Issues and Research at UCR on PM and Toxics Impacts of VOCs

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Outline

- Factors affecting impacts of VOCs on secondary toxics and modeling study of aldehyde and PAN formation potentials of VOCs
- Factors affecting impacts of VOCs on PM and qualitative UCR chamber data on relative impacts of coatings VOCs
- Summary of issues and research needs for developing reactivity scales for impacts of VOCs on SOA and toxic products

Factors Affecting Impacts of VOCs on Air Toxics Formation

Direct Effects

- For toxic VOCs the main factors are their removal rates
- For toxic precursor VOCs the main factors are the rate the VOCs react, the toxic product yields and how they vary with conditions

Indirect Effects

- VOCs that enhance or inhibit radical levels will affect rate of toxic product formation from toxic precursors that are present
- VOCs that affect O_3 will affect the chemical environment that may affect some toxic product yields (e.g., PANs)
- Indirect effects will be highly dependent on the levels of toxic precursors present
- Indirect effects will correlate with O_3 reactivity more than direct effects.

UCR Project for OEHHA to Estimate Aldehyde and PAN Formation Potentials

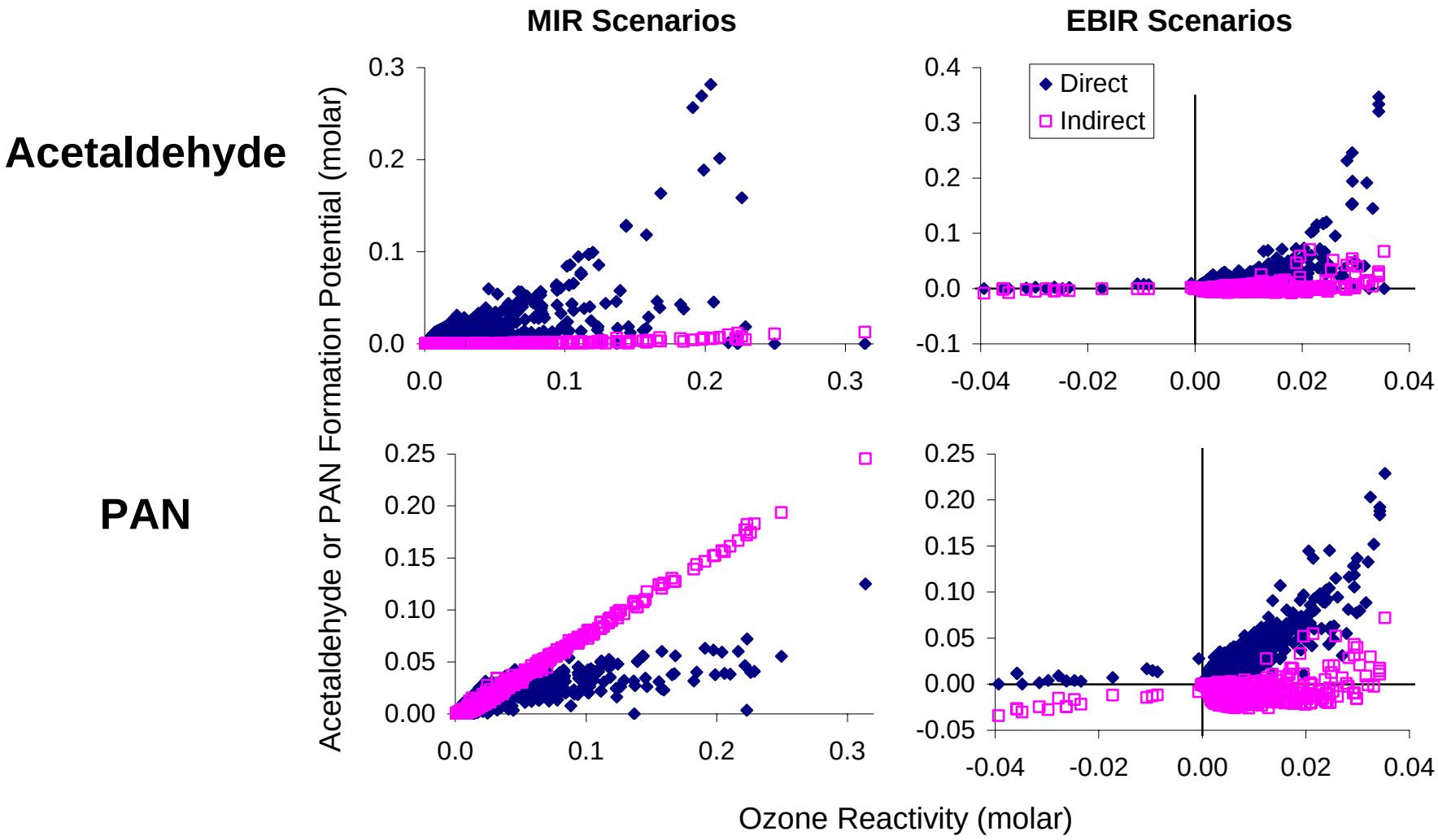
Background

- The California Office of Environmental Health Hazard Assessment needed to evaluate the human and environmental health impacts of motor vehicle fuels
- Quantifying effects on secondary toxics of fuel VOCs on air toxics (aldehydes, nitrates, PANs) was part of this effort
- UCR was contracted to calculate impacts of VOCs on atmospheric aldehyde, nitrate, and PAN levels
- Work was completed in September, 2001. Report now available at http://www.cert.ucr.edu/~carter/absts.htm#aldrpt

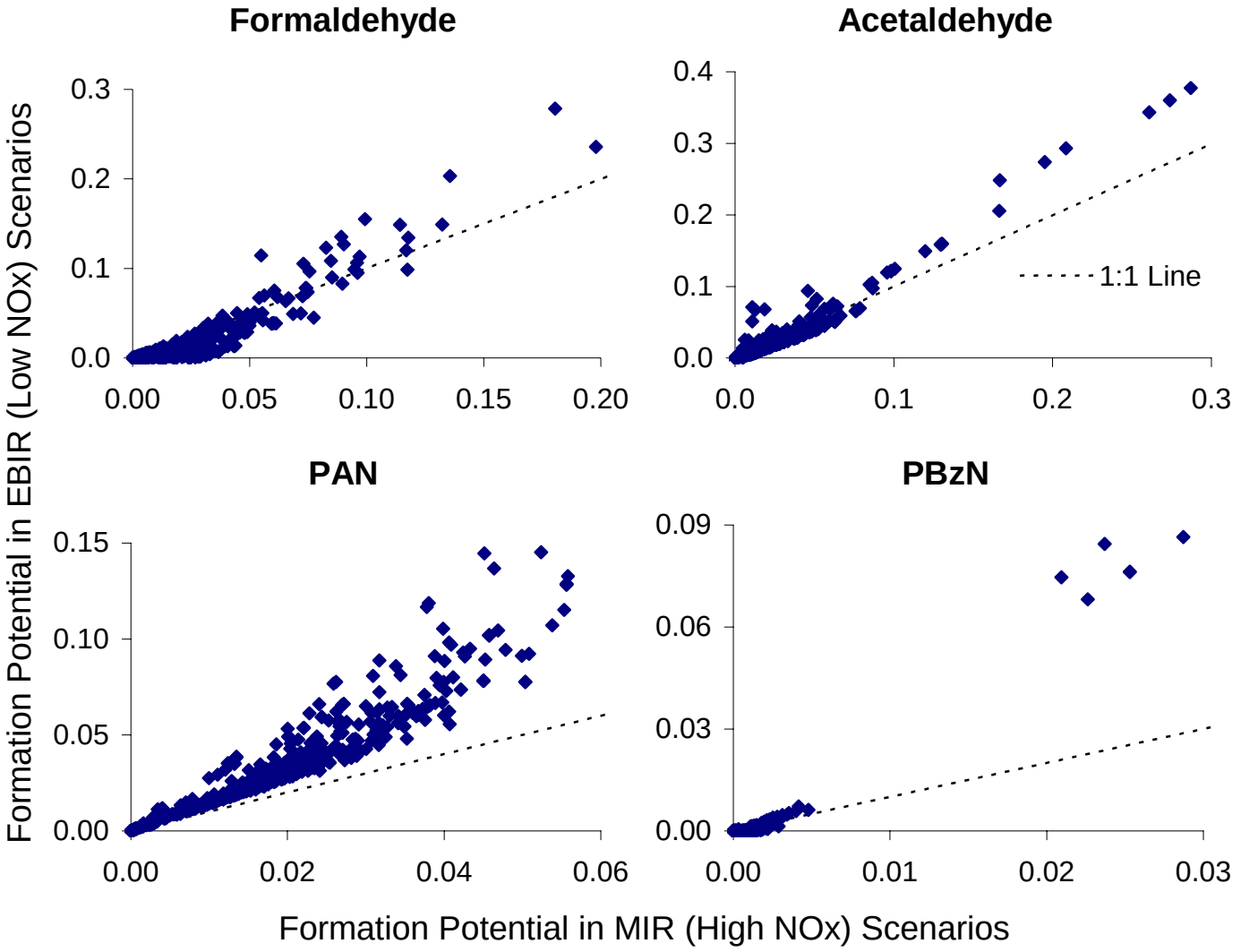
Project to Estimate Aldehyde and PAN Formation Potentials: Approach

