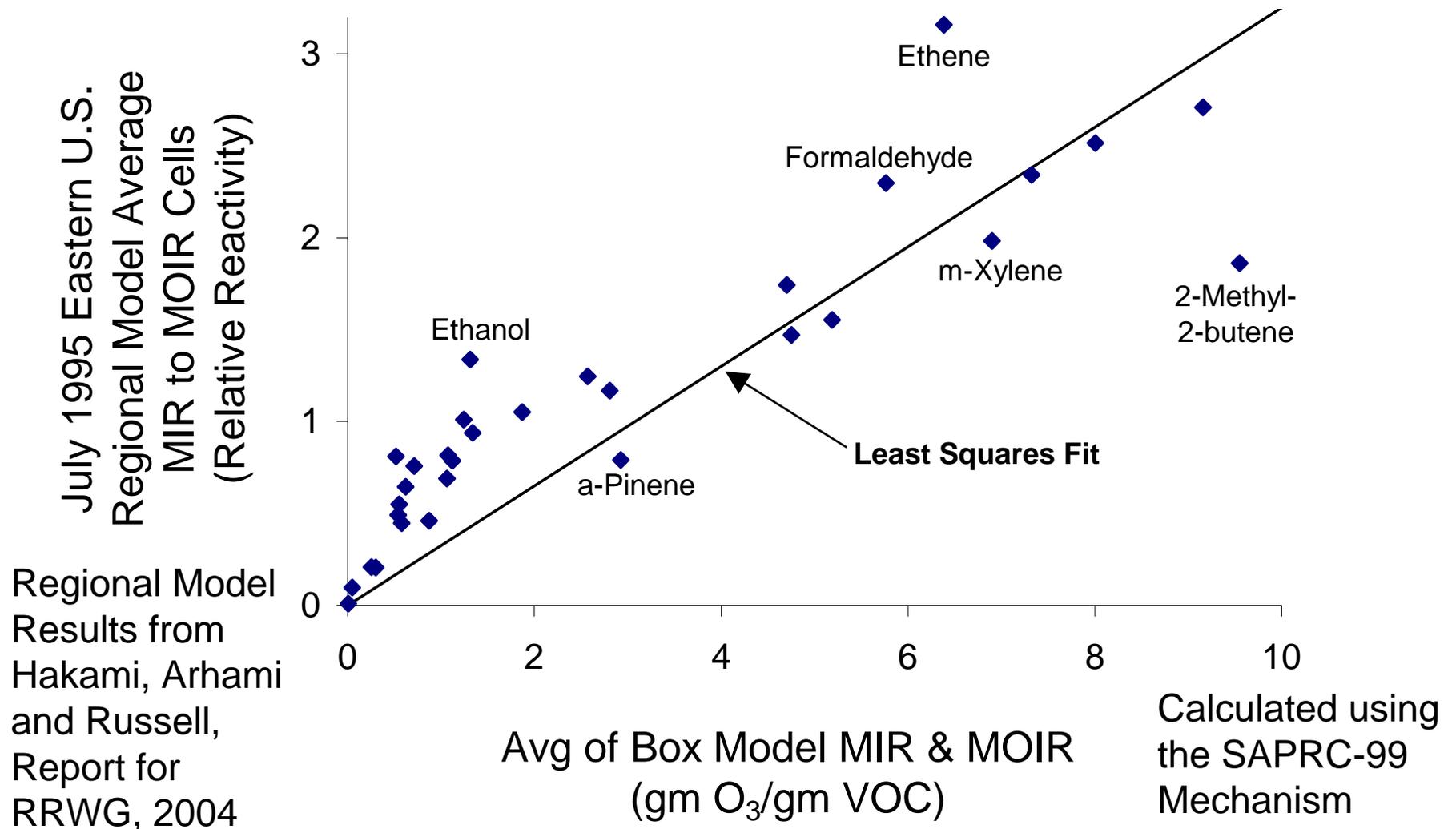
Requirements

- Must represent the current state of the science and be acceptable for predicting O₃ in ambient scenarios for regulatory applications
- Must include appropriate representation of how the hundreds of types of VOCs differ in their effects on O₃ formation
- Ability to predict O₃ impacts for the major types of VOCs should be experimentally evaluated using environmental chamber data

