CHAMBER STUDIES OF OZONE FORMATION POTENTIALS OF VOCs

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Outline

- Quantification of VOC reactivity: issues and data needs
- Recent data concerning ozone impacts of specific types of VOCs
  - Ambient surrogate
  - Aromatics
  - Glycols, Glycol ethers, esters, etc.
  - Petroleum distillates
- Summary of current status, ongoing work, and data needs

VOC REACTIVITY

- Ground level O_3 is formed from the reactions of VOCs and NO_x in sunlight
- VOCs differ significantly on their effects on O_3 formation ("reactivity"). Mechanistic factors affecting reactivity 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
- Regulations that take VOC reactivity into account could potentially result in more cost-effective O_3 control strategies.

QUANTIFICATION OF O_3 REACTIVITY

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

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

- This depends on the condition of the “Base Case” 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
  - Chamber experiments have wall effects, static conditions, higher levels of test VOCs, 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.
- **Therefore, Chamber experiments are necessary to test the reliability of chemical mechanisms to predict reactivity**.

UNCERTAINTIES IN REACTIVITY QUANTIFICATION

- Uncertainty in most appropriate environmental conditions to use to derive the reactivity scale
  - No single scale can represent all environments. Not obvious how to derive a general scale
  - California adopted MIR scale. U.S. EPA wants more research before adopting regulatory scale
- Chemical composition uncertainties
  - Applicable to complex mixtures such as exhausts and petroleum distillates
- 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.

CHEMICAL MECHANISM

- Chemical mechanisms for reactivity assessment must explicitly represent reactions of the hundreds of types of VOCs
- Most appropriate are those that explicitly represent the many types of VOCs (e.g, SAPRC-99 and the “Master Mechanism”
- SAPRC-99 mechanism probably the most extensively evaluated against chamber data.

Experiments Used in initial SAPRC-99 Evaluation	# Runs	# VOCs
Characterization	76	
Single Simple VOC - NO_x	484	37
Incremental reactivity	447	80
Miscellaneous mixtures	95	
“Base Case” mixtures with reactivity runs	591	

- Base and individual VOC mechanism uncertainties remain

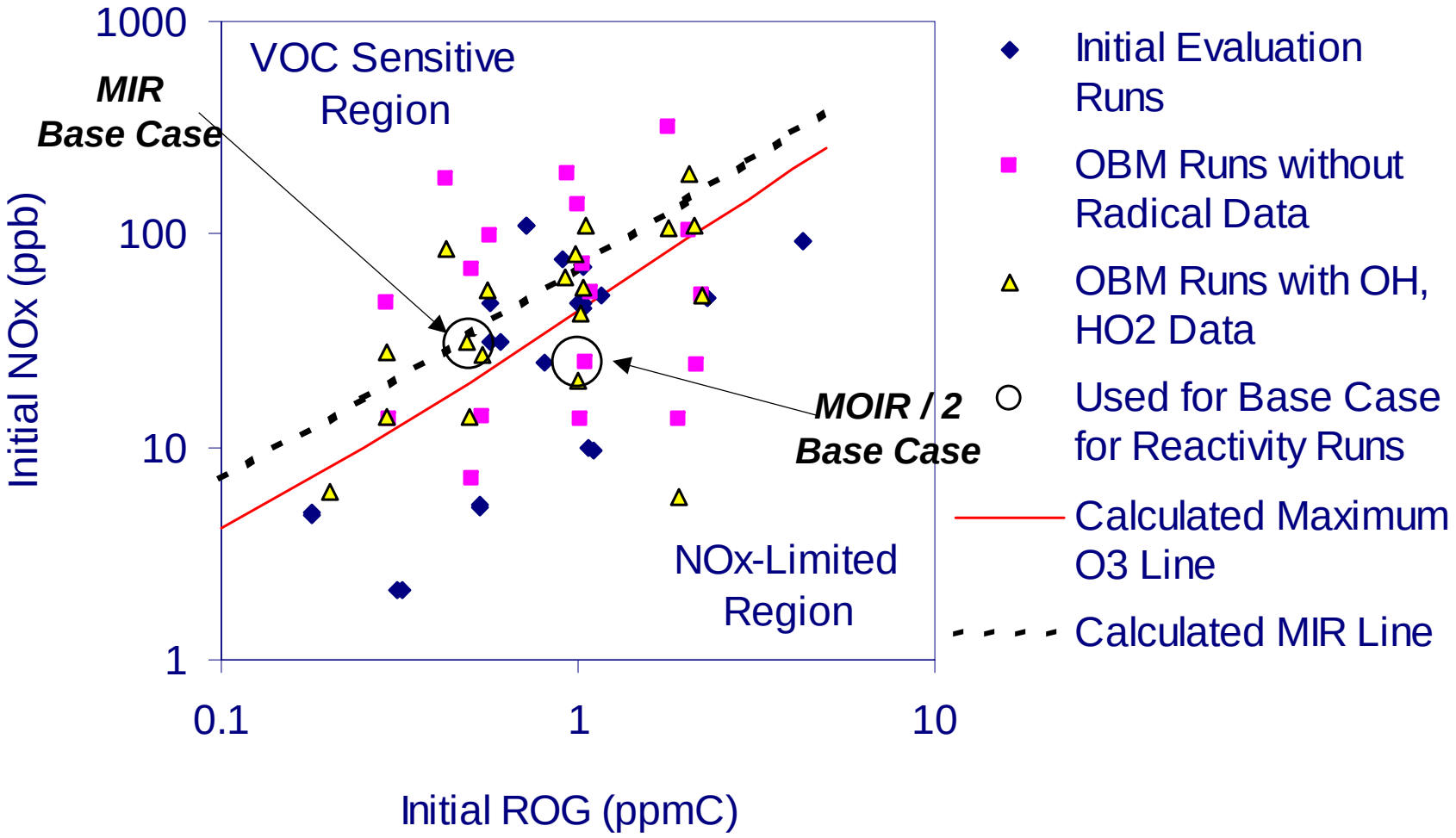
SUMMARY OF NEW UCR CHAMBER DATA RELEVANT TO O_3 IMPACT ASSESSMENT

- Data to test O_3 predictions of base mechanism
  - Ambient ROG surrogate - NO_x experiments
  - Aromatic – NO_x and aromatic – CO – NO_x experiments
- Data to test O_3 mechanisms of major solvent VOCs
  - Selected glycols, glycol ethers and glycol esters
    - Important water-based coatings solvents
    - Provide data to test SAPRC-99 mechanism estimates
  - Selected petroleum distillates
    - Widely used in solvents and coatings
    - Complex mixtures of C_{8+} alkanes with varying amounts of aromatics.
    - Predicted reactivity will depend on choice of compounds used to represent unidentified components