- SAPRC-99 mechanism used
- Duplicate organic product species added to permit separate assessments of direct and indirect effects
- Same scenarios employed as used to calculate MIR, MOIR, and EBIR ozone reactivity scales
- Incremental reactivities of VOCs were calculated with respect to direct and indirect formation of:
  - Formaldehyde
  - Acetaldehyde
  - Lumped higher aldehydes
  - PAN
  - PBzN
  - Lumped Other PANs
  - Acrolein
  - Organic nitrates
  - Lumped aromatic products

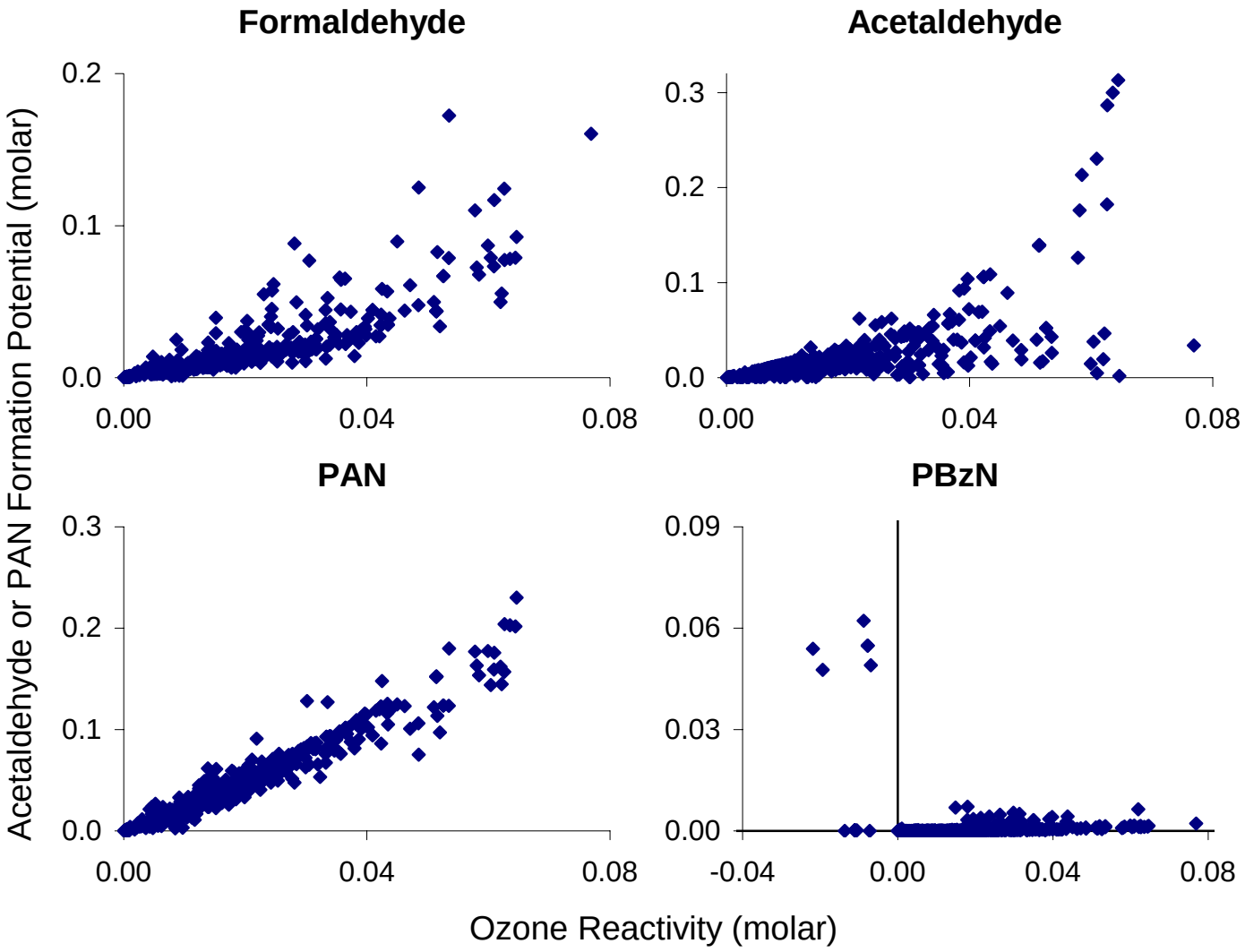
Direct and Indirect Acetaldehyde and PAN Formation Potentials vs. Ozone Reactivity



