Environmental Chamber Studies of Ozone And PM Impacts of VOCs

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Outline

- VOCs and air quality
- Need for mechanisms to predict atmospheric impacts of VOCs
- Role of environmental chamber data in mechanism development
- Recent mechanism evaluation data with new low-NOx chamber
- Recent chamber data on secondary PM from m-xylene
- Ongoing research

VOCs and Air Quality

- Volatile Organic Compounds (VOCs) enter the atmosphere from a variety of anthropogenic and biogenic sources

- Impacts of VOCs on air quality include:
  - Direct effects (for toxic VOCs very near large sources)
  - Formation of toxic or persistent oxidation products
  - Promotion of ground-level ozone formation
  - Contribution to secondary particle matter (PM) formation

- 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 ozone

- But need to reduce PM has also become a priority. VOC control may also be necessary to reduce secondary PM.

Mechanism of VOCs Impact on 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:

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

$$O(^3P) + O_2 \rightarrow O_3$$

$$O_3 + NO \rightarrow O_2 + NO_2$$

Overall:
$$NO_2 + O_2 \overset{h\nu}{\Leftrightarrow} O_3 + NO$$
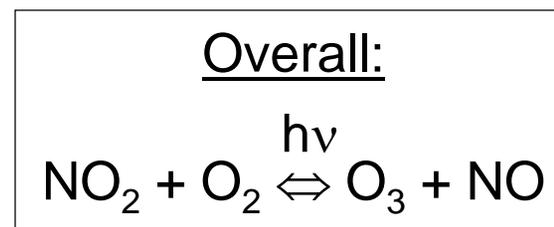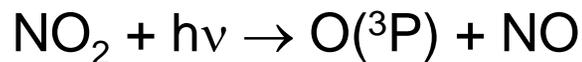
- VOCs promote O_3 by forming radicals that convert NO to NO_2 and shift the photostationary state towards O_3 formation, e.g.:

$$RH + OH \rightarrow H_2O + R$$

$$R + O_2 \rightarrow RO_2\cdot$$

$$RO_2\cdot + NO \rightarrow RO\cdot + NO_2$$

$$RO\cdot \rightarrow \rightarrow HO_2 + \text{other products}$$

$$HO_2 + NO \rightarrow OH + NO_2$$

Overall:
$$\overset{h\nu, NO_x, O_2}{VOC + O_2 \rightarrow \rightarrow \rightarrow O_3 + \text{products}}$$
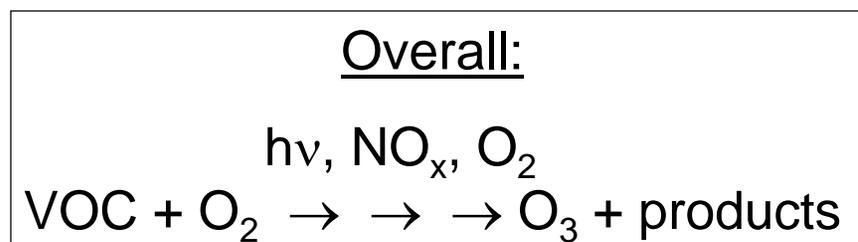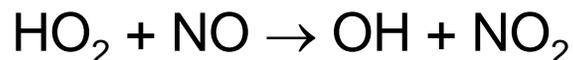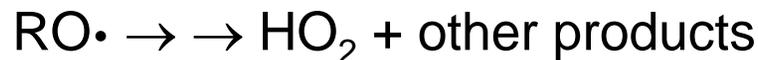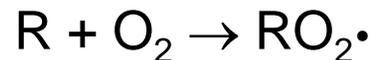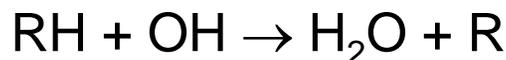
Factors Affecting Impacts of VOCs on O_3

- Ground level O_3 is formed from the reactions of NOx. 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 impacts 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

- Models must take these factors into account to evaluate effective VOC control strategies to reduce O_3.

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 may also vary with atmospheric conditions

- Identity, yields, formation mechanisms, and partitioning coefficients 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.

- Inadequately tested and highly simplified parameterized models are used for predicting effects of emissions on secondary PM

Importance of Environmental Chamber Data to Air Pollution Models

- **Chemical mechanisms** are needed for models to predict secondary pollutants such as O_3 and PM

- Mechanisms in current airshed models have many uncertain estimates, simplifications and approximations

- **Environmental chambers**, simulating atmospheric reactions under controlled conditions, are essential to:
  - Develop predictive mechanisms when basic mechanistic data insufficient.
  - Testing approximations and estimates in mechanisms for almost all VOCs under simulated atmospheric conditions
  - Testing entire mechanisms under the necessary range of conditions

- Results of experiments are influenced by chamber effects, so developing an appropriate chamber effects model is important

Relationship Between Mechanisms, Chamber Data and Airshed Models

Basic kinetic and mechanistic data and theory	**Environmental Chamber Experiments**	Chamber Characterization Data

Mechanism Under Development	Model Simulations of Chamber Experiments	Chamber Effects Model

Evaluated Mechanism	Airshed Model	Airshed Scenario Conditions

Airshed Model Predictions
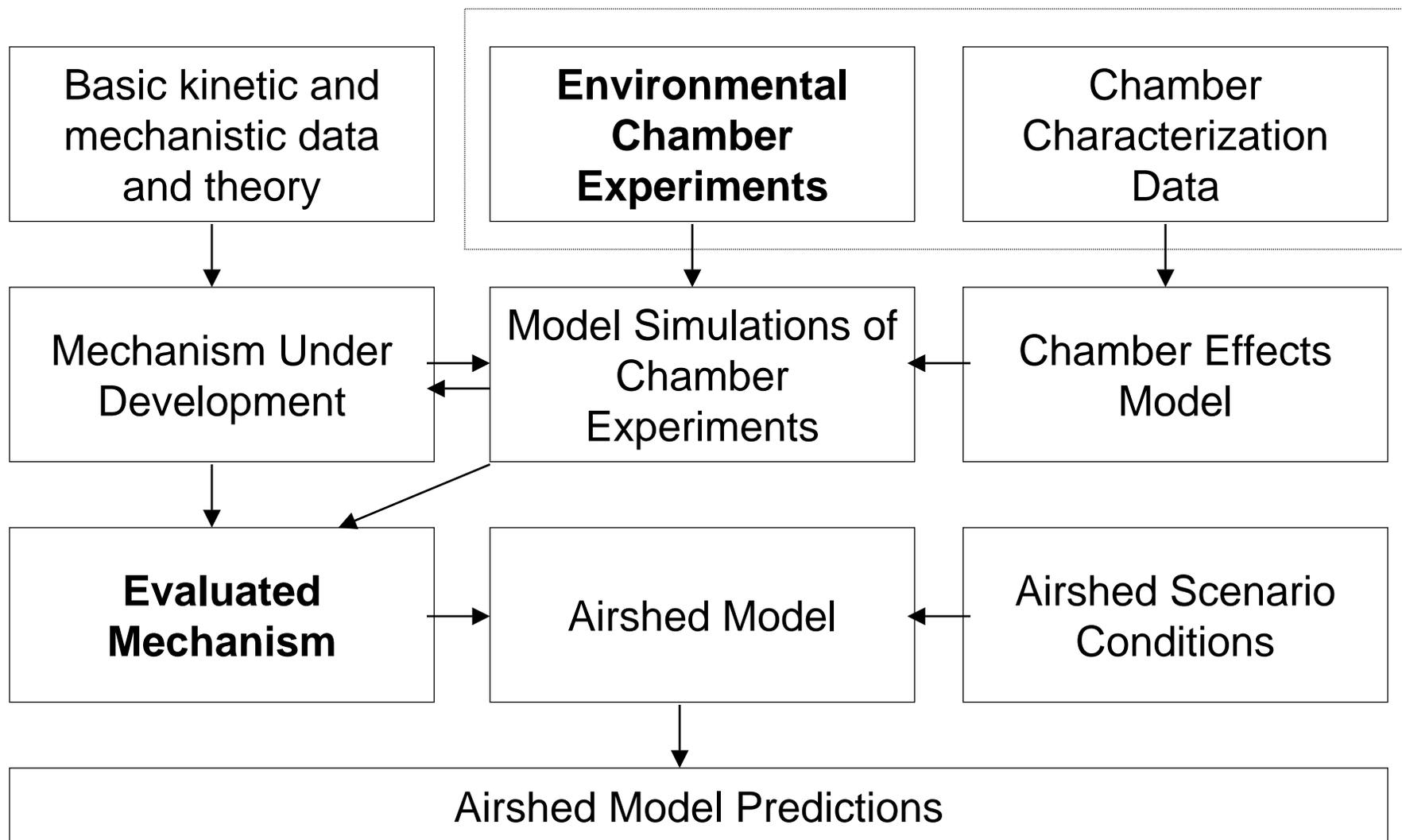
Examples of Chemical Mechanisms for Airshed Models