TESTS OF BASE MECHANISM

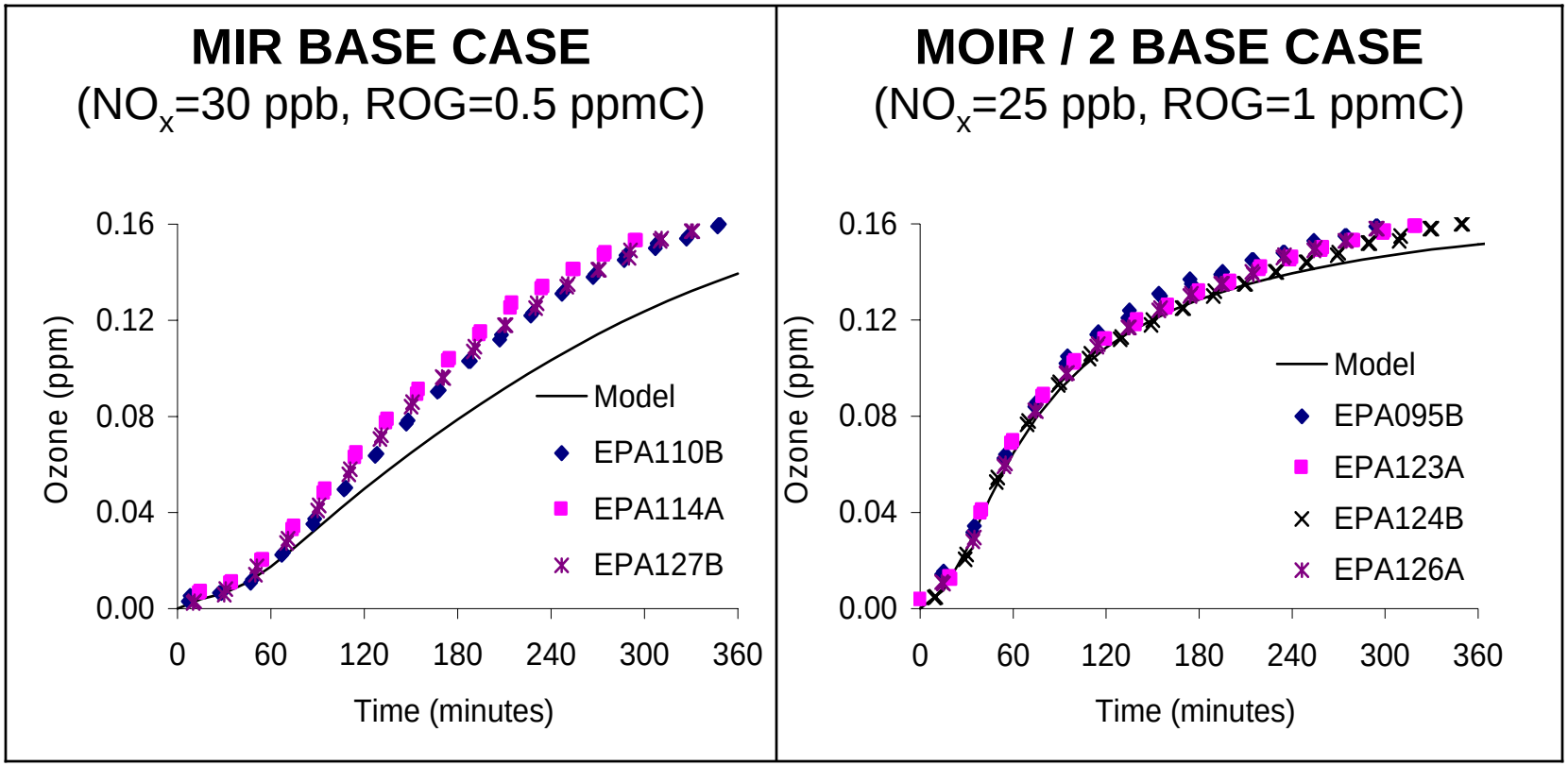
- Ambient ROG surrogate – NO_x experiments
  - 8-component ROG surrogate used to represent major classes of emitted VOCs (n-butane, n-octane, ethene, propene, trans-2-butene, toluene, m-xylene, formaldehyde)
  - Test ability to predict O_3 as function of ROG and NO_x
  - Establish model performance for “base case” used in incremental reactivity experiments
- Aromatic mechanism evaluation experiments
  - Aromatics have significant impact on predicted ambient O_3 but also have highly uncertain mechanisms
  - Parameterized mechanisms adjusted to fit chamber data
  - New aromatic – NO_x and Aromatic – NO_x + CO experiments provide new type of test for aromatics mechanism.