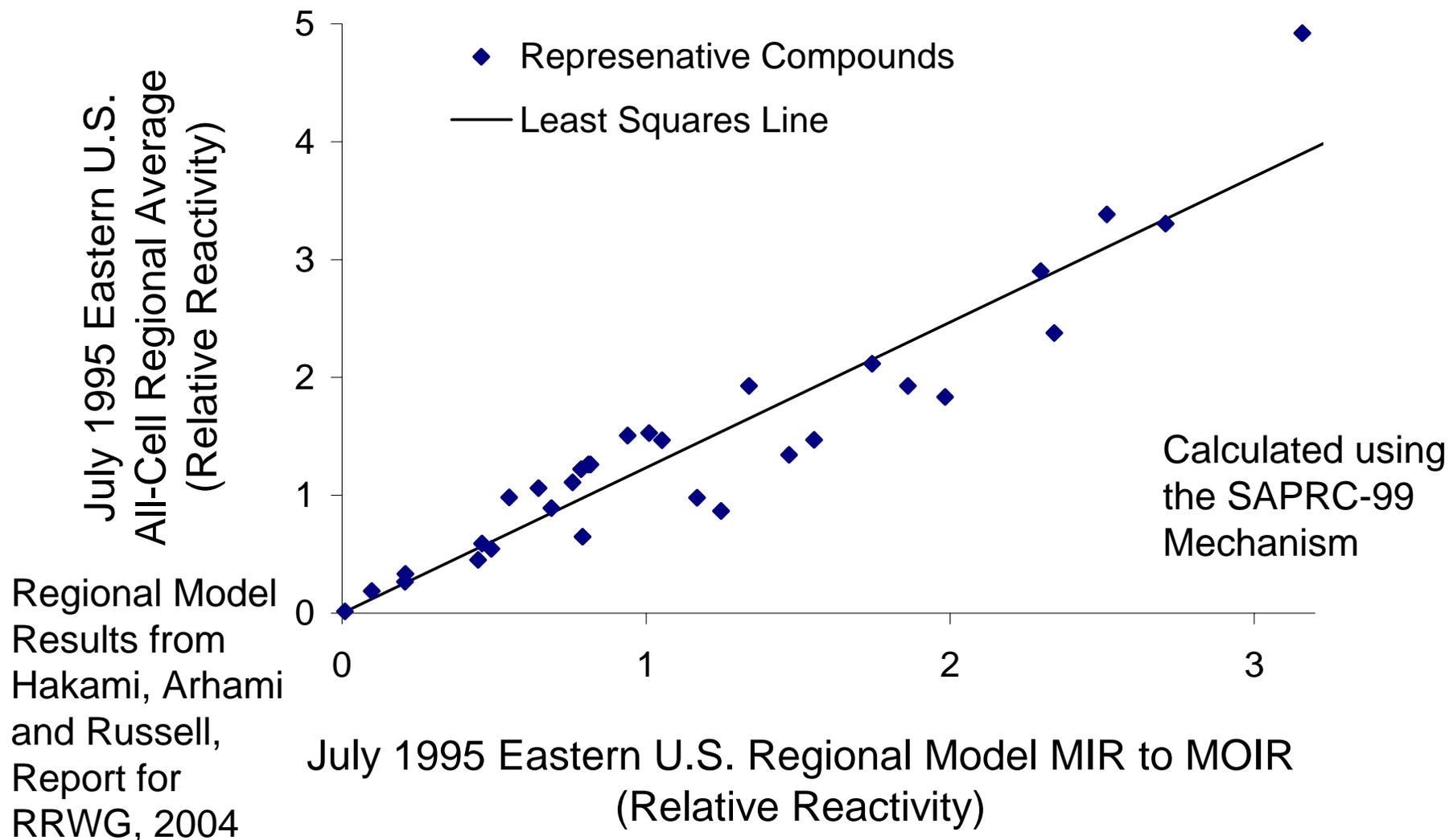
Available Options

- **SAPRC mechanisms:** designed for this purpose and extensively evaluated against chamber data
- **European MCM:** much more chemically detailed but fewer types of VOCs represented and not as extensively evaluated

