

Ozone and PM Reactivities of VOCs

William P. L. Carter
CE-CERT, University of California, Riverside, CA
September 25, 2007

Outline

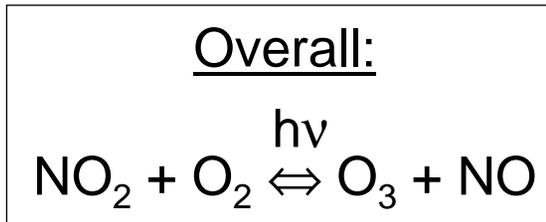
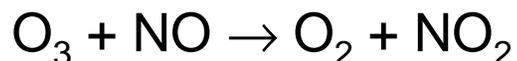
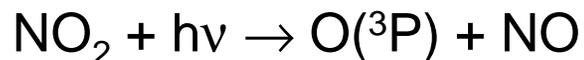
- Factors affecting ozone reactivity, ozone reactivity scales, and recent work on ozone reactivity
- Considerations of PM reactivity and recent work at CE-CERT/UCR
- Recommendations for work needed

VOCs and Air Quality

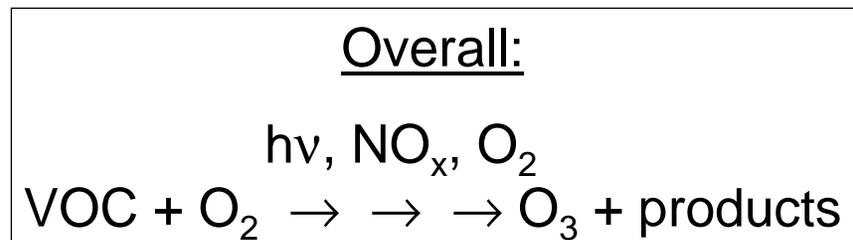
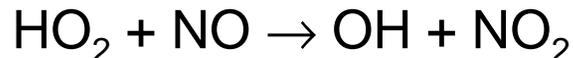
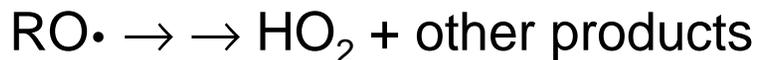
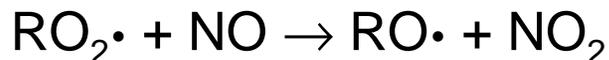
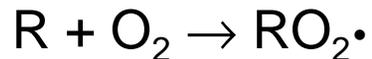
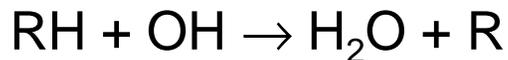
- Volatile Organic Compounds (VOCs) enter the atmosphere from a variety of anthropogenic and biogenic sources
- Impacts of VOCs on air quality include:
 - Direct effects (for toxic VOCs very near large sources)
 - Formation of toxic or persistent oxidation products
 - Promotion of ground-level ozone 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
 - 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:



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



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**

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

- 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:
 - Models for airshed conditions
 - Chemical mechanism for VOC's Atmospheric Reactions
- But reactivity calculations can be no more reliable than the chemical mechanism used. Chamber experiments are needed to test if mechanisms can predict reactivity.

Uncertainties in Reactivity Quantification

- Uncertainty in most appropriate methods and environmental conditions to use to derive the reactivity scale
 - No single scale can represent all environments. Not obvious how to derive a general scale
 - Current reactivity scales derived using box models, which greatly oversimplify environmental conditions
- Chemical mechanism uncertainties
 - Base mechanism uncertainties cause uncertainties for reactivity quantifications for all VOCs
 - VOC mechanisms have uncertainties because most have uncertain estimates and approximations. Not all VOCs have the chamber data needed to test reliability of predictions.

Options for Derivation of Reactivity Scales: Type of Model

Use 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 all existing comprehensive reactivity scales (e.g., MIR)

Use Multi-Cell, 3-D Regional Models

- Only way model how O₃ varies with time and space in *actual* airsheds. Only type of model acceptable for SIP demonstrations
- Now possible to model reactivity of individual VOCs, but expensive and computer-intensive
- Has been used for selected compounds for comparison with box model reactivities, but not yet used to for comprehensive scales

Options 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

Average Base Case or Regional Average

- Represents effects on O_3 throughout wide regions, including those not sensitive to VOC controls
- Variants include averages for cells over the O_3 standard or population-weighted averages (regional models only)

Minimum Substitution Error

- Minimizes ozone differences in reactivity-weighted VOC substitutions. Considers all regions but gives greater weight to VOC-sensitive areas

