Development of Reactivity Scales for Volatile Organic Compounds

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October 17, 2013

Topics

- VOCs and air quality
- Factors affecting ozone reactivity and ozone reactivity scales
- Use of VOC reactivity in ozone control strategies
- Quantifying other VOC impacts: fine particle pollution; global warming; ozone depletion, Toxics
- Recommendations

VOCs and Air Quality

- Volatile Organic Compounds (VOCs) enter the atmosphere from a variety of anthropogenic and biogenic sources
  - Vehicle exhaust and evaporative emissions
  - Solvents and coatings
  - Industrial emissions
  - VOCs from vegetation (e.g., isoprene and terpenes)
- Impacts of VOCs on air quality include:
  - Promotion of ground-level ozone formation (“bad ozone”)
  - Contribution to secondary particle matter (PM) formation
  - Direct effects of toxic VOCs very near large sources
  - Formation of toxic or persistent oxidation products
  - Stratospheric ozone depletion (“good ozone”)
  - Global warming impacts

VOCs and Ground Level Ozone

- VOCs react in the presence of oxides of nitrogen (NO_x) to form ground-level ozone, an air quality problem in many urban areas
- Reducing ground level O_3 requires both VOC and NO_x control
  - NO_x is formed in combustion (O_2 + N_2 + high temperature)
  - NO_x is required for ground-level ozone to be formed and limits how much O_3 can be formed.
  - VOCs enhance the rate of ozone formation from NO_x. Without VOCs O_3 would not exceed air quality standards
- **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 or downwind ozone

Mechanism of How VOCs Affect O_3

- Ground level O_3 is actually formed from the photolysis of NO_2, with O_3 in a photostationary state relation with NO and NO_2:

$$NO_2 + h\nu \rightarrow O(^3P) + NO$$
$$O(^3P) + O_2 \rightarrow O_3$$
$$O_3 + NO \rightarrow O_2 + NO_2$$

<u>Overall:</u>

$$NO_2 + O_2 \overset{h\nu}{\Leftrightarrow} O_3 + NO$$

- VOCs promote O_3 by forming radicals that convert NO to NO_2 and shift the photostationary state towards O_3 formation, e.g.:

$$RH + OH \rightarrow H_2O + R$$
$$R + O_2 \rightarrow RO_2\bullet$$
$$RO_2\bullet + NO \rightarrow RO\bullet + NO_2$$
$$RO\bullet \rightarrow \rightarrow HO_2 + \text{other products}$$
$$HO_2 + NO \rightarrow OH + NO_2$$

<u>Overall:</u>

$$VOC + O_2 \overset{h\nu,\ NO_x,\ O_2}{\rightarrow \ \rightarrow \ \rightarrow} O_3 + \text{products}$$

Factors Affecting Impacts of VOCs on O_3

- No O_3 is formed without NO_x. 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 reactivities 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
- All these factors must be taken into account when developing effective VOC control strategies to reduce O_3.

