

# EVALUATION OF ATMOSPHERIC IMPACTS OF COATINGS VOCs

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## Outline

- Background and Objectives
- Environmental Chamber Experiments – Ozone Impacts
- Environmental Chamber Experiments – PM Impacts
- Exploratory Glycol Availability Experiments
- Estimation of Hydrocarbon Solvent Reactivities
- Direct Reactivity Measurement
- Summary and Conclusions

# Recent UCR Coatings Reactivity Projects

## Evaluation of Atmospheric Impacts of Selected Coatings VOCs

- CARB Contract 00-333
- Objective: Reduce uncertainties in estimations of ozone impacts of coatings VOCs
- Final report at <http://www.cert.ucr.edu/~carter/coatings>

## Environmental Chamber Studies of VOC Species in Architectural Coatings and Mobile Source Emissions

- SCAQMD Contract No. 03468
- Relevant Objectives:
  - Evaluate O<sub>3</sub> impacts of selected water-based coatings VOCs
  - Determine PM impacts for Coating VOCs studied for CARB
  - Evaluate use of chamber for availability studies
- Final report in preparation

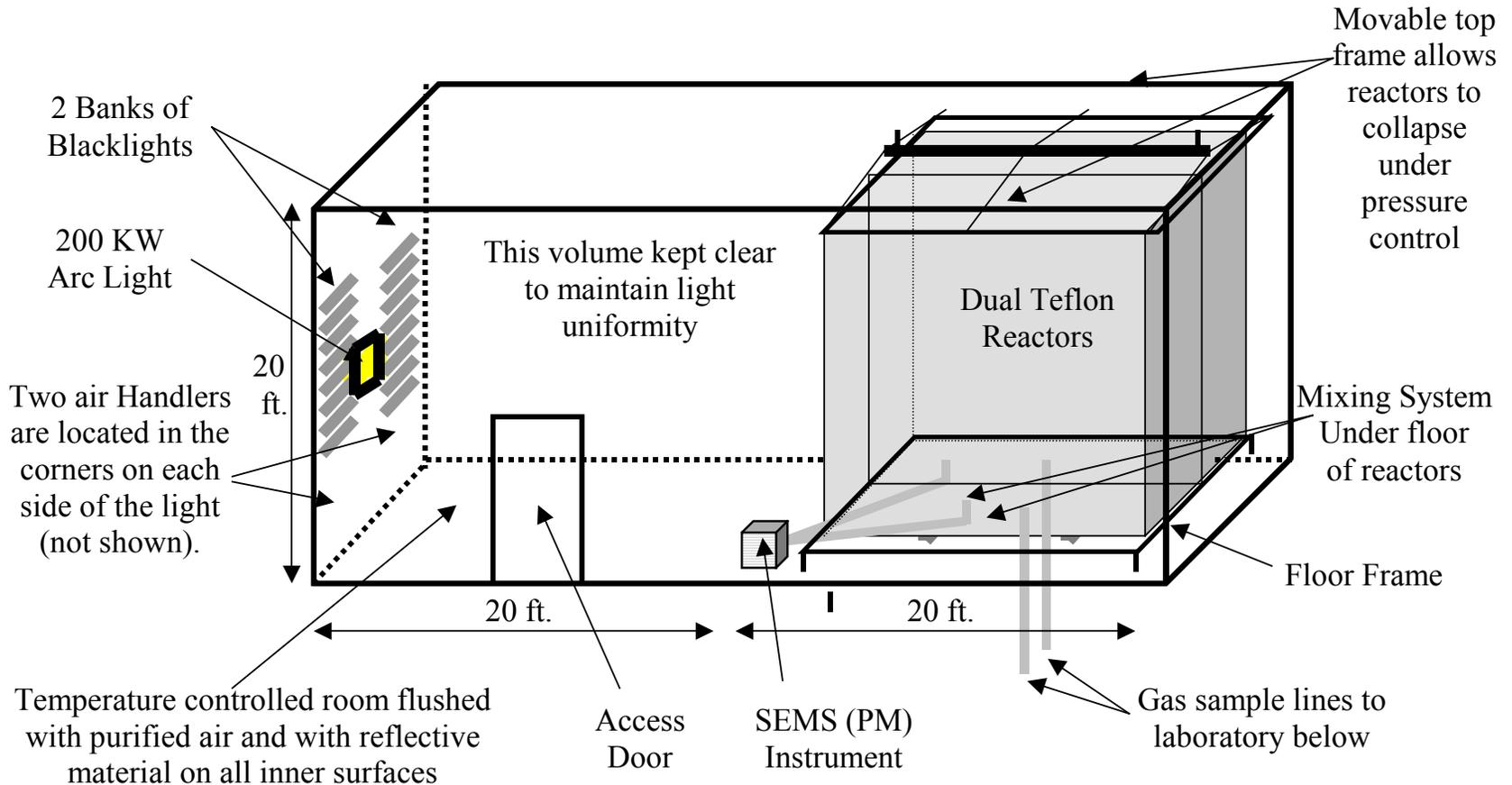
# Components of Coatings Projects

- Environmental chamber studies
  - Six complex hydrocarbon solvents and four water-based coatings VOC compounds chosen for study
  - UCR EPA chamber employed
  - Chamber results used to evaluate ozone reactivity predictions of the SAPRC-99 mechanism
  - PM measurement results used to derive *qualitative* estimates of *relative* PM impacts of solvents studied
  - Exploratory studies of effects of aerosol and humidity on glycol availability
- Development and evaluation of general procedures to estimate reactivities of complex hydrocarbon solvents
- Further development and evaluation of direct reactivity measurement methods

# Measurement or Calculation of Ozone Reactivities of VOCs

- VOC Reactivities measured in chamber experiments **are not exactly the same** as VOC reactivities in the atmosphere.
  - Impractical to duplicate all relevant conditions
  - Chamber experiments have wall effects, static conditions, higher levels of test VOCs, etc.
- Atmospheric Ozone impacts of VOCs must be calculated using **computer airshed models**, given:
  - Models for airshed conditions
  - Chemical mechanism for VOC's Atmospheric Reactions
- BUT mechanisms have uncertainties. reactivity calculations can be no more reliable than the chemical mechanism used.
- **Therefore, the purpose of chamber experiments is to test the ability of the mechanisms to predict reactivity in models**

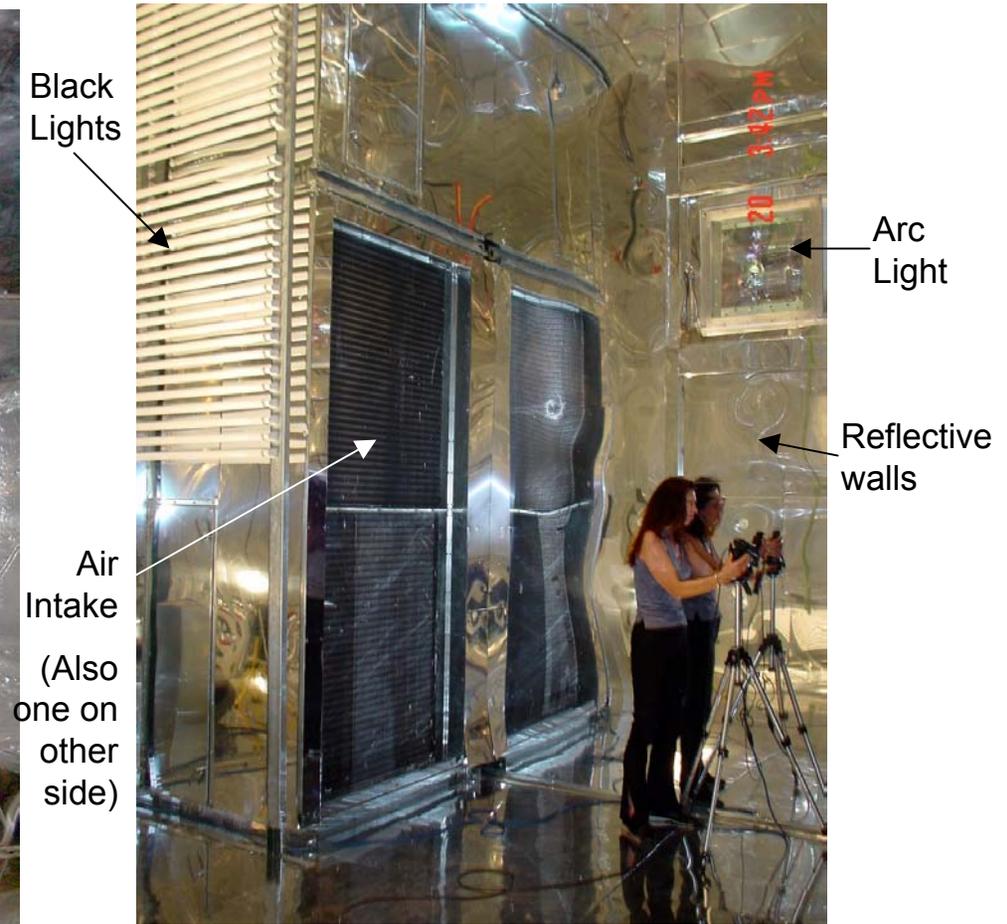
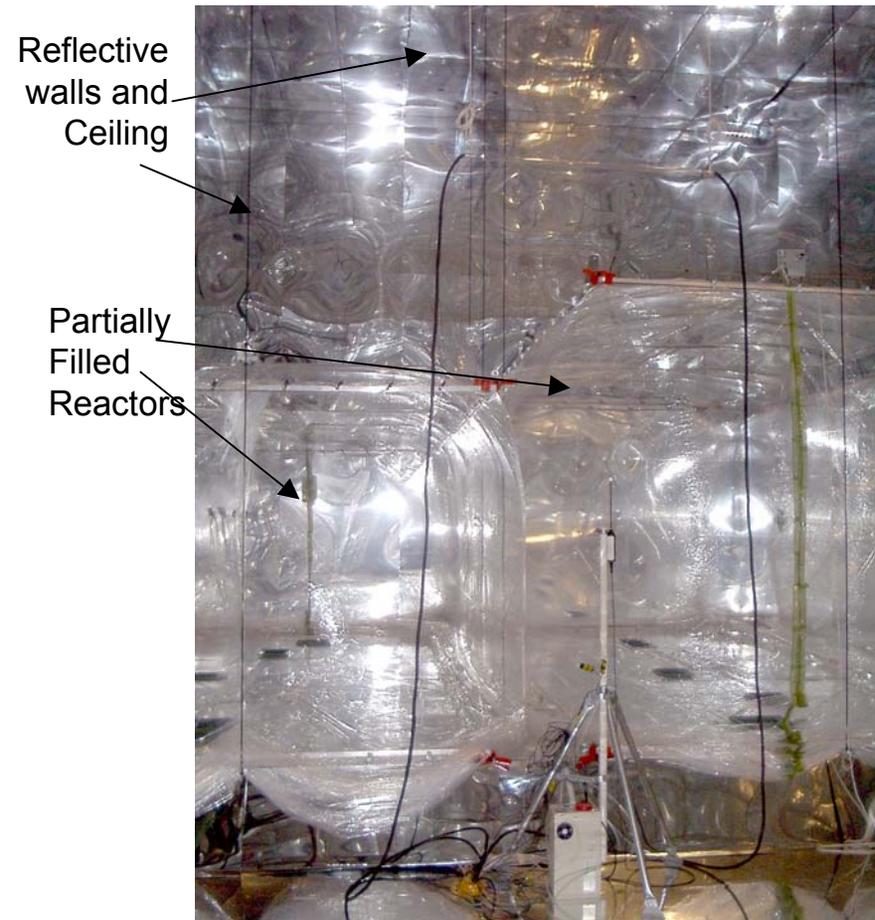
# Diagram of UCR EPA Chamber



# Photographs of Chamber and Lights

Looking Towards Reactors (from light)

Looking Towards Lights and Air Inlet



# Incremental Reactivity Experiments

- Objective is to determine effects of VOC's reactions in *chemical environments* representing a range of atmospheric conditions.
- Approach is to conduct two simultaneous experiments in the dual chamber
  - Base Case Experiment: Irradiate surrogate ROG – NO<sub>x</sub> mixture simulating an ambient chemical environment
  - Test Experiment: Same as base case experiment except that a test compound or solvent added
- Effect of added VOC on O<sub>3</sub>, radicals, etc, provides a means to test model predictions reactivities of VOCs under similar conditions in the atmosphere
- Base case experiments should reflect range of atmospheric chemical conditions relevant to VOC reactivity.

# Choice of Base Case for Incremental Reactivity Experiments

- Major atmospheric chemical condition relevant to VOC reactivity is relative availability of NO<sub>x</sub> (relative ROG/NO<sub>x</sub> ratio). E.g.,

Condition	Relative NO <sub>x</sub>	ROG/NO <sub>x</sub>	O <sub>3</sub> sensitivity
MIR	High	Low	Most sensitive to VOCs
MOIR	Moderate	Moderate	Optimum conditions for O <sub>3</sub>
Low NO <sub>x</sub>	Low	High	Most sensitive to NO <sub>x</sub>

- Different aspects of the mechanism affect O<sub>3</sub> impacts under different NO<sub>x</sub> conditions
  - High NO<sub>x</sub> experiments: test effects of VOCs on radical levels
  - Low NO<sub>x</sub> experiments: test effects of VOCs on NO<sub>x</sub> removal
- Therefore, *minimum* of two base case experiments is needed

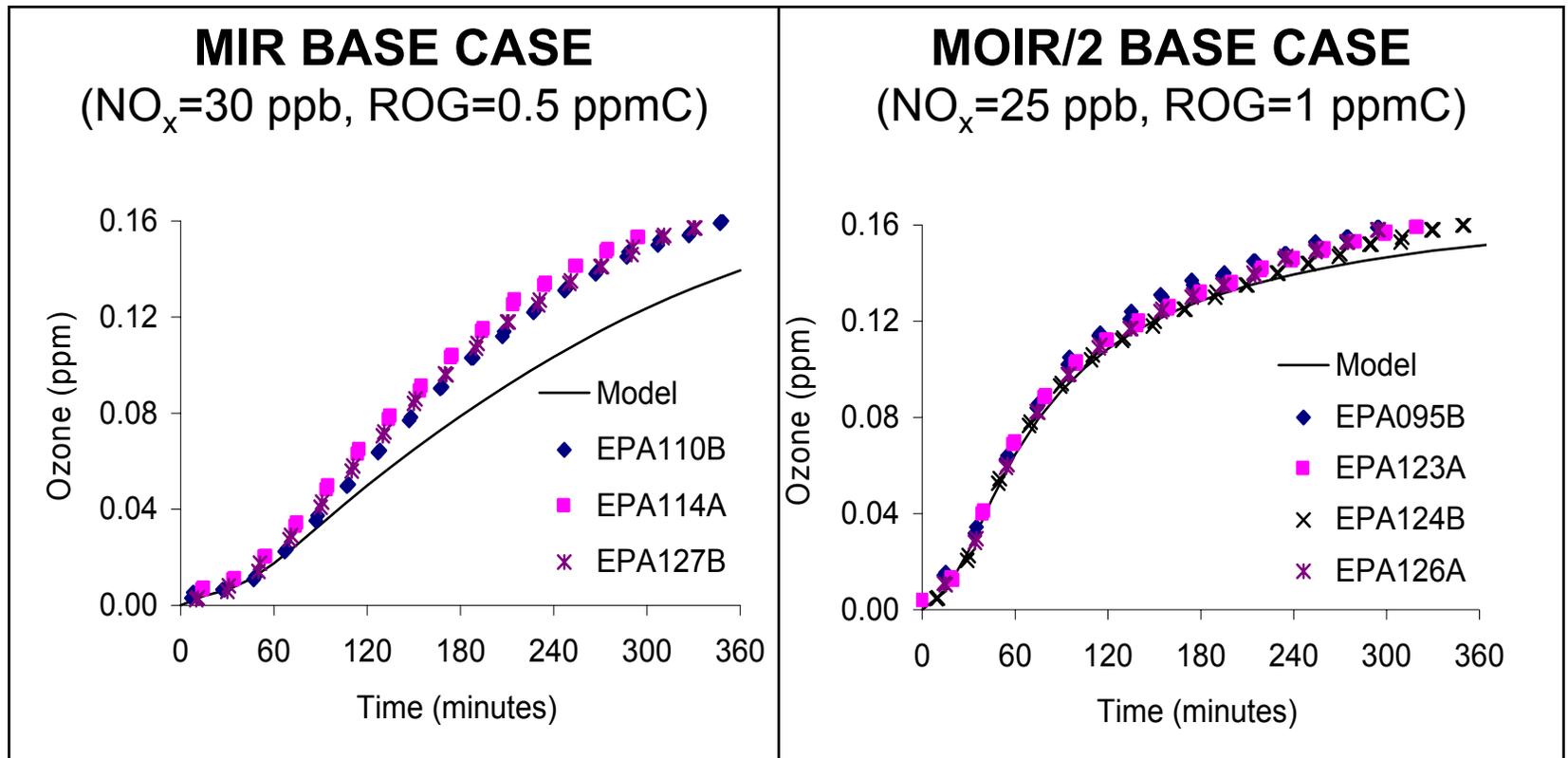
# Base Case Experiments used in Coatings Reactivity Studies

Experiment	NO <sub>x</sub> (ppb)	ROG (ppmC)	Discussion
MIR	30	0.5	ROG levels calculated to yield MIR conditions
MOIR/2	25	1.0	½ MOIR NO <sub>x</sub> levels. NO <sub>x</sub> relatively low but not so low that O <sub>3</sub> insensitive to VOCs.