Aldehyde and PAN Formation Potentials in High vs. Low NO_x Scenarios



Aldehyde and PAN Formation Potentials vs. Ozone Reactivity in MOIR Scenarios



Summary and Recommendations - Toxic Product Reactivity

Summary

- Toxic product reactivities depend on details of VOC mechanisms which vary from compound to compound
- Aldehyde formation potentials are insensitive to NO_x conditions. PAN potentials more sensitive but trends are consistent.
- Correlation with O_3 reactivity depends on product. Ranking is PAN > Formaldehyde > Acetaldehyde >> PBzN

Recommendations

- Issues and research needs similar to those for O_3 scales except:
  - Greater requirement for chemical detail in mechanism and greater mechanism uncertainty
  - Choice of scenario conditions may be slightly less important except for composition of base ROG mixture.

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 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.
- Current models use inadequately tested and highly simplified parameterized models to predict secondary PM

Requirements for Predictions of PM Impacts
(in addition to requirements for O_3 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

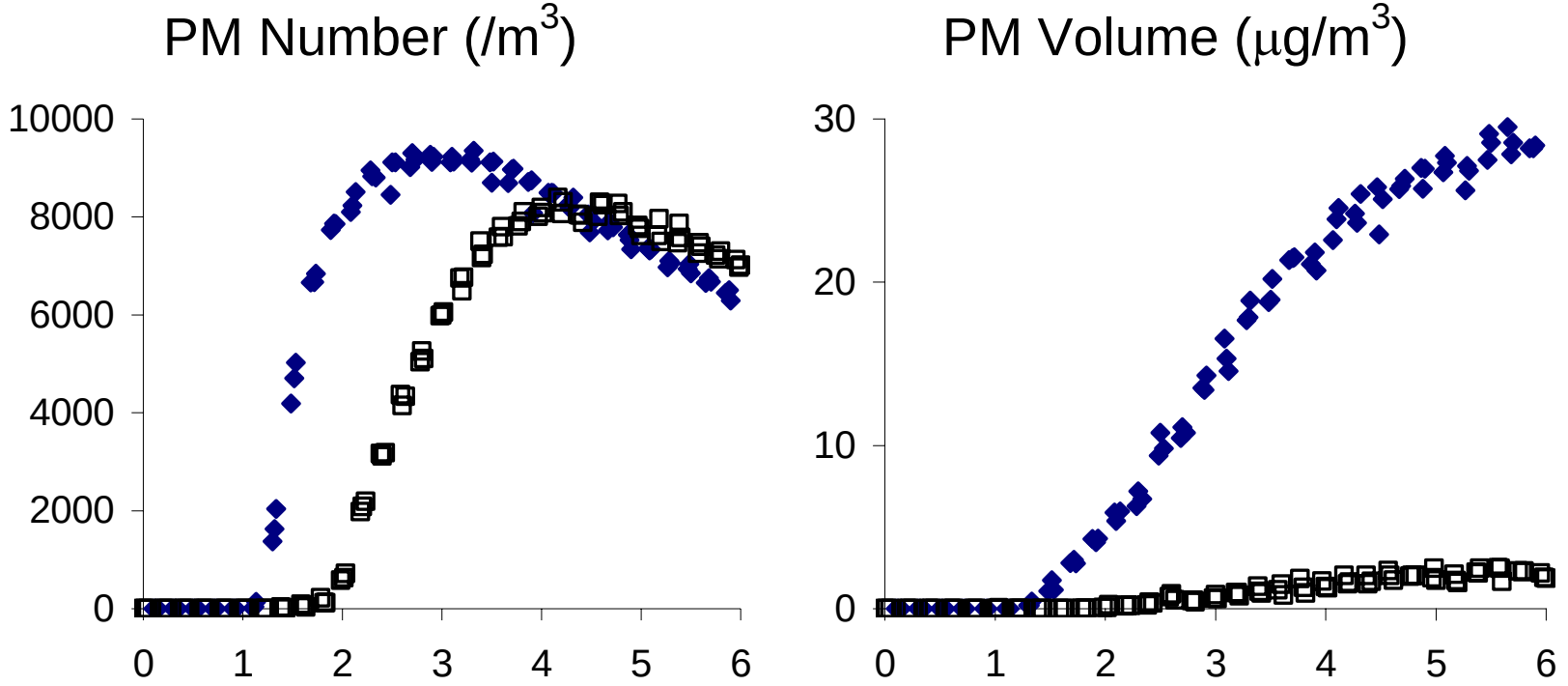
Model for Environmental Conditions

- Appropriately representing temperature, humidity, absolute concentrations *much more important* for PM than for O_3
- Appropriately represent *primary* and *background* PM that may affect partitioning or condensed-phase processes
- Use base case scenarios that give representative PM levels
- Appropriately represent PM loss processes