Options for Derivation of Reactivity Scales: Ozone Quantification

Base Scale on Effect of VOCs on Daily Maximum Ozone

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

Base Scale on Effect of VOCs on 8-Hour Average Ozone

- Representative of new 8-hour standard

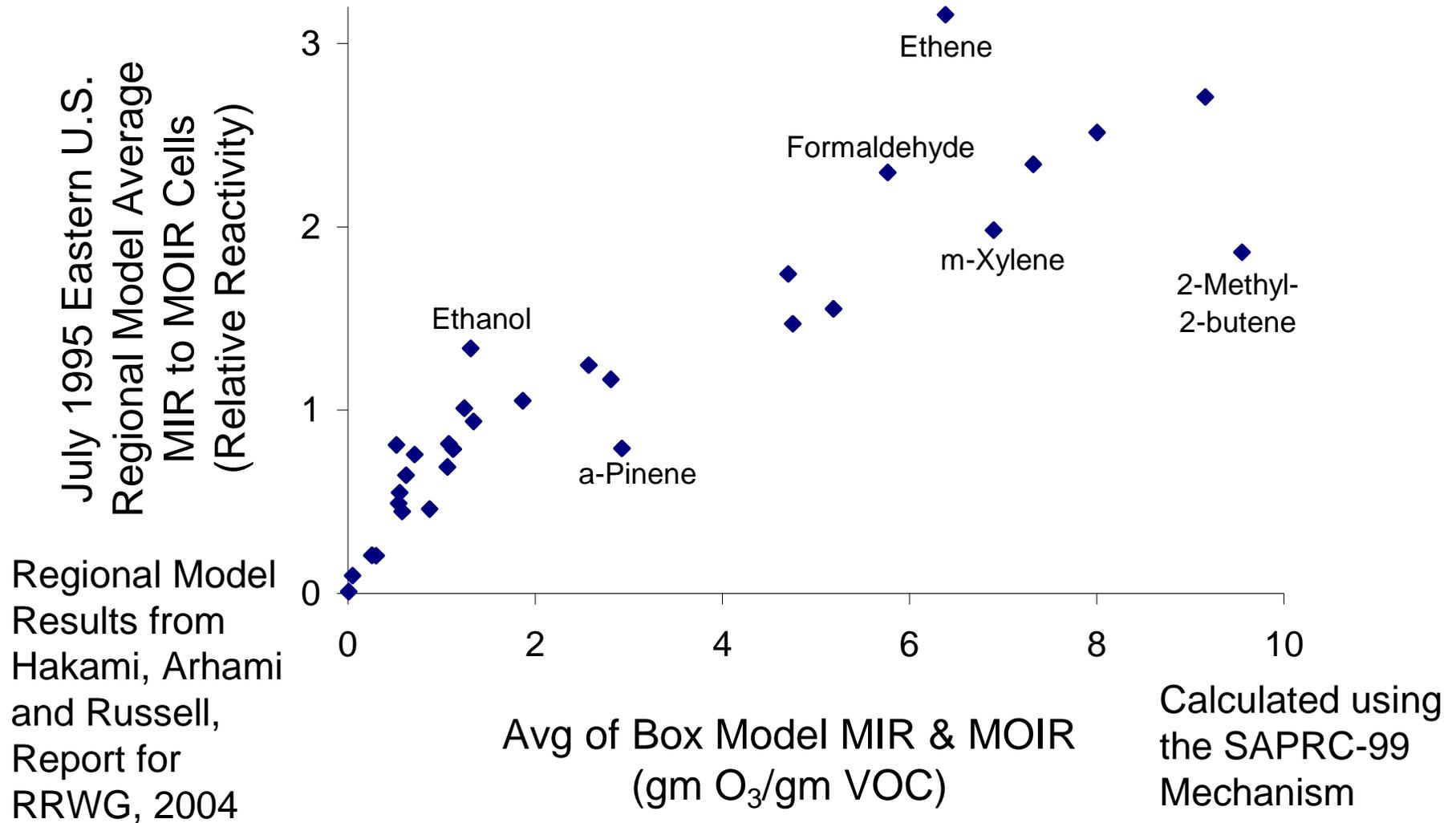
Base Scale on Effect on Ozone Exposure

- Represents impacts VOC controls on the population.
- Option for regional model reactivity scales.

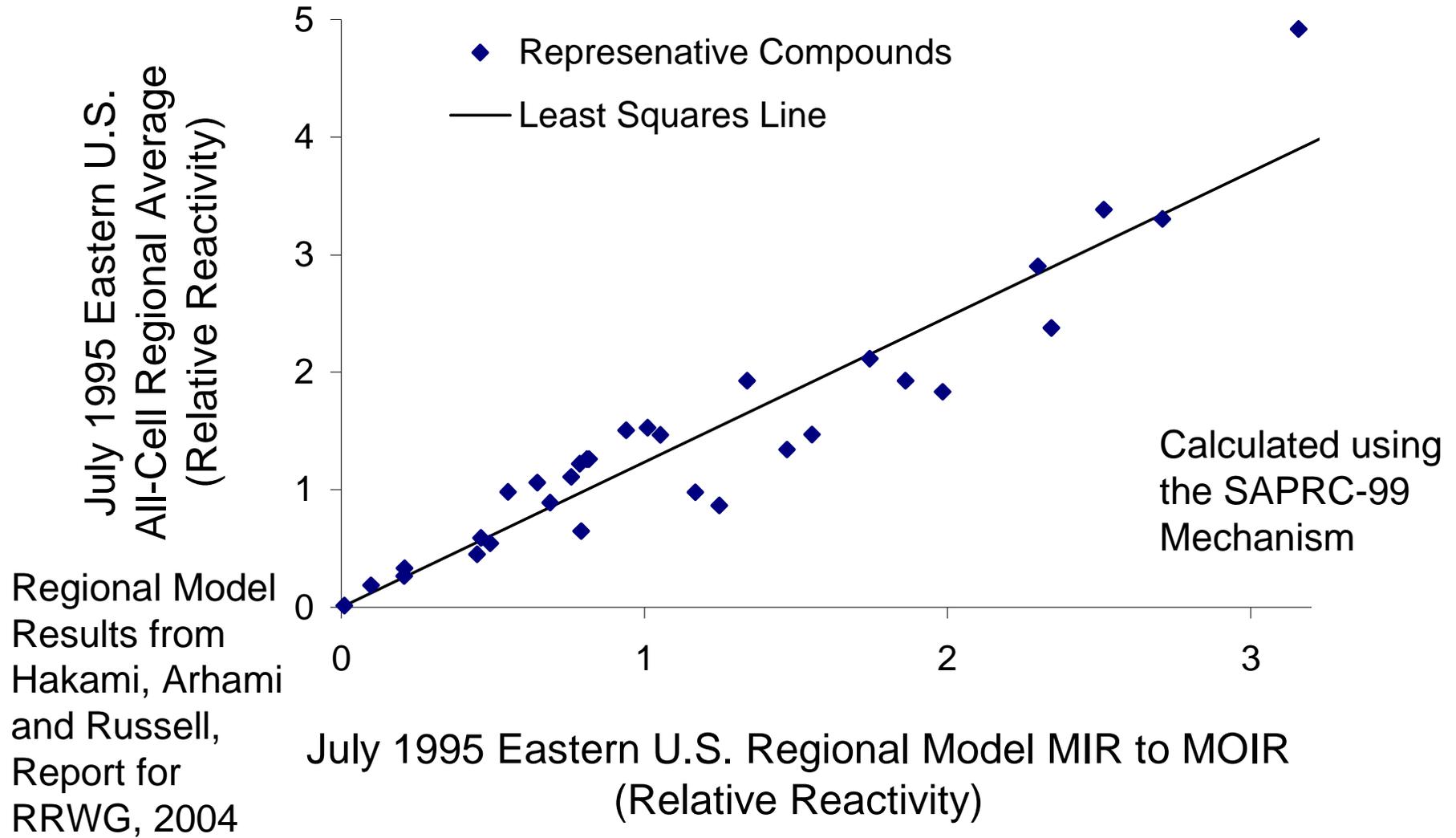
Derivation of MIR Scale used in Current California Reactivity Regulations

- Box models for 39 U.S. cities derived in 1990 for regulatory impact analysis using the EKMA method used as starting point
 - Scenario development not well documented
 - Do not represent current conditions (e.g., base case “Los Angeles” scenario has >550 ppb maximum O₃)
 - Single day scenarios; multi-day effects not considered. May underestimate O₃ impacts of slowly reacting compounds
- NO_x levels adjusted to give highest sensitivities of O₃ to VOC emissions.
 - Higher than NO_x levels in most regions, including regions with highest O₃.
- Scale based on effect of VOCs on daily maximum O₃ levels. Reflects the older 1-hour standard