Quantification of VOC O_3 Reactivity

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

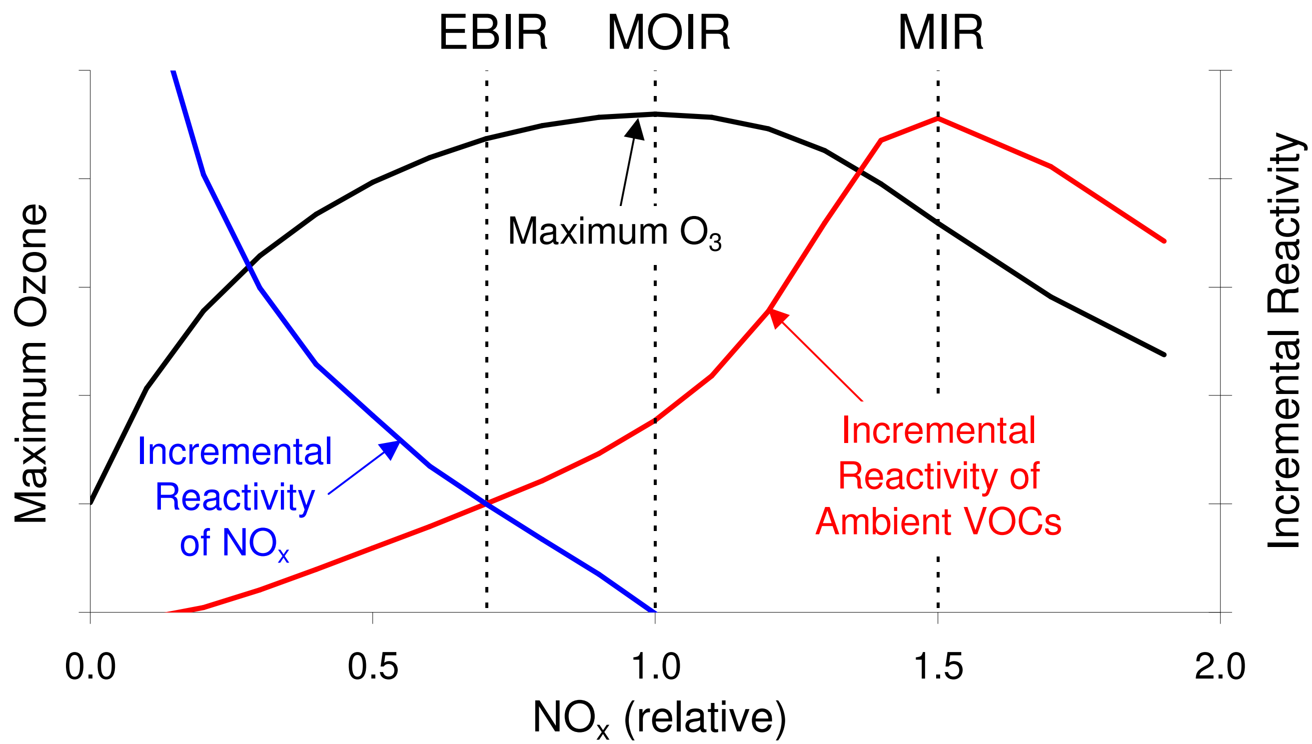
$$\text{Incremental reactivity of a VOC in an episode or experiment (scenario)} = \lim_{[\text{Added VOC}] \to 0} \frac{\left(O_3 \text{ formed after VOC added}\right) - \left(O_3 \text{ formed in scenario (“Base Case”)}\right)}{\text{Amount of VOC added}}$$