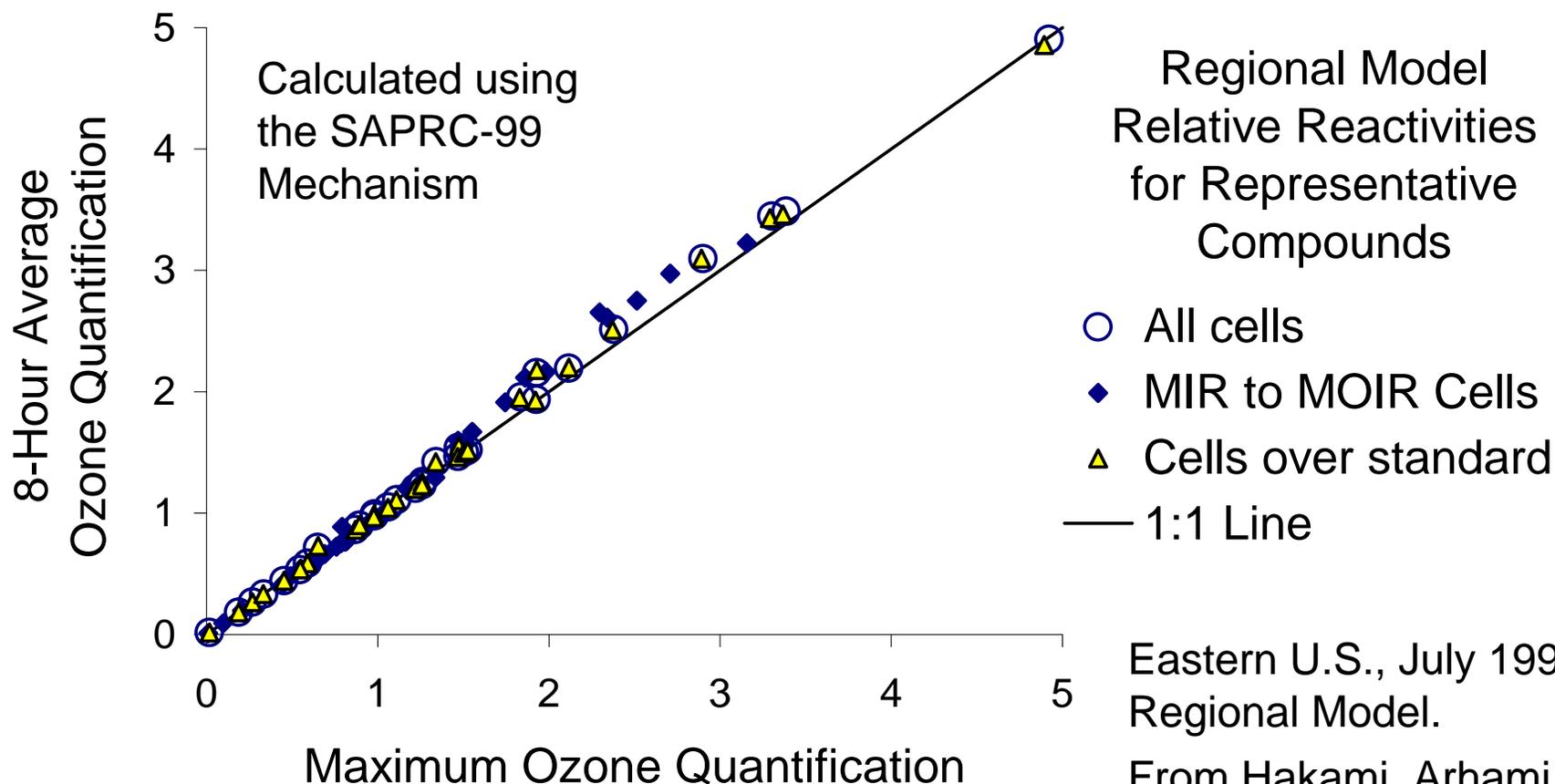
Comparison of Regional vs. Box Model Reactivities for Comparable Conditions



