

# Recent Development in VOC Reactivity Research and Regulations in California

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*Diamond Bar, California*

*VOC Reactivity Technology Forum  
and Roundtable Discussion*

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**California Environmental Protection Agency**



**Air Resources Board**

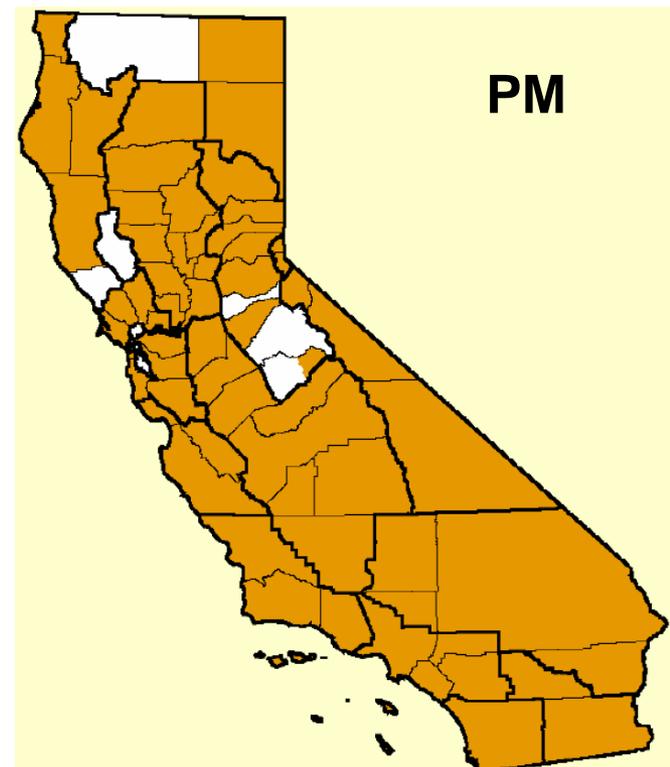
# The Road Map



- **Background**
  - Air Quality Status
  - SIP Requirements
- **VOC Reactivity**
  - Ozone Formation
  - Recent Reactivity Research
- **Reactivity-based Programs in California**
  - Low Emission Vehicle Program
  - Aerosol Coatings Regulation
  - CaRFG Program
  - VOC Exemptions
- **Summary**
- **Resources**