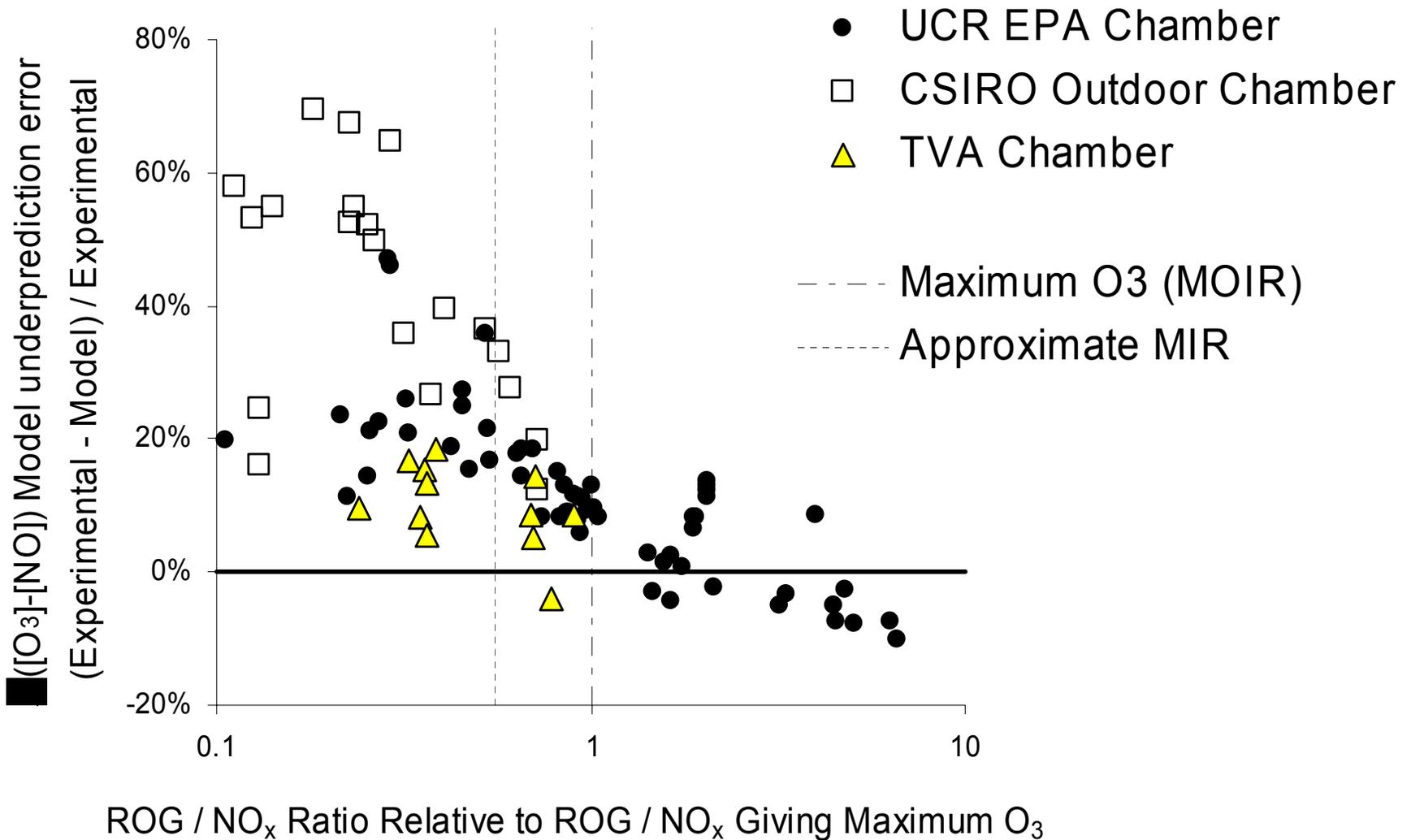
- NO<sub>x</sub> levels of 25-30 ppb, based on CARB recommendations of range of NO<sub>x</sub> that represents urban conditions in California
- 8- component ROG surrogate (used previously) employed to represent major classes of VOCs present in ambient air
  - Formaldehyde removed in later experiments and other VOCs increased by 10% to simplify experiments
  - Calculated to give essentially the same reactivity results as base ROG mixture used to calculate reactivity scales.

# Experimental and Calculated O<sub>3</sub> for Representative Base Case Experiments

SAPRC-99 Model simulations of representative experiments



# Dependence of SAPRC-99 Underprediction Bias on Relative ROG/NO<sub>x</sub> Levels



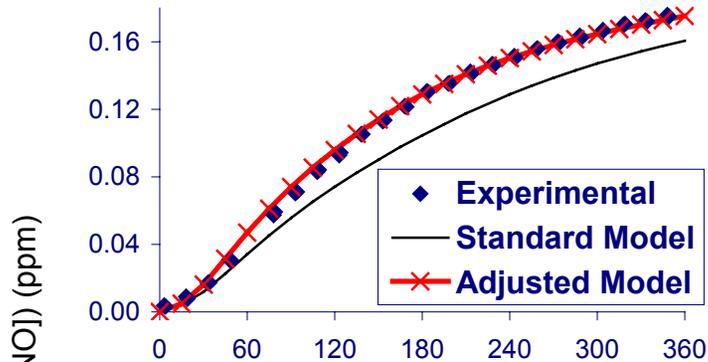
# Aromatic Mechanism Adjustments to Improve Base Case Simulations

- Biases in model simulations of base case experiment attributed to aromatics mechanism. So far, no aromatic mechanism found that gives satisfactory fits all the available chamber data.
- Base case biases may cause biases in simulations of reactivity.
- To investigate this, mechanisms for aromatics in the base ROG was adjusted to remove biases in base case simulations.
  - Yields of aromatic fragmentation products AFG2 and AFG3 for toluene and m-xylene increased by factor of 1.75
  - Rate of reaction of AFG1 with O<sub>3</sub> increased by factor of 10
- Comparing simulations with and without this adjustment shows effects base mechanism biases on reactivity predictions
- *Not a “better” aromatics mechanism* because this adjustment makes fits to single aromatic – NO<sub>x</sub> experiments worse.

# Effects of Mechanism Adjustments on Simulations of Representative Experiments

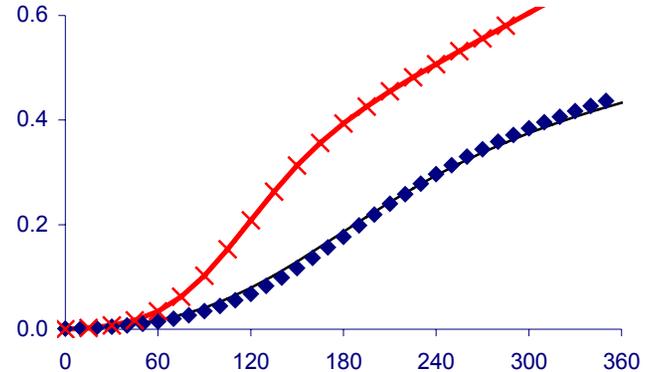
## Surrogate - NOx Runs

EPA188A: Low ROG/NOx (MIR)

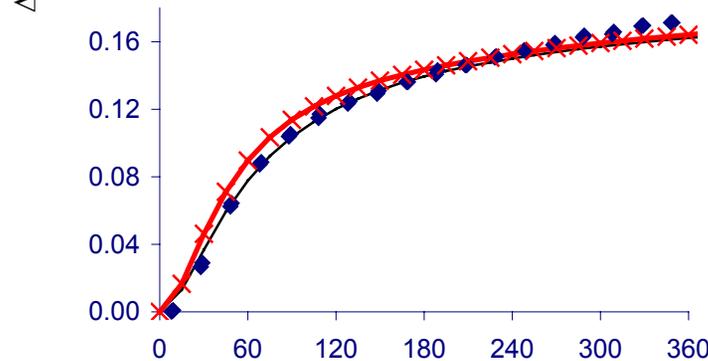


## M-Xylene - NOx Runs

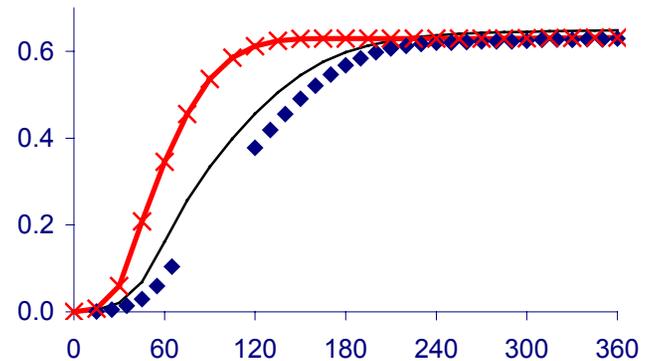
CTC036: Low ROG/NOx



EPA124B: High ROG/NOx (MOIR/2)

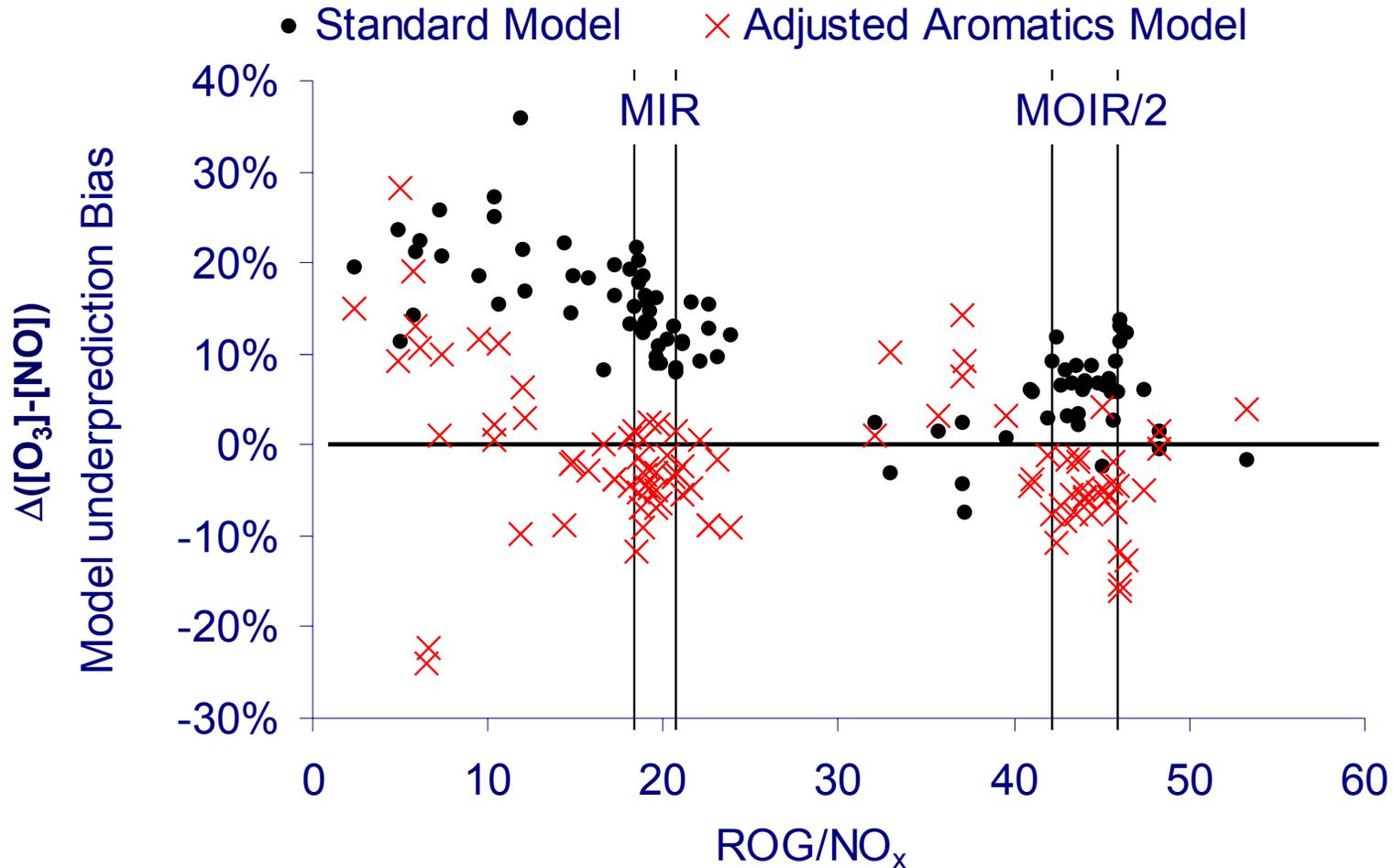


CTC029: High ROG/NOx

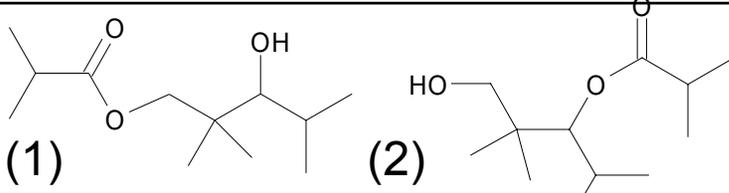
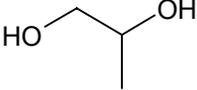
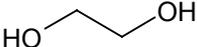
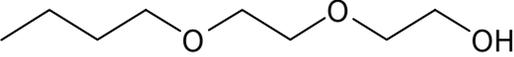
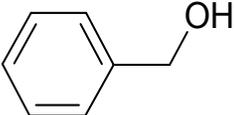


Time (minutes)

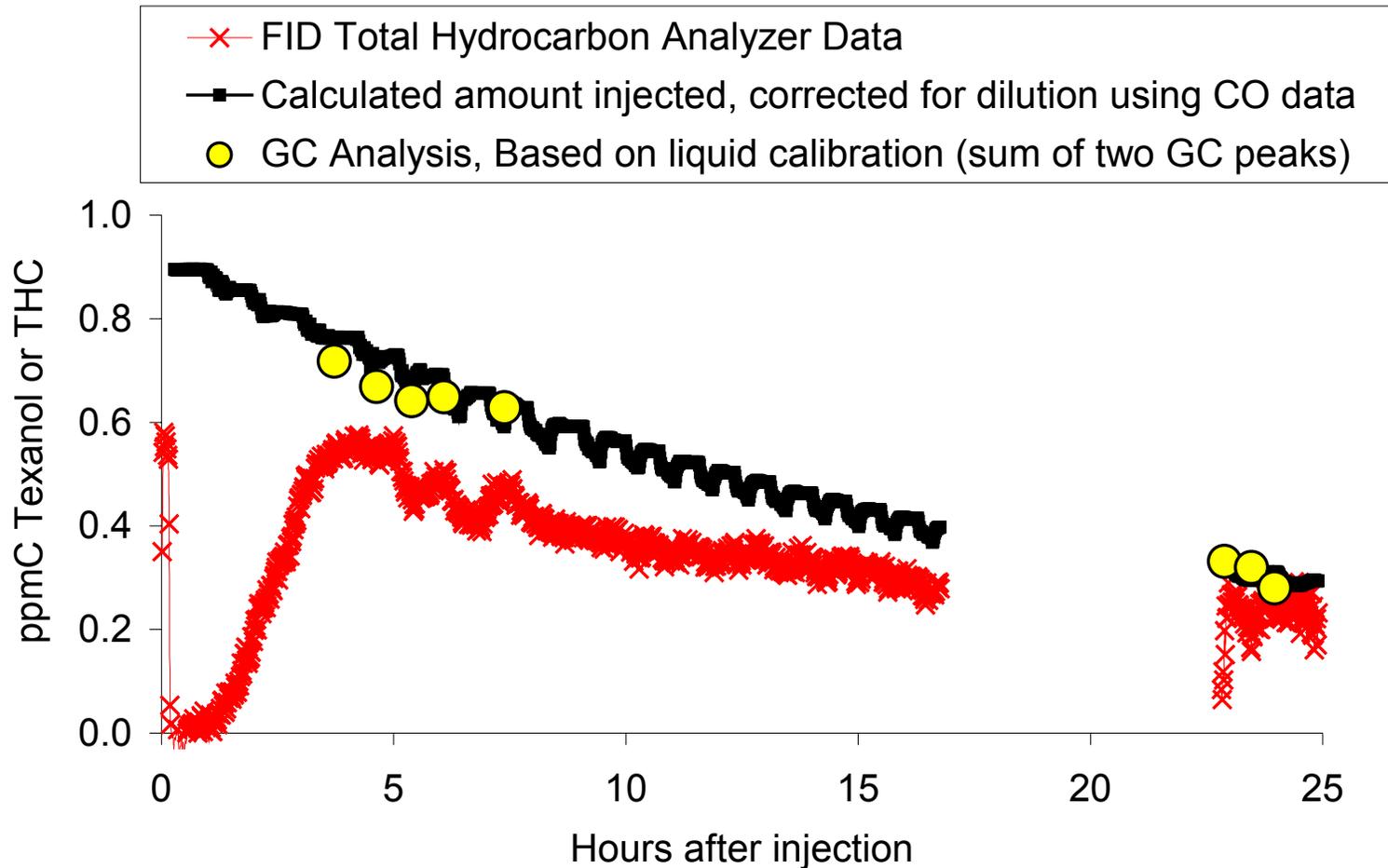
# Effect of Aromatic Mechanism Adjustment on Base Case Model Underprediction Bias



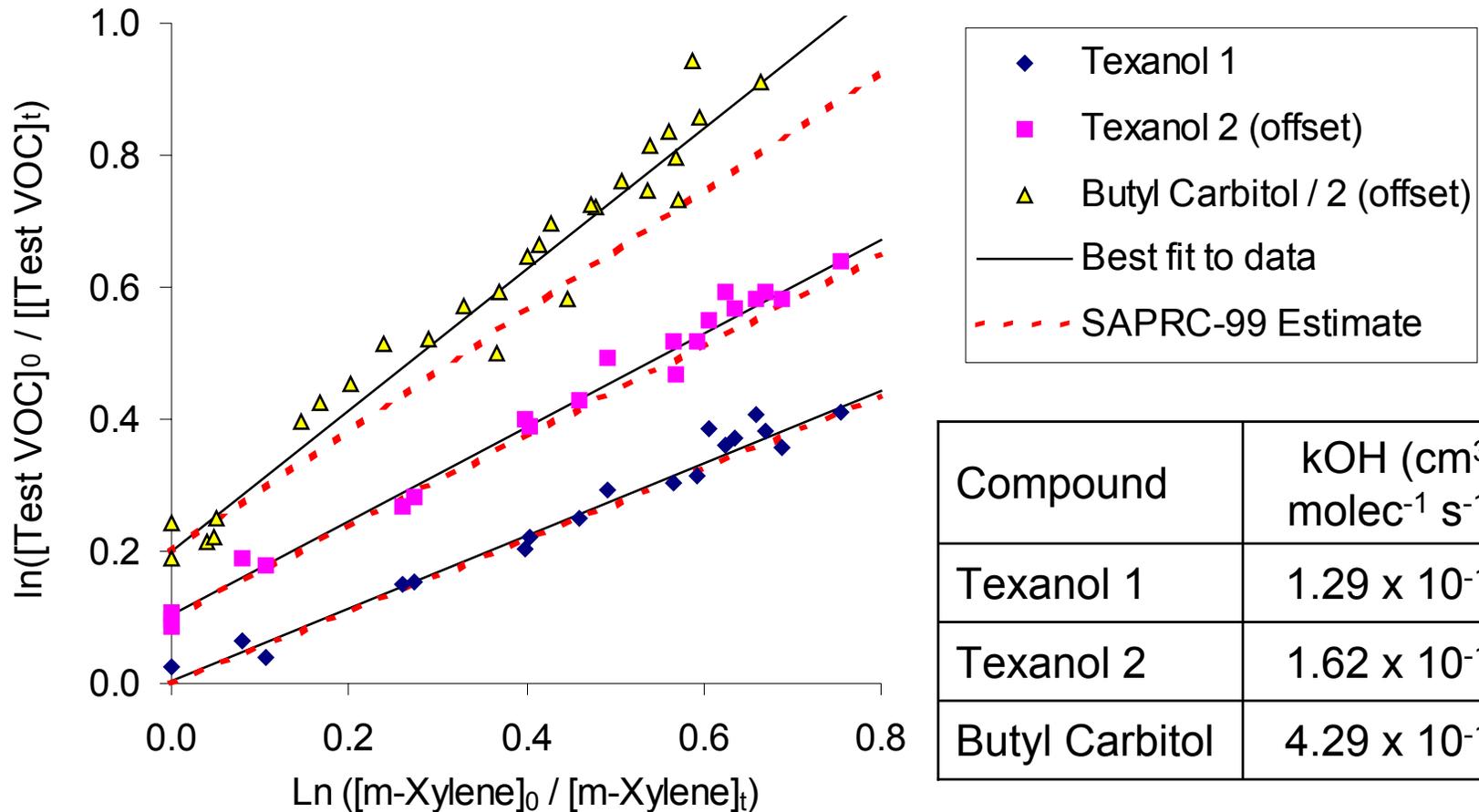
# VOCs Identified in the 2001 CARB Survey of Water-Based Architectural Coatings