MATRIX OF ROG SURROGATE – NO_x EXPERIMENTS IN UCR EPA CHAMBER

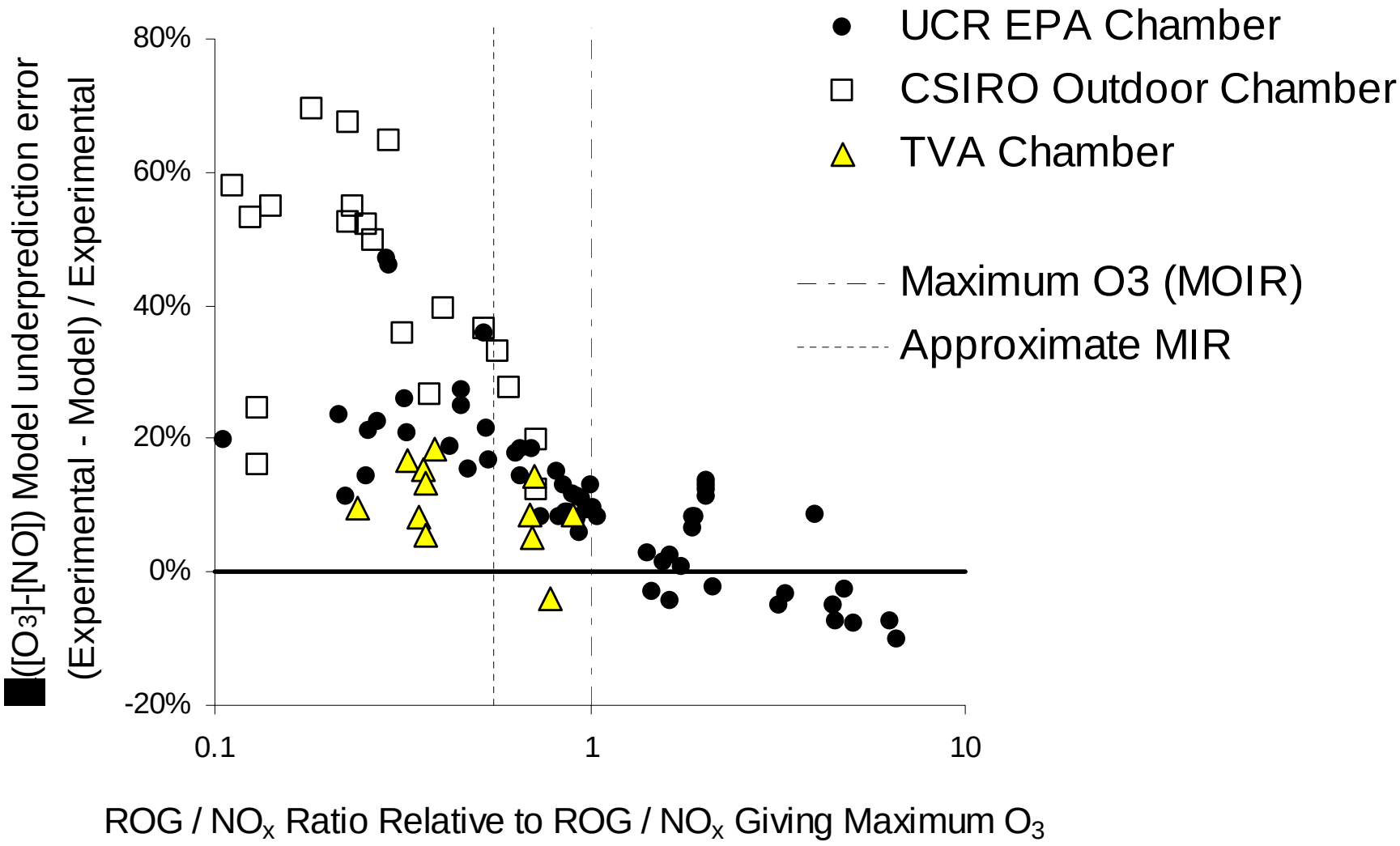


EXPERIMENTAL AND CALCULATED O_3 FOR CURRENT BASE CASE REACTIVITY EXPERIMENTS

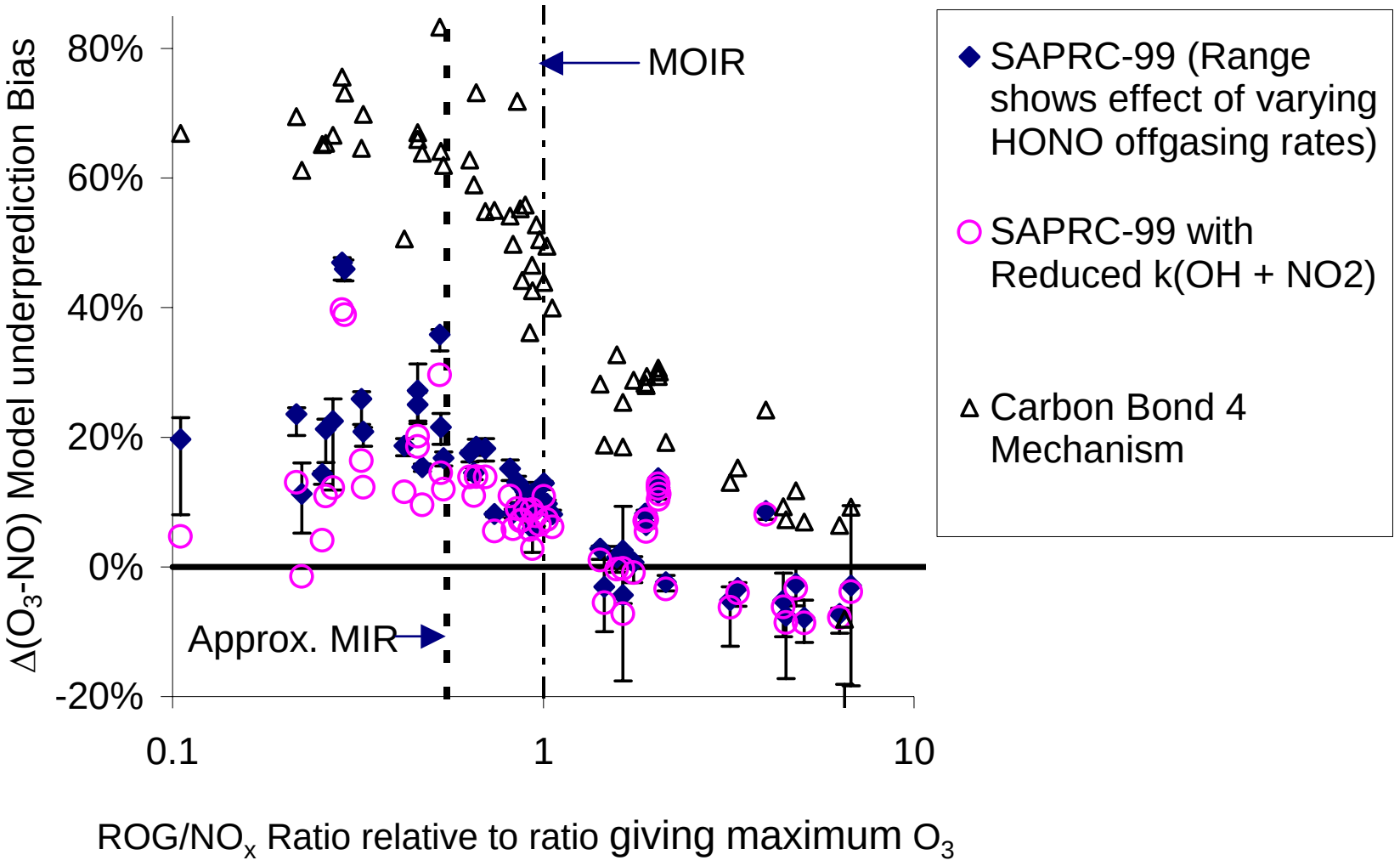
SAPRC-99 Model simulations of representative experiments