- Carbon Bond 4 Mechanism (~20 organic model species)
  - Highly condensed. Designed for computational efficiency
  - Developed in the late 80's with some more recent updates
  - Limited testing against older chamber data
  - Widely used in regulatory modeling in the U.S.
  - Not suitable for secondary PM prediction

- European "Master Mechanism" (~4500 organic model species)
  - Highly explicit representation of major reaction routes for ~130 VOCs and their major oxidation products.
  - Development and testing against chamber data ongoing.
  - Used in trajectory models in Europe to estimate relative reactivity factors for VOCs. Too large for grid models
  - Being adapted for secondary PM prediction

Examples of Chemical Mechanisms
for Airshed Models (cont'd)

- SAPRC-99 Mechanism (~60 to ~600 organic model species)

  - Can separately represent reactions of >550 types of VOCs. Condensed representation of oxidation products

  - Developed in late '90's and comprehensively evaluated against then-available chamber data

  - "Lumped" version widely used for research and some regulatory modeling in the U.S.

  - Versions with selected VOCs represented explicitly used for calculating VOC reactivity scales for O_3

  - Not designed for secondary PM prediction, but some modeling groups have adapted it for this purpose

  - Evaluation against newer chamber data ongoing.

  - Updated version under development

Chamber Data Base Used when Developing and Evaluating the SAPRC-99 Mechanism

| Type of Experiment	No. of Runs	No. of VOCs	NO$_x$ Range (ppb)
Chamber Characterization	76		0 - 660
Single VOC - NO$_x$	481	37	100 - 1000
VOC Mixture - NO$_x$	117		80 - 1000
Incremental Reactivity (effect of adding VOC to Surrogate - NO$_x$)	447	84	100 - 550
Base Case for Incremental Reactivity Reactivity	556		100 - 550

Measure of Model Performance for Ozone

Model performance for simulating both ozone formation and NO oxidation is measured by ability to predict $\Delta([O_3]-[NO])$:

$$\Delta([O_3]-[NO]) = ([O_3]-[NO])_{FINAL} - ([O_3]-[NO])_{INITIAL}$$

Legend:
- $\Delta([O_3]-[NO])$
- O3
- NO

Concentration (y-axis)

Time (x-axis)