Compound	Mass %	Structures
Texanol®; Isobutyrate esters of 2,2,4-Trimethylpentyl-1,3-diol	31%	
Propylene Glycol	25%	
Ethylene Glycol	21%	
Various Hydrocarbon Solvents	4%	Mixtures of C <sub>8</sub> -C <sub>12</sub> alkanes and aromatics
Butyl Carbitol; 2-(2-Butoxyethoxy)-Ethanol	3%	
Benzyl Alcohol	3%	

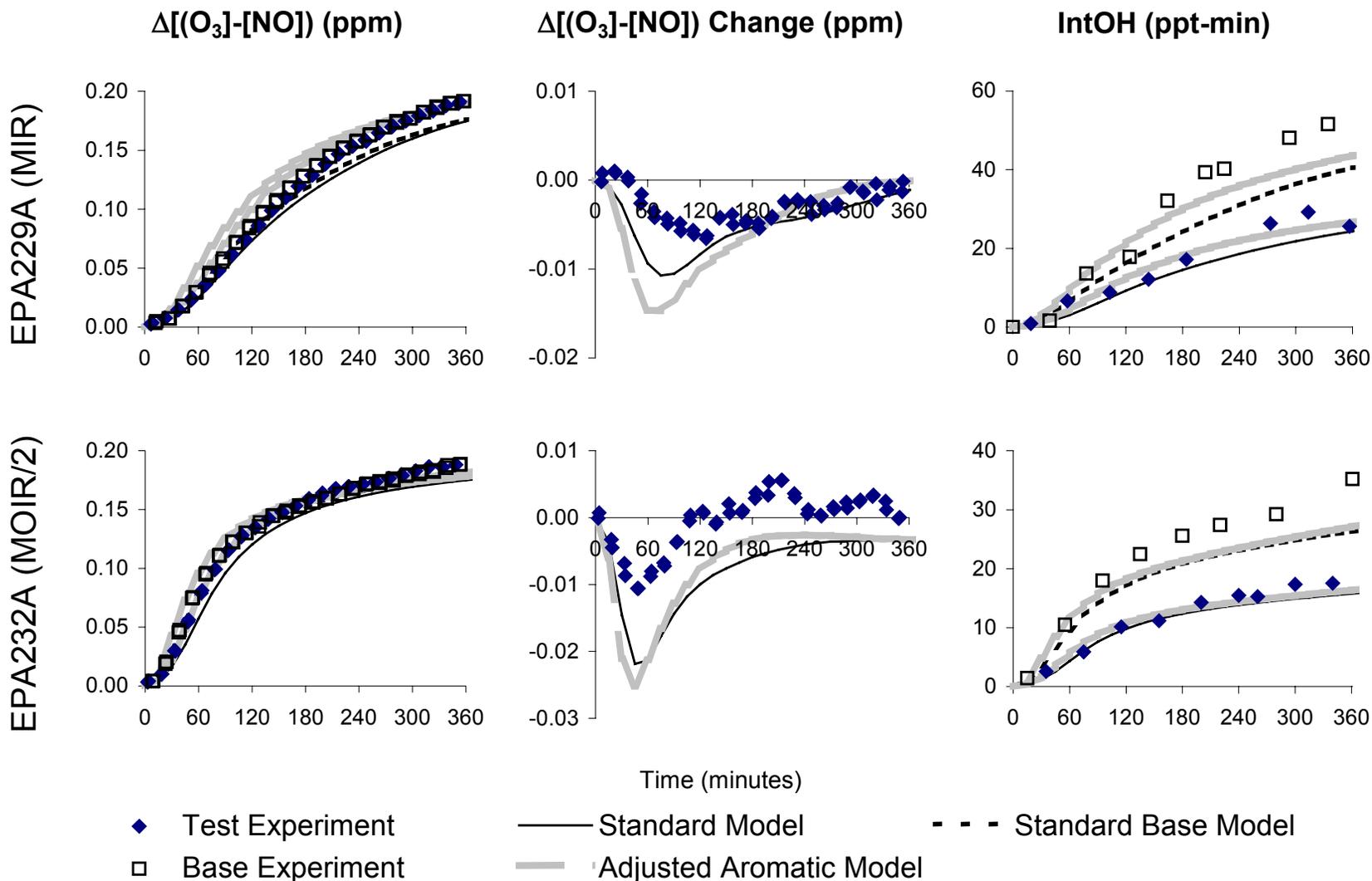
# Results of a Texanol® Injection Test



# OH Radical Rate Constants Derived from Chamber Data

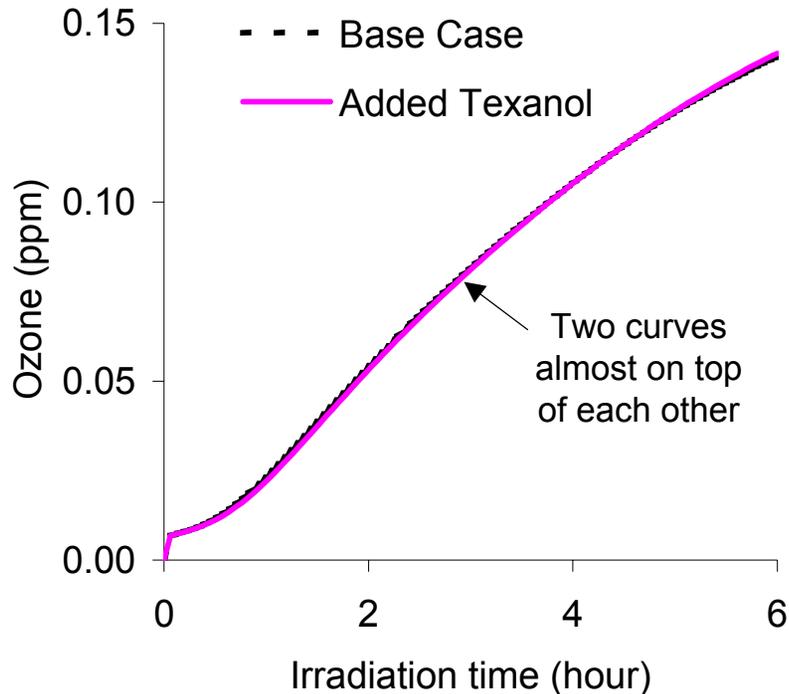


# Reactivity Data for Texanol®

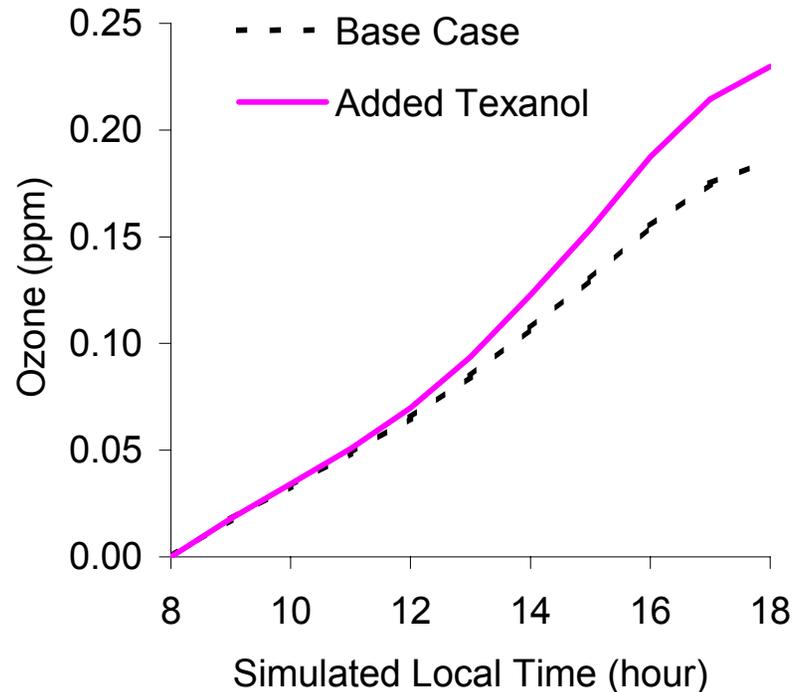


# Comparison of Chamber and Ambient Reactivity Calculation For Texanol®

**"MIR" Incremental Reactivity Chamber experiment**

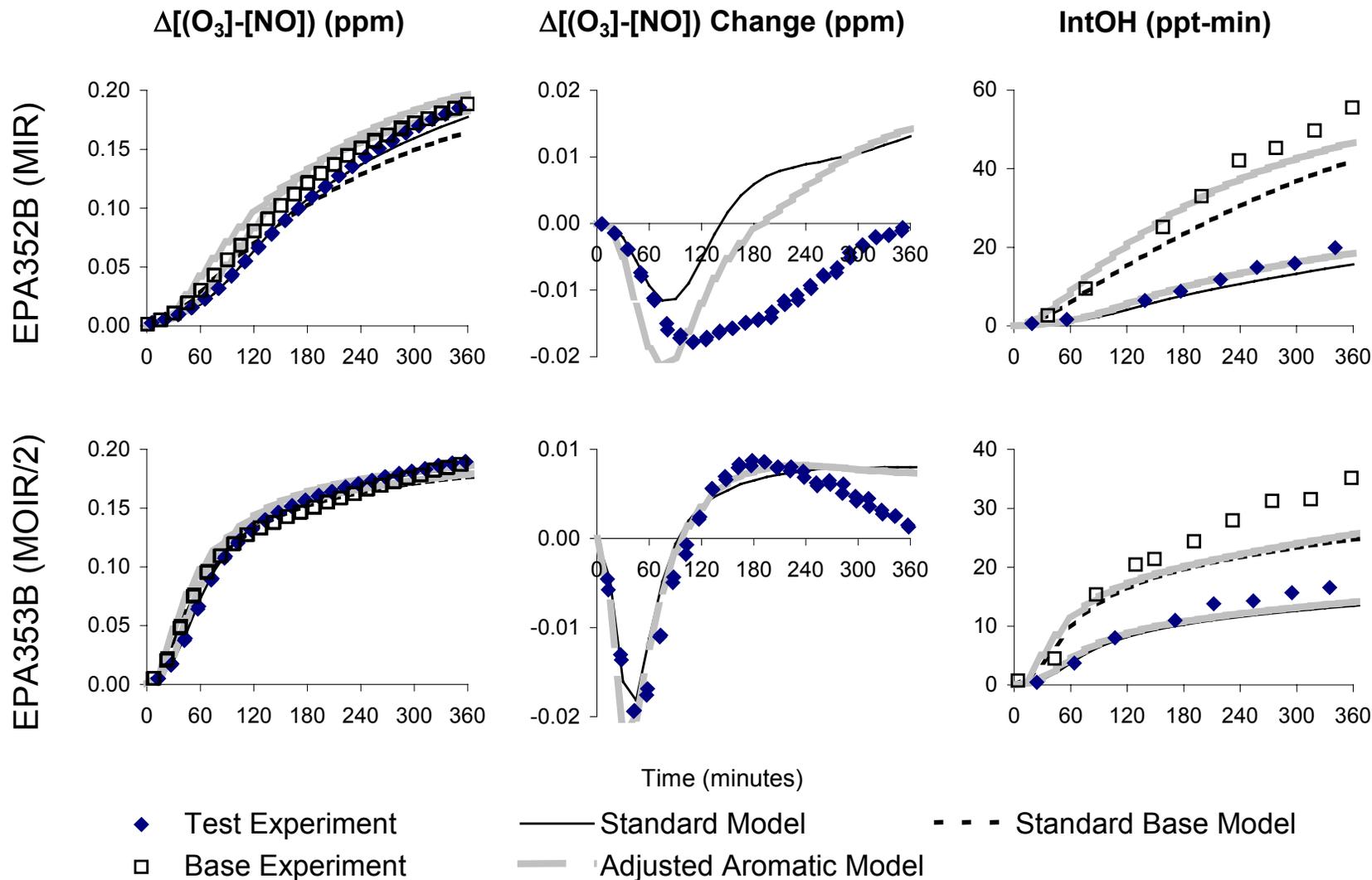


**"Averaged Conditions" MIR Box Model Airshed Scenario**

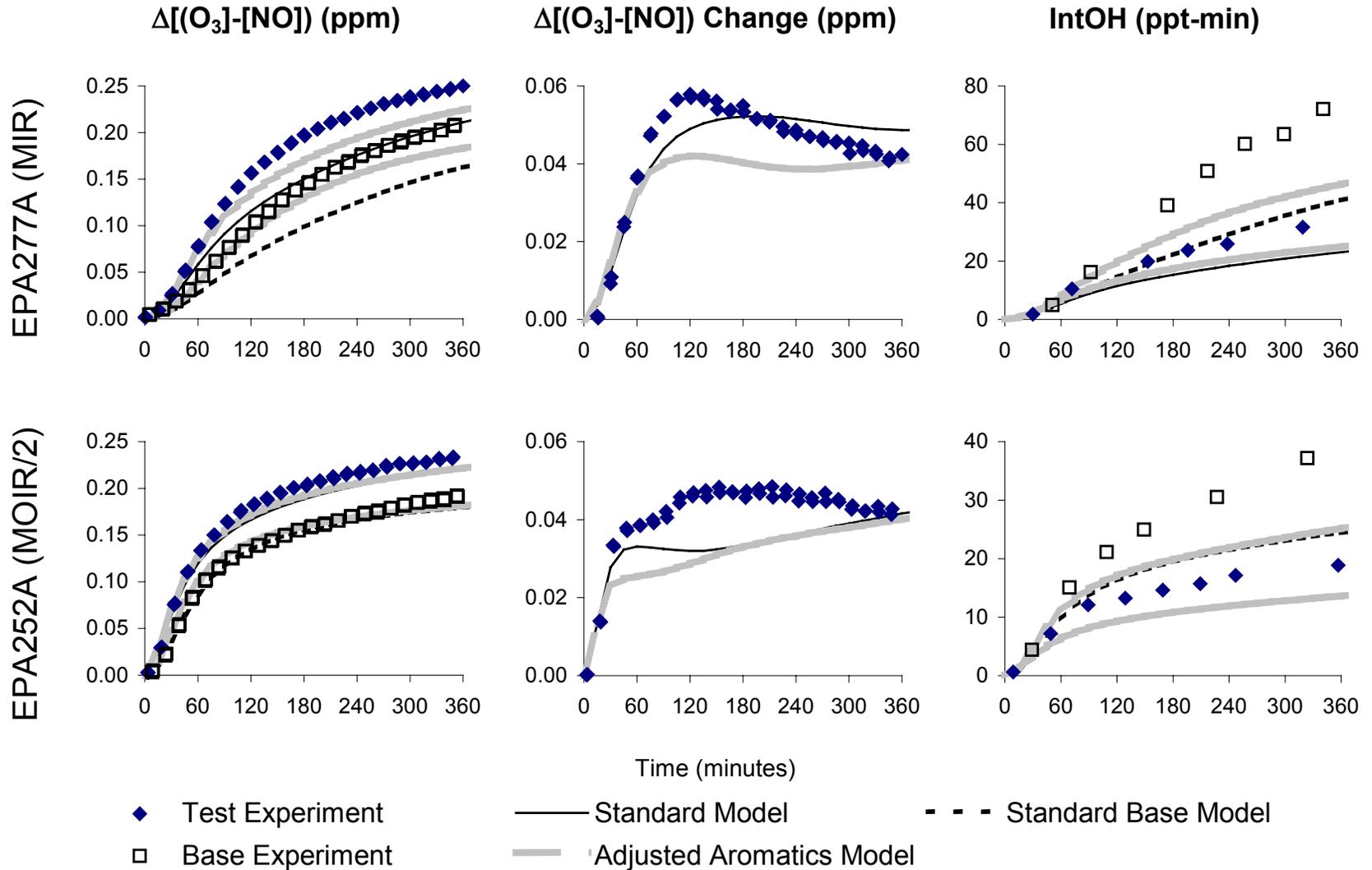


**Both Cases: Moles Texanol added = 5% of moles Carbon in Base Case ROGs**  
**Both simulations predict measurable effect of Texanol on OH radical levels.**