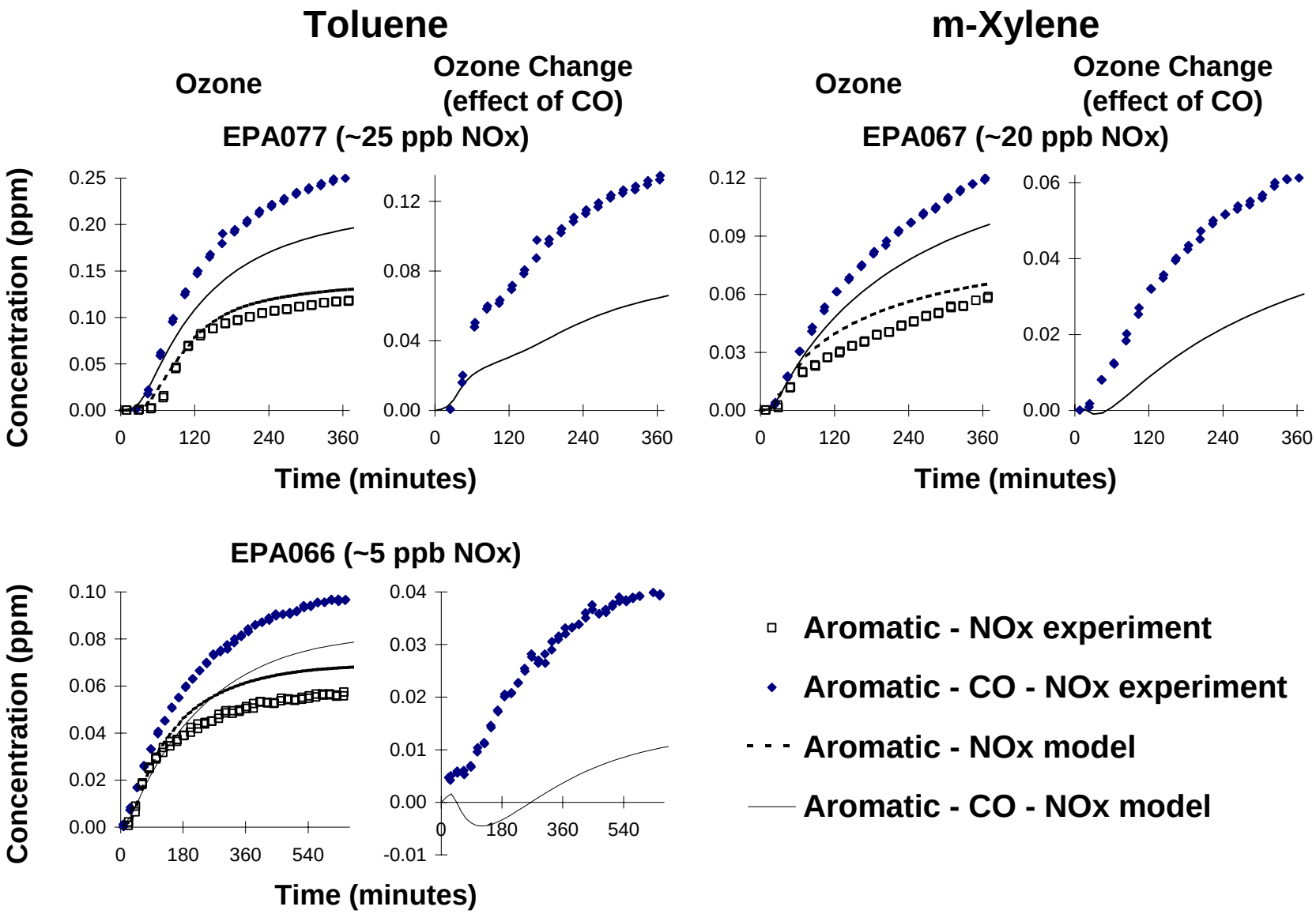
DEPENDENCE OF SAPRC-99 UNDERPREDICTION BIAS ON RELATIVE ROG/NO_x LEVELS



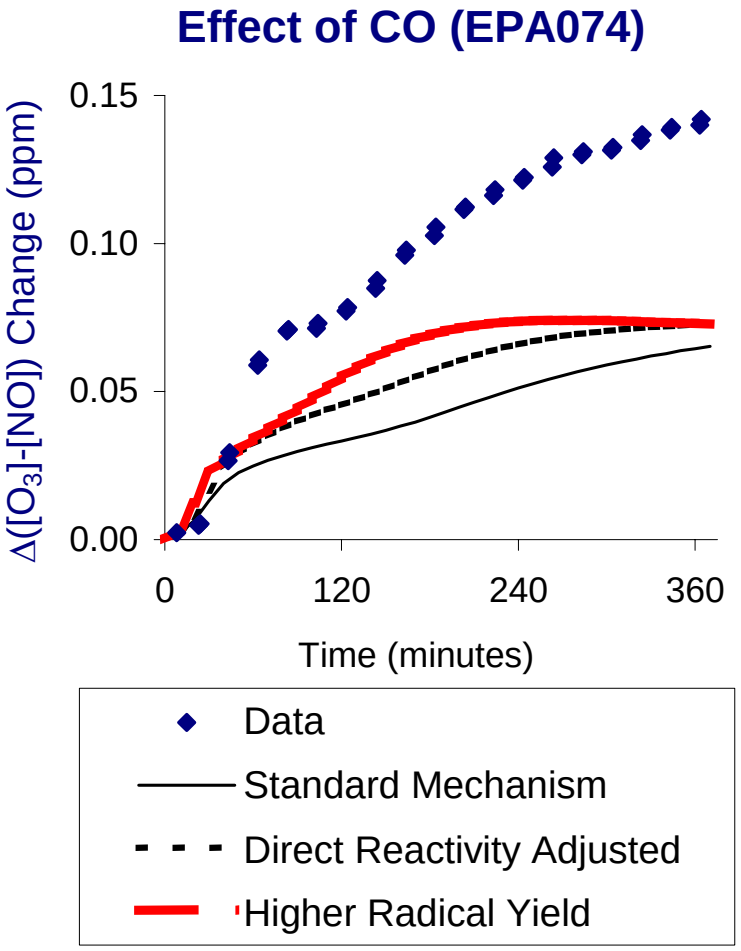
EFFECT OF PARAMETERS AND MECHANISM ON O_3 PREDICTIONS FOR UCR EPA SURROGATE RUNS

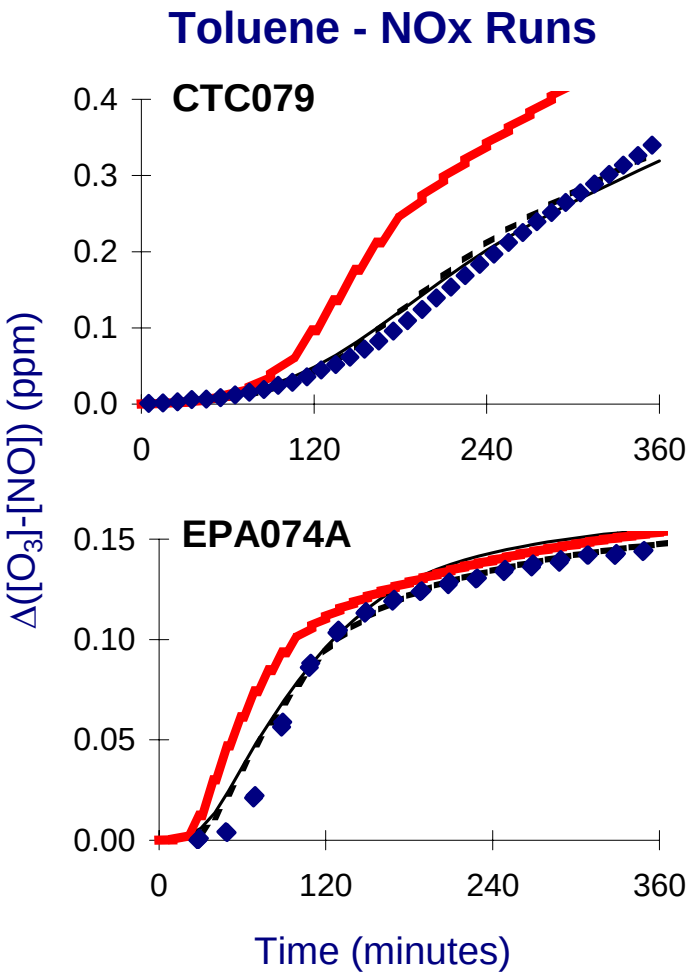


EFFECT OF CO ON AROMATIC - NO_x RUNS



EFFECTS OF ADJUSTMENTS TO PARAMETERIZED TOLUENE MECHANISM

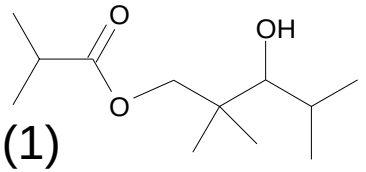
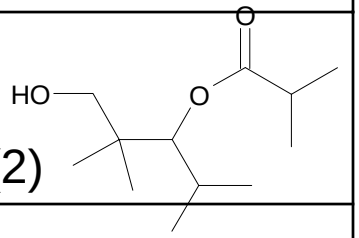
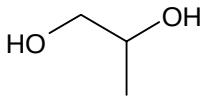
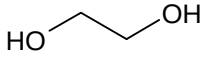
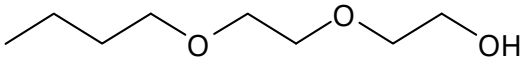




PRELIMINARY CONCLUSIONS FROM NEW BASE CASE REACTIVITY AND AROMATICS DATA

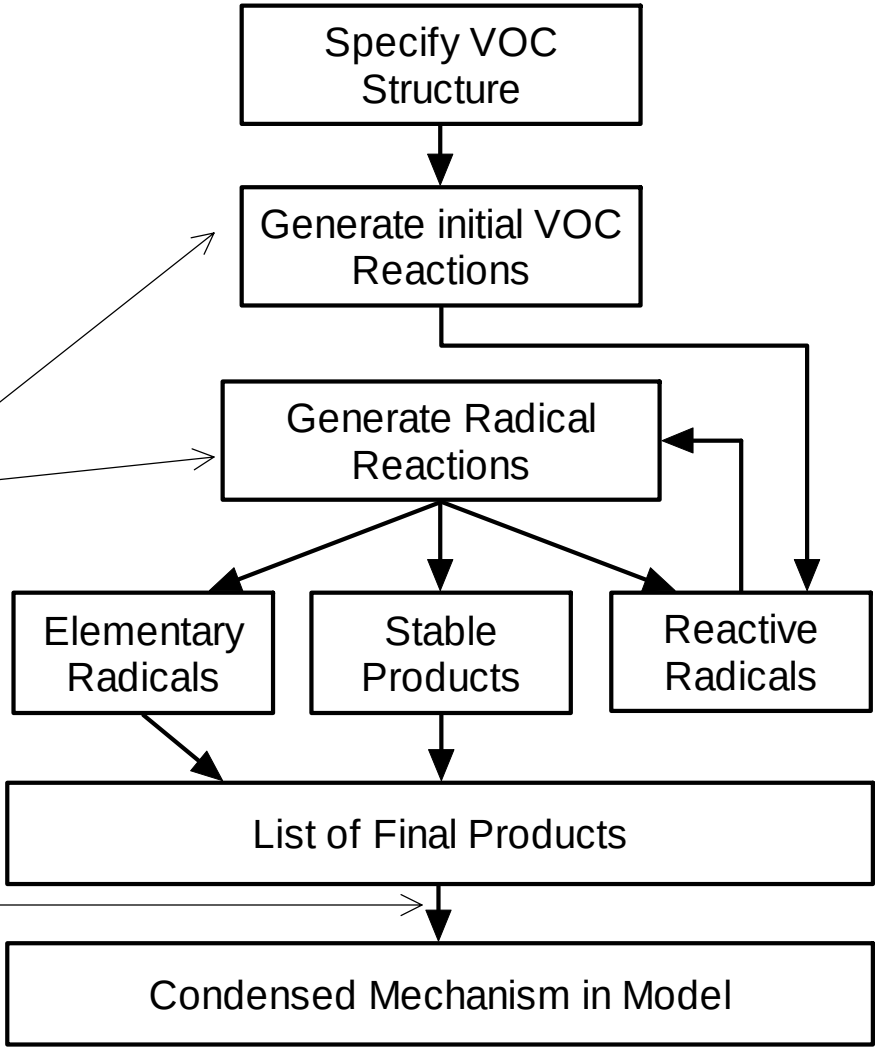
- SAPRC-99 mechanism predicts O_3 reasonably well in low NO_x and high ROG/NO_x ambient simulation experiments
- SAPRC-99 consistently underpredicts O_3 in low ROG/NO_x ambient simulation experiments
  - Problem even worse with CB4
  - Conditions where O_3 is most sensitive to VOCs (MIR)
  - Complicates use of MIR incremental reactivity experiments to assess mechanisms for added VOCs
- Results of new aromatic – NO_x + CO experiments suggest problems with formulation of current aromatics mechanisms
- Aromatics mechanism formulation problems may be reason for O_3 underprediction in low ROG/NO_x ambient simulations