Comparison of MIR to MOIR vs. Regional Average Reactivities



Maximum Ozone vs. 8-Hour Average Ozone Regional Model Relative Reactivities

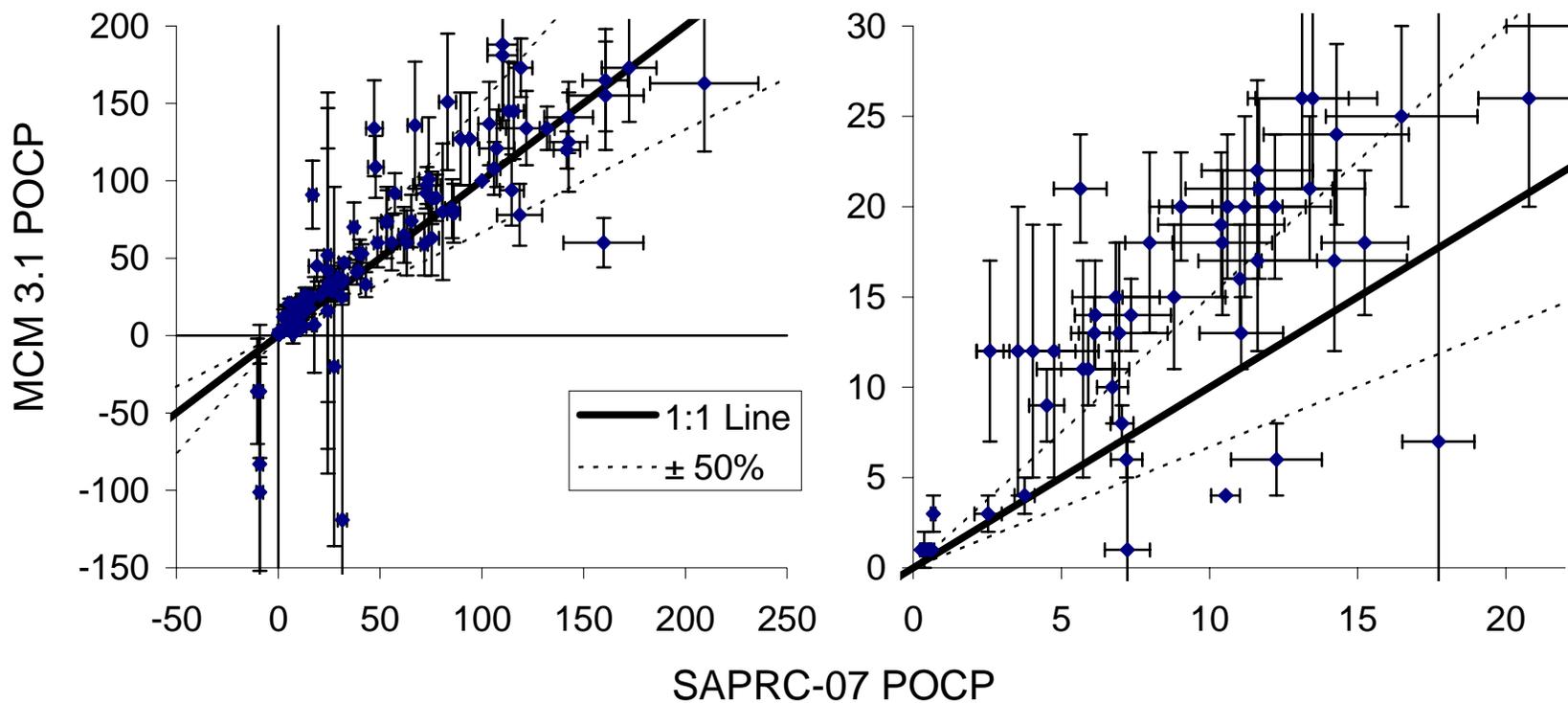


Eastern U.S., July 1995
Regional Model.