This gives a useful measure for both high NO and high O_3 conditions

Measures initial NO oxidation rate

Measures O_3 formation once NO is consumed
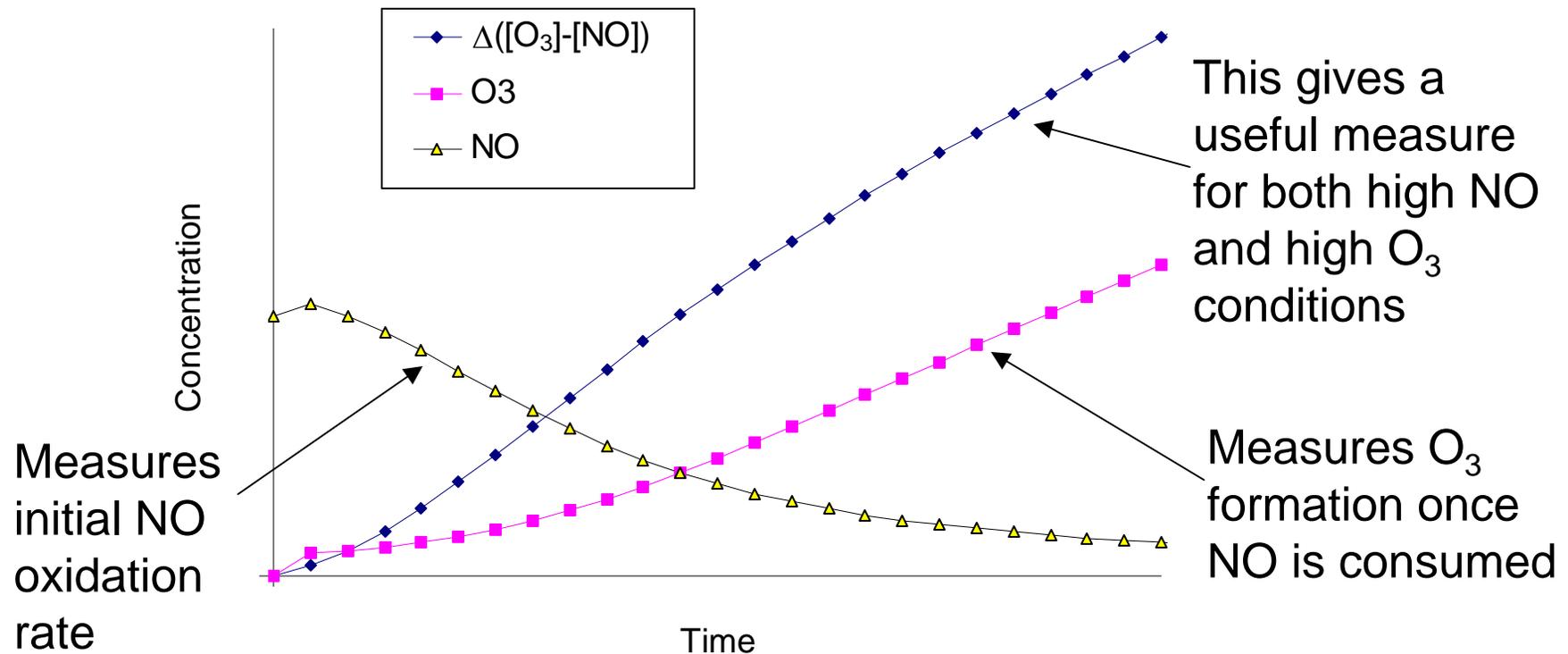
Distribution of Model Errors for $\Delta([O_3]-[NO])$ in the Initial SAPRC-99 Evaluation
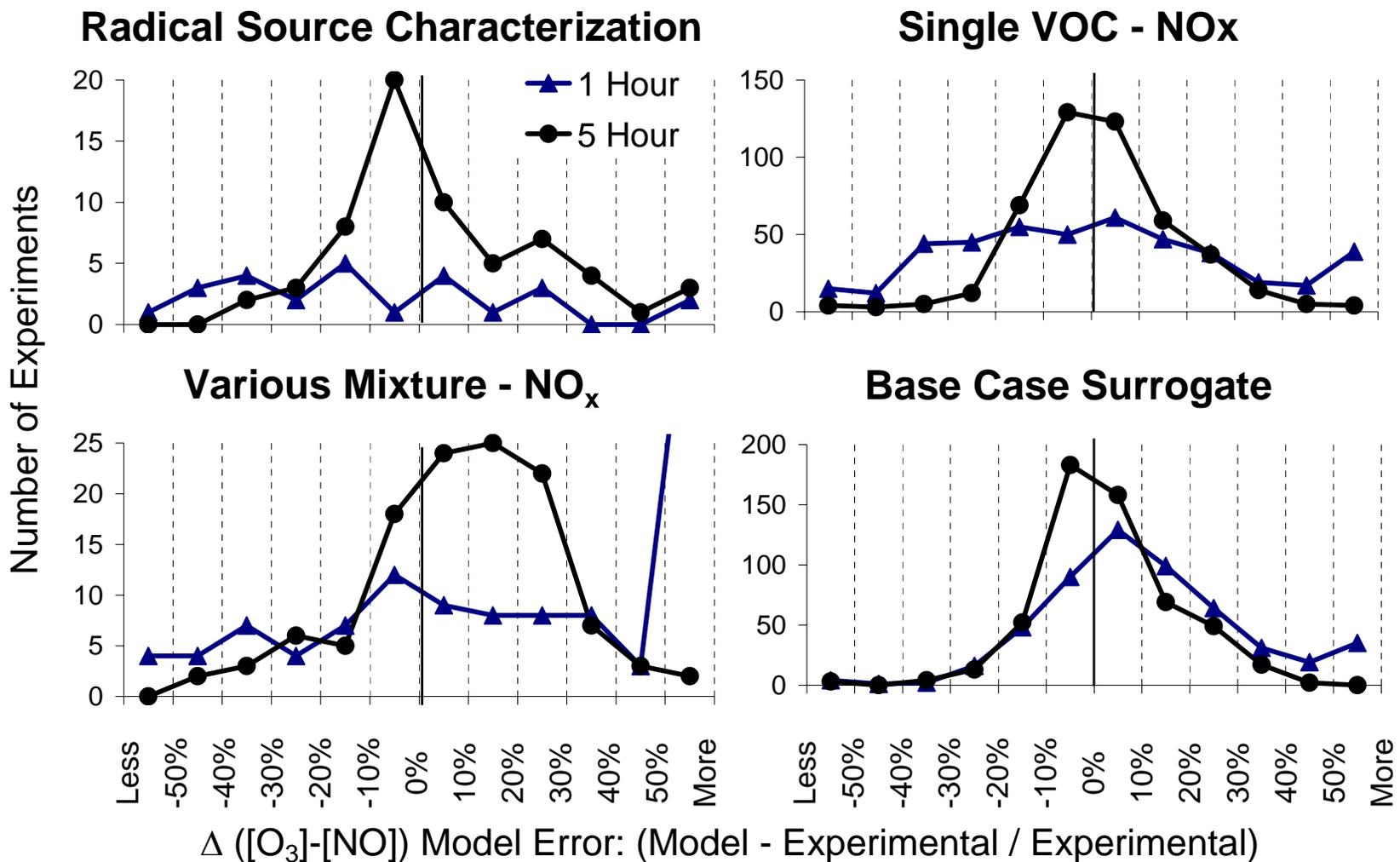
Need for Improved Chamber Facility for Mechanism Evaluation

- Because of chamber effects and analytical limitations, most mechanism evaluation experiments conducted at higher pollutant levels than ambient.

- Large volume chambers are needed to reduce chamber effects and allow equipment with high sampling rates. But large outdoor chambers are difficult to control and characterize

- Most chambers are not suitable to test predictions on how temperature affects O_3 and PM formation.

- Most U.S. chambers lack the analytical instrumentation needed to monitor many important trace species

- **The new UCR EPA Chamber was developed to address these needs**

Characteristics of New UCR EPA Chamber

- Indoor chamber design used for maximum control and characterization of conditions

- Dual reactor design for experimental productivity and to simplify reactivity assessment

- Largest practical volume for indoors (two ~100,000-L reactors)

- 200 KW filtered argon arc solar simulator

- Replaceable Teflon reactors in "clean room" to minimize background

- Positive pressure reactor volume control to minimize dilution and minimize contamination

- Temperature controlled to ±1°C in ~5°C to ~50°C range.

- Improved array of analytical instrumentation and provision for additional instrumentation in the future

Diagram of UCR EPA Chamber

2 Banks of Blacklights

200 KW Arc Light

Two air Handlers are located in the corners on each side of the light (not shown).

20 ft.

This volume kept clear to maintain light uniformity

Dual Teflon Reactors

Movable top frame allows reactors to collapse under pressure control

Mixing System Under floor of reactors

Floor Frame

20 ft.

20 ft.

Temperature controlled room flushed with purified air and with reflective material on all inner surfaces

Access Door

SEMS (PM) Instrument

Gas sample lines to laboratory below

Diagram of Reactor and Framework
(One of Two)