VOCs IDENTIFIED IN 1998 CALIFORNIA SURVEY OF WATER-BASED ARCHITERCURAL COATINGS

Compound	Mass %	Structures
"Texanol®" Isobutyrate esters of 2,2,4-Trimethylpentyl-1,3-diol	28%	(1)  (2) 
Propylene Glycol	28%	
Ethylene Glycol	16%	
Various Petroleum Distillates (Main constituents of solvent-based coatings)	5%	C_{8+} Alkanes and Aromatics
"Butyl Carbitol": 2-(2-Butoxyethoxy)-Ethanol	4%	

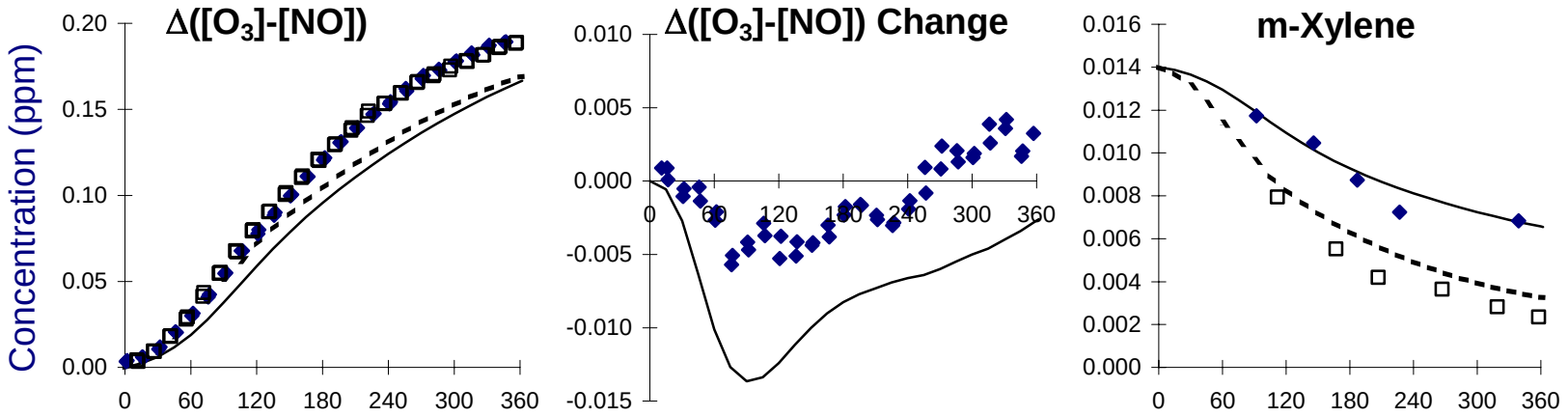
SAPRC-99 MECHANISM GENERATION SYSTEM

- Automated mechanism generation procedure
- Used to derive SAPRC-99 mechanisms for alkanes, glycols, esters, etc.
- Estimation methods used to derive unknown rate constants and ratios
- Measured rate constants and branching ratios used where known.
- "Lumping Rules" use to derive condensed mechanism for model

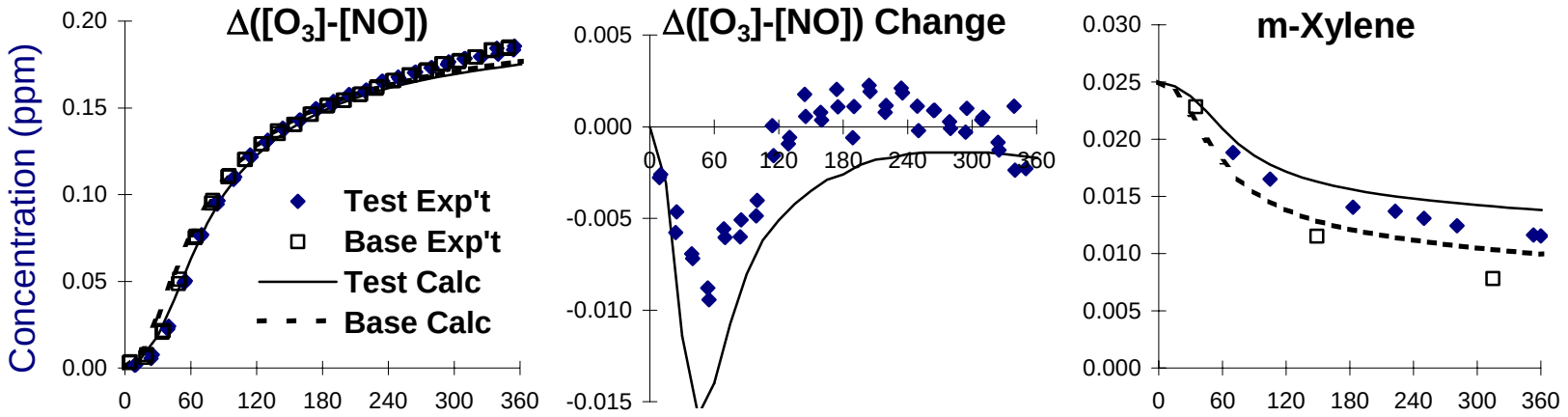


REACTIVITY DATA FOR TEXANOL®

MIR Conditions (EPA230)

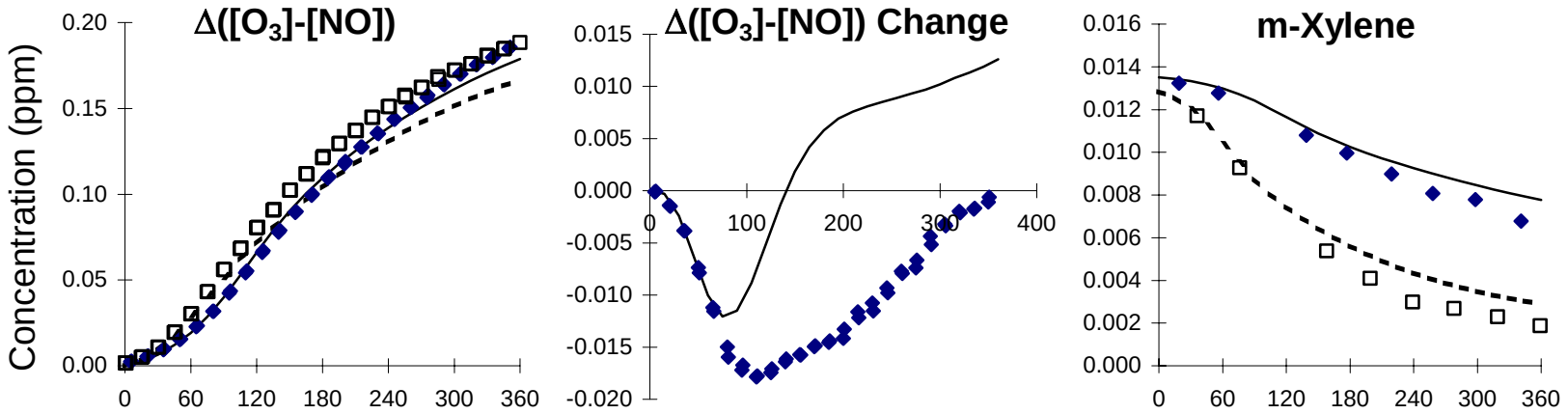


Low NOx Conditions (EPA231)