# Air Quality Status

## State Non-attainment Areas



# Annual Ozone Impacts\*

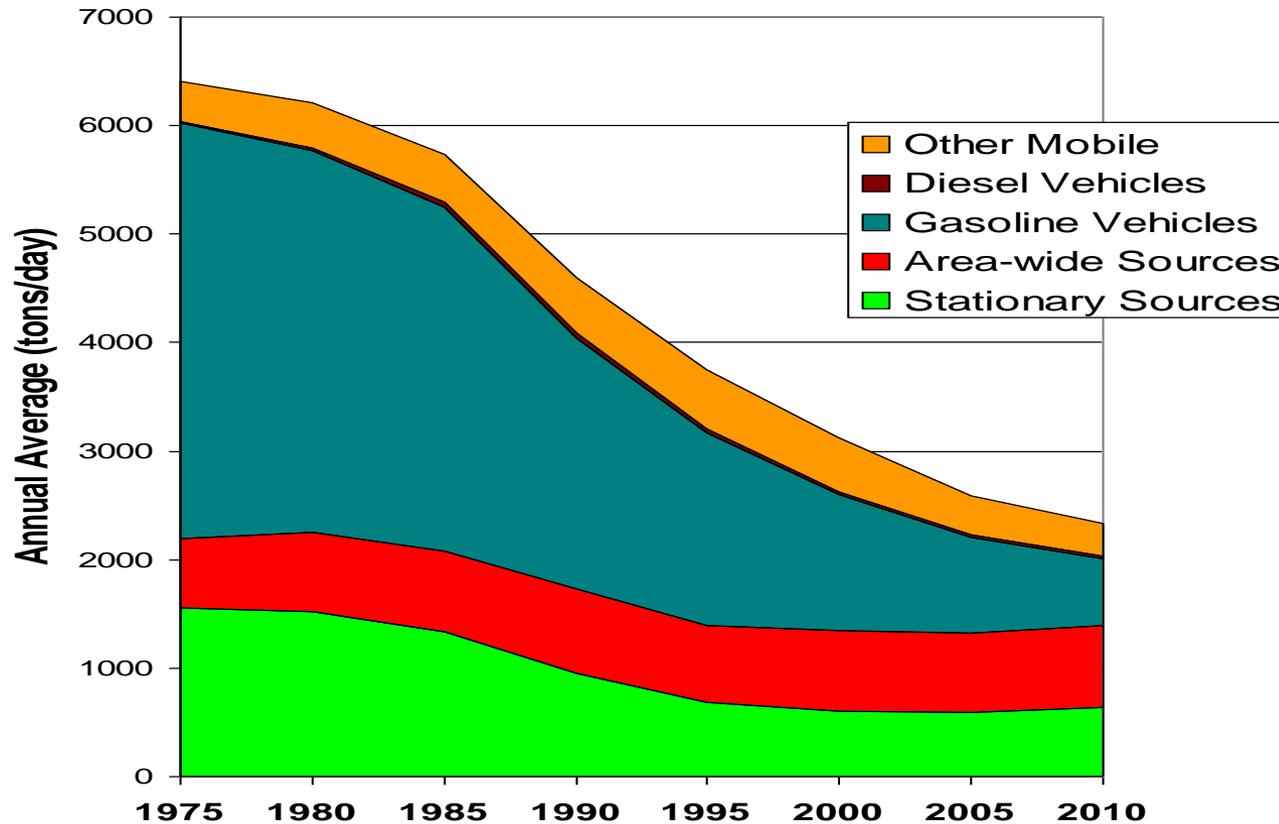


- 630 Premature Deaths
- 4,200 Hospitalizations
- 4,700,000 School Absence Days
- 3,100,000 Minor Restricted Activity Days

\* Ostro et al. *AWMA* (2006)

# VOC Emission Trends by Category

## Statewide ROG Emission Trends



# State Implementation Plan (SIP)



- Mandated by the Federal Clean Air Act
- California's Emission Reduction Commitments
- Developed in consultation with all interested parties
- 2007 SIP Commitments

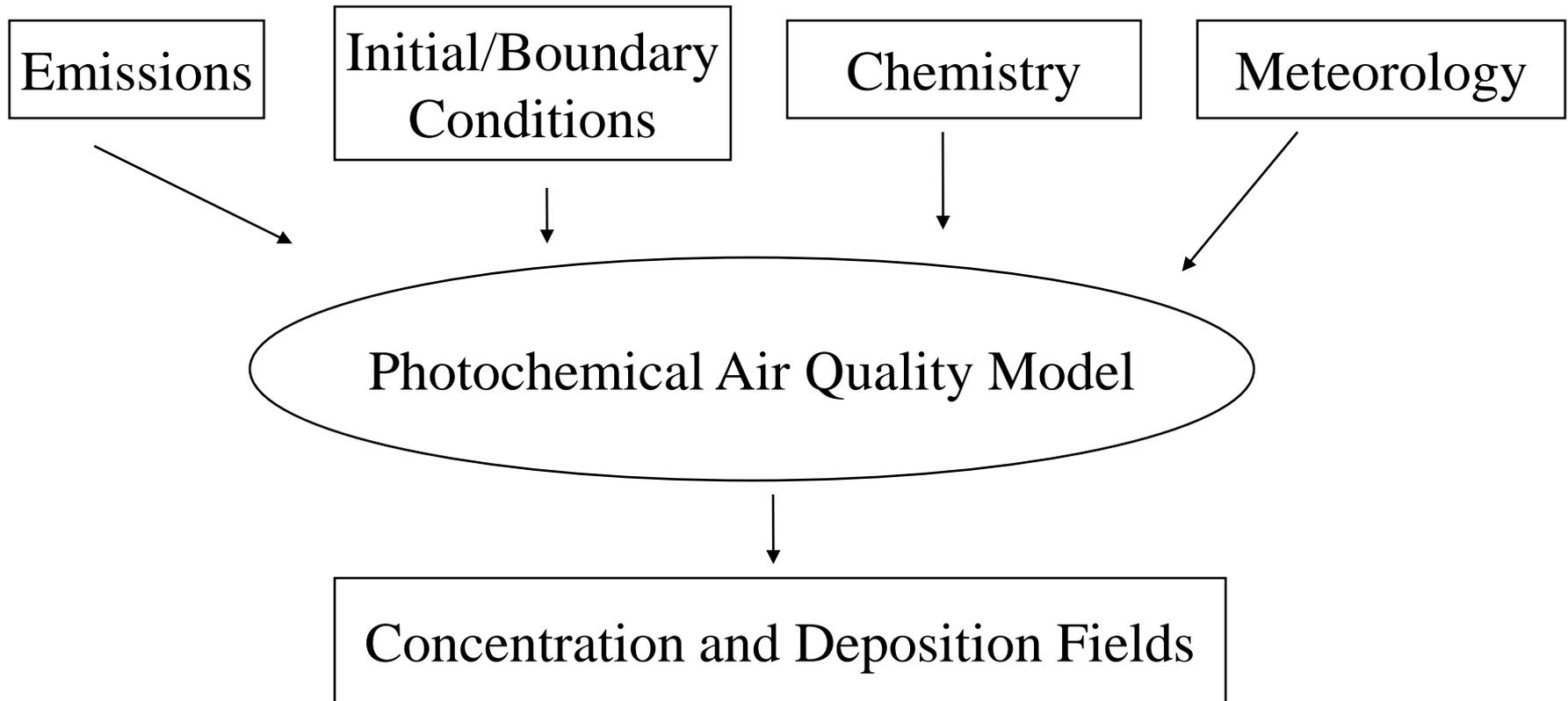
# VOC Reactivity: Ozone Formation & Control