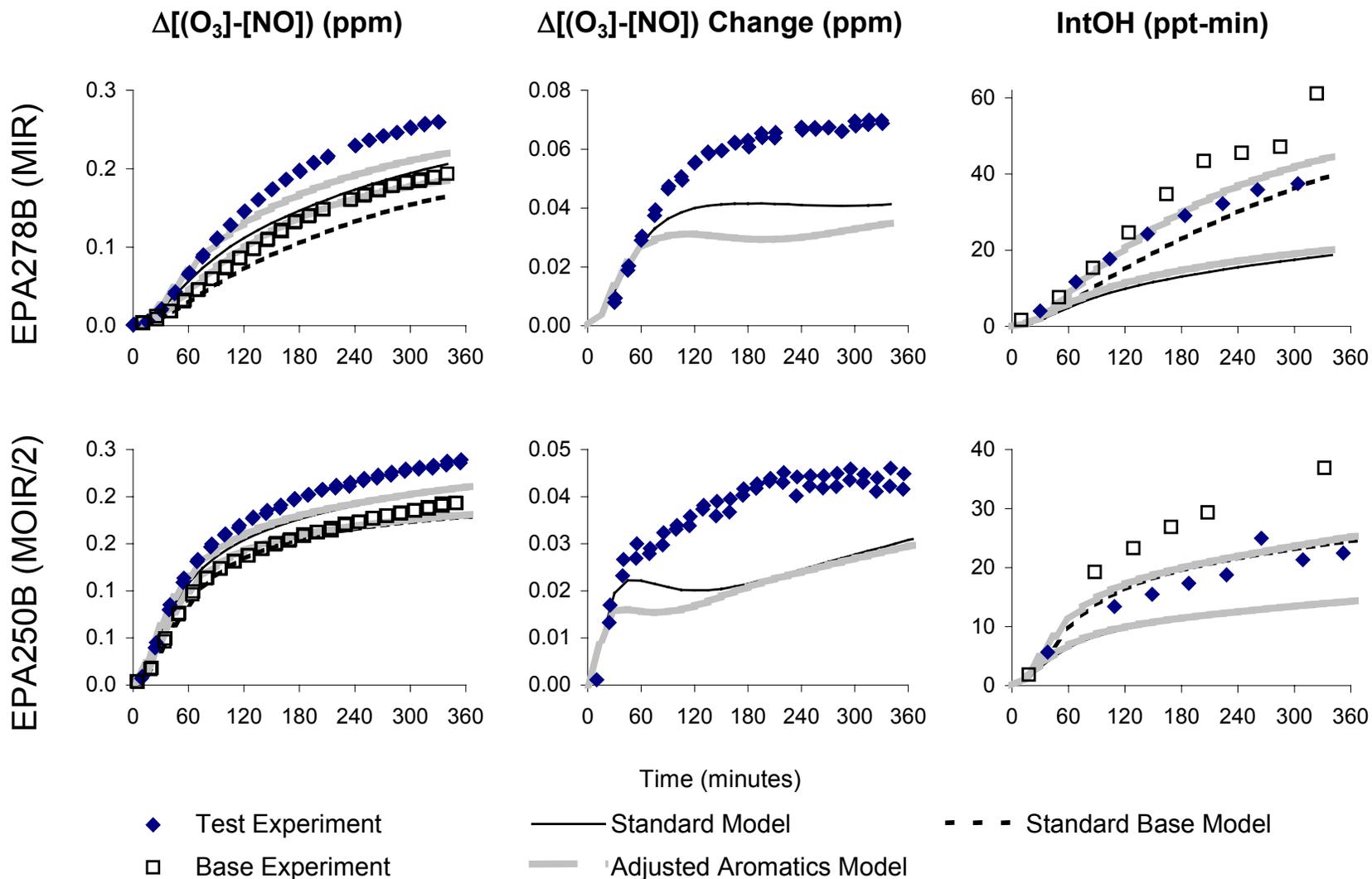
# Reactivity Data for Butyl Carbitol



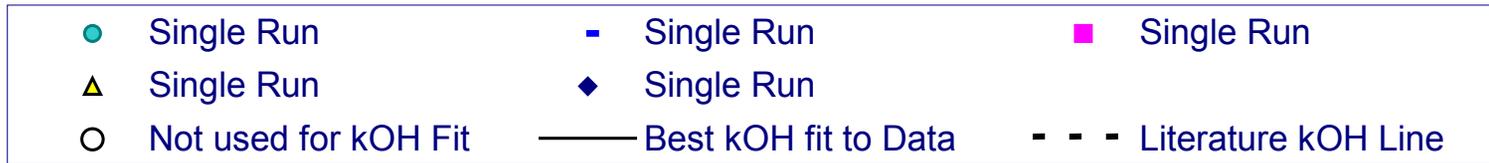
# Reactivity Data for Propylene Glycol



# Reactivity Data for Ethylene Glycol

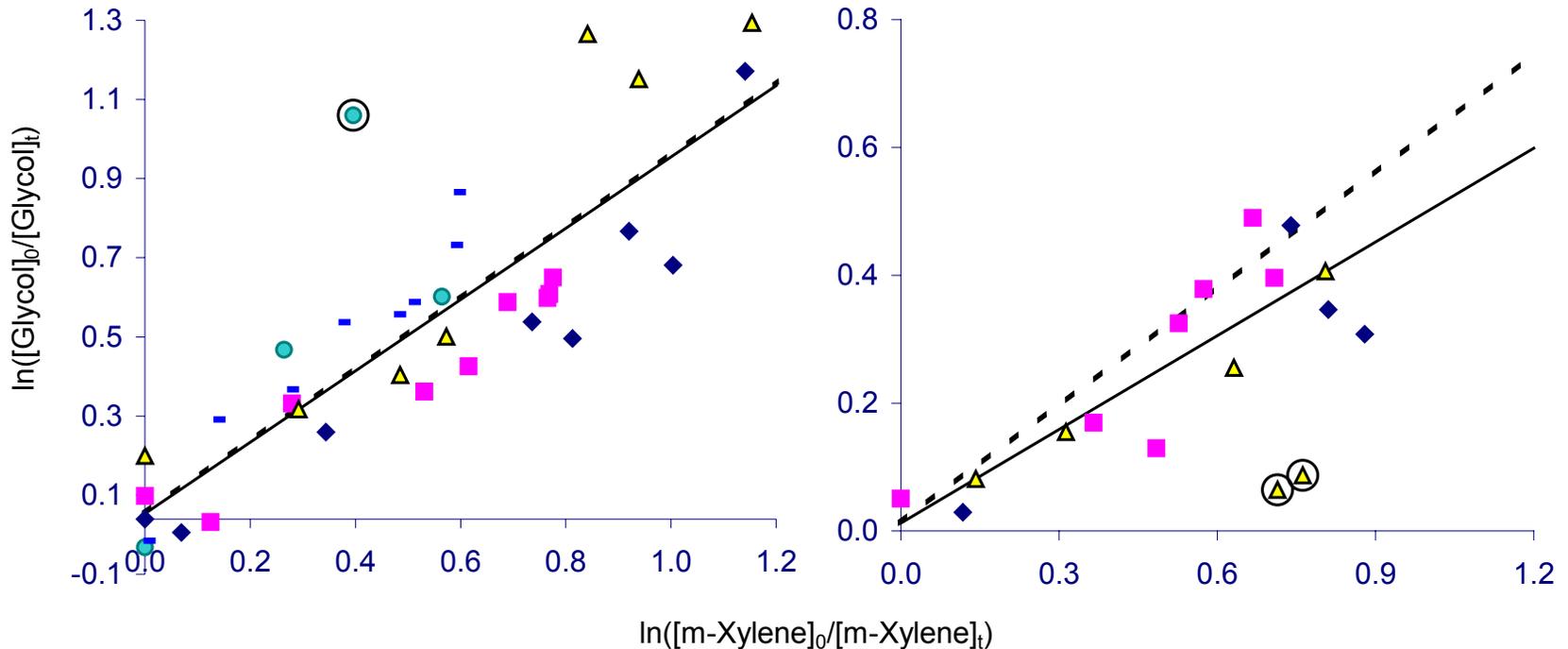


# Glycol Decay Rates in Reactivity Runs: Comparison with Literature k(OH) Values

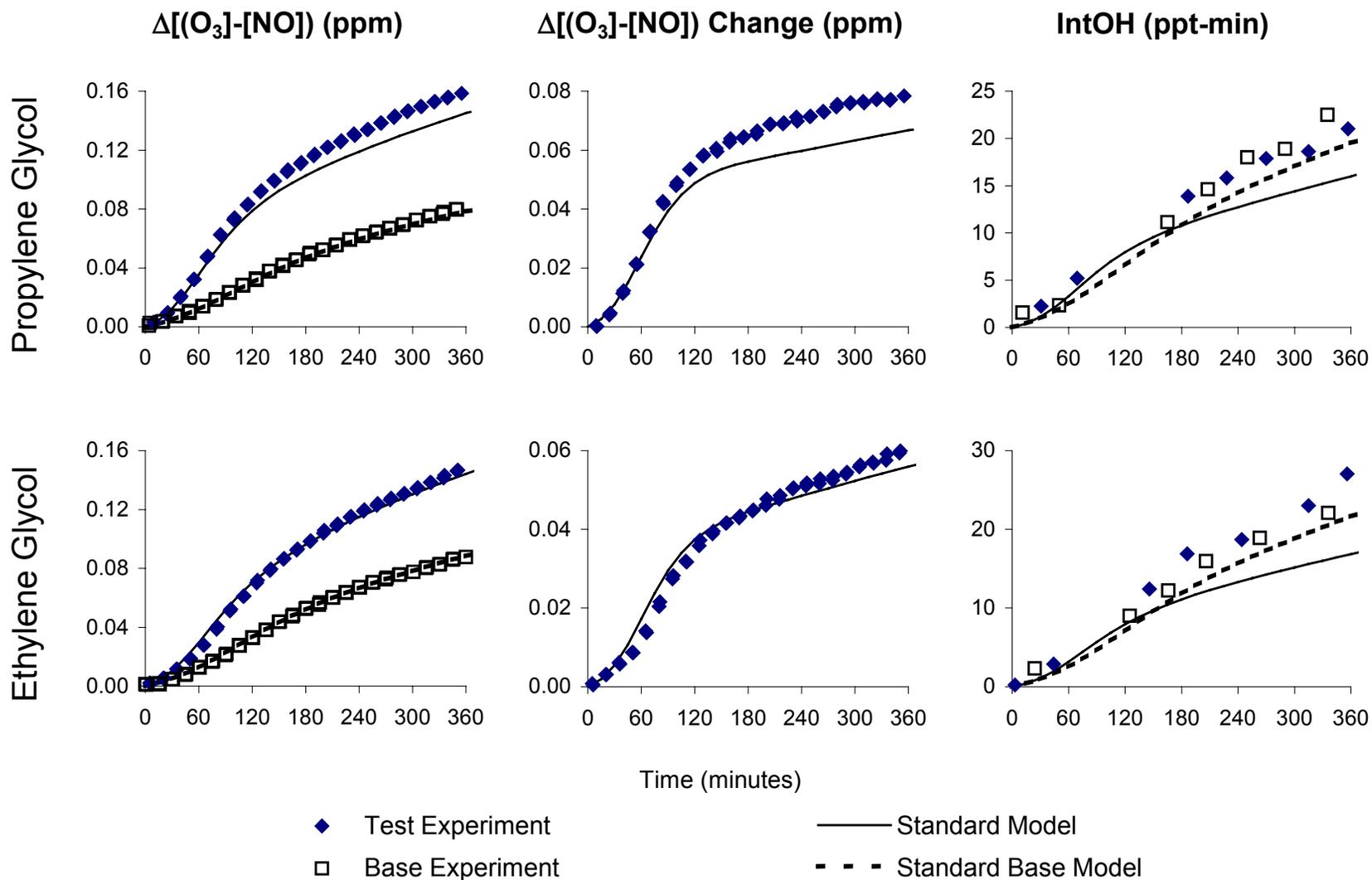


Propylene Glycol vs m-Xylene

Ethylene Glycol vs. m-Xylene



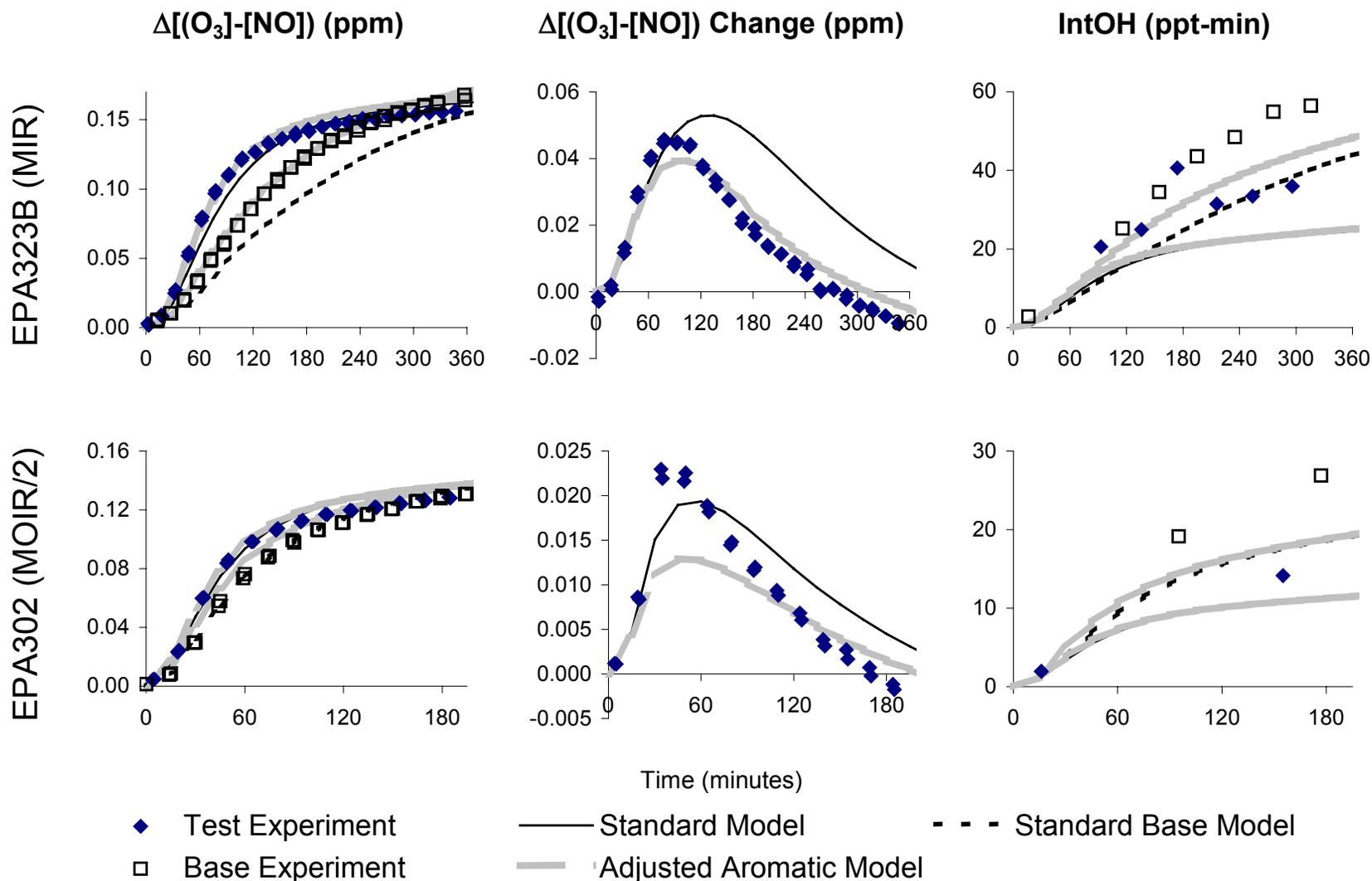
# Glycol Reactivity Data with a Non-Aromatic Surrogate



# Development of a Benzyl Alcohol Mechanism

- Reaction with OH radicals assumed to dominate.
- Single measurement of  $k(\text{OH})$  given by Atkinson (1989) used
- Reaction at  $-\text{CH}_2\text{OH}$ , forming Benzaldehyde +  $\text{HO}_2$  assumed to occur 30% of the time, to fit benzaldehyde data in experiments
- Mechanism of OH addition to ring based on that used for toluene
- Overall nitrate yield adjusted to be 5% to give best fits to data
- Benzaldehyde –  $\text{NO}_x$  experiments also carried out to provide additional basis for developing adjusted mechanism.

# Reactivity Data for Benzyl Alcohol



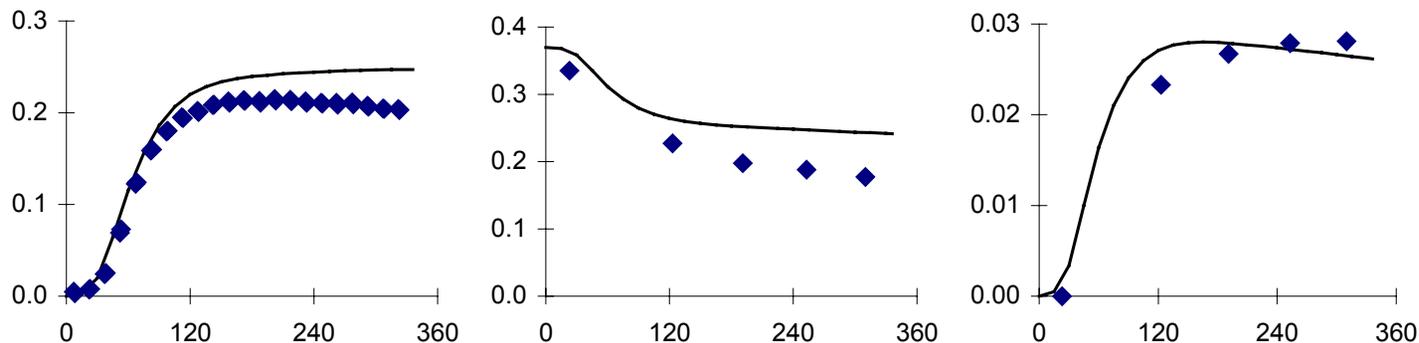
# Simulations of Representative Benzaldehyde – NO<sub>x</sub> Experiments

$\Delta([\text{O}_3]-[\text{NO}])$  (ppm)

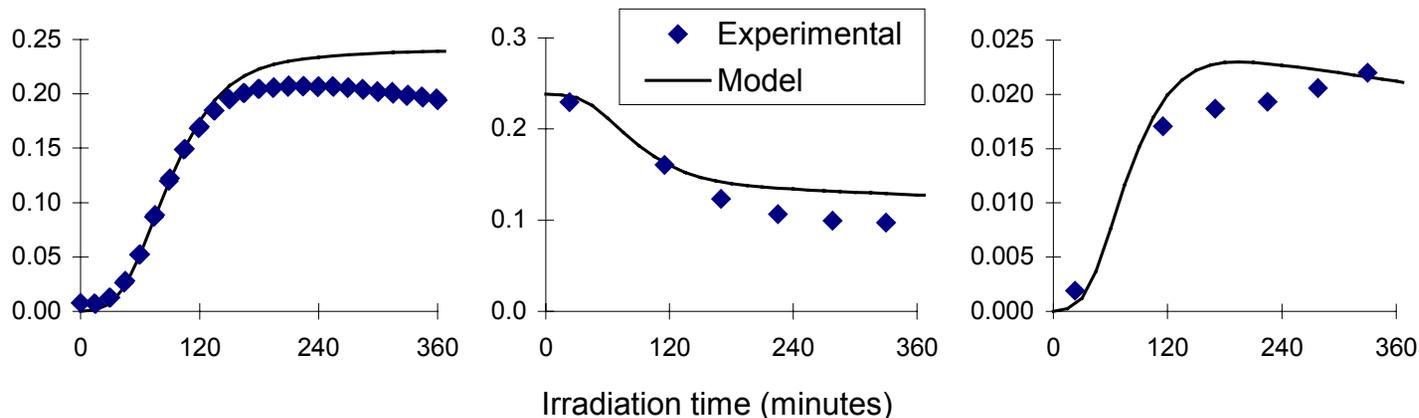
Benzyl Alcohol (ppm)

Benzaldehyde (ppm)

EPA322A (0.41 ppm Benzyl alcohol, 26 ppb NO<sub>x</sub>)



EPA325A (0.27 ppm Benzyl alcohol, 55 ppb NO<sub>x</sub>)



Irradiation time (minutes)

# Summary of Mechanism Evaluation Results for Water-Based Coatings VOCs

Compound	Mechanism Performance and Modifications	MIR * (mass basis)
Texanol® isomers	Previous mechanisms simulated data satisfactorily. Not changed.	0.88
Propylene Glycol	Mechanism may underpredict ozone impact, but uncertain whether change is appropriate. Not changed.	≥ 2.7
Ethylene Glycol	Mechanism may underpredict ozone impact, but uncertain whether change is appropriate. Not changed.	≥ 3.4
Butyl Carbitol	Previous mechanism simulated data satisfactorily. Not changed.	2.9
Benzyl Alcohol	No previous mechanism. Parameterized mechanism adjusted to fit data.	4.9