Ceiling

Cable

Takeup Drum

Pulleys

Shaft Supports

Motor

Shaft

Upper Frame

Light Source

~ 90,000 Liters Maximum Volume

Wall

Ports for Mixing, Low Volatility Injection and Exchange System

Teflon Film

Access Hatch and Sampling Port Holder

Lower Frame

Enclosure Floor

Supports
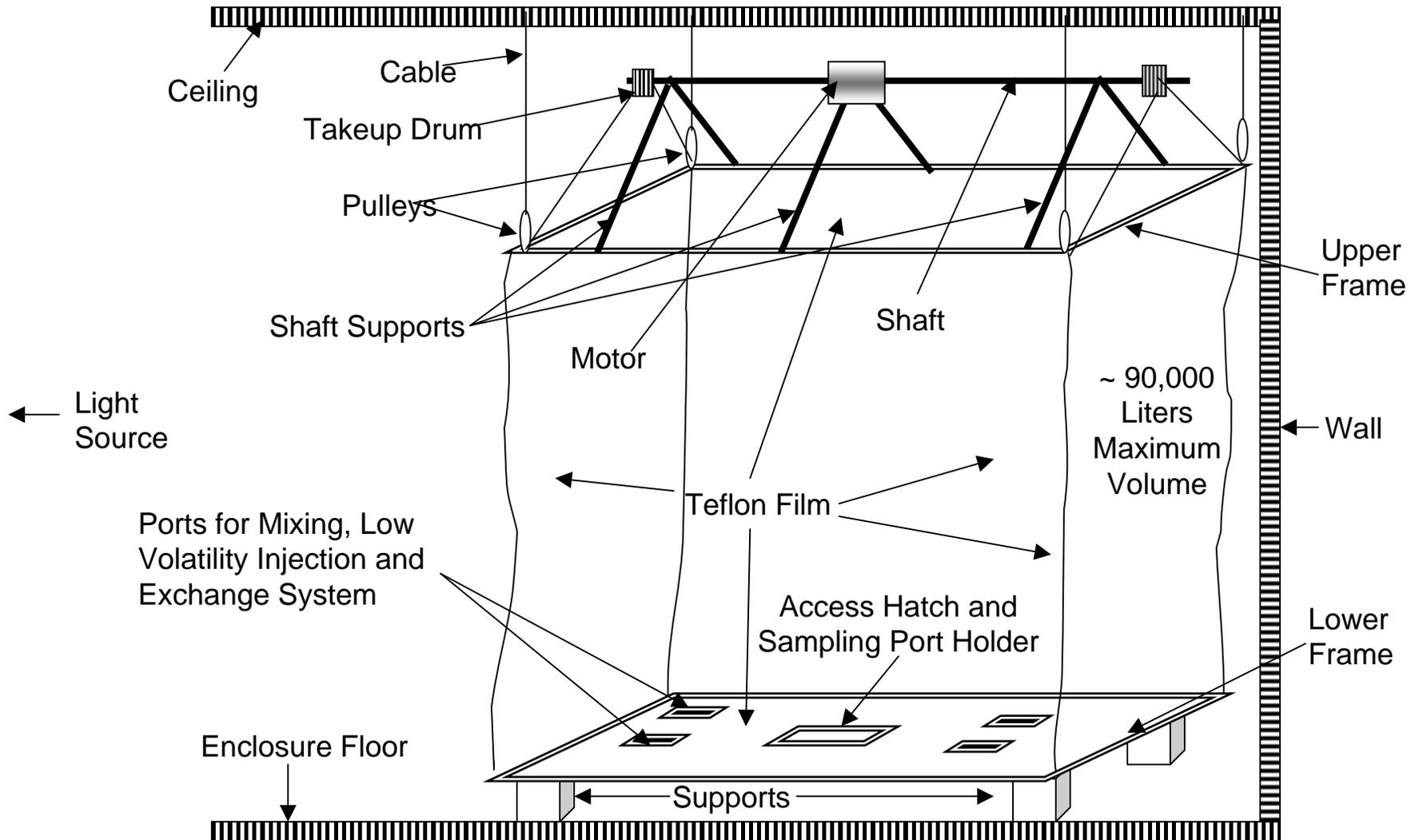
Photographs of Chamber and Lights

Looking Towards Reactors (from light)
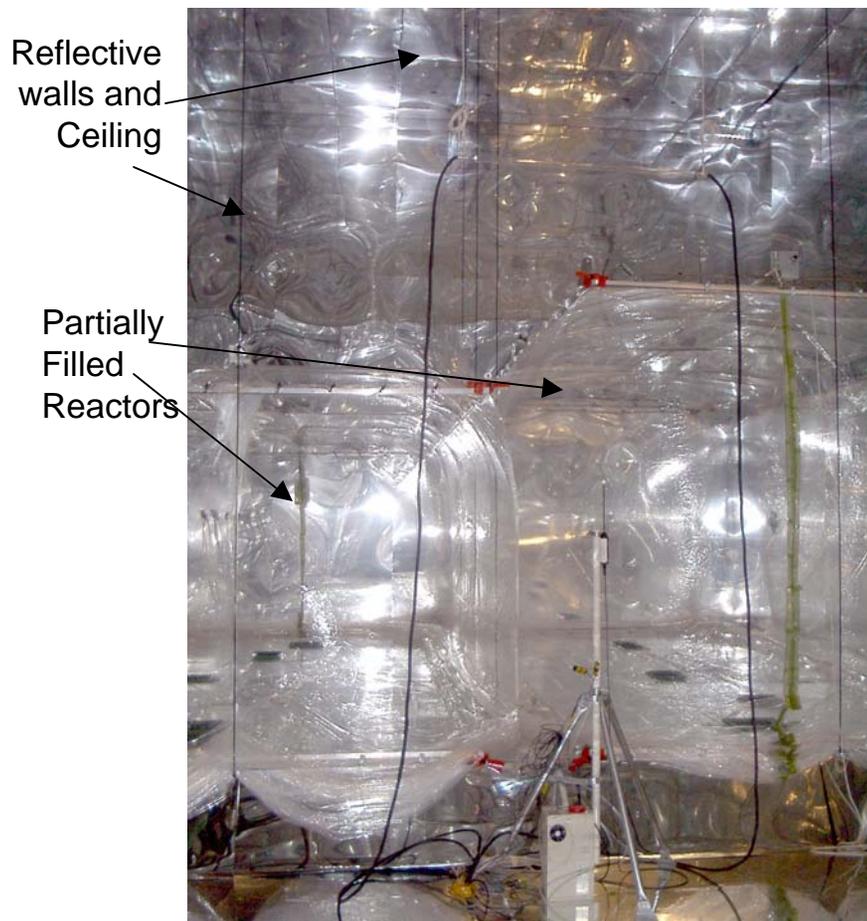
Looking Towards Lights and Air Inlet