- $\text{NO}_x$  control has the greatest benefits on ozone downwind.
- VOC control has the greatest benefits on ozone near the source areas.
- Any comprehensive ozone control strategy should take both VOC and  $\text{NO}_x$  into consideration.
- Control strategies aimed at reducing emissions of more reactive VOCs may be more effective than those reducing all VOCs equally.

# Measures of Reactivity

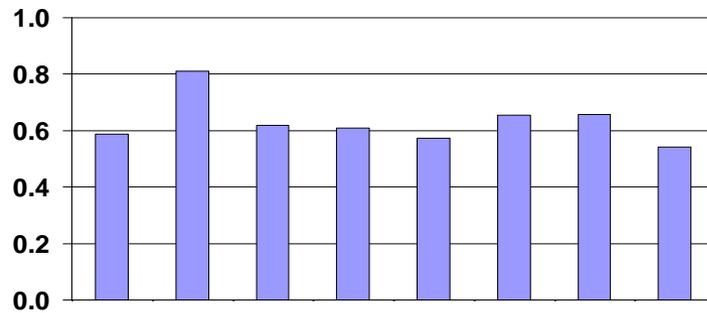
- **Maximum Incremental reactivity (MIR)**
  - Single-box model
  - Detailed chemical mechanism developed using smog chamber experiments
  - 39 scenarios used that represent a realistic distribution of environmental conditions
  - Calculated for over 1000 VOCs
  - Concerns: multi-day transport et al.
- **3-D Reactivity Scales:**
  - Regional MIR (MIR-3D)
  - Least Squares Relative Reactivity (LS-RR)
  - Others