From Hakami, Arhami
and Russell, Report for
RRWG, 2004

Average Relative Reactivities for Five MIR Scenarios: MCM vs. SAPRC

Incremental Reactivities relative to Ethene = 100



Representative Compounds with Significant Differences in MCM vs. SAPRC Reactivities

Compound	POCP		Possible Reason for POCP difference
	S-07	MCM	
Methyl Acetate	0.7	3	MCM forms more reactive products (formaldehyde)
Tetrachloroethylene	0.3	1	Phosgene photolyzes in MCM. Inert in SAPRC
Glyoxal	160	60	Glyoxal photolysis 4 x faster in SAPRC
Acetylene	11	4	
Methacrolein	67	136	Methacrolein photolysis 3 x faster in MCM
Isoprene	119	173	
d-Limonene	47	135	MCM terpene mechanisms too complex to readily assess
α -Pinene	48	109	

Methods for Deriving the MIR Scale Used in California Reactivity Regulations

Airshed model

- Single cell EKMA-type box model

Atmospheric conditions

- Single day EKMA scenarios representing 39 U.S. cities derived in 1990 for regulatory impact analysis used as the starting point
- NO_x inputs adjusted to give highest sensitivity of O₃ to VOCs (MIR)

Ozone quantification method

- Daily maximum (final) ozone concentration

Method to derive a single scale

- Average of incremental reactivities in the 39 MIR scenarios

Chemical Mechanism

- SAPRC mechanisms (updated periodically)

Updates to the MIR Scale Used in California Reactivity Regulations

Chemical Mechanism

- Original scale developed in 1993 used SAPRC-90
- Updated to SAPRC-93 in 1994
- Updated to SAPRC-99 in 2000 (minor updates in 2002)
- Now updated to SAPRC-07

VOCs Represented

- ~330 types of VOCs in SAPRC-93 scale used in 1994 regulations
- ~780 types of VOCs and mixtures in latest SAPRC-99 scale
- ~1140 types of VOCs and mixtures in new SAPRC-07 scale

Airshed model, Atmospheric Conditions, Quantification methods

- No updates since original scale developed in 1993 except for minor software and methodology improvements

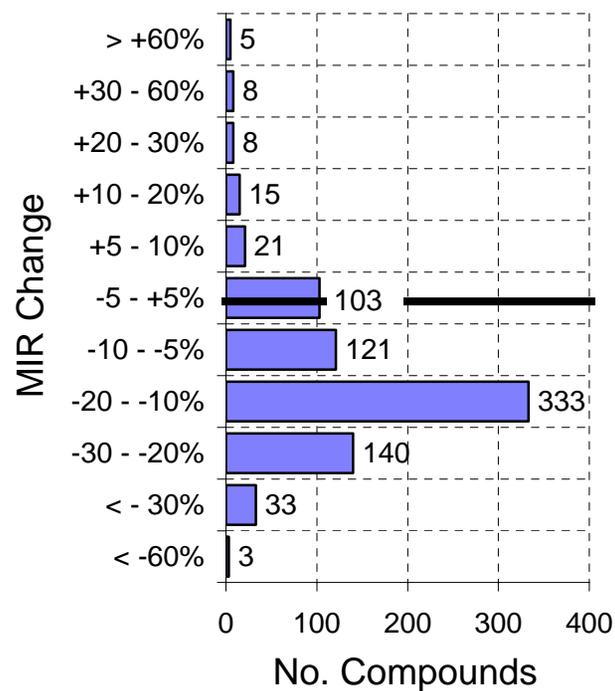
Recent Reactivity Research at UCR: SAPRC-07 Mechanism Update

- Rate constants and reactions updated to the current state of science
- Chlorine chemistry added
- The mechanisms for aromatics have been improved, but major uncertainties and inconsistencies with available data remain
- The method used to estimate and generate explicit mechanisms have been enhanced to derive mechanisms for more compounds
- The capability to be adapted to secondary PM models has been improved, though much additional work is needed for PM modeling
- The mechanism has been evaluated against a larger database of chamber experiments, including many recent experiments at UCR
- The mechanism was peer reviewed by four independent scientists and approved by the CARB Reactivity Science Advisory Committee