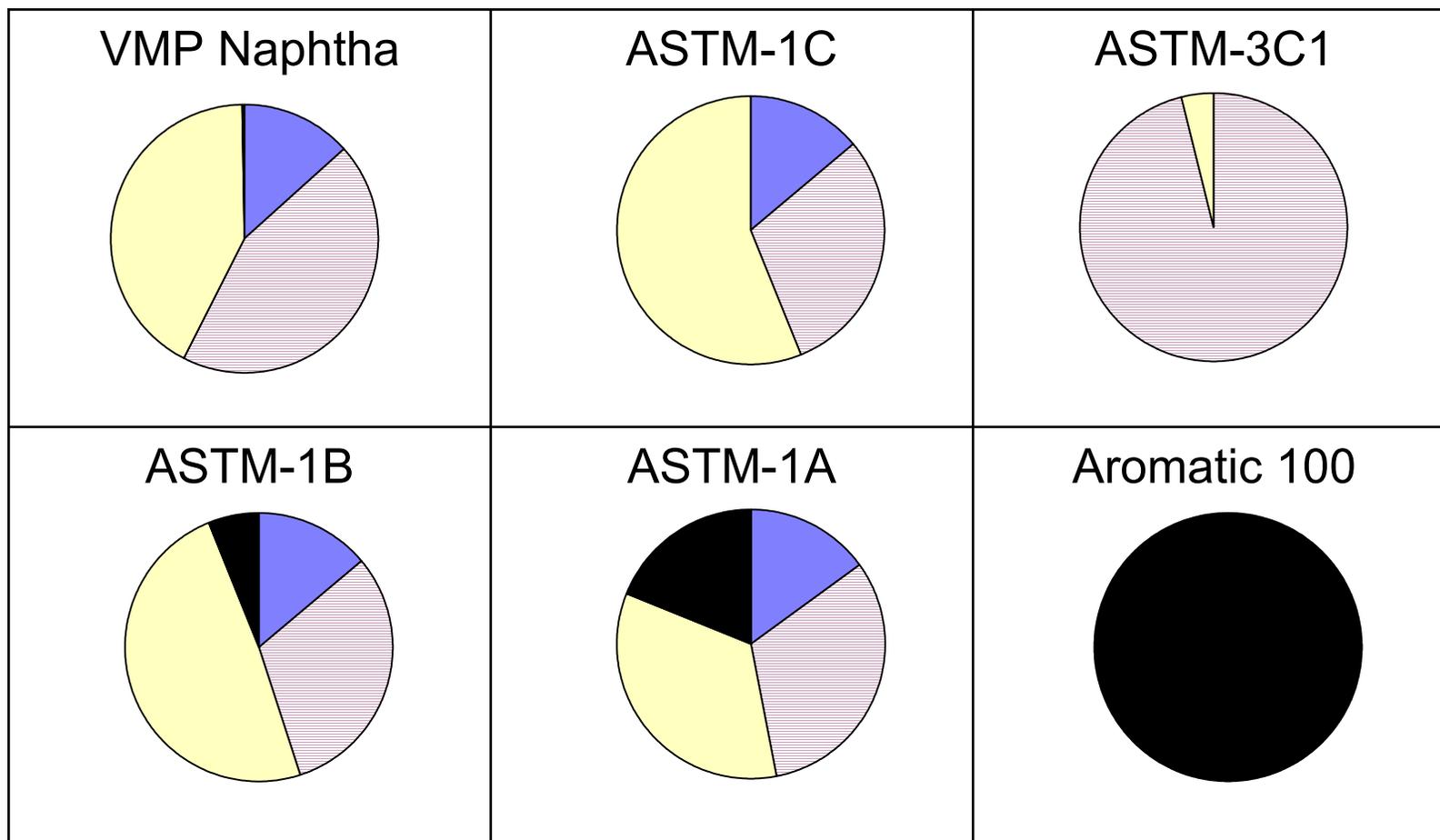
\* MIR of base ROG (Ambient Mixture) = 3.7 gm O<sub>3</sub> / gm VOC

# Representative Hydrocarbon Mixtures Chosen For Reactivity Experiments

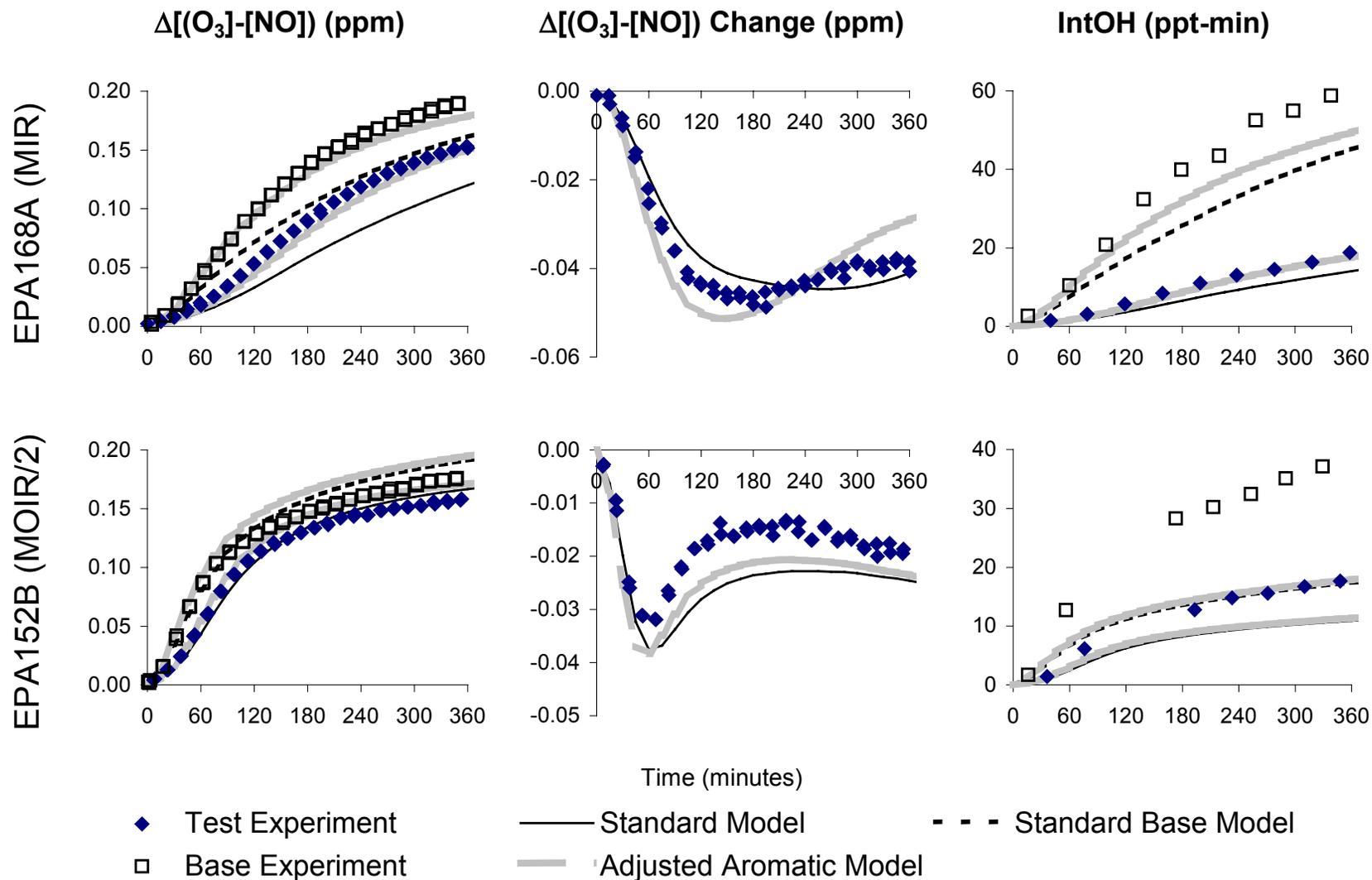
<b>Designation</b>	<b>Description</b>	<b>Carbon No. Range</b>	<b>Aromatic Content</b>	<b>CARB Bin No.</b>
VMP-NAPH	VMP Naphtha	8-9	0.2%	6
ASTM-1C	Dearomatized Mixed Alkanes	9-12	-	11
ASTM-3C1	Synthetic isoparaffinic alkane mixture	Mostly 11	-	12
ASTM-1B	Reduced Aromatics Mineral Spirits	9-12	6%	14
ASTM-1A	Regular Mineral Spirits	9-12	19%	15
AROM-100	Aromatic 100	Mostly 9	100%	22

# Chemical Type Distributions for Hydrocarbon Mixtures Studied

■ n-Alkane    ■ Br-Alkane    ■ Cyc-Alkane    ■ Aromatic

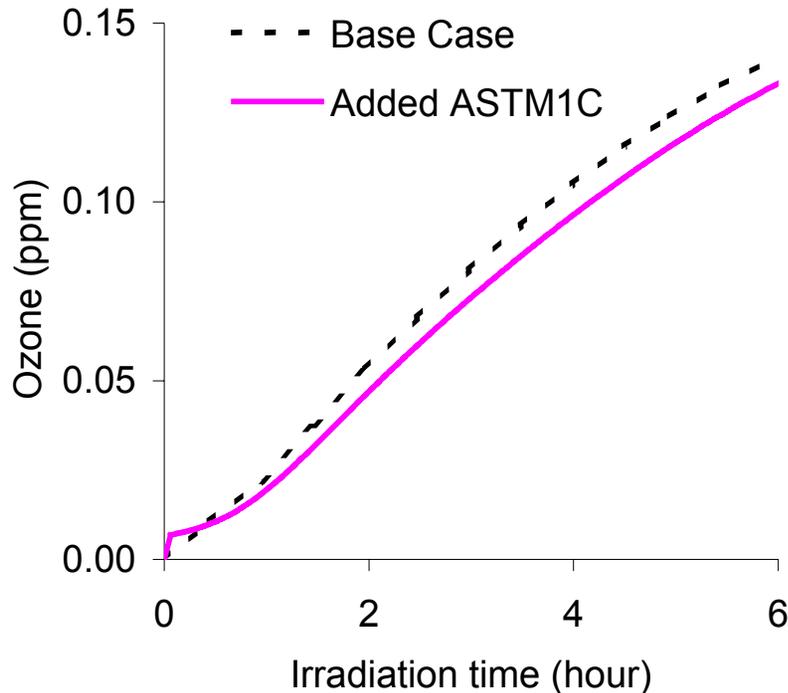


# Reactivity Data for Dearomatized Mixed Alkanes (ASTM-1C)

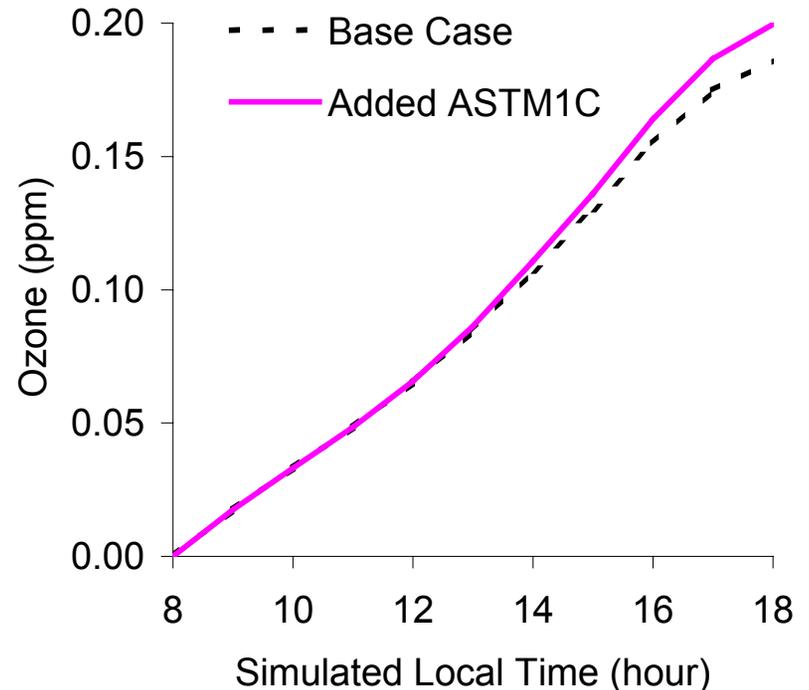


# Comparison of Chamber and Ambient Reactivity Calculation for ASTM-1C

**"MIR" Incremental Reactivity Chamber experiment**

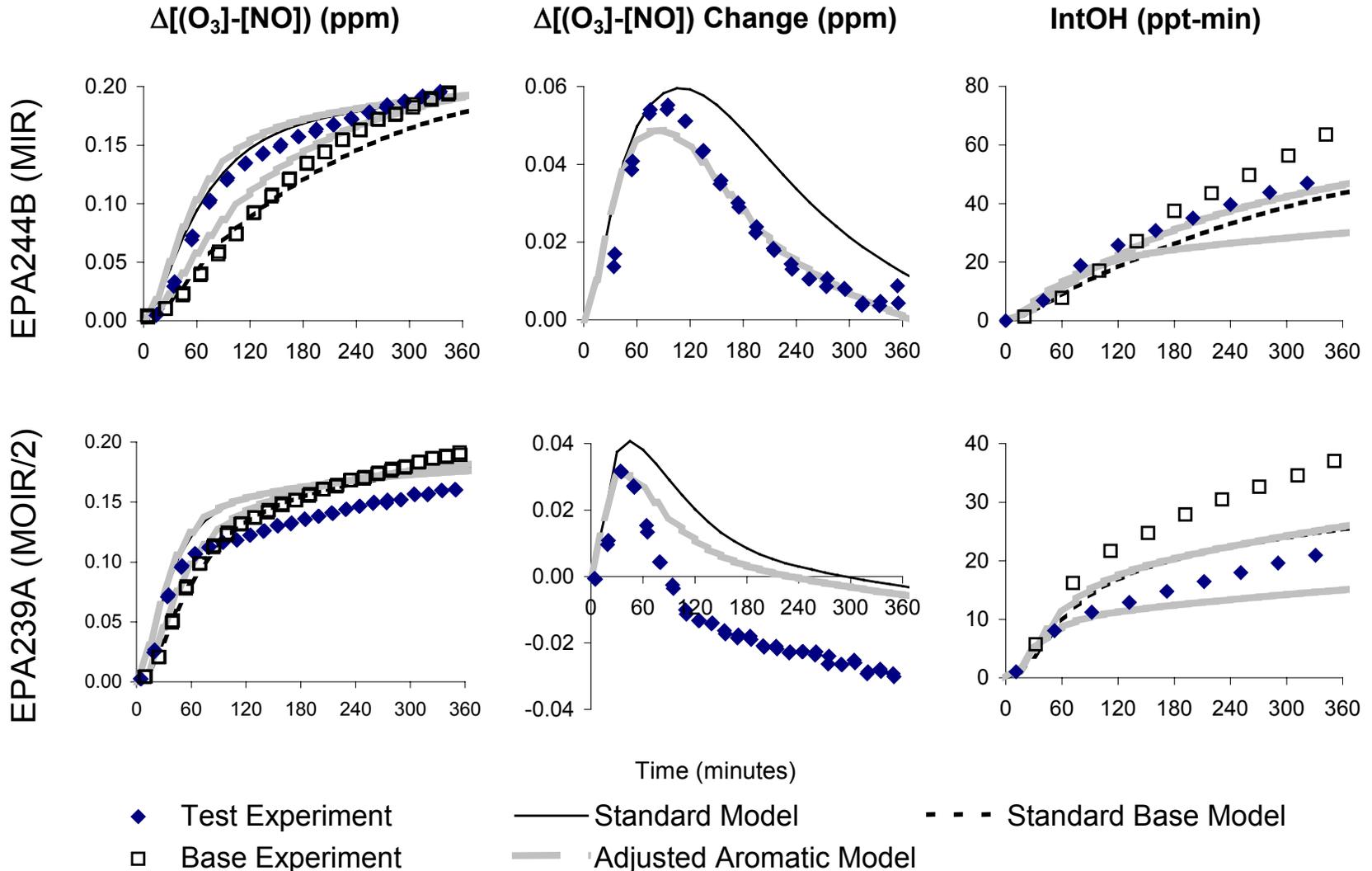


**"Averaged Conditions" MIR Box Model Airshed Scenario**



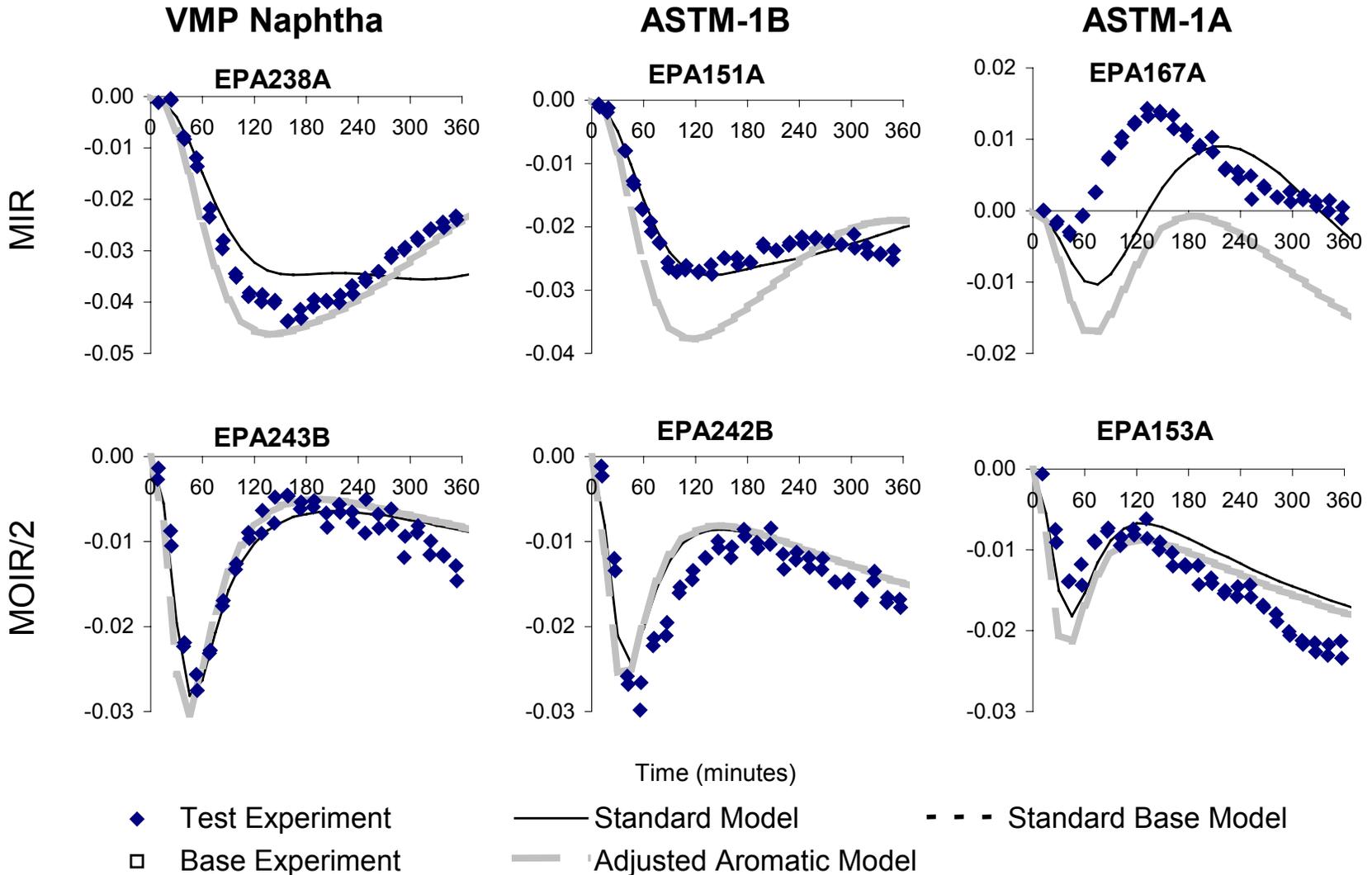
**Moles Carbon Mixture added = 25% of Moles Carbon in Base Case ROGs**  
**Both simulations predict measurable effect of Mixture on OH radical levels.**