# 3-D Air Quality Modelling

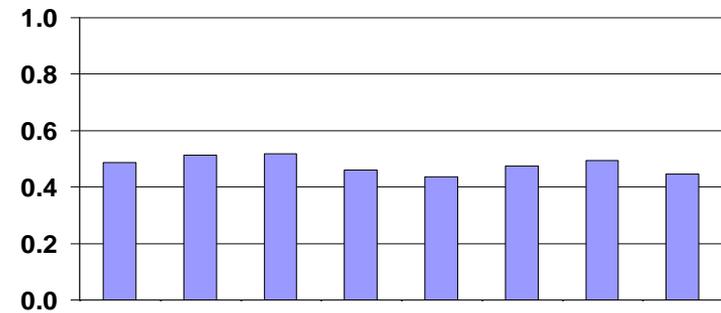


# Temporal (Day-to-Day) Variability: n-C4

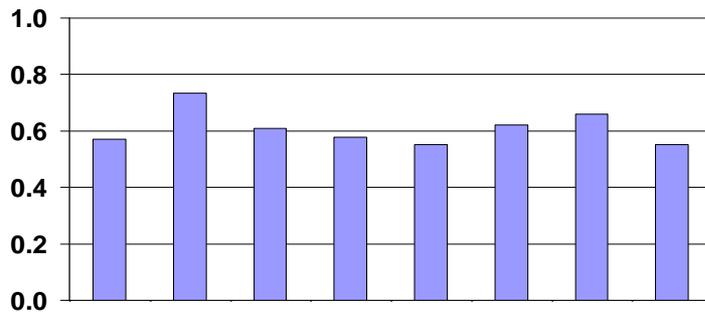
**MIR-3D**



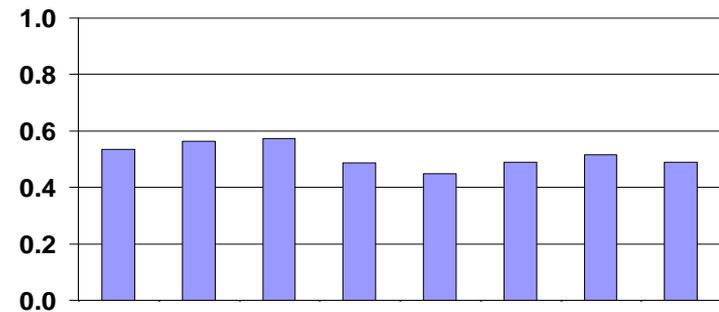
**RR-LS-8hr**



**MIR-3D-8hr**

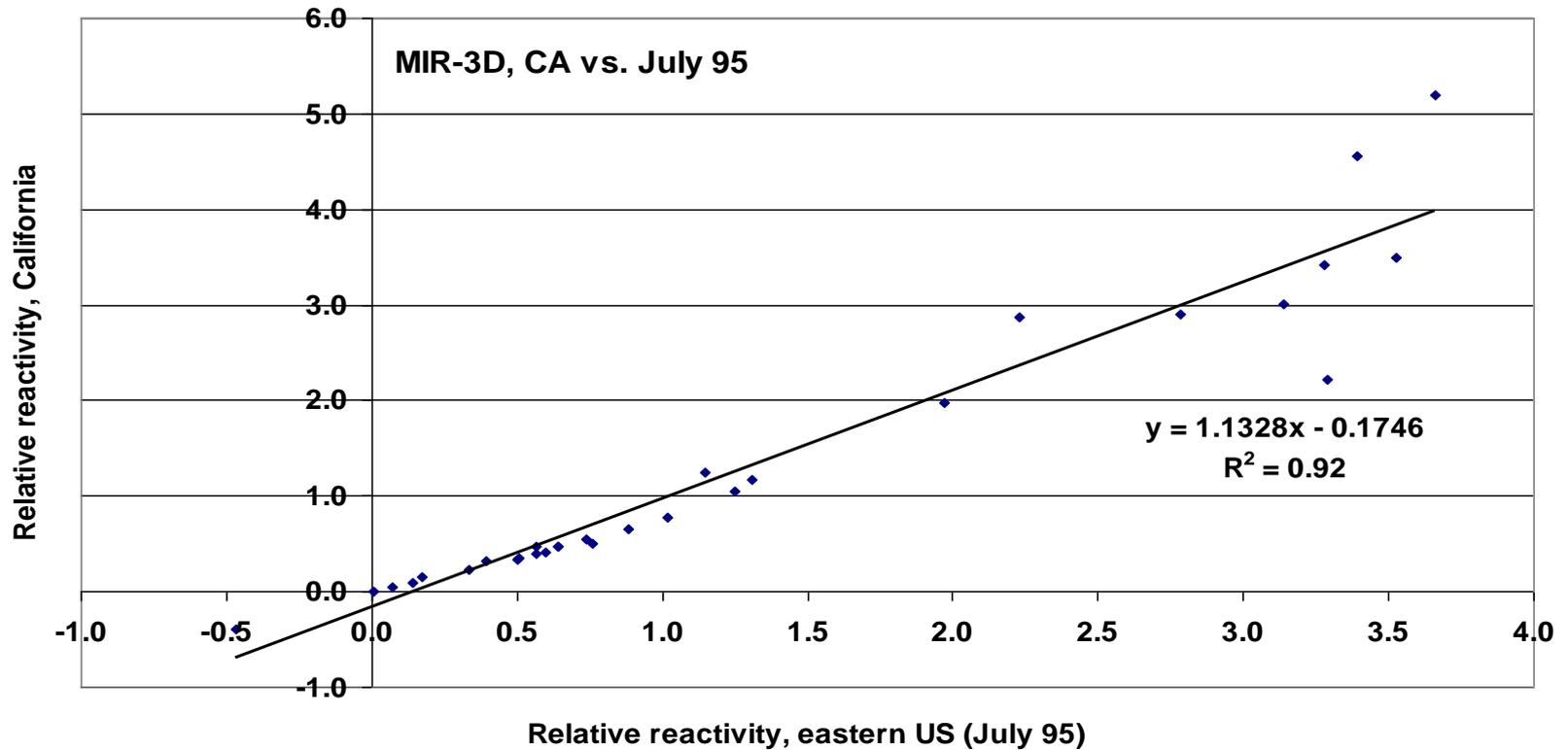


**RR-LS**



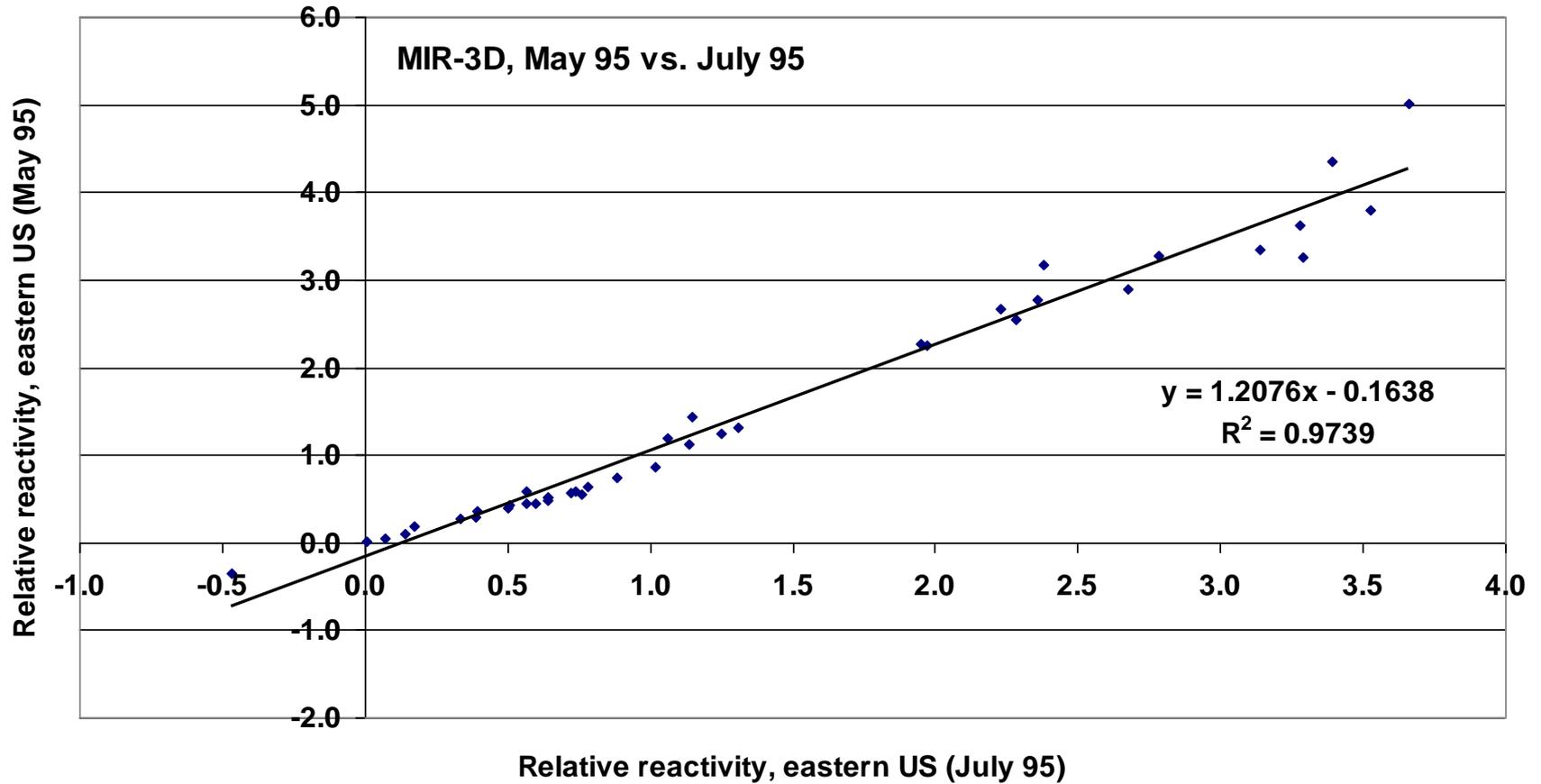
Source: Russell, 2003

# Geographical Validity



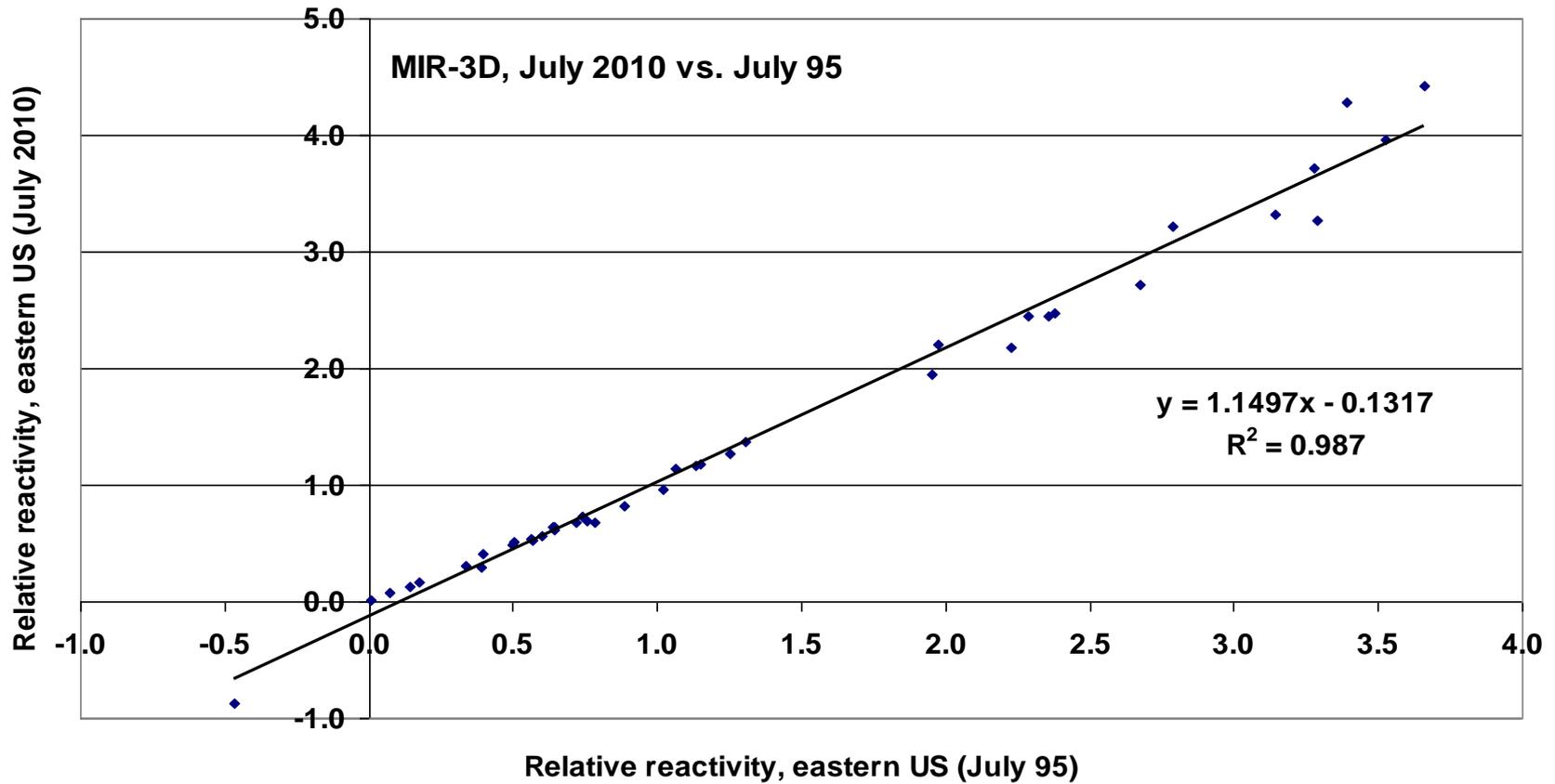
Source: Russell, 2003

# Meteorological Validity



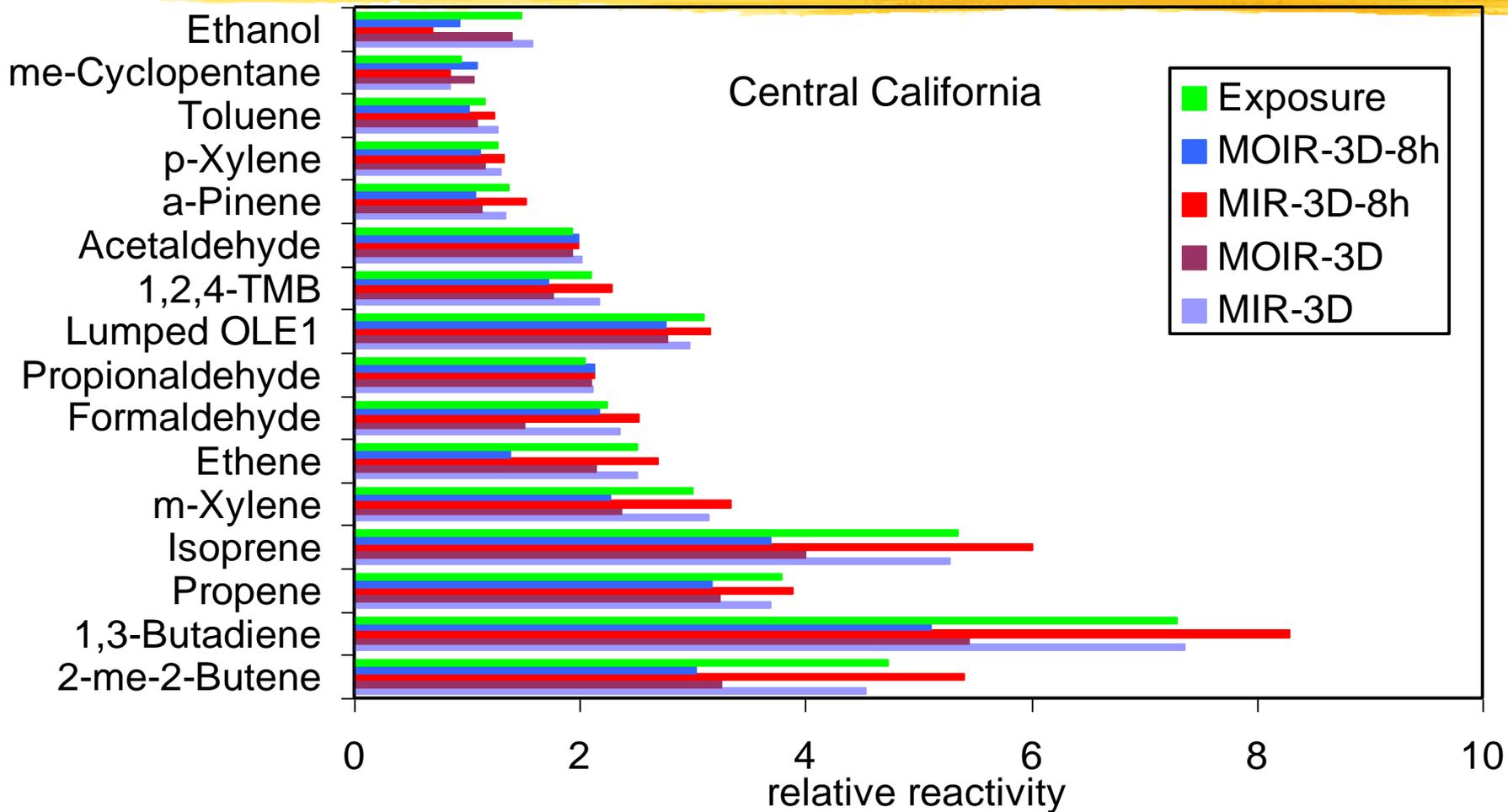
Source: Russell, 2003

# Emission Validity



Source: Russell, 2003

# Comparison of 3-D Metrics



Source: Harley, 2002