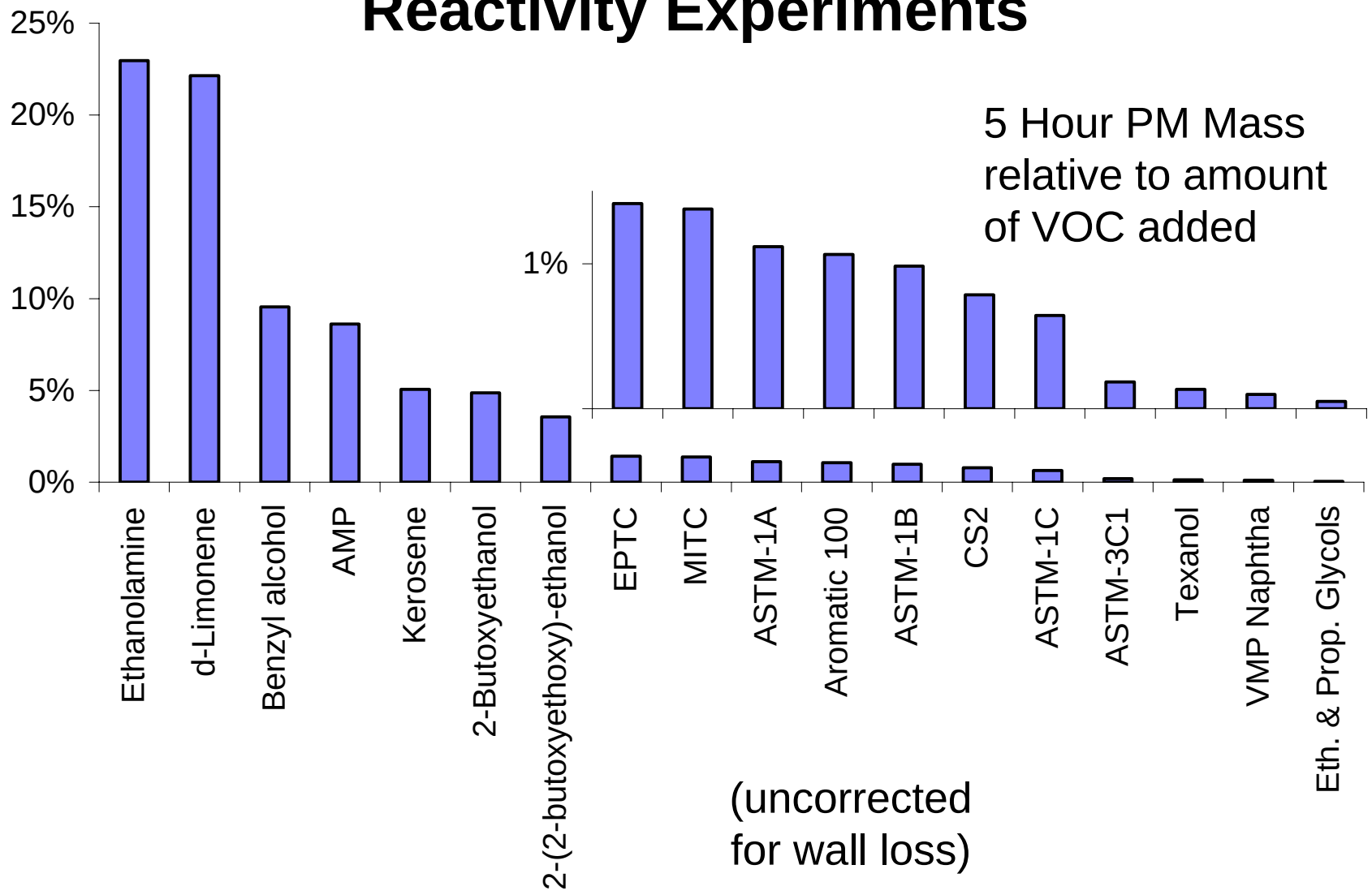
PM Measurements in the UCR EPA Chamber

- 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, CS_2, 