# Reactivity Data for Aromatic 100

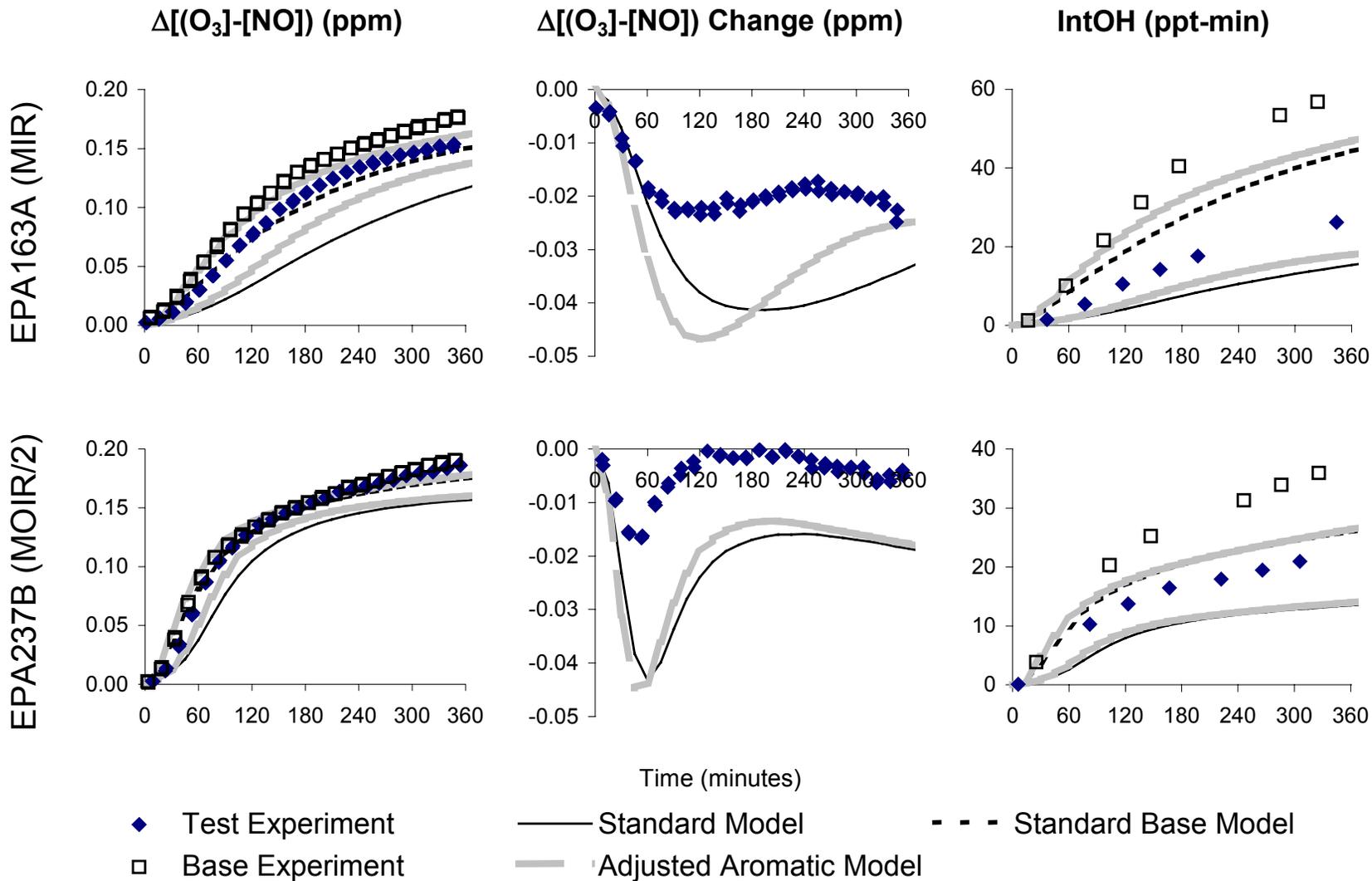


# Results for Other Petroleum Distillates

## Change in $\Delta([O_3]-[NO])$ (ppm)



# Reactivity data for Synthetic Hydrocarbon Mixture (ASTM-3C1)



# Assessment of Model Performance and MIRs for the Hydrocarbon Solvents Studied

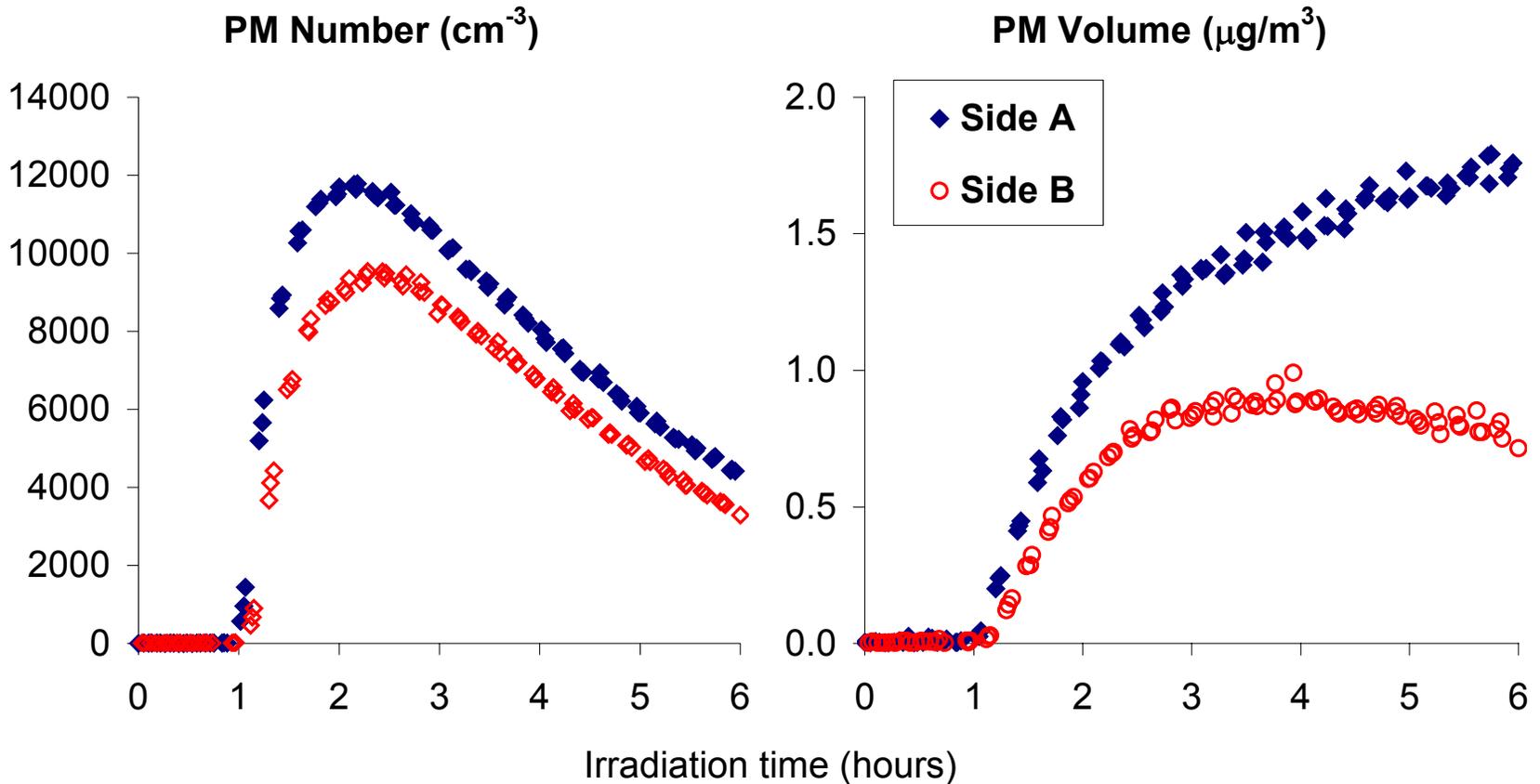
Designation	Components	O <sub>3</sub> Model Performance	Bin MIR	Best Est. MIR
VMP Naphtha	C <sub>8</sub> -C <sub>9</sub> Alkanes	Reasonably consistent with data	1.41	1.35
ASTM-1C	C <sub>9</sub> -C <sub>12</sub> Alkanes	Reasonably consistent with data	0.91	0.96
ASTM-3C1	C <sub>11</sub> Branched Alkanes	Model underestimates O <sub>3</sub> impact by 40-80%	0.81	Approx. 1.1 – 1.5
ASTM-1B	C <sub>9</sub> -C <sub>12</sub> Alkanes, ~6% Aromatics	Reasonably consistent with data	1.26	1.21
ASTM-1A	C <sub>9</sub> -C <sub>12</sub> Alkanes, ~20% Aromatics	Reasonably consistent with data.	1.82	1.97
Aromatic 100	Methyl ethyl and trimethyl Benzenes	Consistent with data for MIR. Underpredicts O <sub>3</sub> inhibition at low NO <sub>x</sub>	7.51	7.70

# PM Measurements

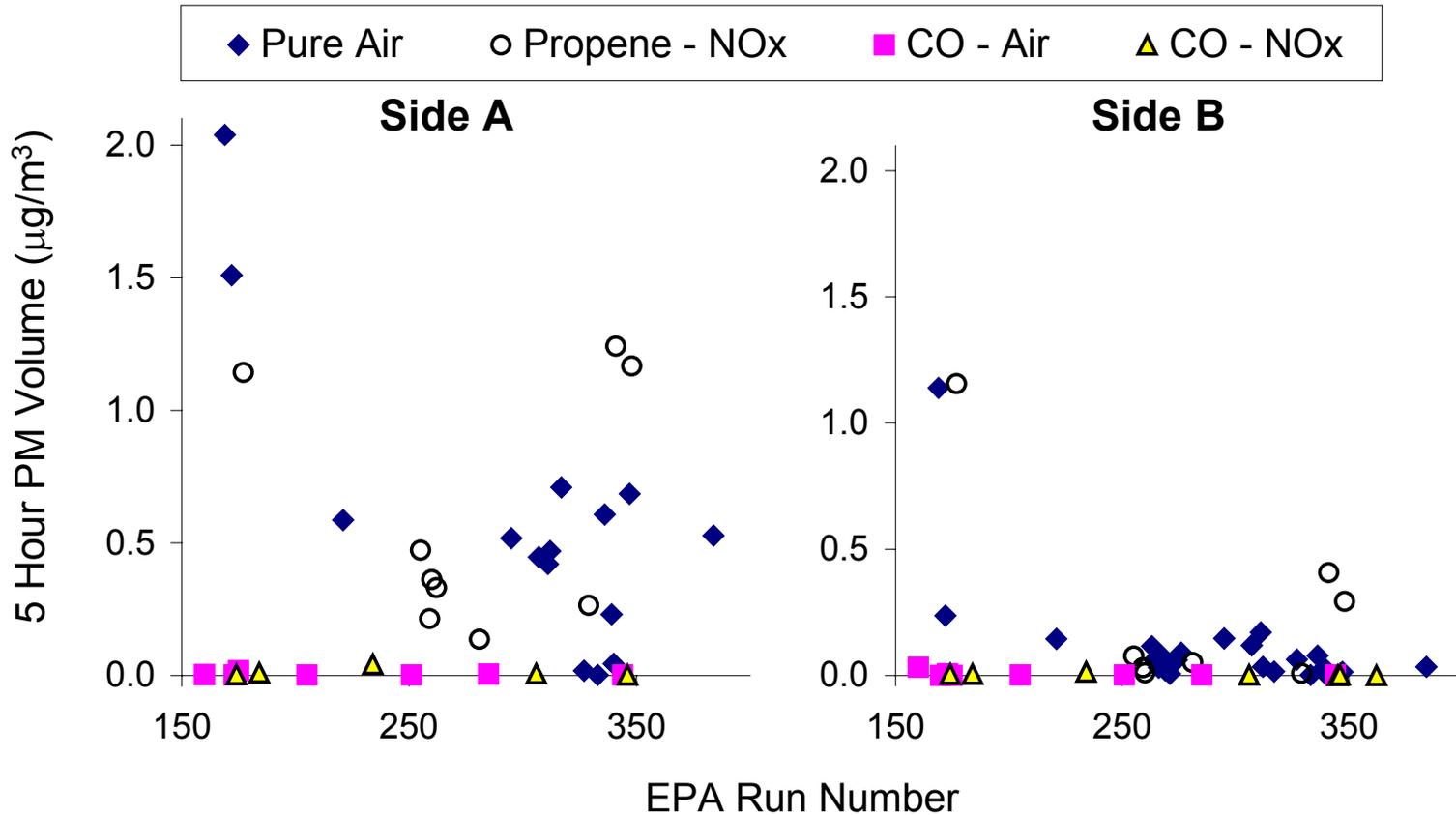
- Number densities of particles in 71 size ranges (28 - 730 nm) measured using a Scanning Electrical Mobility Spectrometer
- Data used to compute total particle number and volume (measured as mass assuming density of H<sub>2</sub>O) per unit volume
- PM alternately sampled from each of the two reactors, switching every 10 minutes (15.3 data points/hour/reactor)
- PM measurements made during most incremental reactivity experiments for the coatings projects
- Background PM measurements made in experiments where PM precursors not expected
- Seed aerosol not used in most experiments

# PM Data in Base Case Experiment

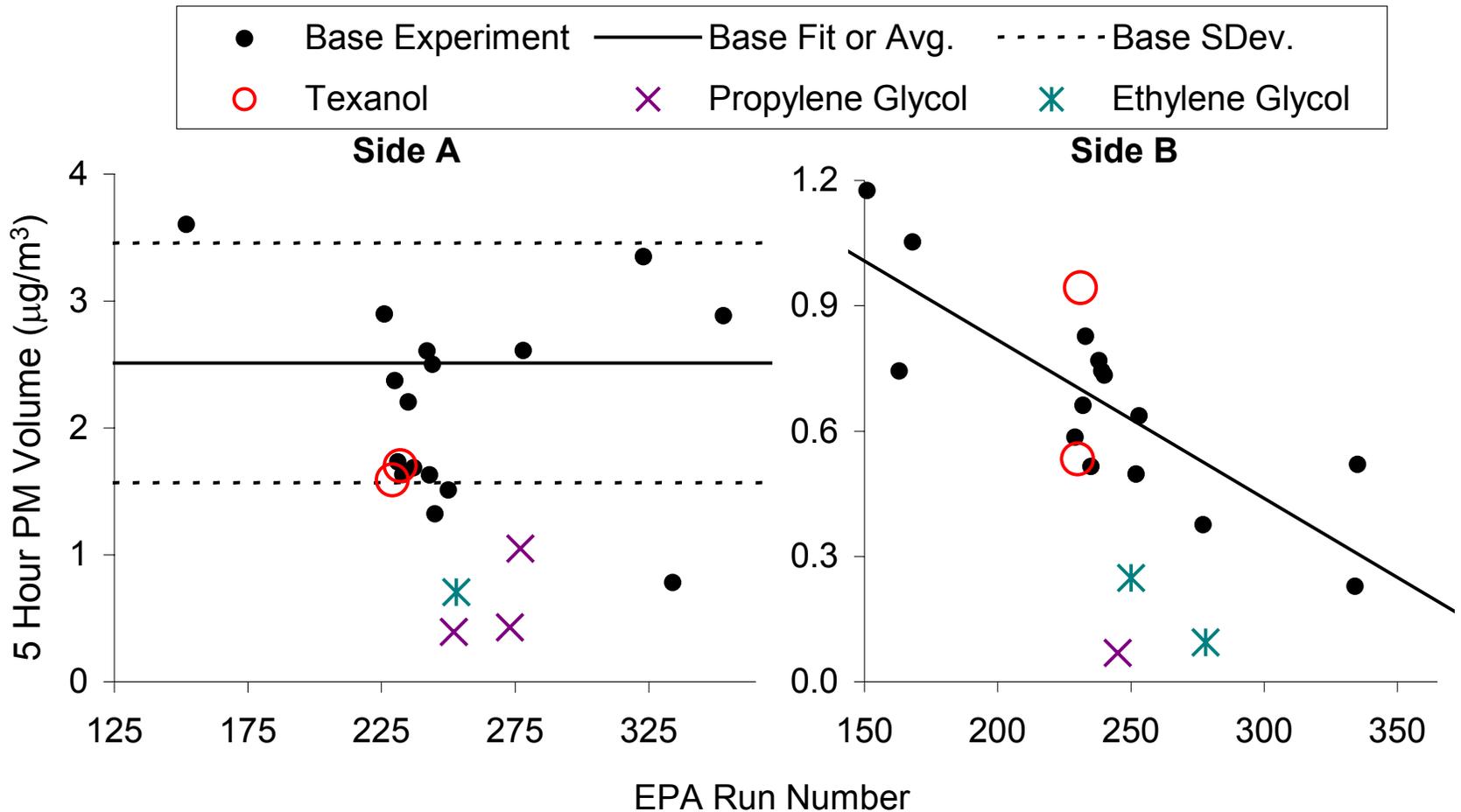
## EPA233: MOIR/2 Surrogate (Side Equivalency Test)