- This depends on the condition of the episode or experiment 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
  - Environmental 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**.

Ozone Formed and Incremental Reactivities as a Function of NO_x Levels



Calculated for the averaged conditions box model scenario using the SAPRC-99 chemical mechanism

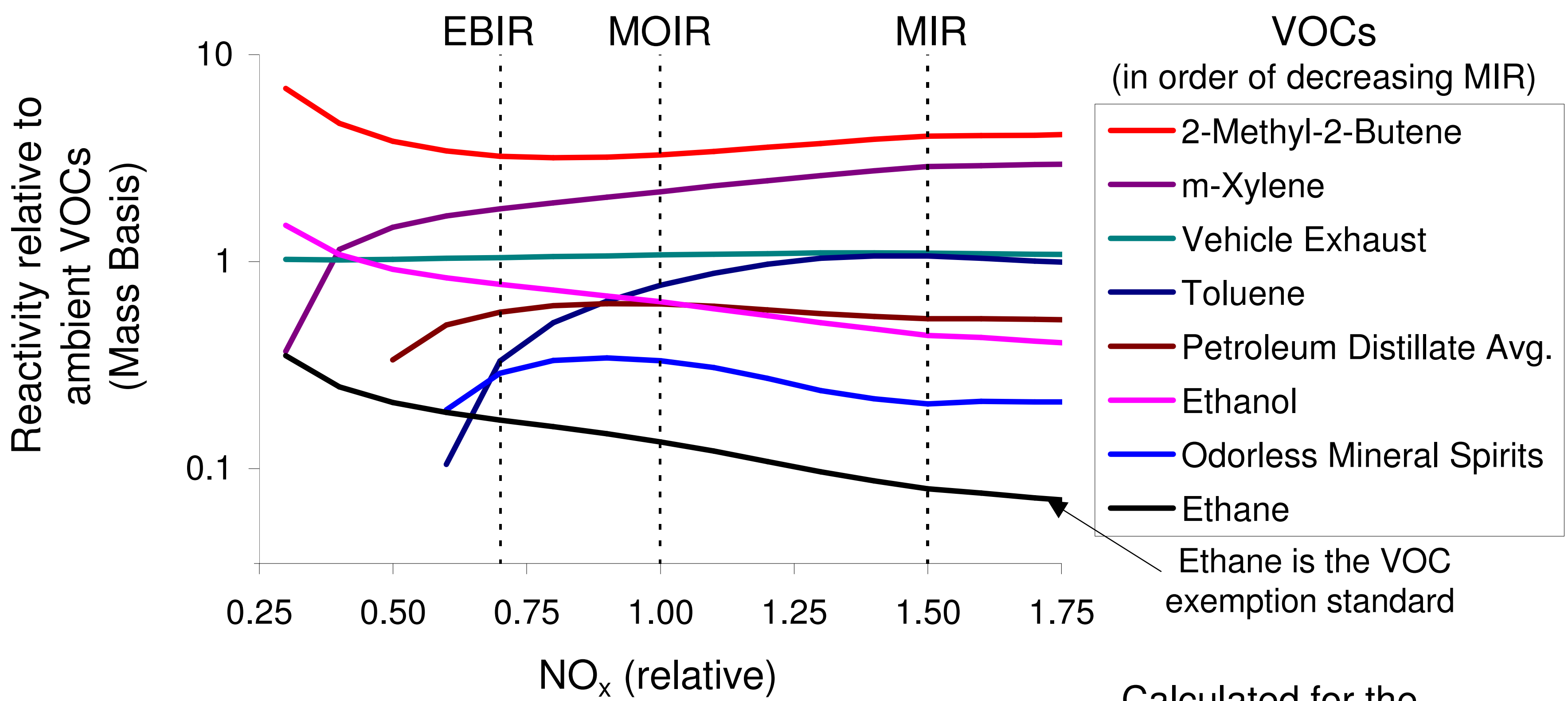
Note that NO_x inhibits O_3 when NO_x > MOIR