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

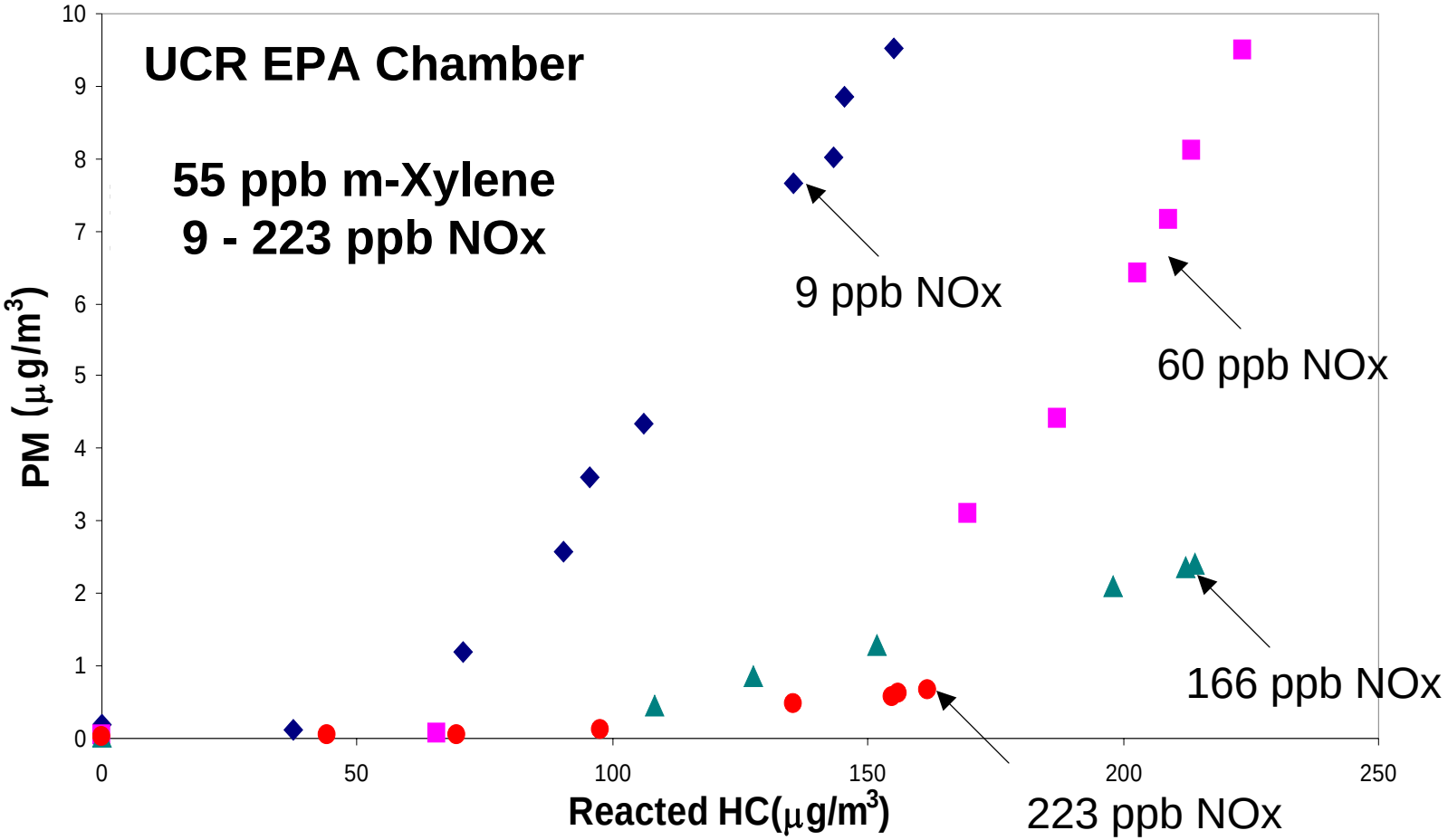
Representative PM Data from Reactivity Experiments