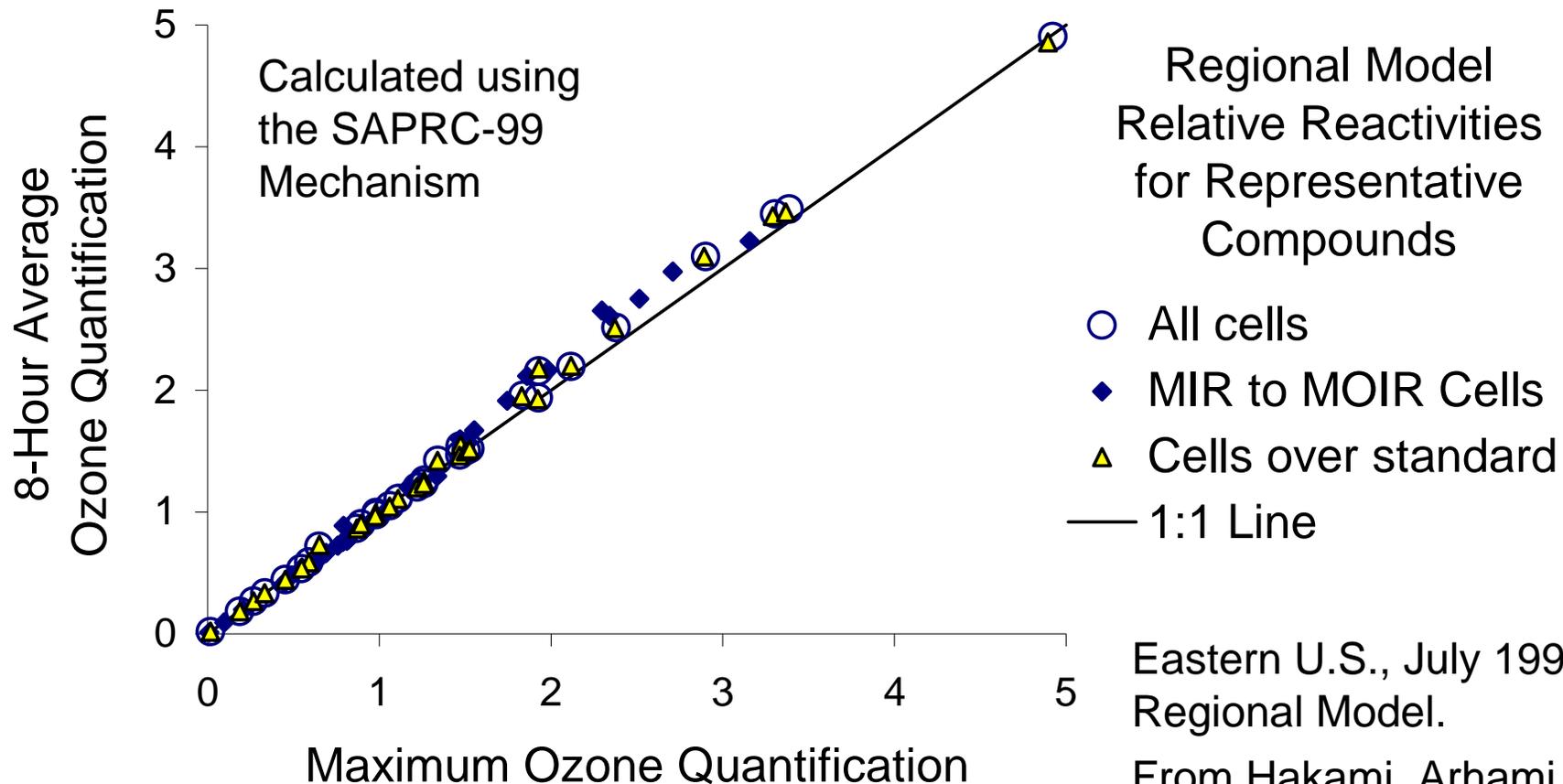
Comparison of Regional vs. Box Model Reactivities for Comparable Conditions



Comparison of MIR to MOIR vs. Regional Average Reactivities



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

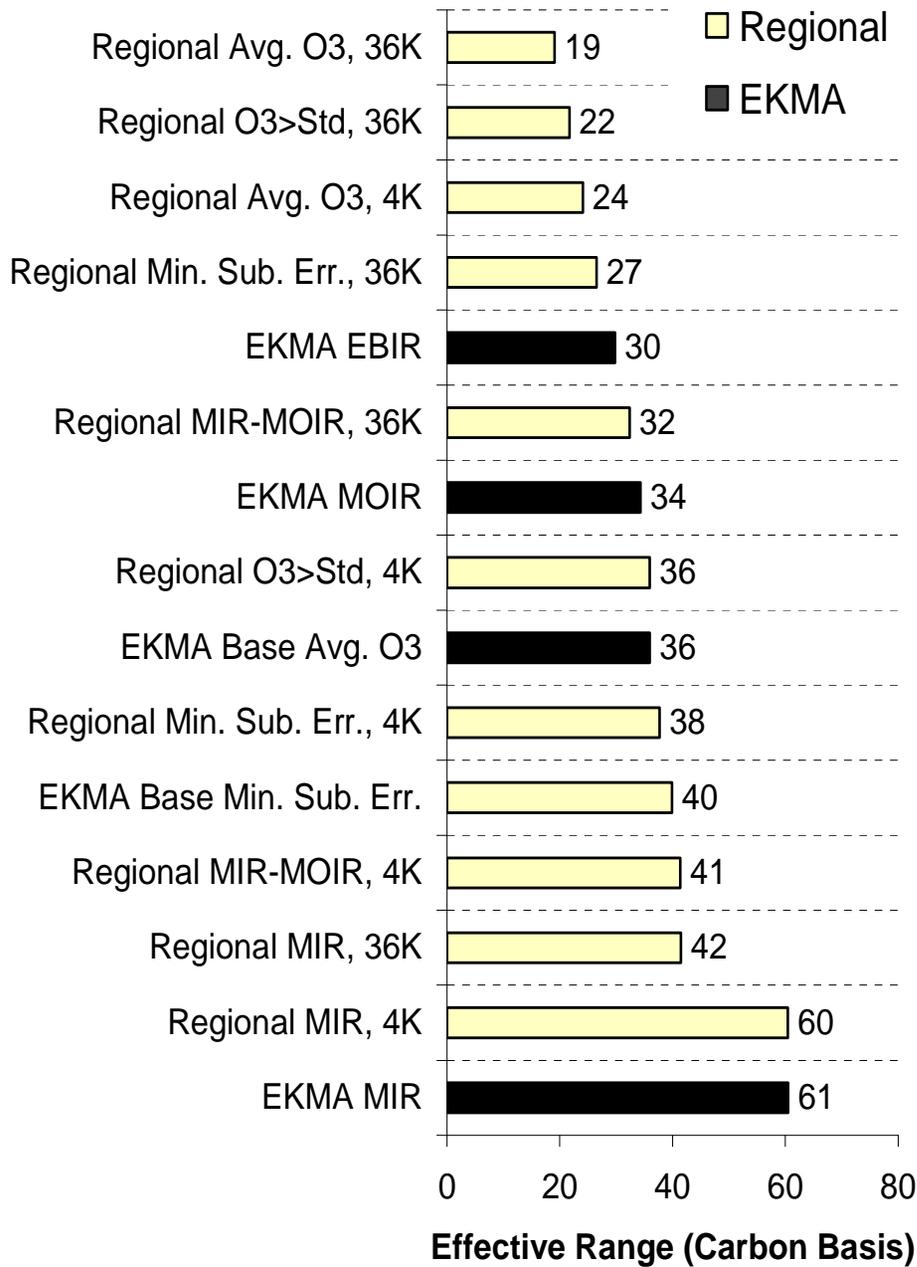


Eastern U.S., July 1995
Regional Model.