Reflective walls and Ceiling

Partially Filled Reactors

Black Lights

Arc Light

Reflective walls

Air Intake
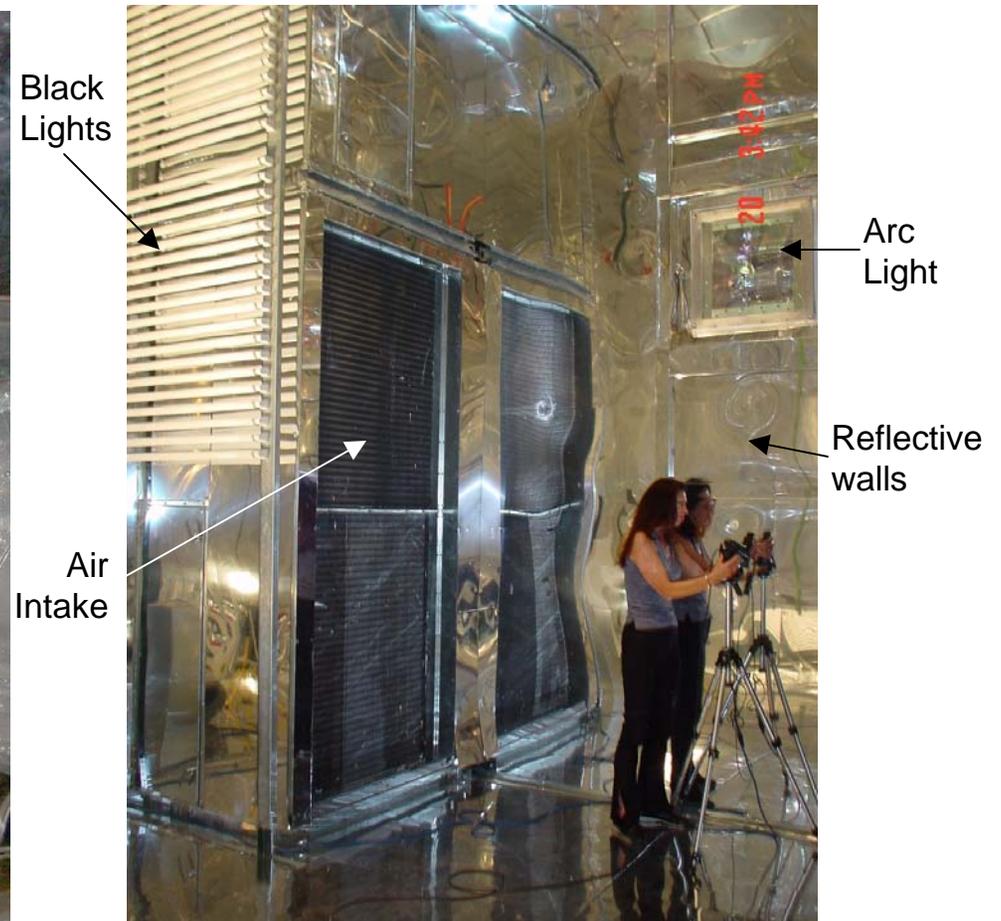
Light Source and Spectrum
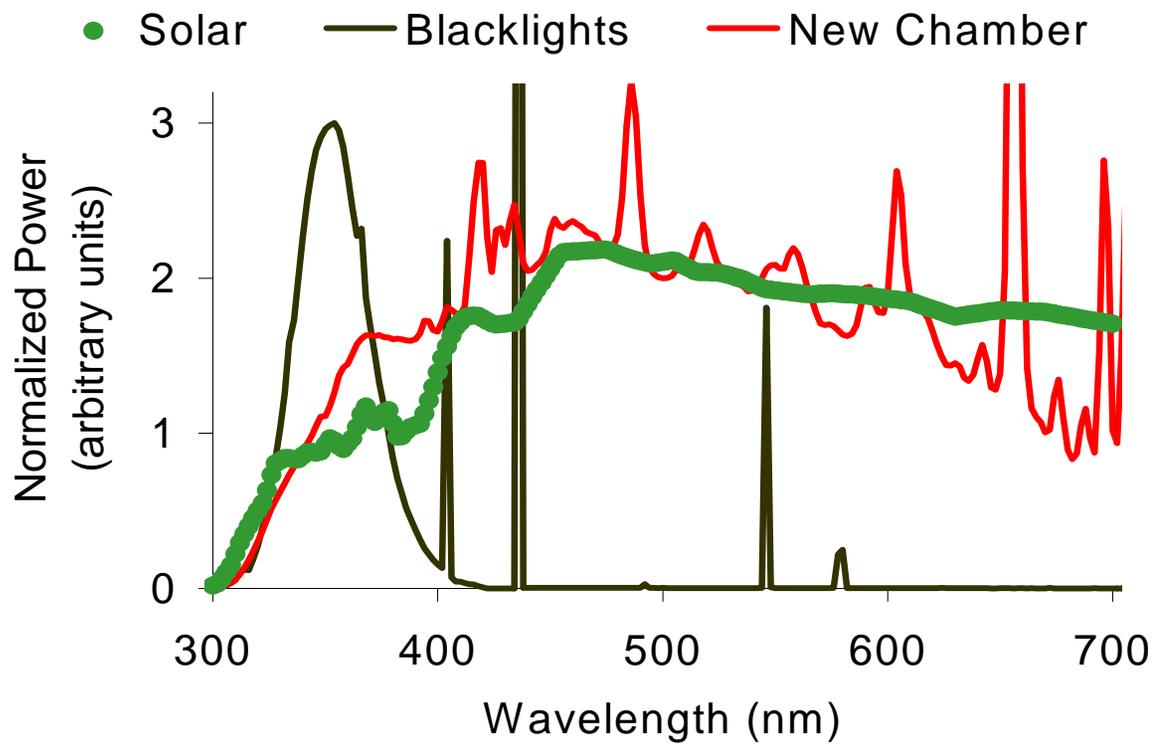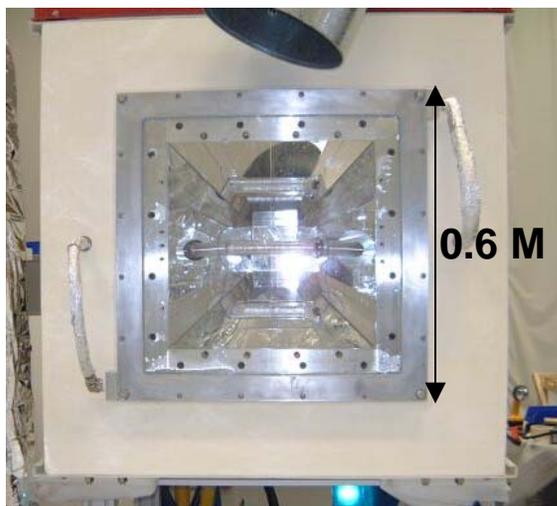
Summary of Characterization Results

- Contamination or dilution by enclosure air is negligible when run on positive pressure control. (Volume decreases as sample is withdrawn)

- Light intensity with argon arc lamp at 80% recommended maximum power gives NO_2 photolysis rate of 0.26 min^{-1}

- Characterization results indicate chamber effects are comparable or lower than in other Teflon film chambers

- Good side equivalency in gas-phase results obtained when the same experiment is simultaneously run in the two reactors (except for some NO_x offgasing-sensitive runs)

- Some background PM formation observed in one of the two reactors before it was replaced, but reproducible results obtained when >10 μg/m^3 PM formed.