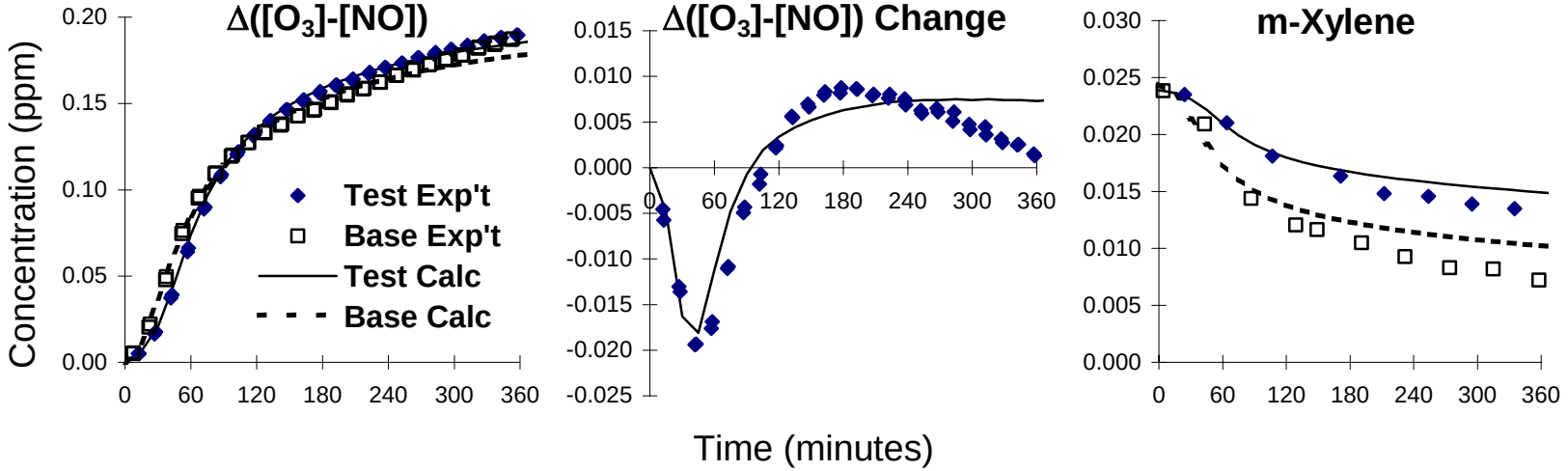


REACTIVITY DATA FOR BUTYL CARBITOL

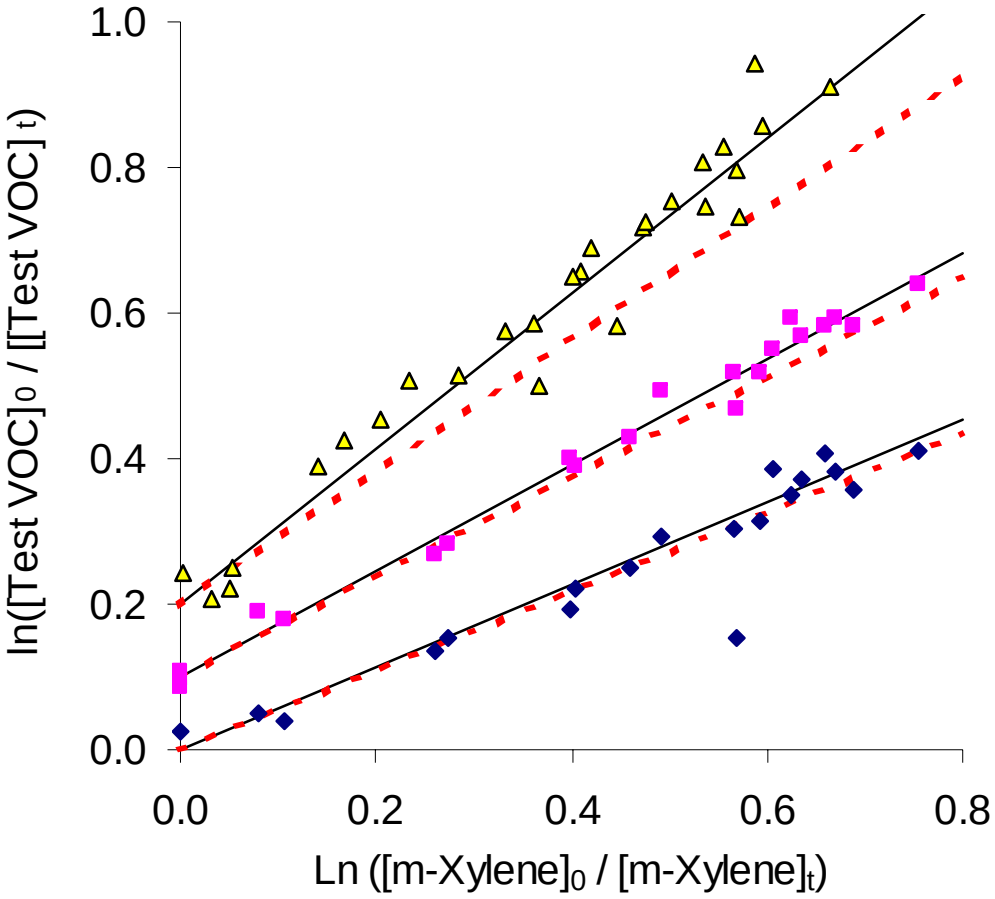
MIR Conditions (EPA352)

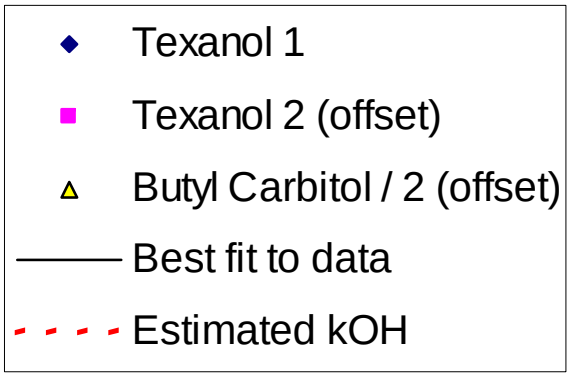


Low NOx Conditions (EPA353)



OH RADICAL RATE CONSTANTS DERIVED FROM CHAMBER DATA





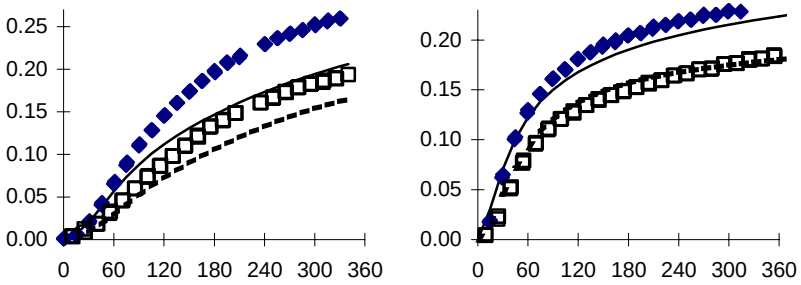
Compound	kOH (cm^3 $molec^{-1}$ s^{-1})
Texanol 1	1.29×10^{-11}
Texanol 2	1.62×10^{-11}
Butyl Carbitol	4.29×10^{-11}