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

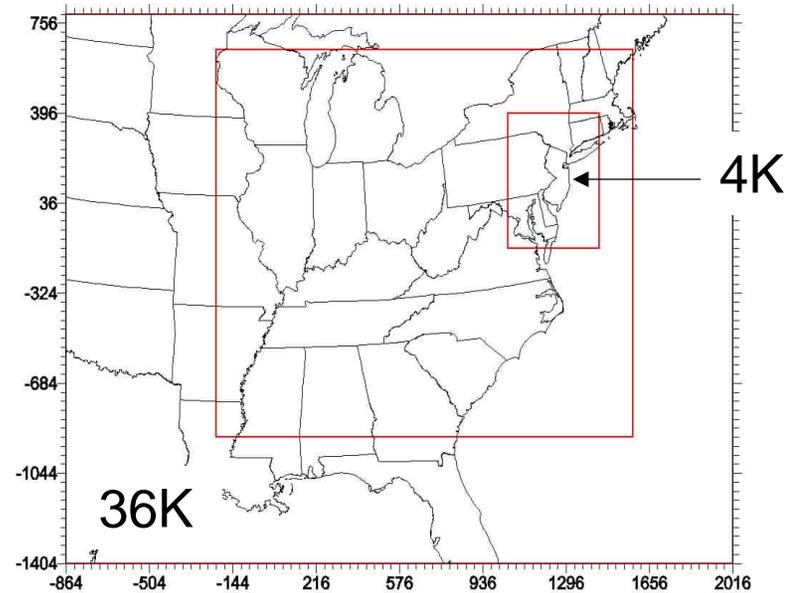
Concept of Effective Range

- Effective range is the ratio of the most reactive compound to compound with borderline negligible reactivity (e.g., ethane)
- Reactivity scales vary in effective ranges
- Effective range provides a measure of the regulatory effect of the reactivity scale.
 - No effective range: Regulating all VOCs equally. No incentive to reduce O_3 by substituting to low reactivity VOCs
 - High Effective range: Greatest incentive for VOC substitutions based on reactivity.
 - But substitutions may cause some measures of O_3 to increase if effective range is too high
- Regulators need to weigh advantages and disadvantages of scales with too high or too low effective ranges



Effective Ranges of Various Reactivity Scales

CB4 Mechanism
OLE / Ethane Ratio
Regional Domains:



Summary of Policy Choices for Reactivity Calculation Methodology

- Continue to use MIR despite outdated scenarios, NO_x adjustments, and no consideration of multi-day effects
- Update the methodology. Then choices become:
 - Use of 3-D regional vs. Box, trajectory, or EKMA models
 - Alternative methods to derive single scale from multiple scenarios or cells, e.g.: Use regional average? Weigh VOC-sensitive cells more? Weigh high O₃ cells more? Use population weighting?
 - Ozone metric to use: 1-hour average, 8-hour average, exposure metric?
 - Develop appropriate reactivity calculation protocol
 - Required software and procedures
 - Reporting requirements

Chemical Mechanism

- Chemical mechanisms for reactivity assessment must explicitly represent reactions of the hundreds of types of VOCs.
 - Examples include the detailed SAPRC mechanisms and the European “Master Chemical Mechanism”
- Because of mechanism uncertainties, their predictive capability should be evaluated as much as possible against chamber data.
- The reactivity scale used for the current California reactivity-based regulations was derived using the SAPRC-99 mechanism
 - Represented the state of the science as of 1999
 - Has reactivity values for 763 types of VOCs
- The SAPRC-99 mechanism has been updated to SAPRC-07
 - Development, evaluation, and documentation completed. Implementation work remains.
 - CARB plans to have mechanism undergo peer review

Major Accomplishments of SAPRC-07 Mechanism Update

- Rate constants and reactions have been updated to the current state of science
- Chlorine chemistry and has been 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 additional work is needed to adapt the mechanism to PM predictions.
- The mechanism has been evaluated against a larger database of chamber experiments
- The number of types of VOCs for which reactivities can be estimated has been increased from 763 to 1097.

Evaluation Against Chamber Experiments

- Mechanism evaluated against available UCR and TVA environmental chamber data base + some UNC experiments

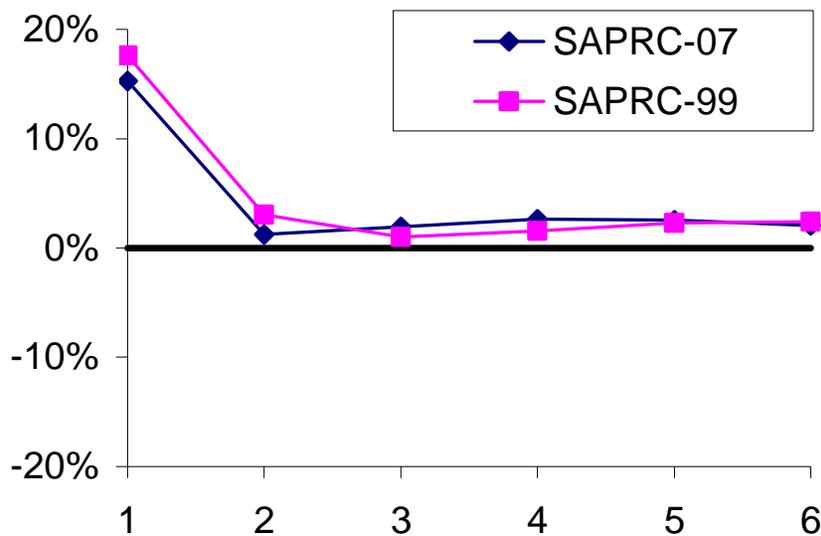
Chambers	UCR	TVA	UNC
Indoor - Blacklight or mixed	4	1	
Indoor - Arc light	4		
Outdoor	1		1

Types of Experiments	Runs	VOCs	Types
Characterization	247		10
Single VOC	671	46	
Incremental Reactivity	571	111	
Mixtures	949		22