MIR: NO_x levels giving maximum VOC incremental reactivities

MOIR: NO_x levels giving maximum ozone concentrations

EBIR: NO_x levels where VOCs and NO_x controls have equal impact

Relative Incremental Reactivities of Representative VOCs as a Function of NO_x



Calculated for the "averaged conditions" box model scenario using the SAPRC-99 chemical mechanism

Note the reactivities of the most and the least reactive VOC subject to mass-based regulations differ by a factor of ~50

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
  - Calculating ambient reactivities requires computer models with a "chemical mechanism" to represent how VOCs react
  - Uncertainties in mechanism for ambient mixtures cause uncertainties for reactivity quantifications for all VOCs
  - Mechanisms for almost all VOCs have uncertain estimates and approximations. Not all VOCs have the environmental chamber data needed to test reliability of predictions.

Options for Derivation of Reactivity Scales: Type of Model

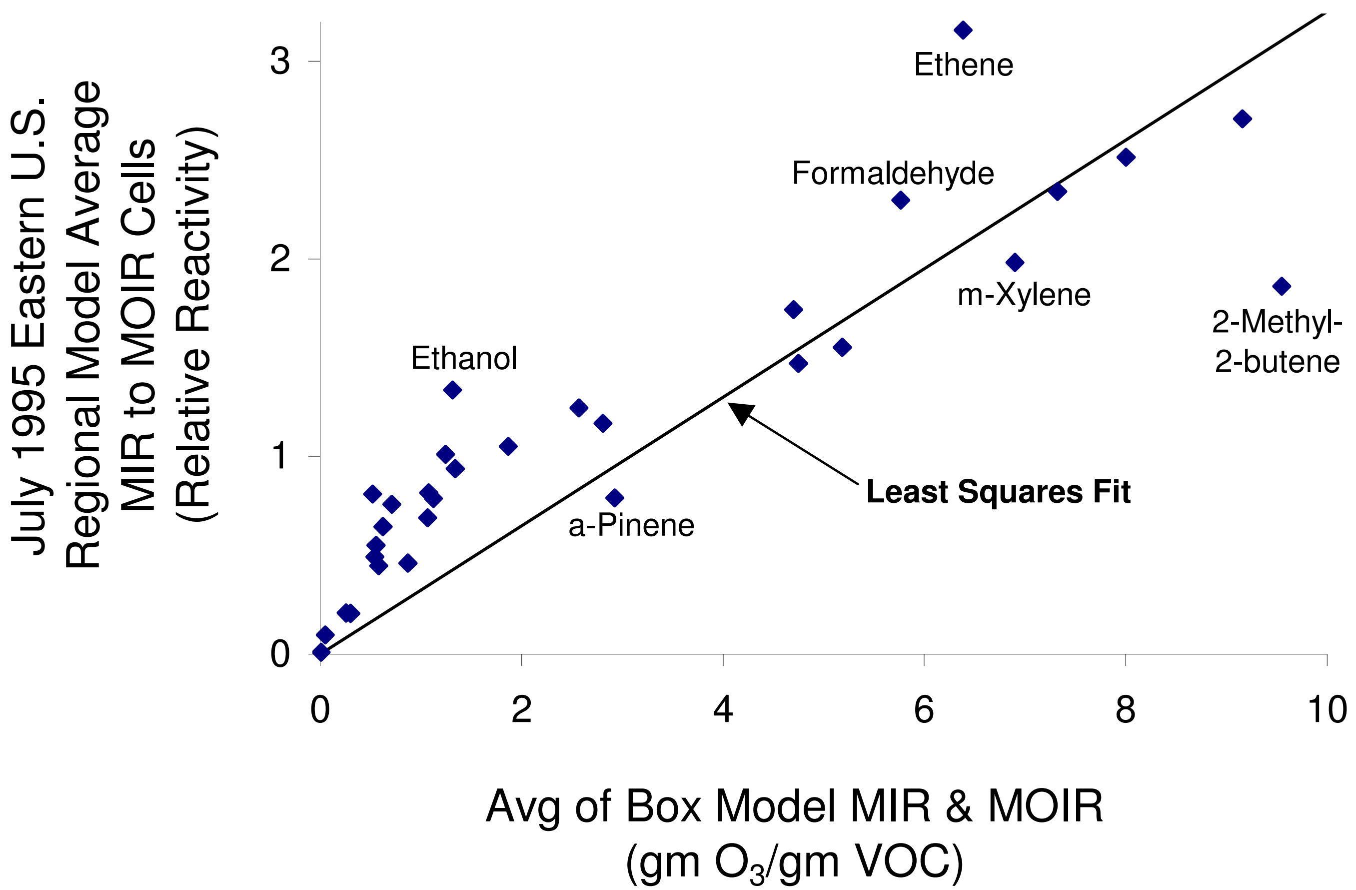
Use Single Cell Box, Trajectory, or "EKMA" models