# Radical or NO$_x$ Offgasing Rates Derived for Various Chambers
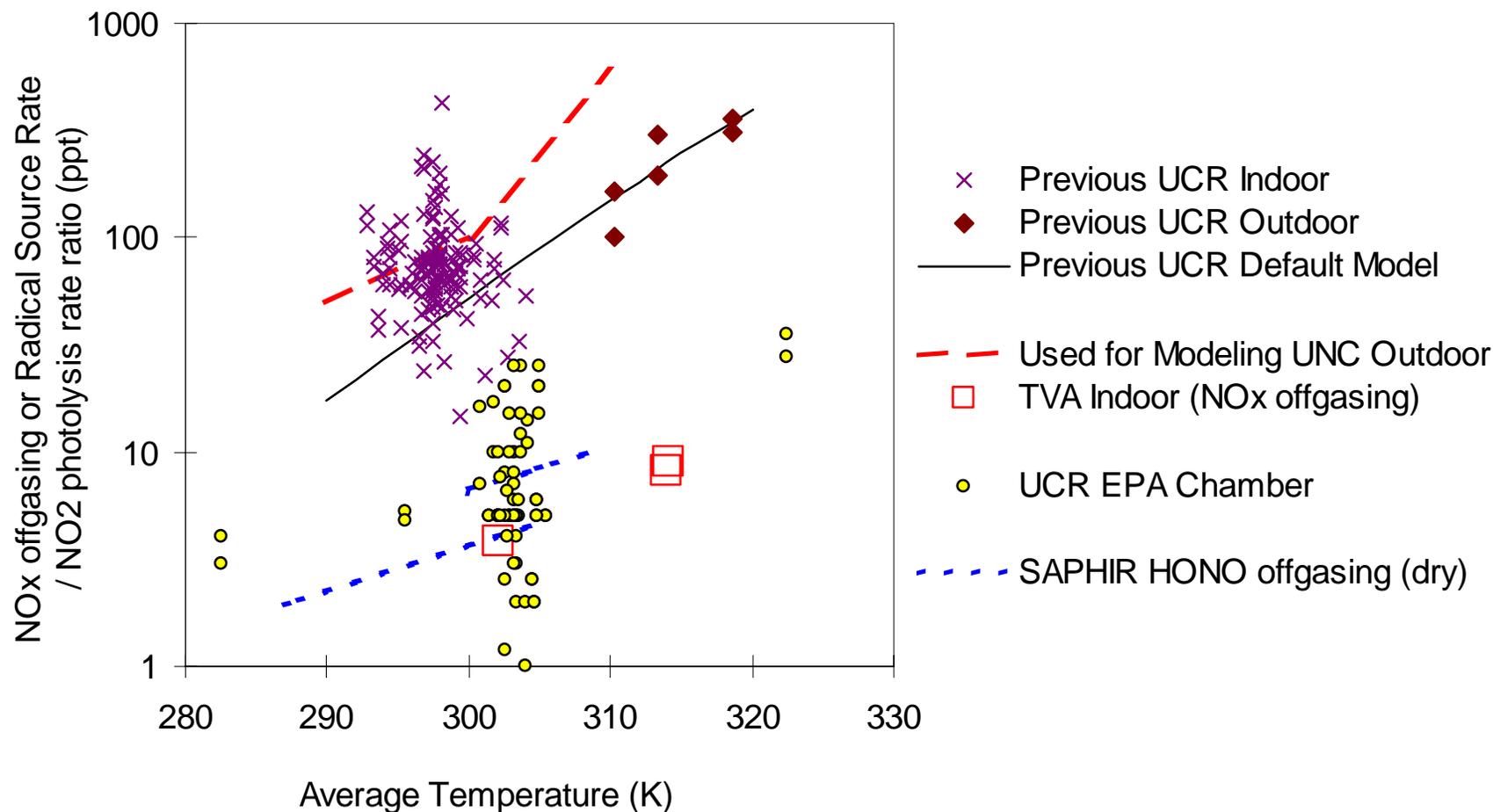
Initial Evaluation Experiments in New Chamber

Run Type	Runs	NO_x Range (ppb)	VOC Range (ppm)
Characterization	32	0 - 200	Varied
Formaldehyde - NO_x	2	8 - 25	0.35 – 0.50
Formaldehyde - CO - NO_x	2	15-20	HCHO: 0.4 – 0.5 CO: 15 - 80
Ethene - NO_x	2	10 - 25	~0.6
Propene - NO_x	2	5 - 25	0.4 – 0.5
Toluene or m-Xylene - NO_x	4	5 - 25	Toluene: 0.6 – 0.16 Xylene: 0.18
Aromatic - NO_x + CO	6	5 - 30	CO: 25 - 50
Ambient Surrogate - NO_x	61	2 - 315	0.2 – 4.2 ppmC

Model Errors in Simulating $\Delta([O_3]\text{-}[NO])$ in the Initial Evaluation Experiments