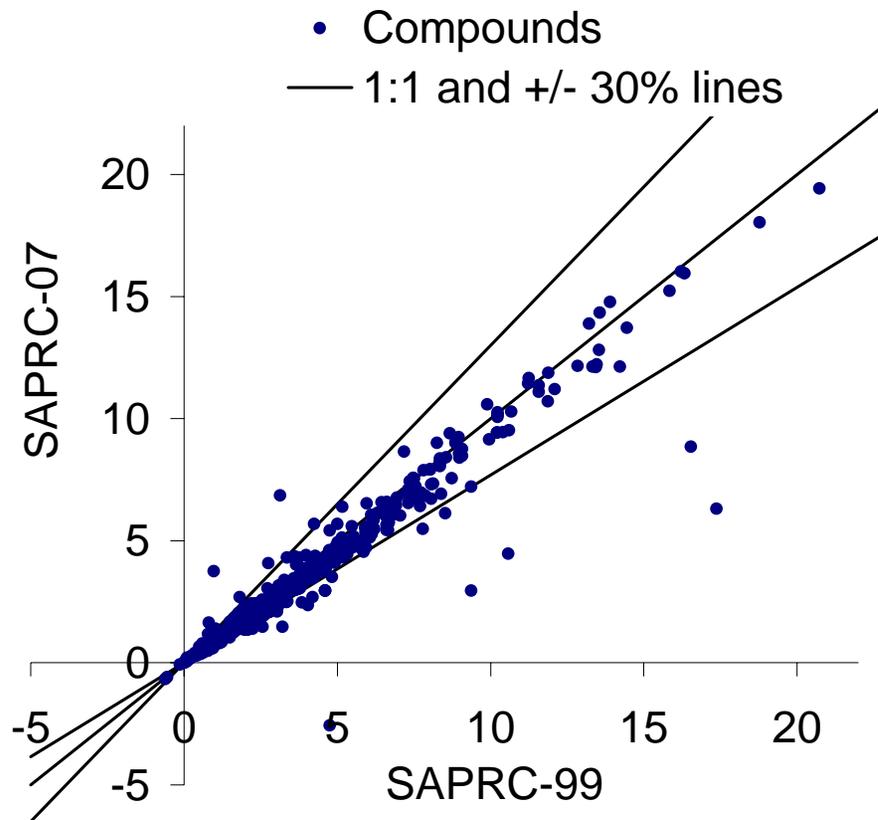
Recent Reactivity Research at UCR: VOCs Studied Since 2005

- Representative coatings VOCs: Various hydrocarbon mixtures; Texanol®; ethylene and propylene glycols; 2-(2-butoxyethoxy)-ethanol; benzyl alcohol
- Representative pesticides: methyl isothiocyanate (MITC); S-ethyl N,N-di-n-propyl thiocarbamate (EPTC); 1-3-dichloropropenes; kerosene; carbon disulfide; methyl iodide
- Representative amines 2-amino-2-methyl-1-propanol (AMP); ethanolamine; isopropyl amine; t-butyl amine
- Representative solvent d-Limonene
- HFC compounds: trans 1,3,3,3- and 2,3,3,3-tetrafluoropropenes

Changes in MIR Ozone Reactivity Values: SAPRC-07 vs SAPRC-99



Base ROG Mixture: -5% Change



MIR Incremental Reactivity
(gm O₃ / gm VOC)

VOCs with Large MIR Changes

Compound	Approx. MIR [*]		Reason for change
	Old	New	
3-Methoxy-1-butanol	1.0	3.8	Rate constant error corrected
2-Amino-2-methyl-1-propanol	4.8	-2.7	New data and mechanisms for amines
2-(Chloromethyl)-3-chloropropene	3.1	6.8	Chlorinated ketones believed to be more photoreactive
1,2-Dibromoethane	0.05	0.1	Approximate representation of Br compounds changed

* grams O₃ / gram VOC

VOCs with Large MIR Changes (continued)

Compound	Approx. MIR [*]		Reason for change
	Old	New	
1,2-Dichloroethane	0.1	0.2	Chlorinated aldehydes believed to be more photoreactive
Trans-1,2-dichloroethene	0.8	1.6	Chlorinated aldehydes believed to be more photoreactive
Dimethyl amine	9.4	2.9	New data and mechanisms for amines
Mesityl oxide (2-methyl-2-penten-4-one)	17.4	6.3	SAPRC-99 mechanism not reasonable. Now represented by the lumped isoprene product.