- 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 O_3 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

Comparison of Regional vs. Box Model Reactivities for Comparable Conditions



Regional Model Results from Hakami, Arhami and Russell, Report for RRWG, 2004

Calculated using the SAPRC-99 Mechanism

Options for Derivation of Reactivity Scales: Type of Scenario Conditions

Maximum Incremental Reactivity (used for MIR scales)

- Represents high NO_x conditions where O_3 most sensitive to VOCs. Representative of urban areas near emissions sources
- Used in California regulations because it represents conditions where VOC control is most effective. Complements NO_x controls

Maximum Ozone Conditions (used for MOIR scales)

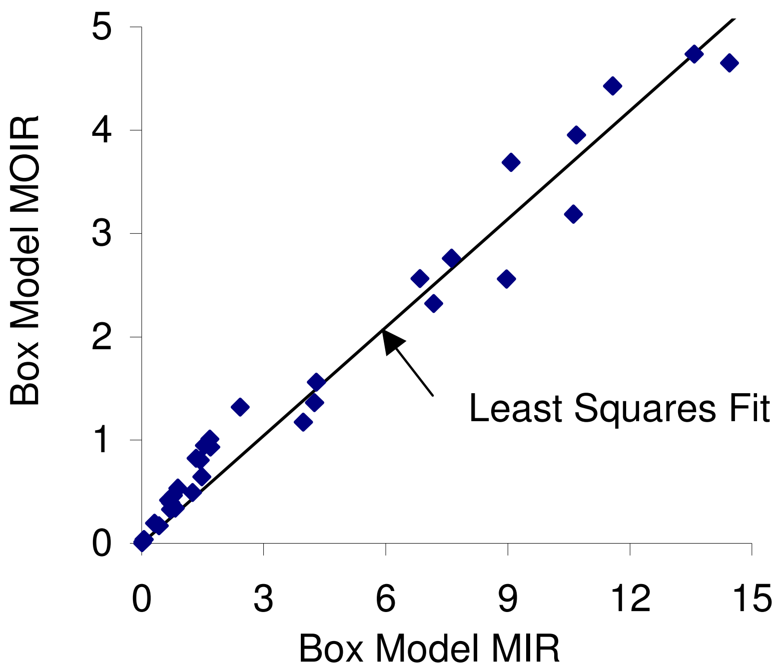
- Represents effects on O_3 under highest O_3 conditions
- Often gives better correlations to reactivities in regional models