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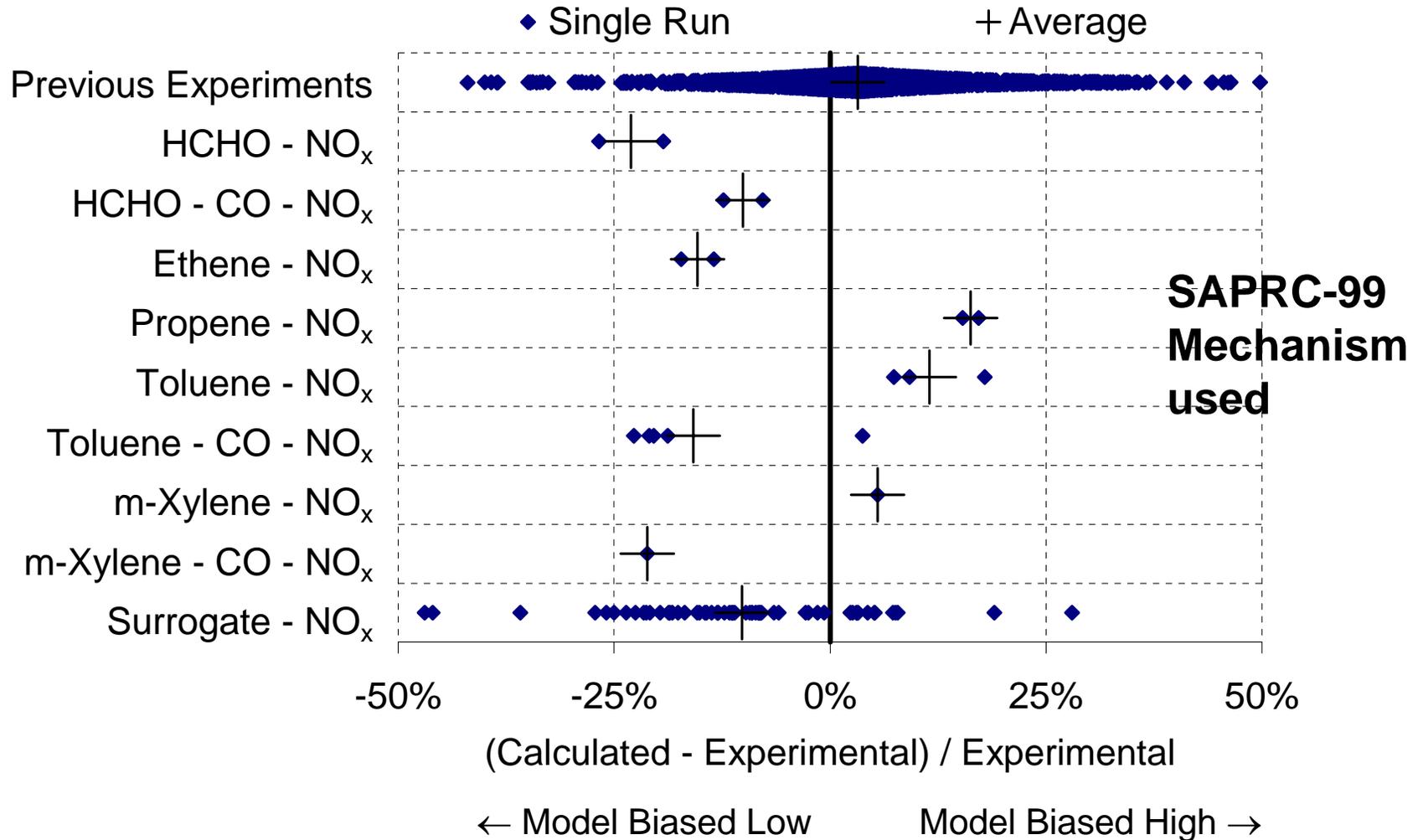
Matrix of ROG Surrogate – NO$_x$ Experiments in the UCR EPA Chamber
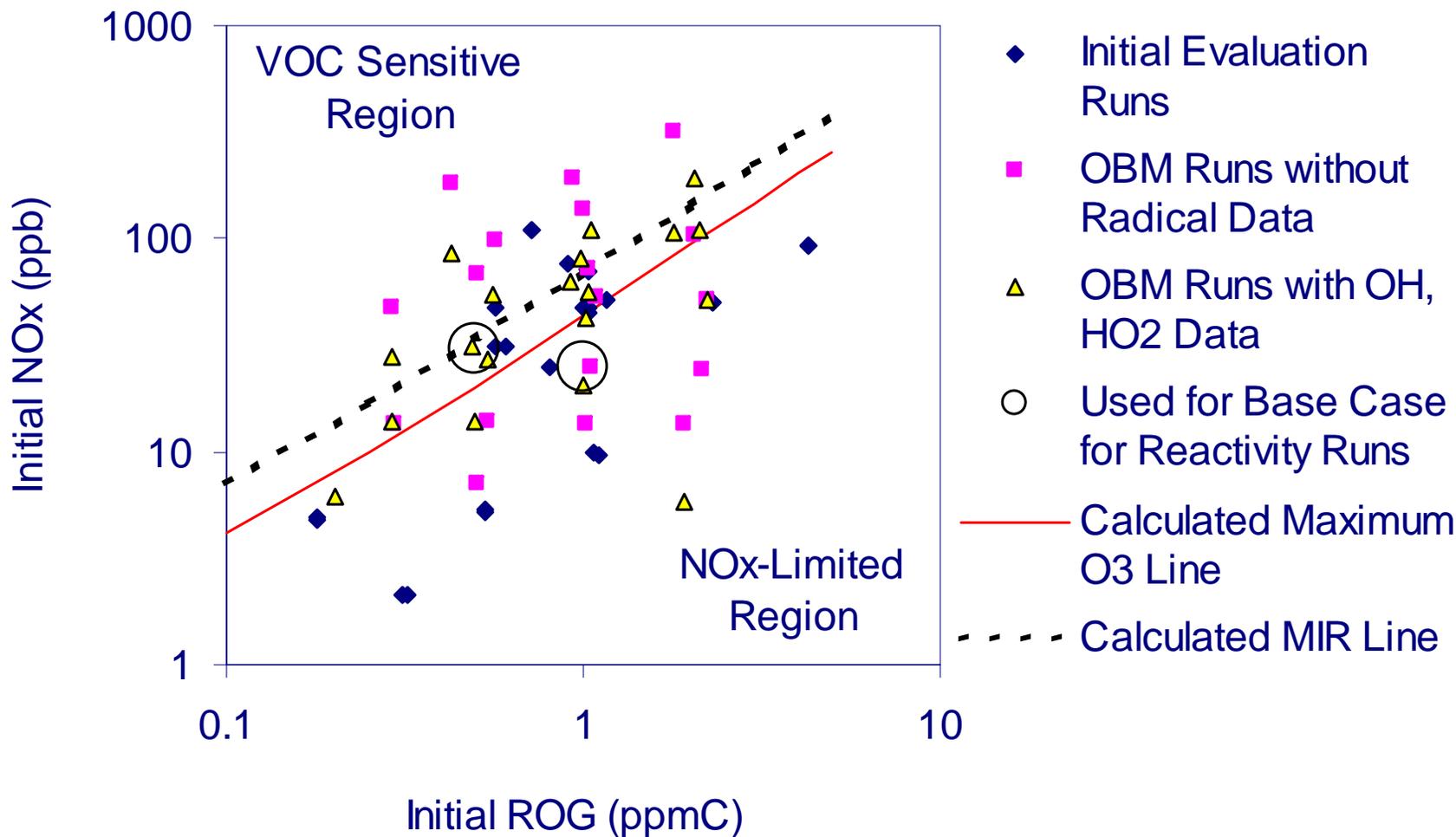
Lowest NO$_x$ Surrogate Experiment
(ROG surrogate = 300 ppbC, NOx = 2 ppb)

◆ Experimental ——— Standard Model
- - - - No HONO Offgasing —·— Maximum HONO Offgasing