Average PM Reactivities in Incremental Reactivity Experiments



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



Upcoming UCR Project: SOA Formation: Chamber Study and Model Development

- Objectives: Develop improved mechanisms to predict secondary organic aerosol (SOA) from aromatics and other compounds.
- Status: Contract pending
- Proposed Overall Approach:
  - This project to be carried out in collaboration with Dr. David Cocker at UCR and Dr. Robert Griffin at Rice University.
  - UCR EPA chamber experiments will be conducted to develop and evaluate models for SOA from aromatics, aromatic products, and selected other VOCs
  - The SAPRC-07 mechanism will be expanded and adapted for SOA modeling based on the results of the experiments.
  - Use the results to develop improved mechanisms for predicting SOA in 3-D airshed models.

Summary and Recommendations - PM Reactivity: Scientific Issues

- Chamber data indicate VOCs vary significantly in PM impacts, and PM impacts are *not* correlated with O_3 impacts.
  - However, current data are qualitative and not representative of ambient conditions
- Improved, and more comprehensive mechanisms need to be developed for modeling secondary PM in the atmosphere
  - Detailed mechanisms have been developed for only few of VOCs and evaluated under unrepresentative conditions
  - Current simplified PM models are not consistent with the limited available chamber data for aromatics
  - 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 O_3 reactivity scales are not appropriate

Summary and Recommendations - PM Reactivity: Policy Issues

- Current models are not yet sufficiently reliable to serve as a basis for deriving PM reactivity scales for regulatory applications
- Near term solution:
  - Use PM formation in appropriate environmental **chamber experiments** to obtain ***qualitative*** **PM reactivity rankings**
  - Modeling and experimental research is needed to develop appropriate experimental procedures for this purpose
- Longer term solution:
  - Continue to support experimental and model development research to improve SOA models.
  - Once sufficiently reliable models are developed, the issues become similar to those for O_3 and toxics reactivity scales.

Additional Information Available

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

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

Report on Aldehyde and PAN formation potentials for the California OEHHA (Dated September 23, 2001)

- http://www.cert.ucr.edu/~carter/absts.htm#aldrpt

Research on Secondary Organic Aerosol Formation in UCR EPA chamber

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