Average Base Case or Regional Average

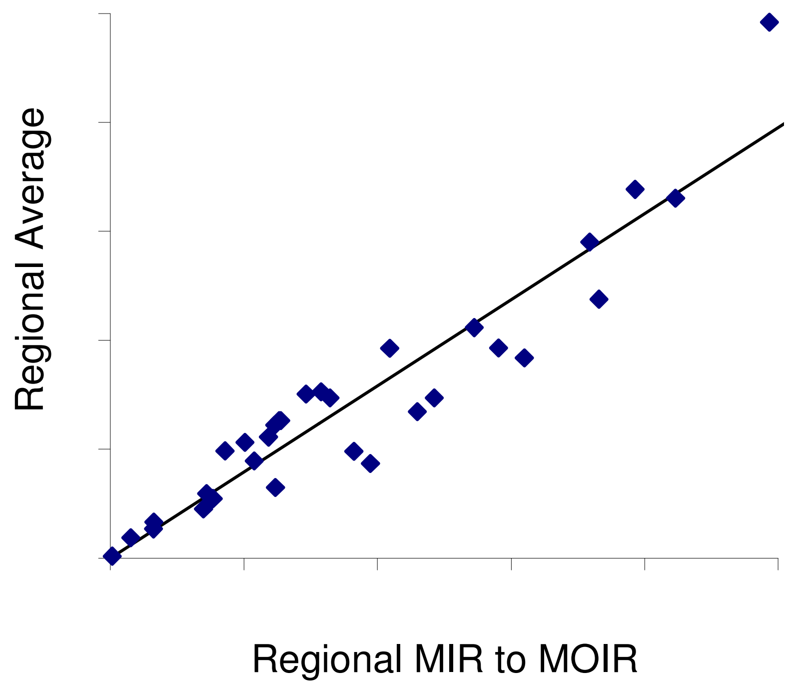
- Represents effects on O_3 throughout wide regions, including those not sensitive to VOC controls
- Very computationally expensive to derive comprehensive scales

Comparison of Reactivities for Differing Scenario Conditions

Box model MOIR vs MIR ($gm\ O_3$ / gm VOC)



Regional Average vs. Regional MIR to MOIR cells (relative)



Box and regional model calculations used the SAPRC-99 Mechanism

Regional Model Results from Hakami, Arhami and Russell, Report for RRWG, 2004

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 against environmental chamber data.
- The reactivity scale used for the current California reactivity-based regulations was derived using the SAPRC-07 mechanism
  - Represented the state of the science as of 2007
  - Has reactivity values for >1100 types of VOCs
- The SAPRC-07 mechanism is being updated
  - Version with updated aromatics, SAPRC-11, now completed
  - Project to comprehensively update SAPRC-11 underway

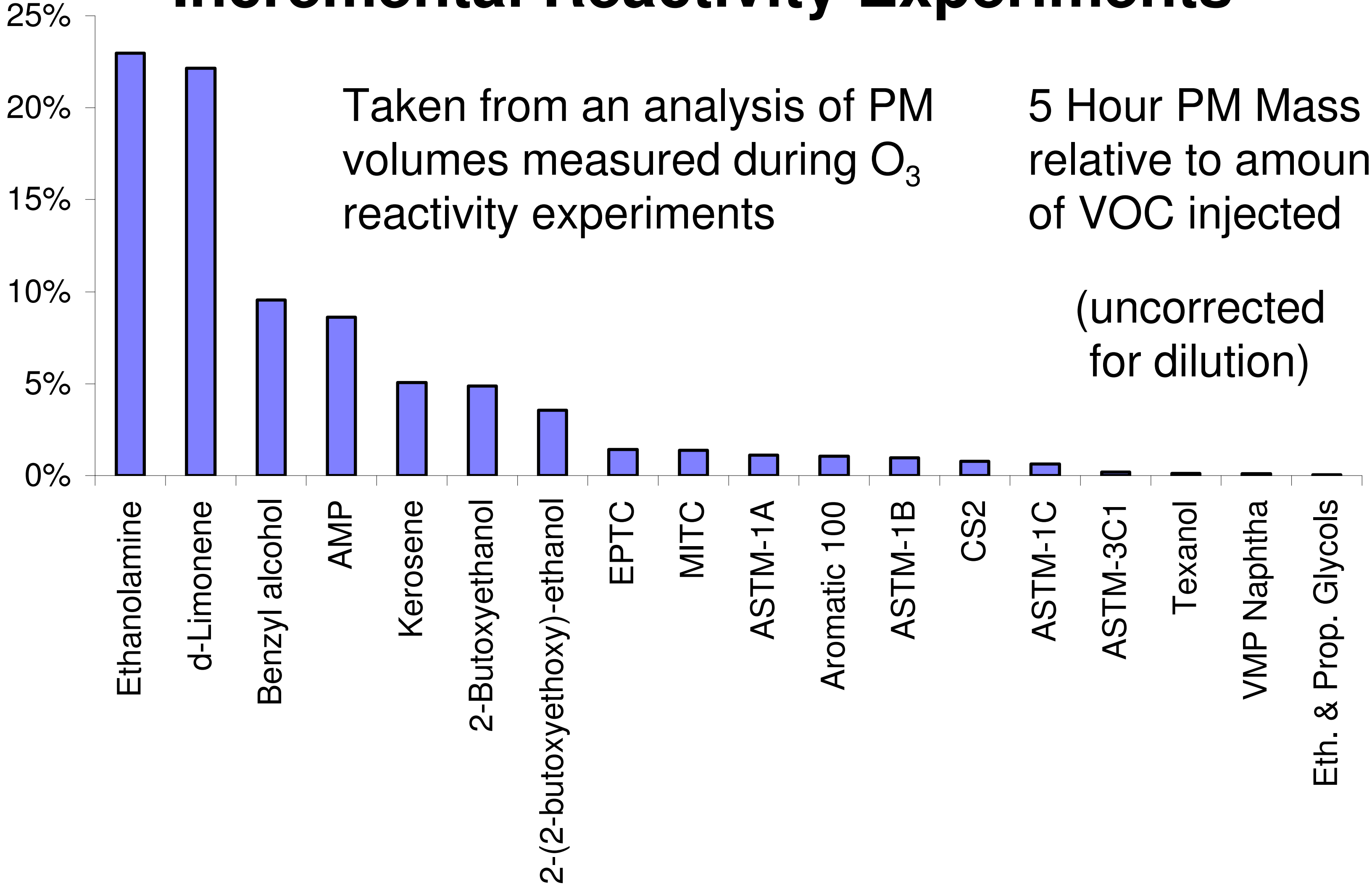
Use of Reactivity Scales in Ozone Control Strategies