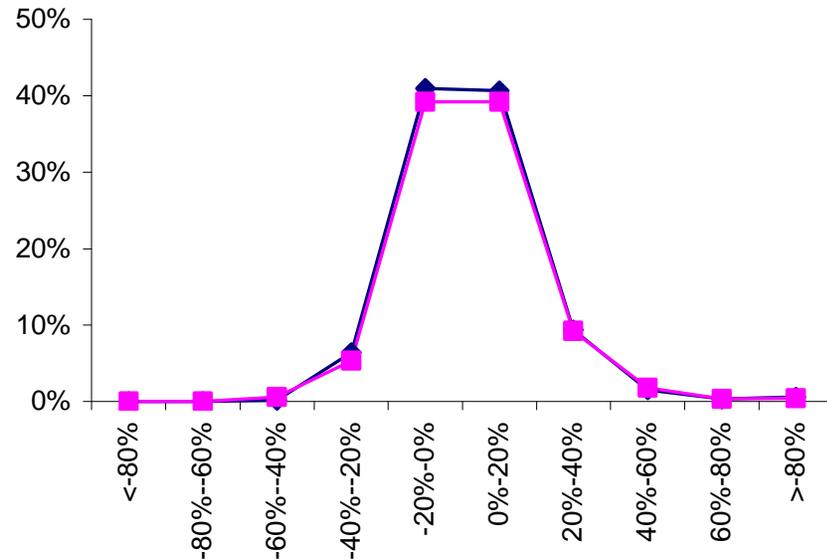
- Performance simulating chamber data comparable to SAPRC99 (somewhat better in some cases, not quite as good in others)

Evaluation Results: Model Errors for All Single VOC Experiments

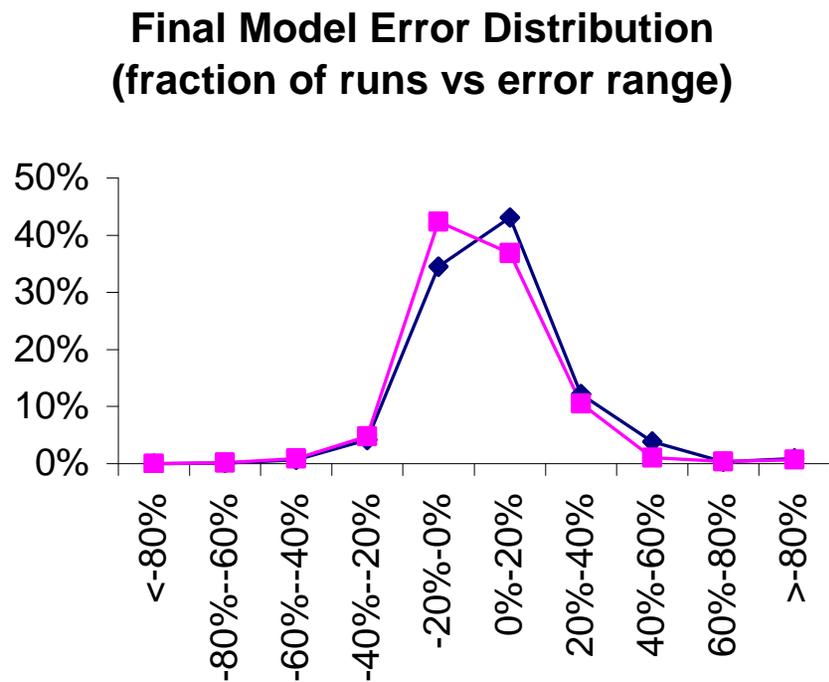
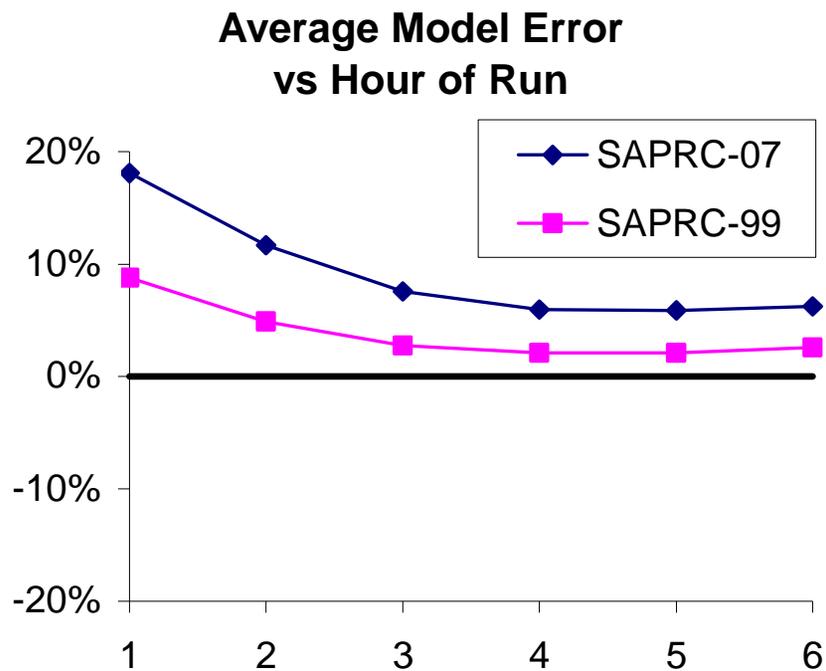
Average Model Error
vs Hour of Run



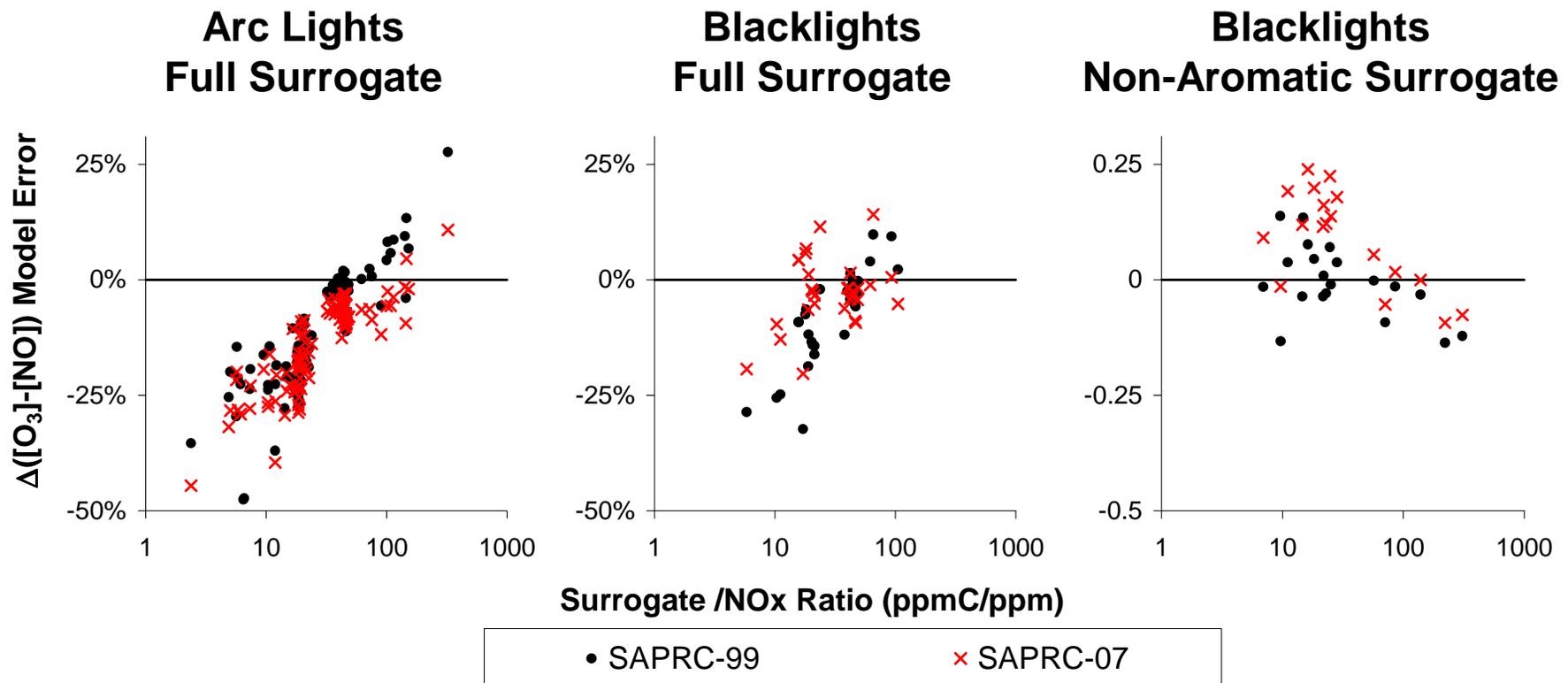
Final Model Error Distribution
(fraction of runs vs error range)