# Summary of 3-D modelling studies

- Reactivity scales developed using 3-D modelling resulted in similar ranking of individual VOC when compared to Carter's box model MIR.
- 3-D reactivity modelling captures temporal and spatial variability in meteorological and chemical regime.
- Results from California (SoCAB and Central California) and Eastern United States are consistent, with a few exceptions.
- Most VOCs behaved similarly in all metrics studied.
- Different meteorology has similar relative reactivities.
- Different emission scenarios result in very similar relative reactivities.

# Other Recent Reactivity Projects



- Reactivity Estimates (Carter)
  - 3-D Air Quality Modelling
    - California (Harley, 05/2002)
    - Eastern U.S. (Russell, 01/2003)
  - Chamber & Box-modelling
    - Architectural Coatings (Carter, 03/2005)
    - Pesticides (Carter, 01/2007)
    - Consumer Products (Carter, 12/2007)

# Other Recent Reactivity Projects (continued)



- Mechanism Development
  - Improved Methods for Reactivity Estimates (Carter, 05/2002)
  - Low NO<sub>x</sub> Mechanism Evaluation (Carter, 05/2004)
  - Improved Aromatics Mechanism (Atkinson, 07/2006)
  - SAPRC-07 (Carter, 08/2007)
- Low Reactivity Survey
  - Consumer Products (Censullo, 05/2002)
  - Automotive Solvents (Wolf, 12/2005)

# SAPRC-2007 and MIR Values



- Major Revision of the Chemical Mechanism (from SAPRC99 to SAPRC07)
- Additions/Changes: Chlorine Chemistry & Improved Aromatic Mechanisms
- Explicit Mechanisms for >700 VOC, MIR Scale for ~1100 VOCs or Mixtures
  - Overall, MIR values changed by ~10%
  - But, 35 VOCs changed by >35%
  - And, 5 VOCs changed by a factor of 2

# 2008 MIR Update Timeline



- Peer Review of SAPRC-07 Mechanism – November 07
- Reactivity Scientific Advisory Committee (RSAC) review – December 2007
- Final MIR Values - December 2007
- ARB Staff's Draft Proposal – early 2008
- ARB Staff Report – March 2008
- ARB Governing Board hearing – June 2008 with hearing for consumer product regulation

# Reactivity-Based Programs



- SIP Equivalent
- Scientifically Sound
- Technically Sound
- Effective
- Enforceable
- Defensible
- Flexible