- Regulations taking ozone reactivity into account are potentially much more efficient and cost effective than current approaches
- But reactivity-based VOC regulations have practical difficulties:
  - Chemical composition information required for all sources
  - Much more complex to implement and enforce
  - Reactivities for some VOCs unknown or very uncertain
  - Some low reactivity compounds need to be regulated because of other impacts, e.g., toxicity and PM formation
- California has used the MIR scale in regulations for
  - Reactivity adjustment factors for alternative fuel vehicles
  - Aerosol coatings VOC content regulations
  - Considered for architectural coatings but not implemented
- Most practical use of reactivity may be prioritizing VOC sources for controls

Other VOC Impacts: Effects on Fine Particle Formation

- 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.
- Developing improved methods to quantify effects of VOCs on PM formation is currently an active area of research
- **PM reactivities can be quite different than ozone reactivities**

PM Reactivities Measured in UCR Incremental Reactivity Experiments

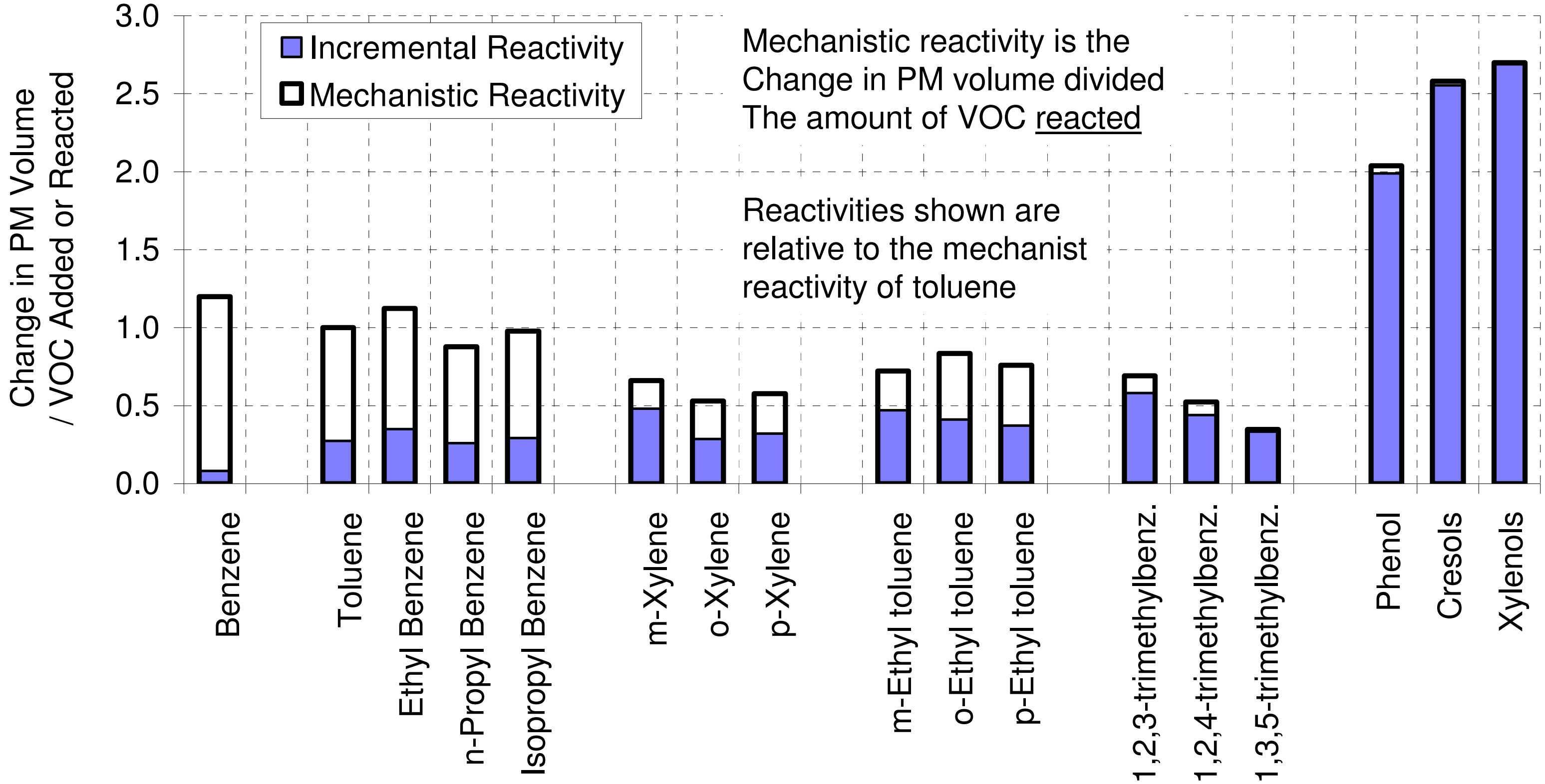


Taken from an analysis of PM volumes measured during O_3 reactivity experiments

5 Hour PM Mass relative to amount of VOC injected

(uncorrected for dilution)