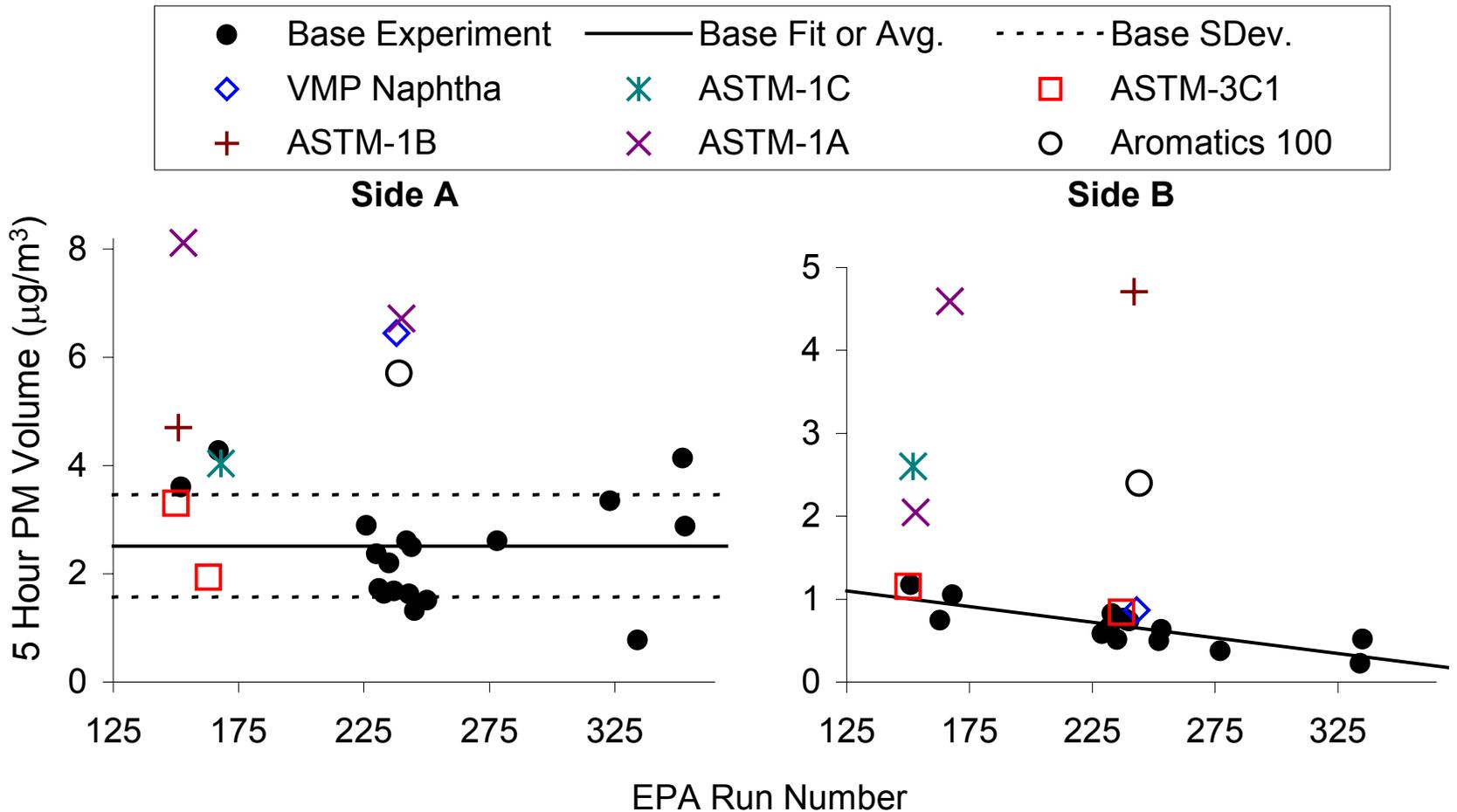
# PM Volume in Background Experiments



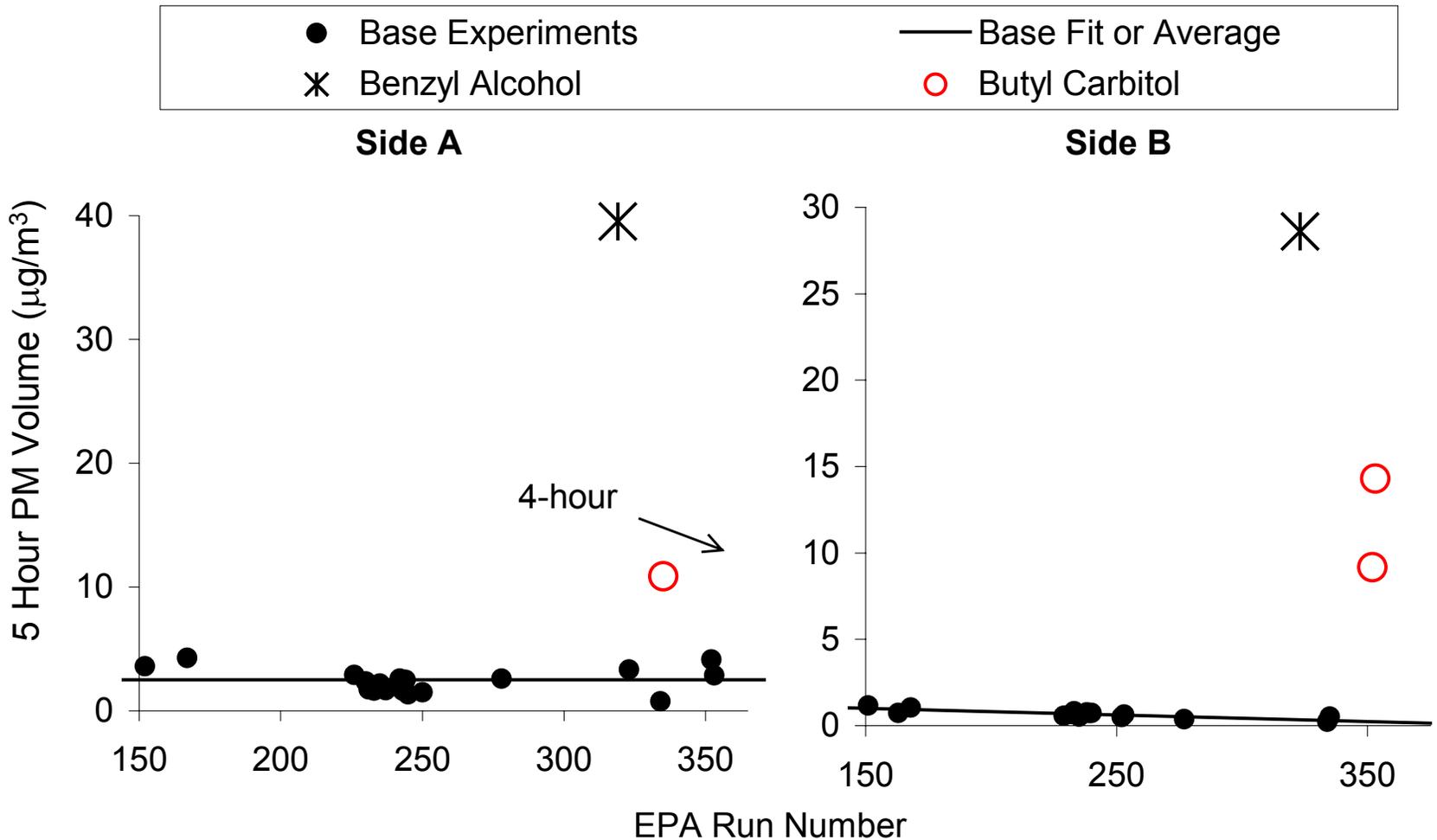
# Effects of Texanol® and the Glycols on 5-Hour PM Volume



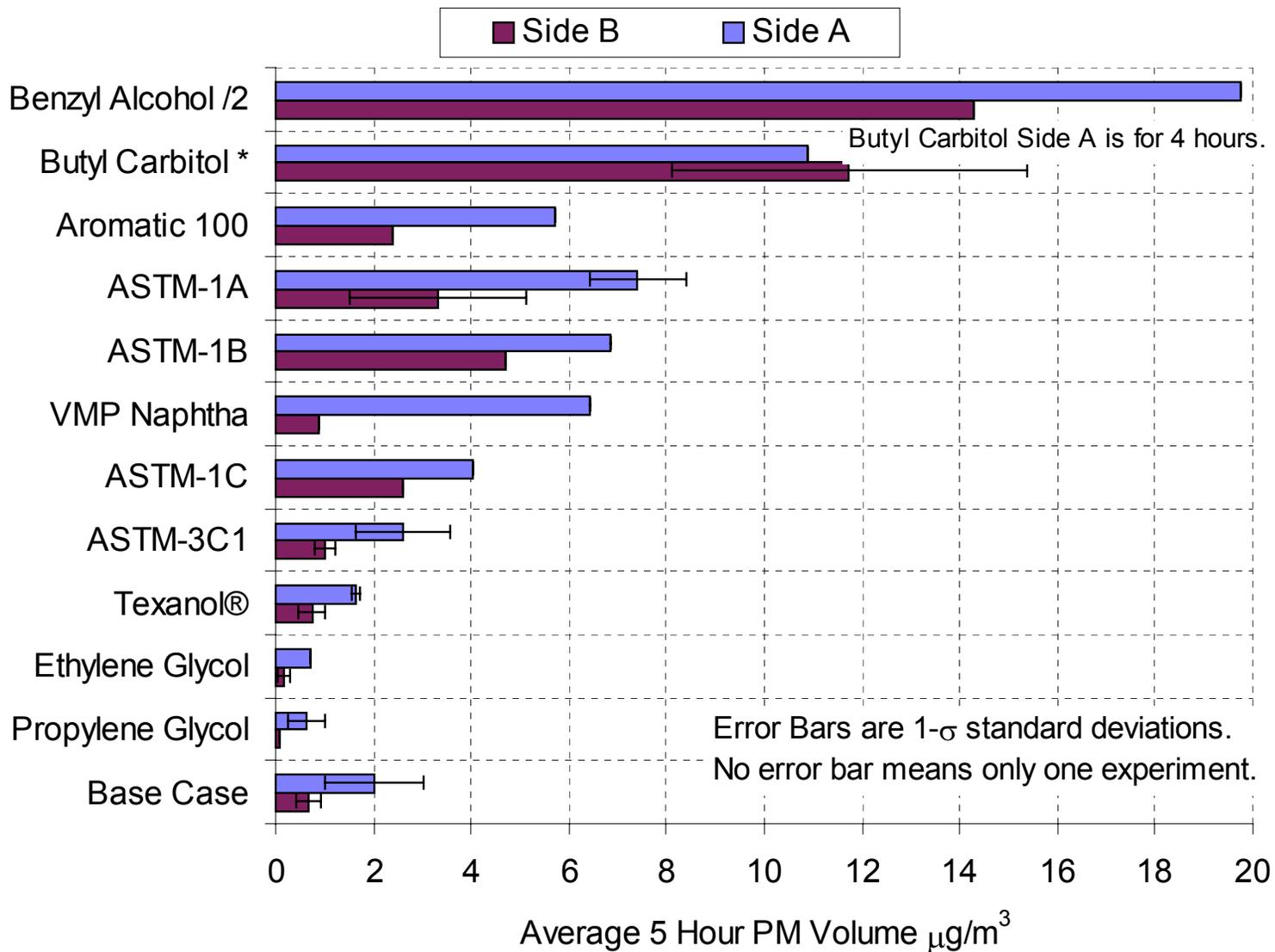
# Effects of Hydrocarbon Solvents on 5 Hour PM Volume



# Effects of Benzyl Alcohol and Butyl Carbitol on 5-Hour PM Volume



# Summary of PM Volume Reactivity Results



# Summary of PM Measurement Results

- Background PM formation in chamber is up to  $\sim 1 \mu\text{g}/\text{m}^3$ , depending on reactor employed
  - Probably due to contaminant reacting with OH, forming SOA
  - Reason for higher background in “A” reactor unknown
- Secondary PM formation from ethylene and propylene glycol, Texanol®, and the ASTM-3C1 synthetic mixture negligible.
- Small but measurable PM from petroleum distillate solvents. Not simply related to aromatic content.
- Highest secondary PM from butyl carbitol and (especially) benzyl alcohol
- Chamber effects PM model needed before PM data can be used for *quantitative* mechanism evaluation

# Glycol Availability Screening Experiments

## Objective

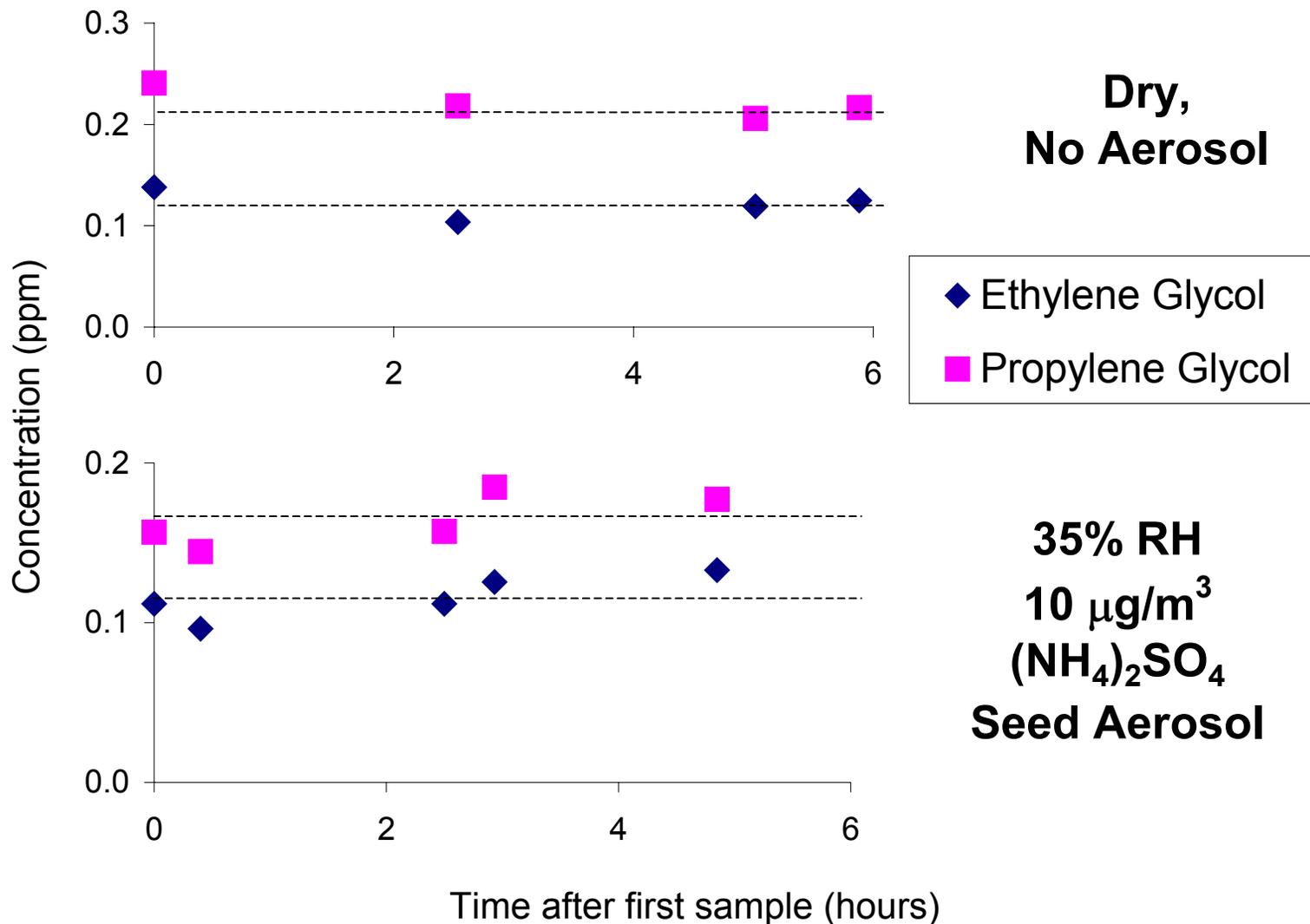
- Determine if added aerosols affect gas-phase consumption rates and reactivities of glycols

## Experiments Carried Out

- Dark decay experiments with ethylene and propylene glycol with  $10 \mu\text{g}/\text{m}^3$   $(\text{NH}_4)_2\text{SO}_4$  seed aerosol at 35% RH.
- ROG –  $\text{NO}_x$  ambient surrogate irradiation with added propylene glycol with  $9 \mu\text{g}/\text{m}^3$   $(\text{NH}_4)_2\text{SO}_4$  seed aerosol at 25% RH.
- ROG –  $\text{NO}_x$  ambient surrogate irradiation with added ethylene glycol with  $7 \mu\text{g}/\text{m}^3$   $\text{NH}_4\text{HSO}_4$  seed aerosol at 30% RH.

Note: Aerosol and humidity added to only one reactor because of limited aerosol generation and humidification capacity.