# Low-Emission Vehicle (LEV) Program



- LEV I Adopted 1990 (Implementation 1994-2003)
- LEV II Adopted 1998 (Implementation 2004-2010)
- Reactivity of Exhaust Emissions First Accounted for in LEV I
- Established Reactivity TLEV, LEV, ULEV Relative to Baseline Fuel
- Generic Reactivity Adjustment Factor (RAF)  
Determined for Different Fuels: Commercial Gasoline, M85, CNG, & LPG
- Manufacturers Options

# Aerosol Coatings Regulation



- Reactivity Limits Adopted in June 2000
- Approved by the U.S. EPA as a SIP Revision in September 2005
- Reactivity-Based Control Strategy may be Cost-Effective and Provide Flexibility to Industry

# California Reformulated Gasoline (CaRFG) Program



- MIR values are used in Predictive Model to allow for certification of alternative formulations.
- Uses mathematical equations to demonstrate that alternative formulations preserve the emissions benefit of the program.
- MIR values play an essential role in providing producers flexibility to produce gasoline in CA while preserving the benefits of the CaRFG program.
- Uses MIR values to allow trade-offs between various emission processes on a reactivity adjusted basis.

# VOC Exemptions: Guideline



- Factors Considered in Environmental Impact Assessment
  - Atmospheric Impact
    - Ozone Forming Potential
    - Secondary Organic Aerosol
    - Stratospheric Ozone Depleting Potential
    - Global Warming Potential
  - Multimedia Impacts
  - Economic Impacts
  - Substitution & Scenario Analyses
  - Health Effects & Impacts

# Recent Exemption Requests



- tert-Butyl Acetate
- Halogenated Chemicals (9)
  - HCFC-225ca & HCFC-225cb
  - HFC-245fa
  - HCFC-365mfc
  - HFC-43-10mee
  - HFE-7100 (2) & HFE-7200 (2)

# VOC Exemptions: Recommendations

## Summary of Adverse Environmental Impacts (ARB, 2007)

Compound	Stratospheric Ozone Depleting Potential <sup>1</sup>	Global Warming Potential (100 years) <sup>2</sup>	Health Effects (Acute Hazard Index) <sup>3</sup>	Exemption Recommendation
HCFC-225ca & HCFC-225cb	0.02 <sup>4</sup> 0.03	122 595	1.75	No No
HFC-245fa	0.00	1,056	0.08	No
HFC-365mfc	0.00	794	0.01	No
HFC-43-10mee	0.00	1,640	0.47	No
HFE-7100 & HFE-7200	0.00	297 59	0.01	No Yes

# Other Potential Applications



- Prioritize control measures using reactivity metrics
- Target emissions of highly reactive VOCs with specific control measures
  - Houston-Galveston area, Texas
- Encourage VOC substitution and composition changes using reactivity-weighted emission limits
- New Source Review/Emission Trading
  - Trades of equal ozone-forming potential

# Challenges



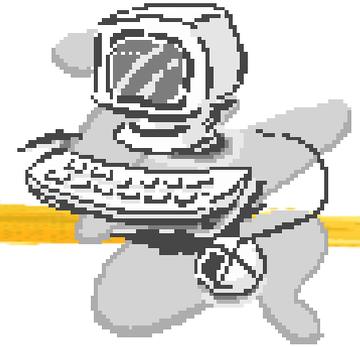
- Improved Chemical Mechanism & Scenarios
- Reactivity Metrics
- Aerosol Forming Potential, Ozone Depleting Potential, & Global Warming Potential
- Multimedia Impacts
- Health Effects and Impacts
- Atmospheric Availability
- Confidentiality & Enforceability

# Summary



- Mass-based VOC control measures are the primary tool today but the reactivity-based control strategies may offer an innovative way to reduce VOC emissions.
- CARB has been the leader on VOC reactivity research and regulations, developed first-in-the-world reactivity-based VOC regulations, and is examining the feasibility of these strategies for CP and architectural coatings.
- The U.S. EPA and other states have endorsed VOC reactivity science in the development of SIPs designed to meet the national air quality standard for ozone and other applications.

# Resources



- **Dongmin Luo, [dluo@arb.ca.gov](mailto:dluo@arb.ca.gov)**
  
- **Reactivity Program website:**
  - <http://www.arb.ca.gov/research/reactivity/reactivity.htm>
  
- **Consumer Products website:**
  - <http://www.arb.ca.gov/consprod/consprod.htm>
  
- **Architectural Coatings website:**  
<http://www.arb.ca.gov/coatings/arch/arch.htm>

# **Our Goal Is Clean Air Everyday for Everyone**



**Thank you!**