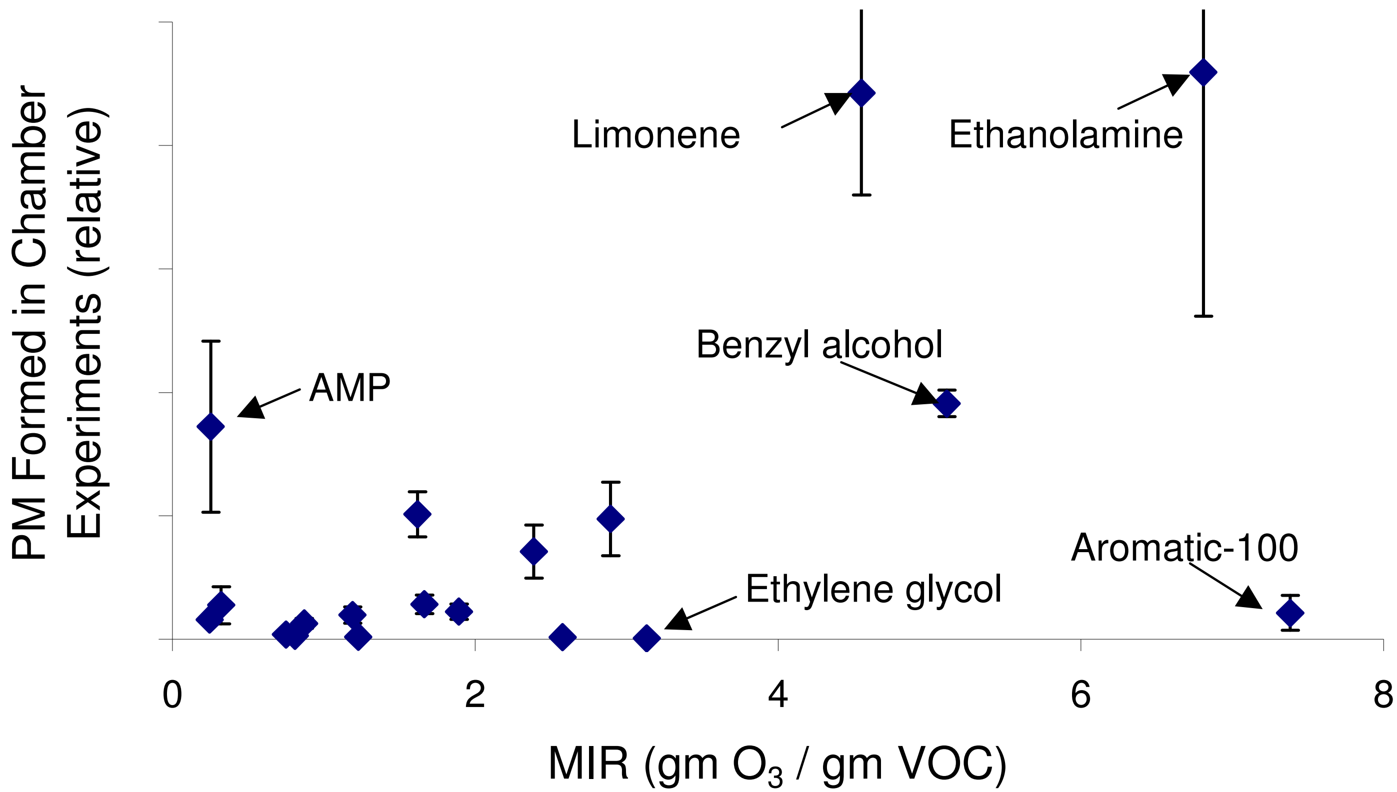
Calculated PM Reactivities of Aromatics



Calculated for the conditions of a standard UCR surrogate – NO_x chamber experiment using the SAPRC-11 aromatics SOA mechanism.

The SAPRC-11 SOA yield parameters were adjusted to fit model simulations of PM in UCR aromatic – H_2O_2 and aromatic – NO_x chamber experiments

Correspondence Between O_3 Impact (MIR) and PM Formed in Chamber Experiments



Other VOC Impacts: Global Warming and Stratospheric Ozone Depletion

- Very slowly reacting VOCs can persist in the atmosphere long enough to have global impacts
  - Global warming: IR absorption affects radiative transfer
  - Stratospheric O_3: Some VOCs release Cl or Br in the stratosphere that catalytically remove “good” O_3
- Relative reactivity scales for these impacts exist and are less uncertain than relative reactivity scales for ground-level O_3
  - Depend only on reaction rates, IR absorption, and halogen contents of the compounds, which are generally known
  - Negative correlation with ground-level O3 reactivity scales
- Global impacts from CO_2 formed from oxidation of reactive anthropogenic VOCs is less important than impacts of CO_2 itself or biogenic VOCs

Other VOC Impacts

Toxicity of VOCs themselves (concern near source areas)

- Difficult to quantify. “Binning” probably best approach

Persistence in the environment (effects on ecosystem)

- Primarily a concern for low reactivity or low volatility VOCs

Formation of toxic or persistent oxidation products

- Reactivity scales for formation of various toxic products can be developed if mechanism is known
- This requires more chemically detailed mechanisms than those currently used used in regulatory models

Recommendations: Ozone Reactivity

Develop workable reactivity-based VOC regulations

- Develop practical reporting and enforcement methods
- Appropriately consider toxicity and other impacts besides O_3

Improve science and regulations on volatility and availability

- Some VOCs may partition onto water or surfaces and not be available for reacting in the atmosphere to promote O_3
- But some current LVP exemptions may be much too lenient

Improve methods and scenarios used for reactivity scales

- MIR method may not be optimal and box model scenarios used are out of date and do not represent the best science

Reduce chemical mechanism uncertainties

- Significant uncertainties and lack of data for many VOCs
- Mechanism uncertainties reduce reliability of SIP modeling as well as reactivity scales

Recommendations: Other VOC Impacts

Improve ability to quantify PM impacts

- Replace parameterized models with process-based models
- This requires development **and evaluating** much more detailed mechanisms than needed for ozone modeling

Improve predictions of formation of toxic or persistent products

- Ozone is not the only toxic product formed when VOCs react
- Also requires developing much more detailed mechanisms

Develop regulations that consider each VOC impact separately

- Reactivities relative to different impacts do not correlate
- O_3 reactivity should not be considered when regulating toxics or PM precursors, and vise-versa

Additional Information Available

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

http://www.cert.ucr.edu/~carter

Current SAPRC mechanisms and reactivity scales

http://www.cert.ucr.edu/~carter/SAPRC

Reactivity Research Working Group reports on VOC reactivity

http://www.narsto.org/voc_reactivity

Reactivity-based VOC regulations in California

http://www.arb.ca.gov/research/reactivity/regulation.htm