Evaluation Results: Model Errors for All Mixture Experiments



Model Performance Simulating UCR-EPA Chamber Surrogate - NOx Runs



- Problem of O₃ underprediction at low ROG/NO_x still exists

Calculation of Updated Reactivity Scales

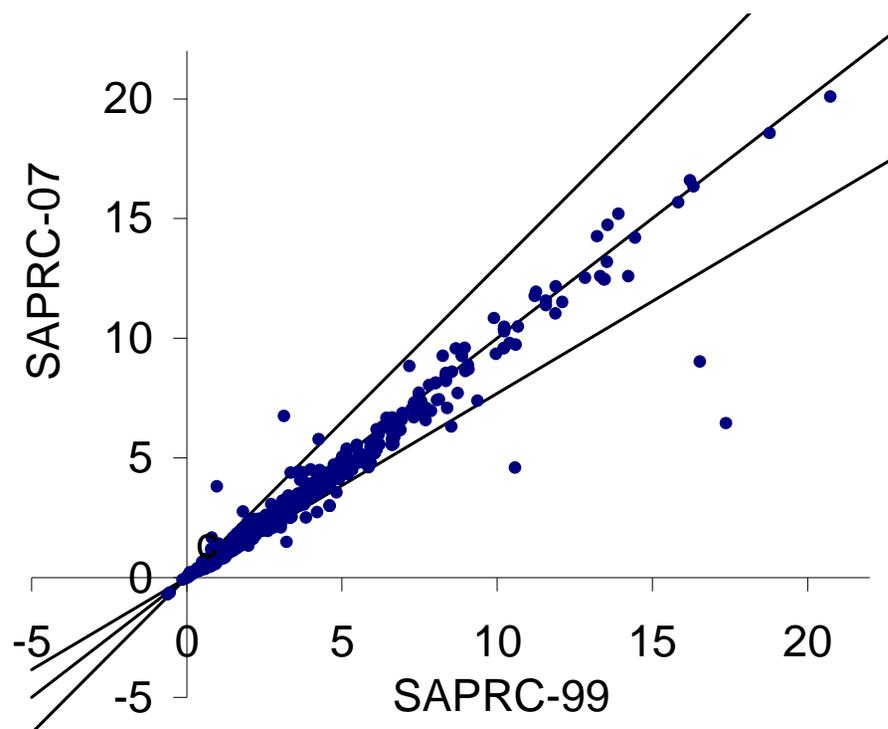
- Updated mechanism used to calculate new MIR scale for use in California reactivity-based regulations
- The scenarios and calculation methodology used is exactly the same as used for SAPRC-99 reactivity scales.
- Reactivities calculated for a total of 1097 Types of VOCs, including
 - 735 VOCs represented explicitly
 - 310 VOCs represented by the “Lumped molecule” method
 - 52 Complex mixtures (e.g., exhausts, petroleum distillates)
- This includes 332 types of VOCs not in 2002 SAPRC-99 scales.
- This also includes 13 amines and 18 other compounds that have just been added

Changes in Ozone Reactivity Values in the MIR Scale

Incremental Reactivity
(gm O₃ / gm VOC)
MIR Scale

• Compounds

— 1:1 and +/- 30% lines



VOCs with Large MIR Changes

Compound	Approx. MIR (mass basis)		Reason for change
	Old	New	
3-Methoxy-1-butanol	1.0	3.8	Rate constant error corrected
2-(Chloromethyl)-3-chloropropene	3.1	6.8	Chlorinated ketones assumed to be more photoreactive
Trans-1,2-dichloroethene	0.8	1.7	Chloroacetaldehyde believed to be more photoreactive
Indene	3.2	1.5	Represented by styrene (was represented by tetralin)
Furan	16.5	9.0	More explicit mechanism (was represented by m-xylene)

(Amines excluded)

Problem of Reactivity Estimates for Amines

- SAPRC-99: Only highly approximate estimates developed. Recommended that “upper limit” MIR’s be used for regulations
- SAPRC-07: Estimated mechanisms developed based on new chamber data, but uncertain how much amine is available for gas-phase reaction or is lost by reaction with HNO₃

Mechanism Version and Method or Assumptions	MIR (gm O ₃ / gm VOC)		
	2-Amino-2-Methyl-1-Propanol	Ethanol amine	Dimethyl amino ethanol
SAPRC-99			
Rough Estimate	4.8	6.0	4.8
Upper Limit	15.1	11.0	15.1
SAPRC-07			
No HNO ₃ Reaction	-2.7	6.6	5.2
Fast HNO ₃ Reaction	-0.2	0.5	0.5

Recommendations - O₃ Reactivity

Update Reactivity Calculation Method

- The work of the RRWG towards developing improved reactivity assessment methods needs to be completed.
- **At a minimum, the out-of-date scenarios used the current MIR calculations need to be updated.**

Reduce Chemical Mechanism Uncertainties

- Uncertainties in the base mechanism and mechanisms for aromatics may affect reactivity predictions for all VOCs
- Many VOCs still have unknown mechanisms
- Chamber experiments currently used to test mechanisms are too insensitive to reactions of oxidation products

Consider Availability and Reduce Availability Uncertainties

- For some VOCs (e.g., amines), the amount of emitted compound available for gas-phase reaction is very uncertain

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, partitioning coefficients, and heterogeneous reactions 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

Requirements for Predictions of PM Impacts (in addition to requirements for O₃ predictions)

Predictive Mechanisms for Chemical and Physical Processes

- Chemical mechanism must predict yields of low-volatility products *and how they change with chemical conditions*
- Predict gas-to-particle phase partitioning and evaporation
- Predict condensed-phase reactions (polymerization, etc)
- Predict PM nucleation and removal processes