REACTIVITY DATA FOR ETHYLENE AND PROPYLENE GLYCOLS

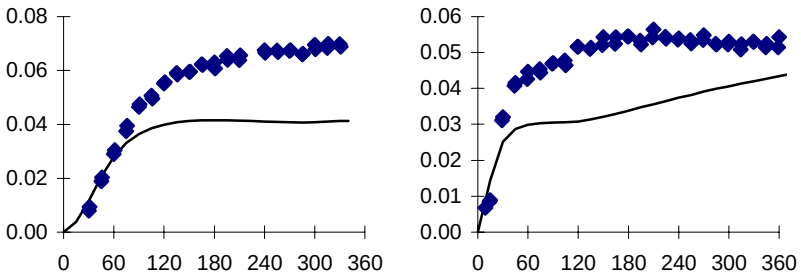
Ethylene Glycol

MIR MOIR / 2

$\Delta([O_3]-[NO])$ vs Time



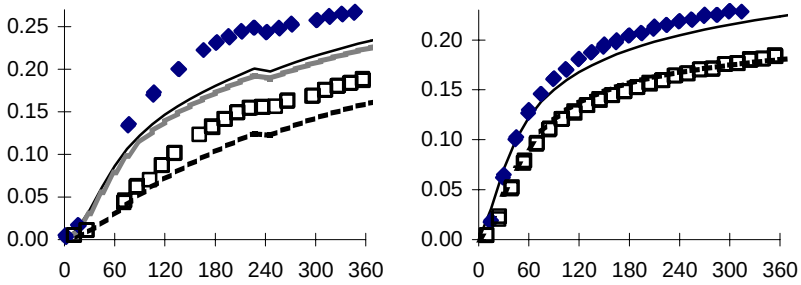
Change in $\Delta([O_3]-[NO])$ vs Time



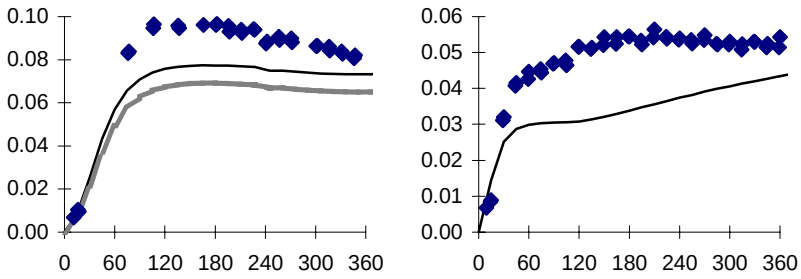
Propylene Glycol

MIR MOIR / 2

$\Delta([O_3]-[NO])$ vs Time



Change in $\Delta([O_3]-[NO])$ vs Time



◆ Test Data ▫ Base Data —— Test Model - - - Base Model

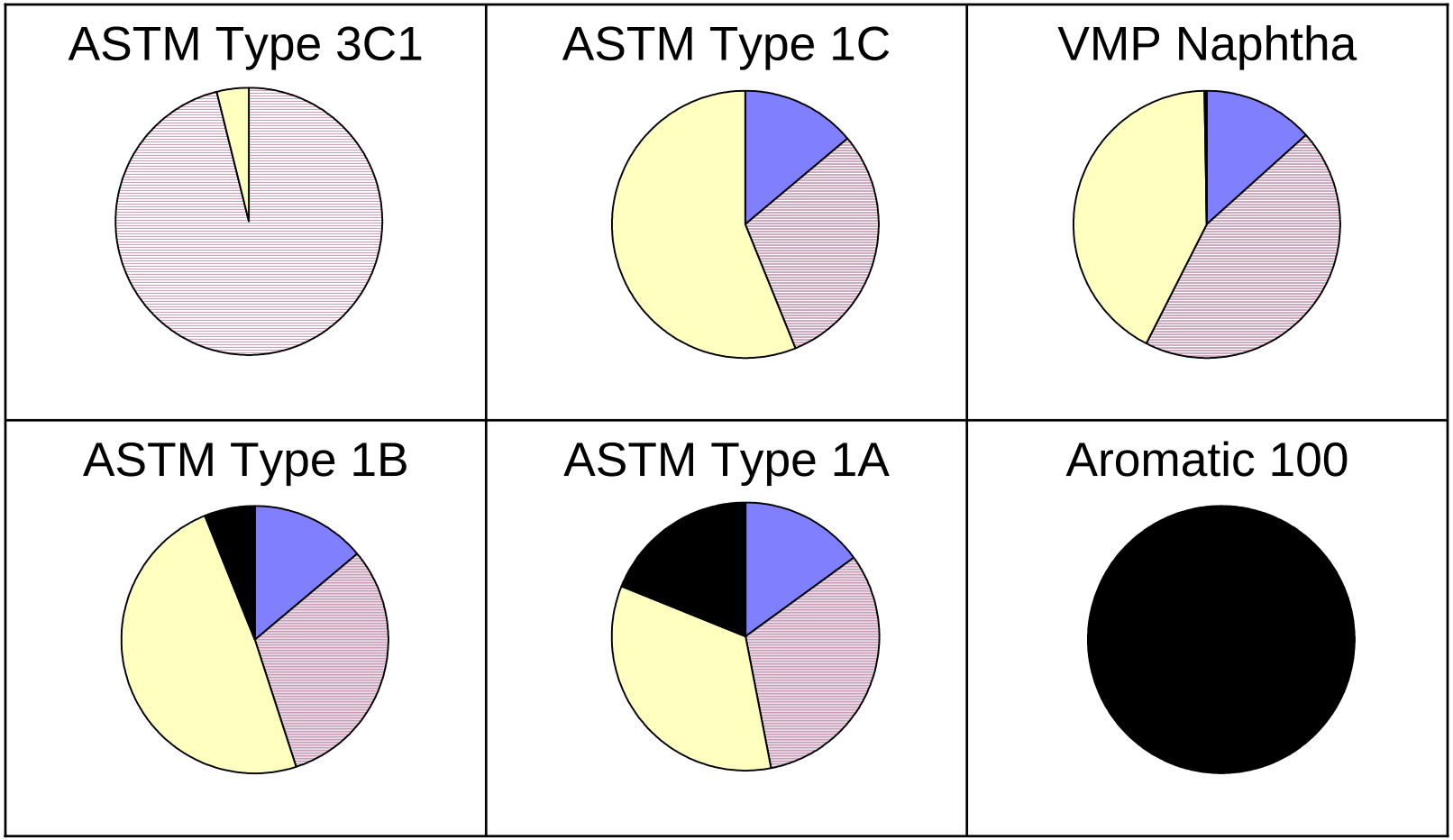
PRELIMINARY CONCLUSIONS FROM WATER-BASED COATINGS SOLVENT EXPERIMENTS

- The new data for Texanol® and butyl carbitol tend to support the estimates of the SAPRC-99 mechanism generation system
  - Excellent predictions of OH rate constants
  - "Acceptable" fits to chamber data without adjustments
- The SAPRC-99 mechanism may somewhat underestimate O_3 impacts of ethylene and propylene glycols
- Need to improve the model simulation of the base case experiment to improve the utility of the MIR incremental reactivity experiments for mechanism evaluation

REPRESENTATIVE PETROLEUM DISTILLATES CHOSEN FOR REACTIVITY EXPERIMENTS

Designation	Carbon Range	Aromatic Content	MIR (gm/gm)	Comment
ASTM Type 3C1	Mostly 11	-	0.87	Mostly branched alkanes
ASTM Type1C	9-12	-	0.98	
VMP Naphtha	8-9	0.2%	1.4	Lower Molecular weight mixture
ASTM Type 1B	9-12	6%	1.3	
ASTM Type 1A	9-12	19%	2.1	
Aromatic 100	Mostly 9	100%	7.5	Detailed analysis provided

CHEMICAL TYPE DISTRIBUTIONS FOR PETROLEUM DISTILLATES STUDIED



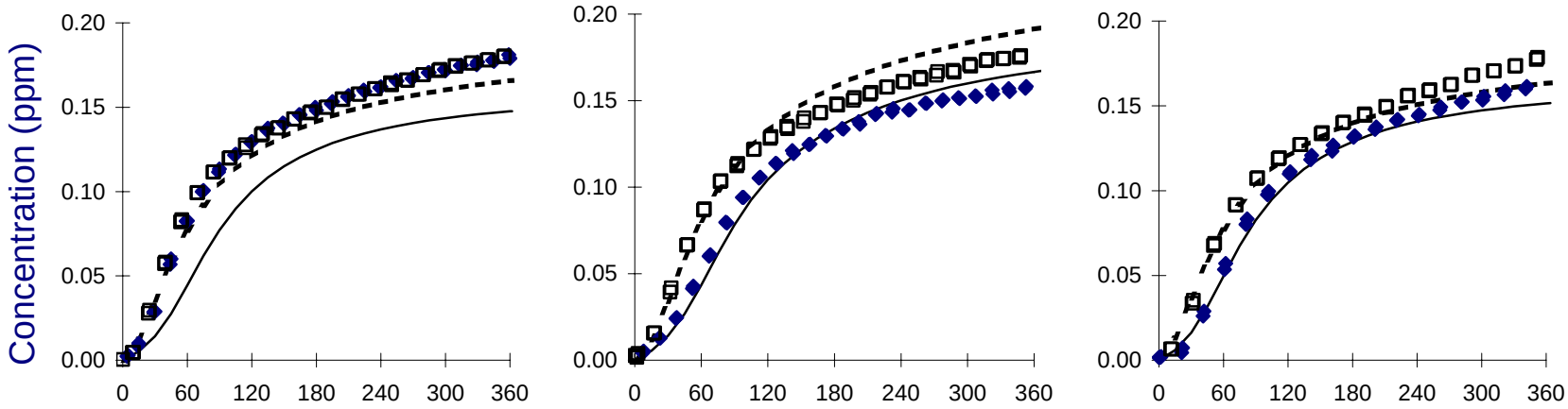
REACTIVITY DATA FOR PETROLEUM DISTILLATES