# Results of Glycol Dark Decay Experiment

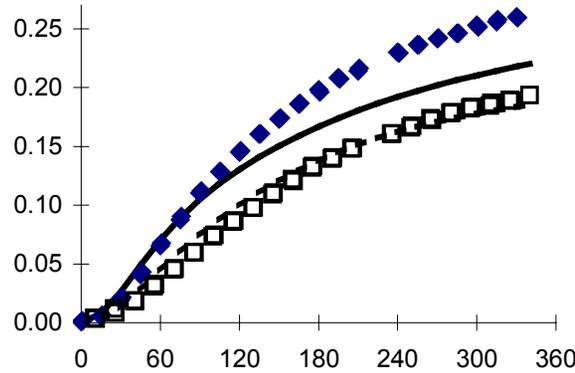
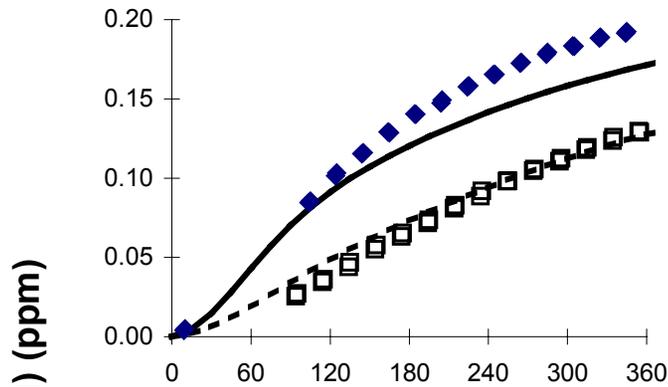


# Effects of Aerosol and Humidity on Glycol Reactivity Experiments

Propylene Glycol

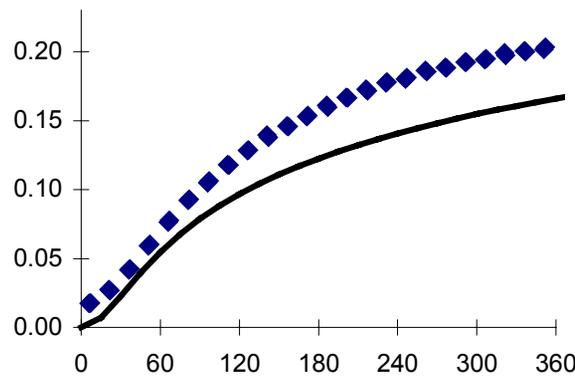
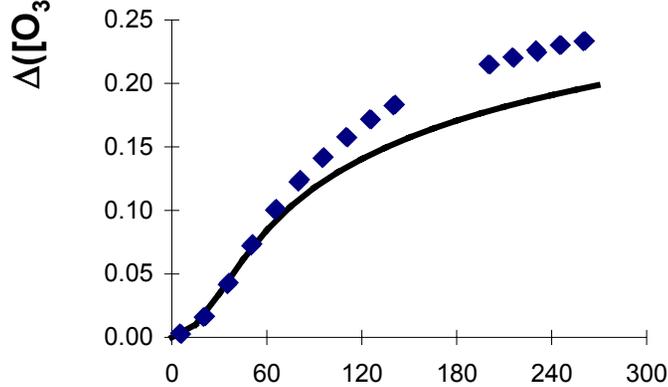
Ethylene Glycol

Dry, no Aerosol



25% RH, 9  $\mu\text{g}/\text{m}^3$   $(\text{NH}_4)_2\text{SO}_4$

30% RH, 7  $\mu\text{g}/\text{m}^3$   $\text{NH}_4\text{HSO}_4$



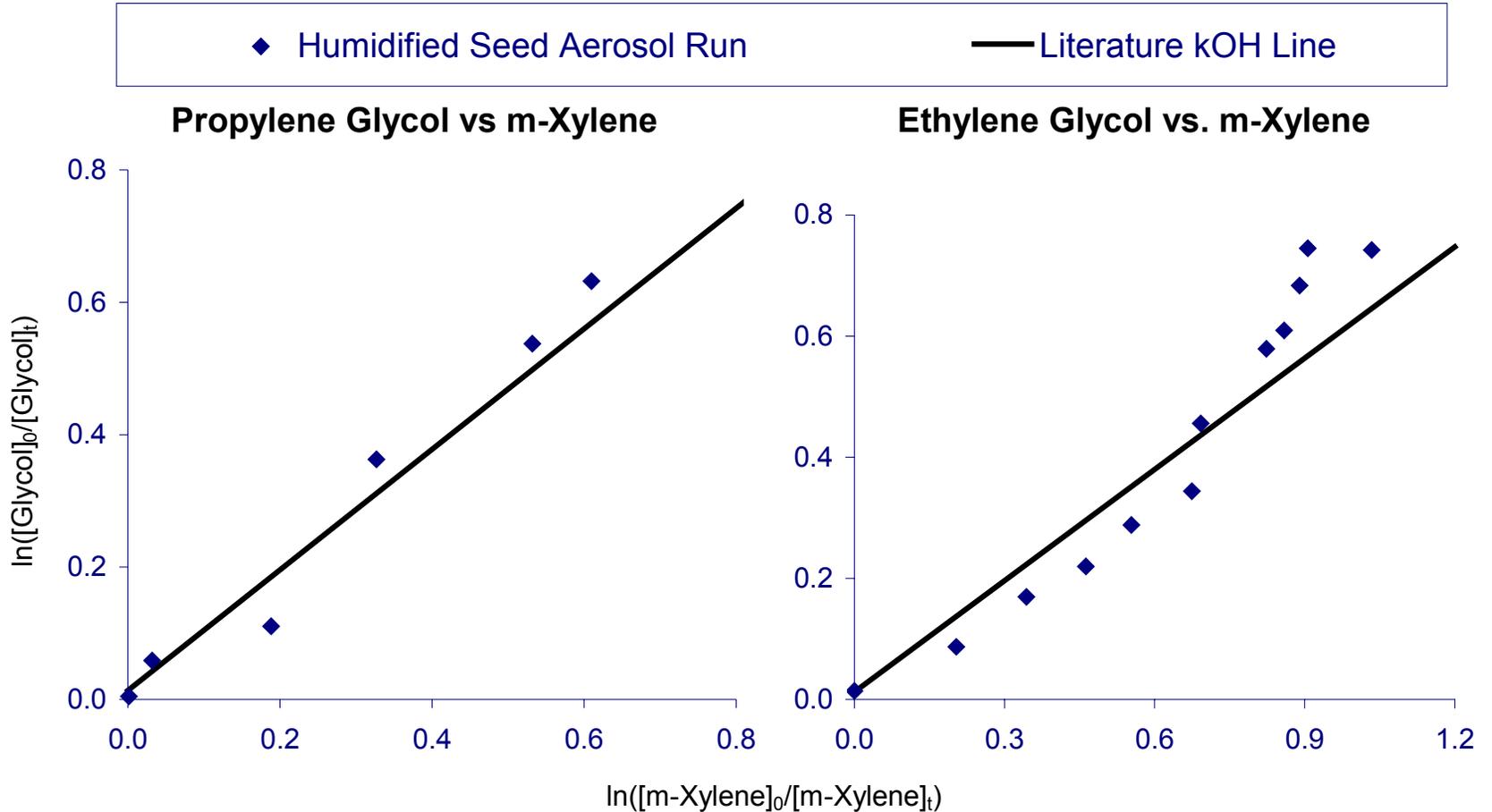
- ◆ Test Data
- Base Data
- Test Model
- - - Base Model

Model calculations used adjusted aromatics base mechanism for best fits.

No base data in added aerosol runs because of limited humidification and aerosol generation capacity.

Irradiation time (minutes)

# Glycol Decay Rates in Availability Runs: Comparison with Literature k(OH) Values



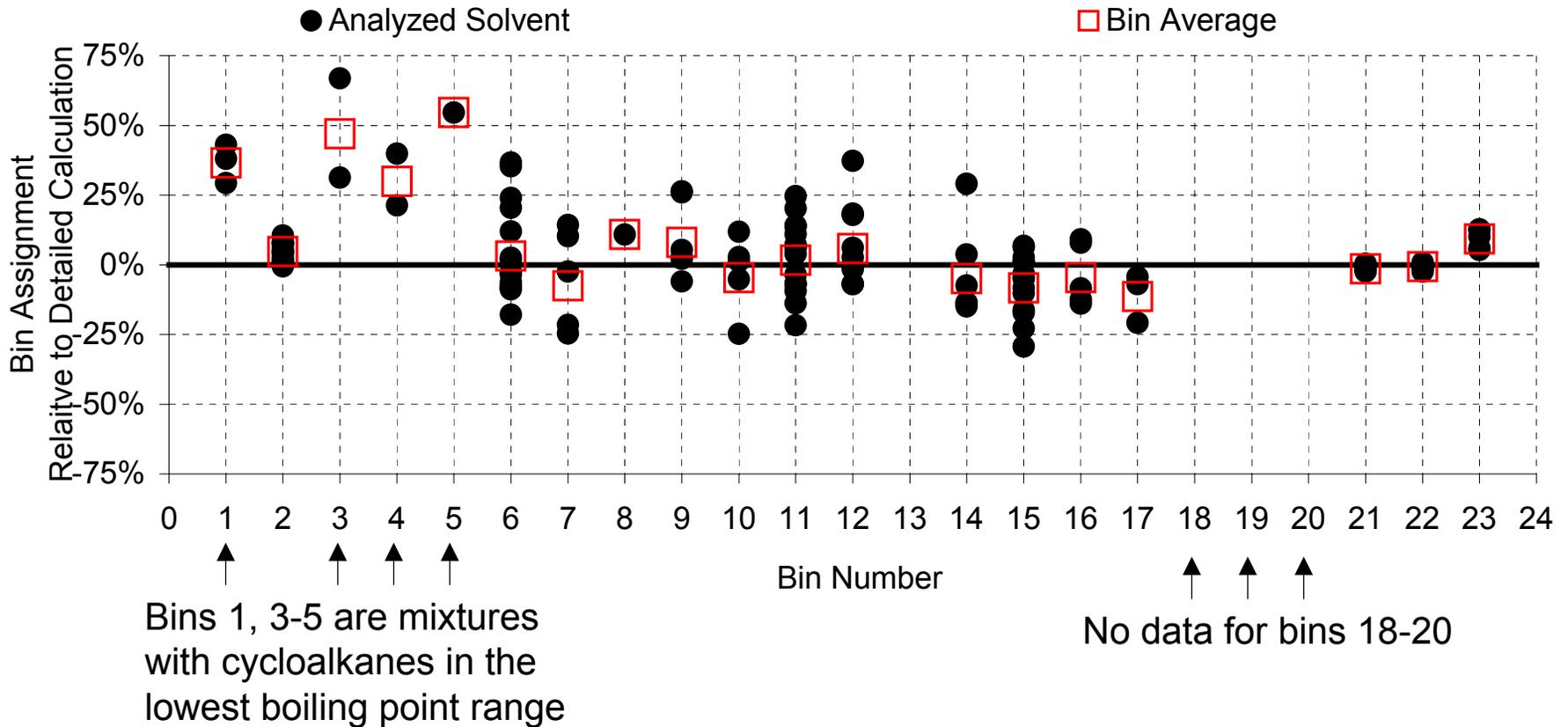
# Glycol Availability Experiments: Preliminary Conclusions

- No clear effect on glycol consumption rate or ozone reactivity for humidity up to 35% and  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{NH}_4\text{HSO}_4$  seed aerosol up to  $10 \mu\text{g}/\text{m}^3$ .
- But there still may be a measurable effect at higher humidity or aerosol concentration, with a different type of aerosol
- Upgrades are being made to the chamber facility to facilitate experiments at higher RH, aerosol levels.
- But experiments that measure increases in aerosol mass when exposed to gas-phase VOCs may give a more sensitive measure of VOC uptake on aerosols

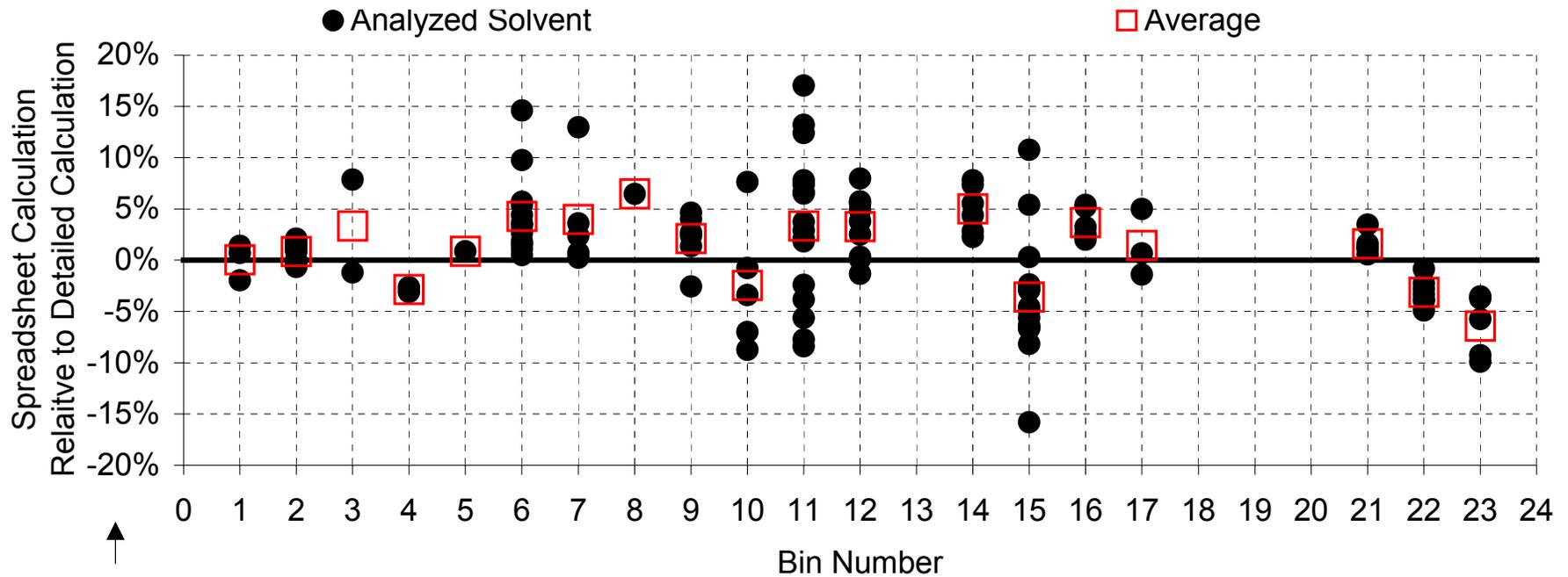
# Evaluation of Methods to Estimate Complex Hydrocarbon Solvent Reactivities

- MIRs for complex hydrocarbon solvents currently estimated using a “binning” procedure based on correlations between carbon numbers, type distributions, and MIRs
- Bin MIRs evaluated by comparison with MIRs calculated using detailed compositional data for a wide variety of solvents
  - Agree within  $\pm 25\%$  except for bins with light cycloalkanes
- An alternative “spreadsheet” method developed for deriving estimated compositions for solvents with limited data
  - Separates compositional and reactivity estimates. Permits derivations in reactivities for other scales besides MIR.
  - Agrees with calculations using detailed compositional data within  $\pm 10\%$  in most cases
  - Can be used as a basis for updating hydrocarbon bin reactivities when reactivity scale is changed or updated.

# Comparison of CARB Bin MIRs with MIRs Calculated Using Compositional Data



# Comparison of Spreadsheet Estimated MIRs with MIRs Calculated Using Compositional Data

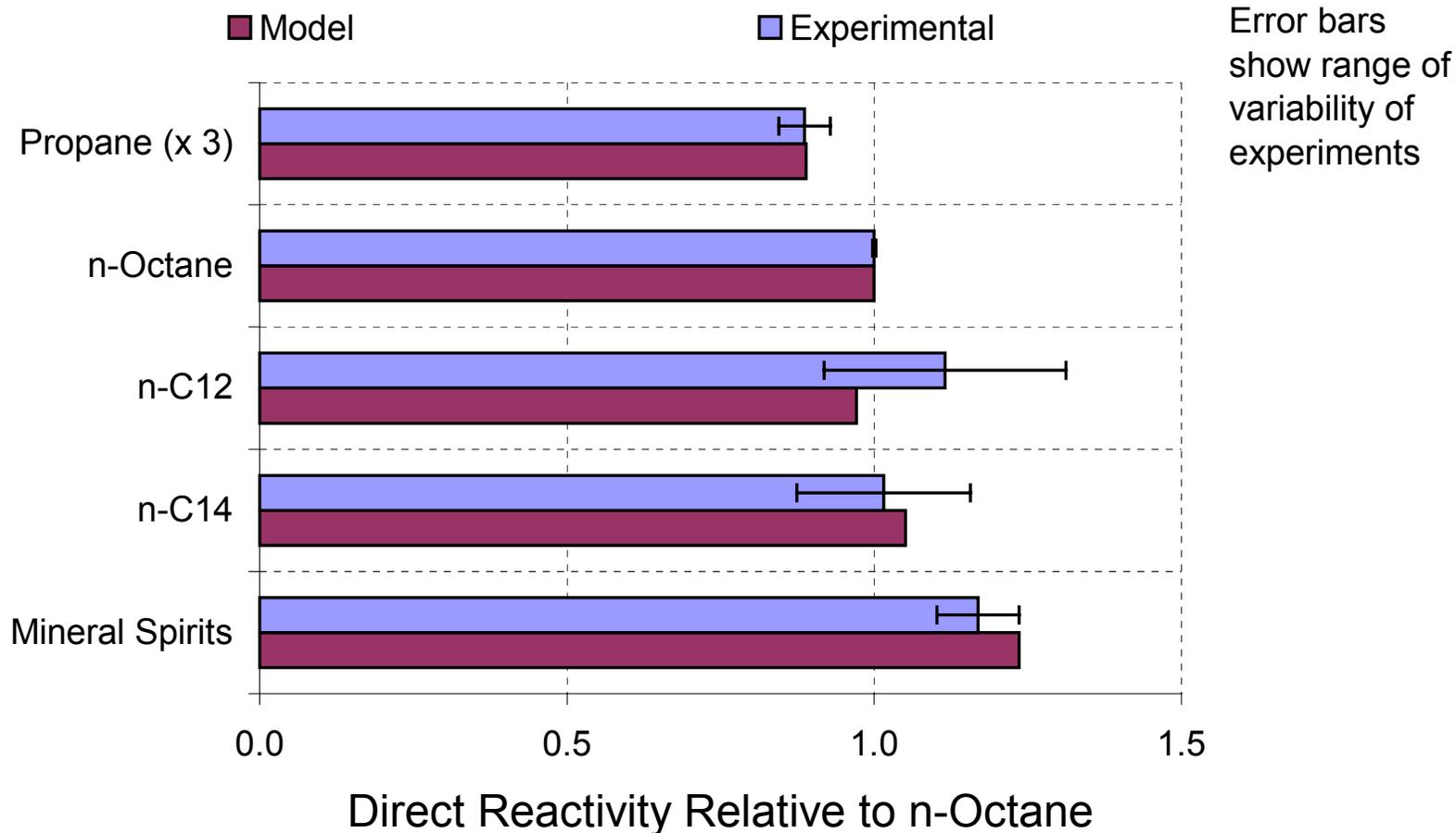


Note that previous plot had  $\pm 75\%$  range

# Further Development of a Direct Reactivity Measurement Method

- VOCs affect O<sub>3</sub> directly through their own reactions or indirectly through the effects of their reactions on radicals and NO<sub>x</sub>.
- A measurement of direct reactivity would reduce uncertainties in mechanism evaluations and provide a reactivity screening tool
- A direct reactivity measurement method was developed in a previous CARB project but was not suitable for coatings VOCs
  - Required GC analysis, so not suitable for complex mixtures or low volatility compounds
- For this project, a total carbon measurement was interfaced to the system to eliminate the need for GC analysis.
- Problems encountered. Absolute direct results not consistent with model predictions; but better agreement with relative results
- Resources for this task exhausted before it could be completed.

# Direct Reactivity Measurements Relative to n-Octane



# Overall Conclusions of Chamber Studies

- Chamber data for Texanol®, butyl carbitol, and primarily alkane petroleum distillates are consistent with SAPRC-99 predictions.
- Chamber data for Aromatics-100 consistent with SAPRC-99 for MIR conditions, but O<sub>3</sub> inhibition at low NO<sub>x</sub> underpredicted.
- Reactivities of at least some synthetic hydrocarbon mixtures may be underpredicted by up to a factor of 2.
- Glycol reactivities underpredicted by ~30% in some experiments, but unclear whether adjustments are appropriate.
- New mechanism developed for benzyl alcohol that simulates chamber data about as well as mechanisms for other aromatics
- Relative secondary PM impacts: benzyl alcohol >> butyl carbitol > petroleum distillates. No measurable PM impacts for others.
- No evidence that humidity and aerosol affects glycol availability at the relatively low aerosol loadings and humidities examined

# Recommendations

- Aromatics mechanisms need to be improved to further reduce uncertainties in reactivity assessments (e.g., glycols)
- Extrapolation of current mechanisms to higher aromatics, such as Aromatics 200, still highly uncertain
- Direct reactivity measurements needed to reduce uncertainties for some VOCs, particularly mixtures of branched alkanes.
- A modified base case experiment that gives better correlations between chamber and atmospheric reactivity would be useful
- No compelling need to change current bin assignments, except perhaps for those with light cycloalkanes and synthetic mixtures. But new procedure will be needed when reactivity scale updated
- Well-characterized environmental chamber data needed to develop predictive secondary PM models. Work needed on background PM characterization in chambers

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