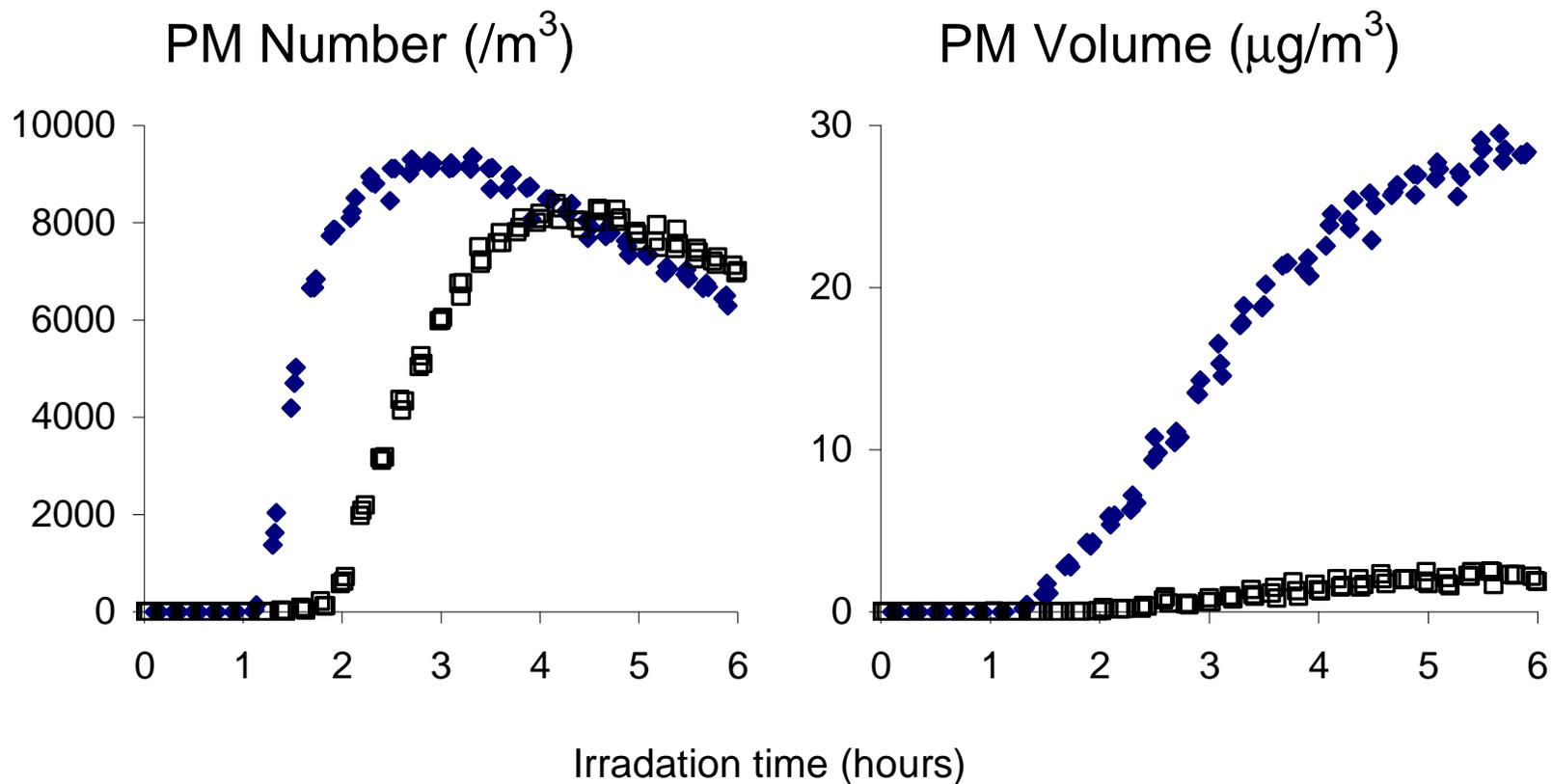
Model for Environmental Conditions

- Appropriately representing temperature, humidity, absolute concentrations *much more important* for PM than for O₃
- Appropriately represent *primary* and *background* PM that may affect partitioning or condensed-phase processes
- Use base case scenario that gives representative PM levels and compositions
- Appropriately represent PM loss processes

PM Measurements in the UCR EPA Chamber

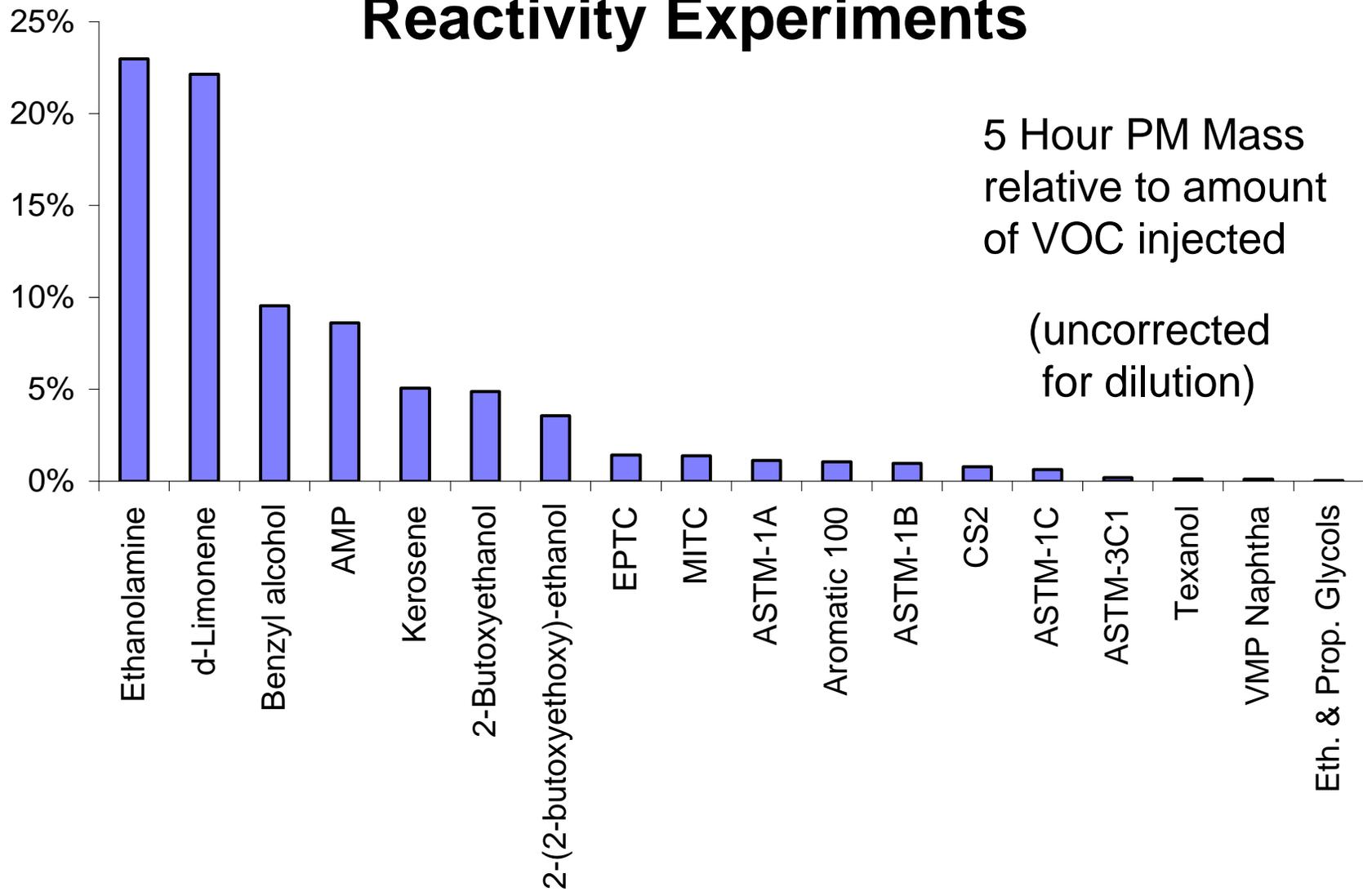
- PM Measurements were made in conjunction with most recent ozone reactivity experiments. Compounds studied include:
 - Representative Water- and Solvent-based coatings VOCs
 - Several pesticide VOCs: MITC, EPTC, CS₂, Kerosene
 - Aminomethylpropanol (AMP), Aminoethanol, d-Limonene
- Research underway to determine effects of reactant (e.g. NO_x) concentrations, humidity, and other factors on PM formation
 - Current emphasis is on aromatics and terpenes
 - Data obtained are needed to develop predictive mechanisms for PM formation in the atmosphere
- Experiments are being carried out at lower reactant concentrations than is practical for most other chambers
- A large array of state-of-science equipment recently was obtained from a grant from the Keck foundation