ASTM Type 3C1

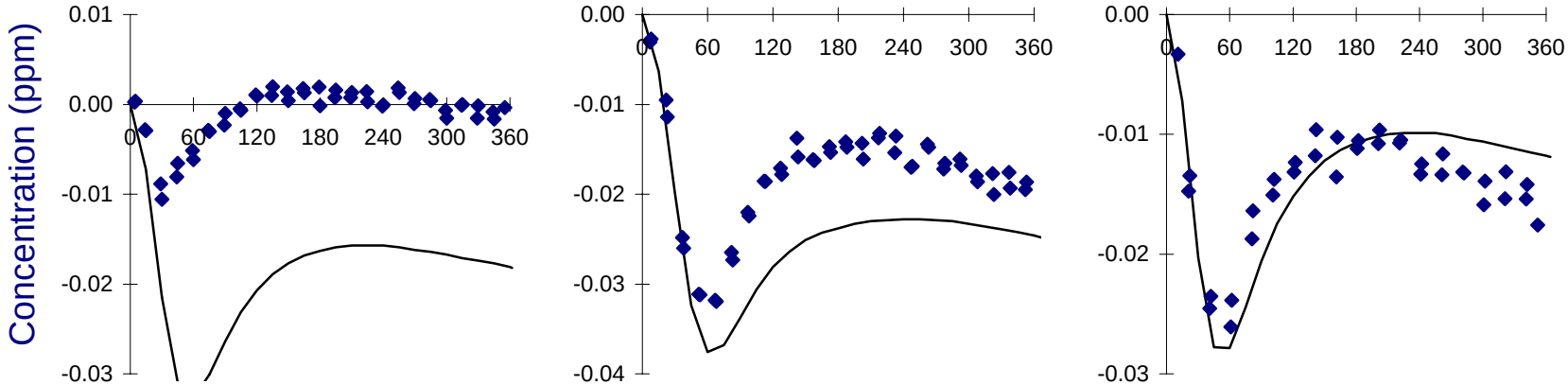
ASTM Type 1C

VMP Naphtha

$\Delta([O_3]-[NO])$ vs Time



Change in $\Delta([O_3]-[NO])$ vs Time



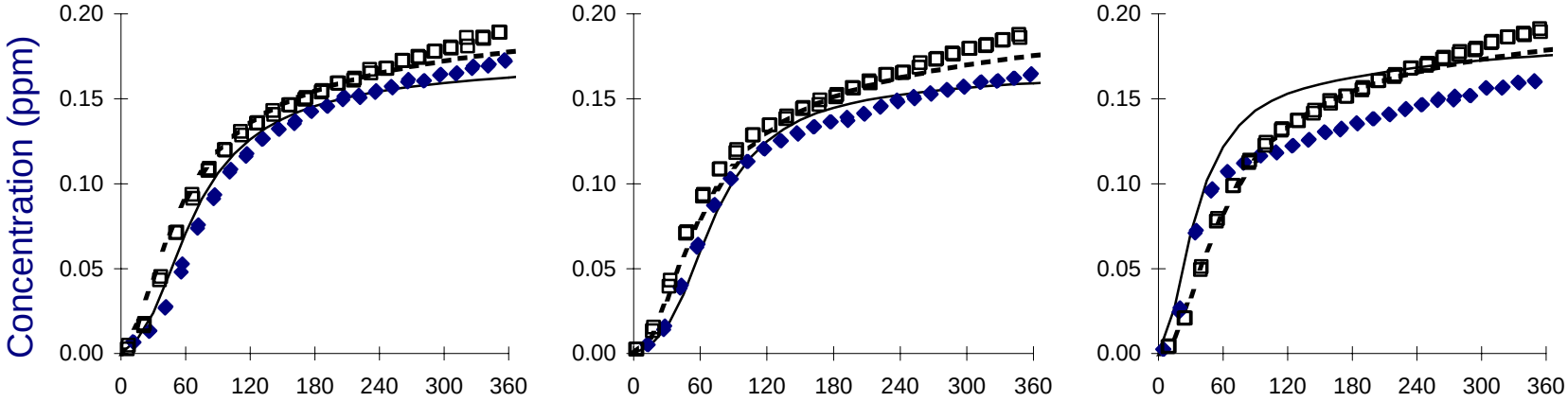
REACTIVITY DATA FOR PETROLEUM DISTILLATES

ASTM Type 1B

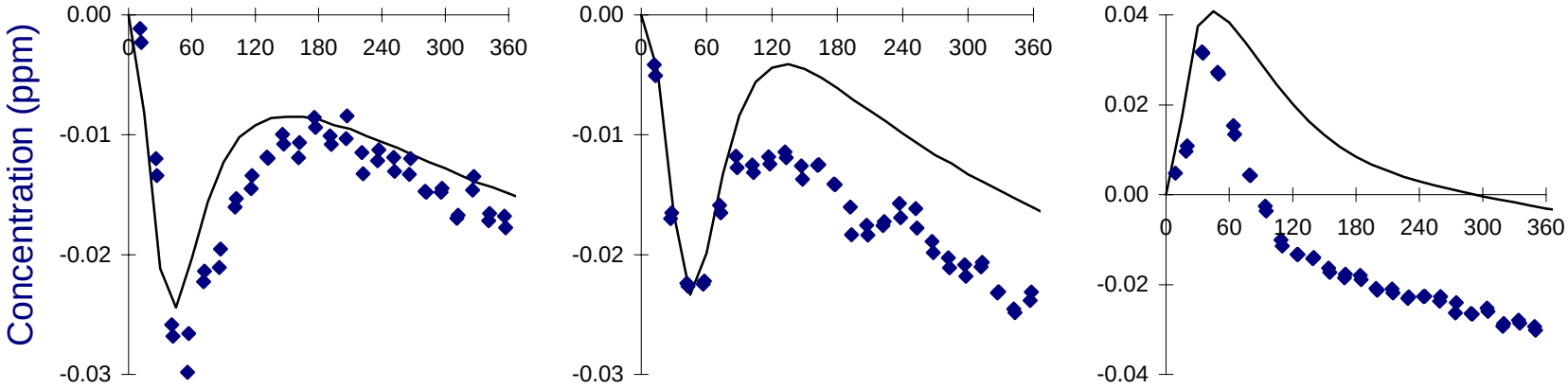
ASTM Type 1A

Aromatic 100

$\Delta([O_3]-[NO])$ vs Time



Change in $\Delta([O_3]-[NO])$ vs Time



PRELIMINARY ASSESSMENT OF MODEL PERFORMANCE FOR PETROLEUM DISTILLATES

Designation	**Major Components**	**Model Performance for O_3**
ASTM Type 3C1	C_{11} Branched Alkanes	Model underestimates O_3 impact
ASTM Type1C	C_9-C_{12} Alkanes	Not inconsistent with data
VMP Naphtha	C_8-C_9 Alkanes	Not inconsistent with data
ASTM Type 1B	C_9-C_{12} Alkanes with ~6% Aromatics	Not inconsistent with data
ASTM Type 1A	C_9-C_{12} Alkanes with ~20% Aromatics	May underpredict low NO_x O_3 inhibition
Aromatic 100	Methyl Ethyl and trimethyl benzenes	Underpredicts low NO_x O_3 inhibition

CURRENT STATUS

- Although progress has been made in our ability to predict ground level O_3, problems still remain
  - Mechanisms underpredict O_3 at in low ROG/NO_x
  - Current aromatics mechanisms not consistent with new data
  - Problems in simulating base case experiment reduces utility of incremental reactivity experiments for mechanism testing
- Attempts are being made to develop new, more explicit aromatics mechanism that fit chamber data, but progress is slow
- Progress has been made in providing data to reduce uncertainties in major classes of stationary source VOCs
  - New results support predictions of estimated mechanisms
  - Problem with models for branched alkane mixtures.
- Studies of temperature effects on O_3 formation are beginning