* grams O₃ / gram VOC

Ongoing Ozone Reactivity Research at UCR

General Mechanism Updates

- Assist CARB and EPA in implementation of versions of SAPRC-07
- Develop and evaluate alternative aromatics mechanisms
- Evaluate effects of using lower OH + NO₂ rate constant

Improve Chamber Experiments for Reactivity Assessment

- Chamber experiments are much less sensitive to secondary reactions of oxidized products than the atmosphere.
- Increasing integrated OH levels by increasing light intensity and duration of experiments is calculated to address this
- Improvements to UCR EPA chamber now underway

Reduce uncertainties in reactivities of coatings VOCs of interest

- Compounds currently being selected for study using new chamber experiment methods

Recommendations

Chemical Mechanism

- Mechanism used in current scales is reasonably up to date, though uncertainties remain where ongoing research is needed

Reactivity Scenarios, Models and Methodology

- *The MIR scenarios and methodology do not represent the current state of the science and need to be updated*
 - The 39 city scenarios are poorly documented and out of date
 - The MIR methodology *may* not be optimum for assessing regional and multi-day impacts
 - Use of box models is questionable because they do not give the best representation of airshed conditions
- **A plan for improving reactivity scenarios and methodology needs to be developed *and executed***

Recommended Steps for Improving Reactivity Scenarios and Methods

Minimum Set of Near Term Policy Decisions Needed

- *Determine available funding level and target schedule for reactivity assessment improvements*
- Determine minimum set of airshed scenarios or episodes that should ideally be used for deriving a national reactivity scale
 - Need to specify a set of regions, episodes and receptors
 - Need to include areas where O₃ may go out of attainment if bad policies are adopted
- Determine optimum ozone quantification and multi-scenario reactivity aggregation method for ozone control policy
 - Consider exactly what impacts we are trying to minimize and how we decide if a reactivity-based substitution is acceptable

Recommended Steps for Improving Reactivity Scenarios and Methods

Near Term Work if Only Minimal Funding or Time is Available

1. Update or replace the 39 box model scenarios to correspond to current VOC, NO_x, and O₃ levels in representative areas
2. Update the base ROG mixture to current measurement data
3. Derive a reactivity quantification method using the updated scenarios that corresponds best to the optimum policy method
4. Derive new scales using the new scenarios and methods using both SAPRC-99 and the current mechanism
5. Compare the SAPRC-99 scale with existing SAPRC-99 3-D reactivities and adjust the box models or method if needed
6. Document and peer review the new scale and its evaluation

Recommended Steps for Improving Reactivity Scenarios and Methods (continued)

Medium Term Work if More Funding and Time is Available

1. Compile a set of 3-D model scenarios to represent episodes and receptors chosen by policymakers for reactivity assessment
 - Purpose: either for deriving the scale itself or to serve as standards against which simpler models can be compared
 - Must represent the state of the science and be acceptable for regulatory modeling
2. Implement optimum policy quantification method to calculate reactivities for representative compounds using these scenarios
3. Derive trajectory or box models and analysis methods that give reactivities closest to those using the 3-D scenarios and method
4. Derive, document, and peer-review a full scale using the trajectory or box model method so derived

Recommended Steps for Improving Reactivity Scenarios and Methods (continued)

Longer Term Work if Sufficient Funding and Time is Available

1. Compile needed set of 3-D model scenarios (Step 1, above)
2. Implement optimum policy quantification method (Step 2, above)
3. Develop software and practical and protocols for deriving full reactivity scale for the >1000 types of VOCs using 3-D scenarios
4. Develop an affordable method and protocol for updating the scales for new compounds or mechanisms as needed
5. Derive, document, and peer review the full reactivity scale

Additional Information Available

W.P.L. Carter research on chemical mechanisms and reactivity

- <http://www.cert.ucr.edu/~carter>

Updated SAPRC-07 mechanism and reactivity scale

- <http://www.cert.ucr.edu/~carter/SAPRC>