Representative PM Data from Reactivity Experiments

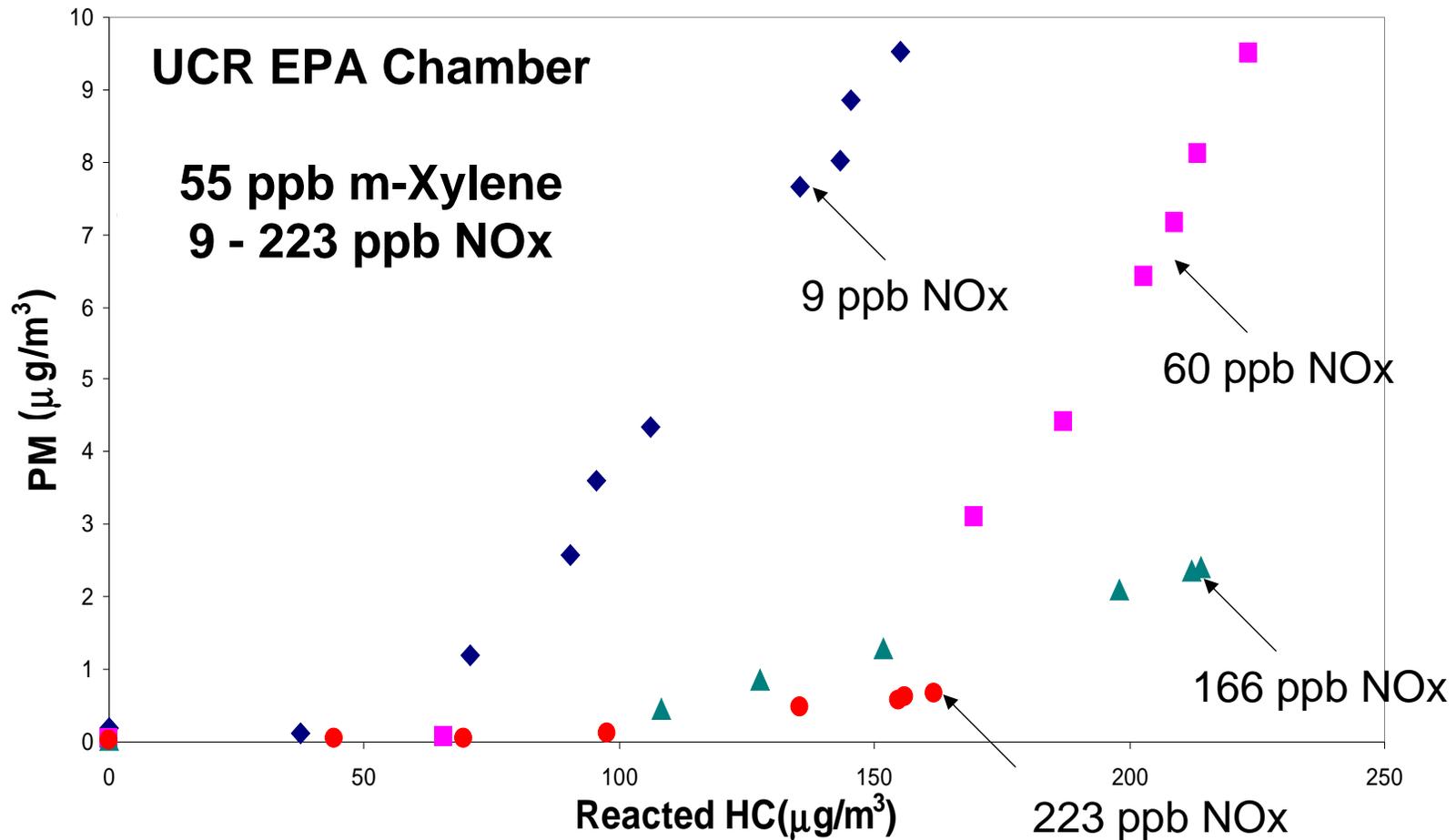


- Base Experiment (30 ppb NO_x, 0.6 ppmC Base ROG)
- ◆ 1.5 ppmC Kerosene Added

Average PM Reactivities in Incremental Reactivity Experiments



Comparison of SOA in Experiments with Same Initial m-Xylene Concentrations



Summary and Recommendations

- PM Reactivity

- Chamber data indicate VOCs vary significantly in PM impacts, and PM impacts are *not* correlated with O₃ impacts.
 - However, current data are qualitative and not representative of ambient conditions
- Improved, and more comprehensive mechanisms need to be developed for simulating secondary PM in the atmosphere
 - Detailed mechanisms have been developed for only few of VOCs and evaluated under unrepresentative conditions
 - Current models use very simplified models for PM formation that is not consistent with the limited available chamber data
 - Well-characterized chamber experiments *simulating ambient conditions* are needed to develop *predictive* PM models.
- Scenarios for assessing PM impacts need to be developed. Existing scenarios for O₃ reactivity scales are not appropriate

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>

Reactivity Research Working Group (RRWG) reports on VOC reactivity

- <http://www.narsto.org/section.src?SID=10>

Research on Secondary Organic Aerosol Formation in UCR EPA chamber

- <http://www.engr.ucr.edu/~dcocker/>