Concentration (ppm) vs Time (minutes)
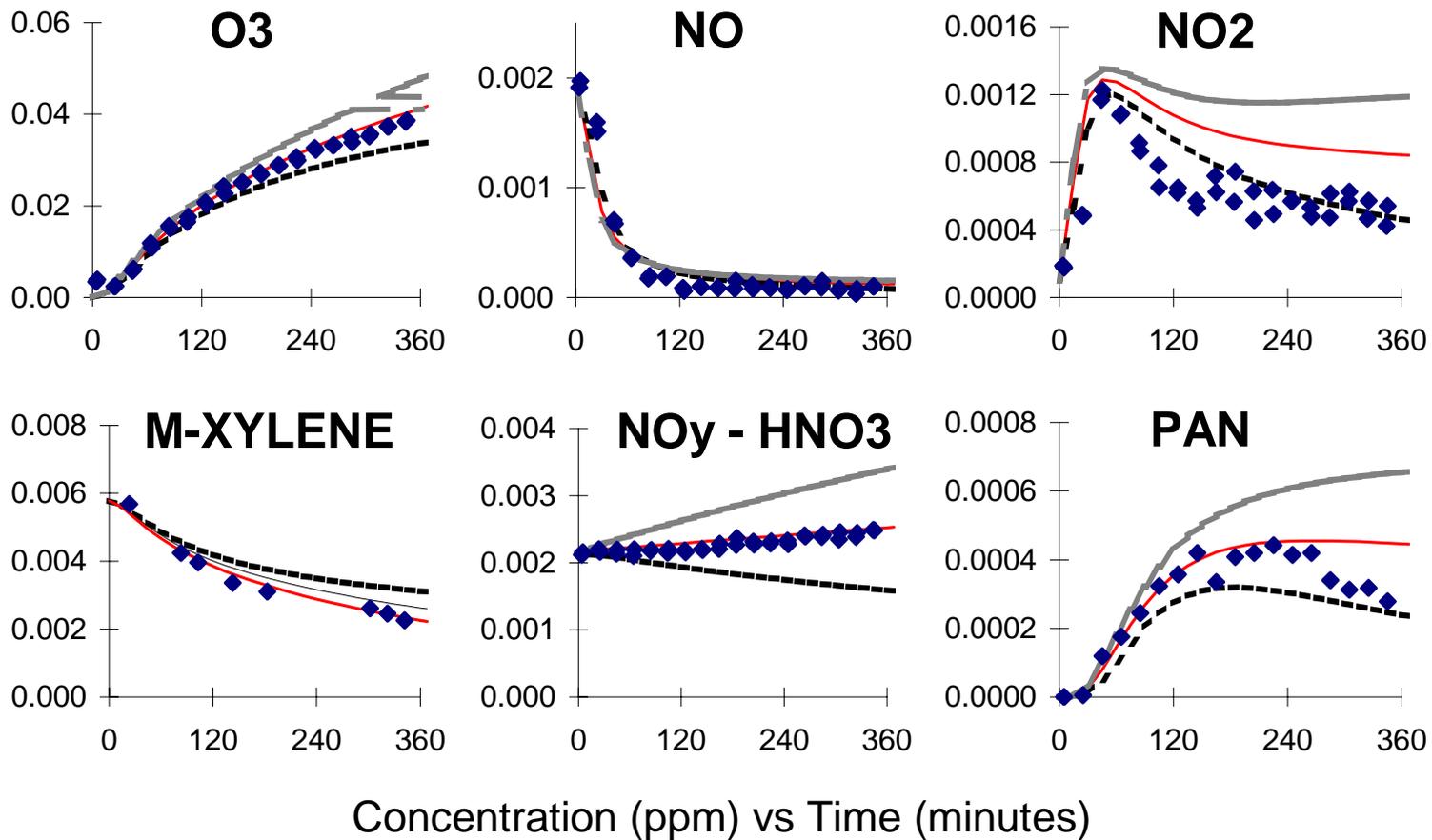
Representative Data from a
Radical Measurement Experiment
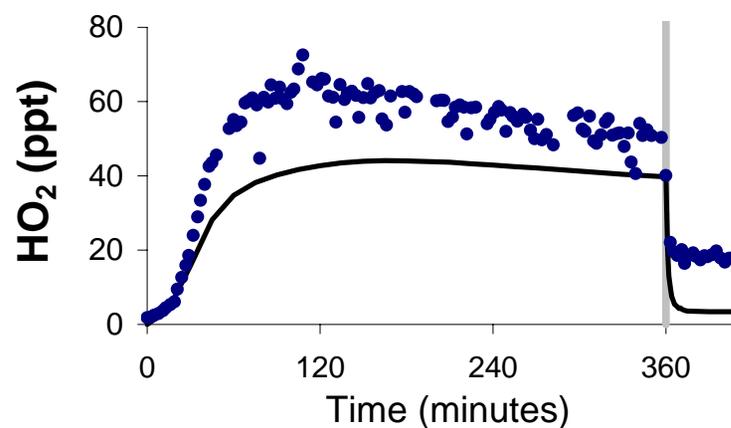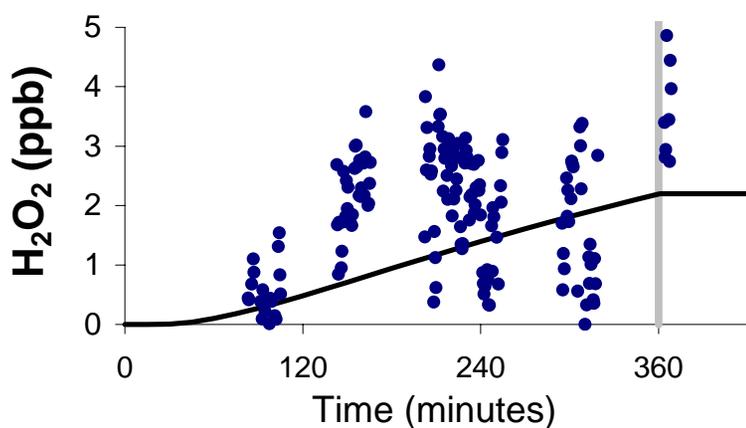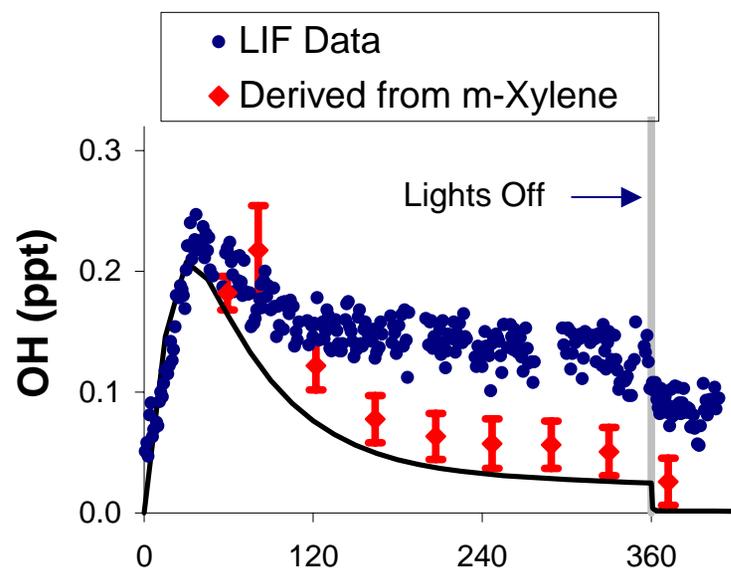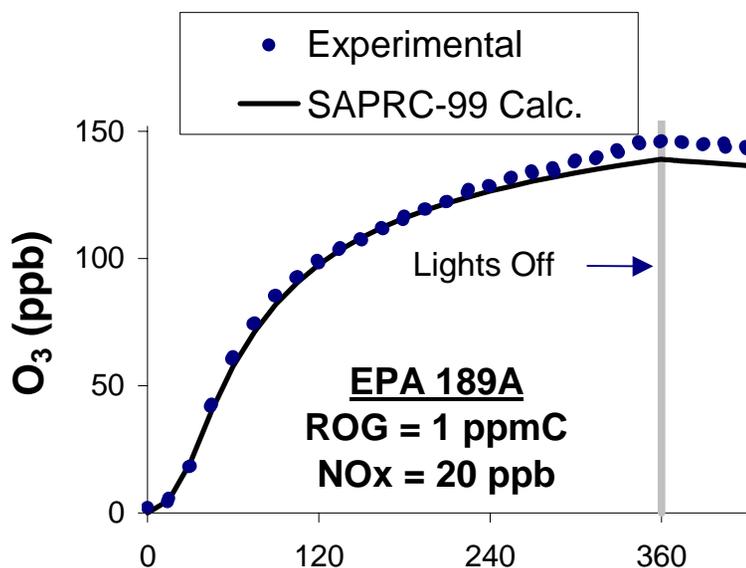
# Model Errors in Simulating $\Delta([O_3]-[NO])$ in the Initial Evaluation Experiments
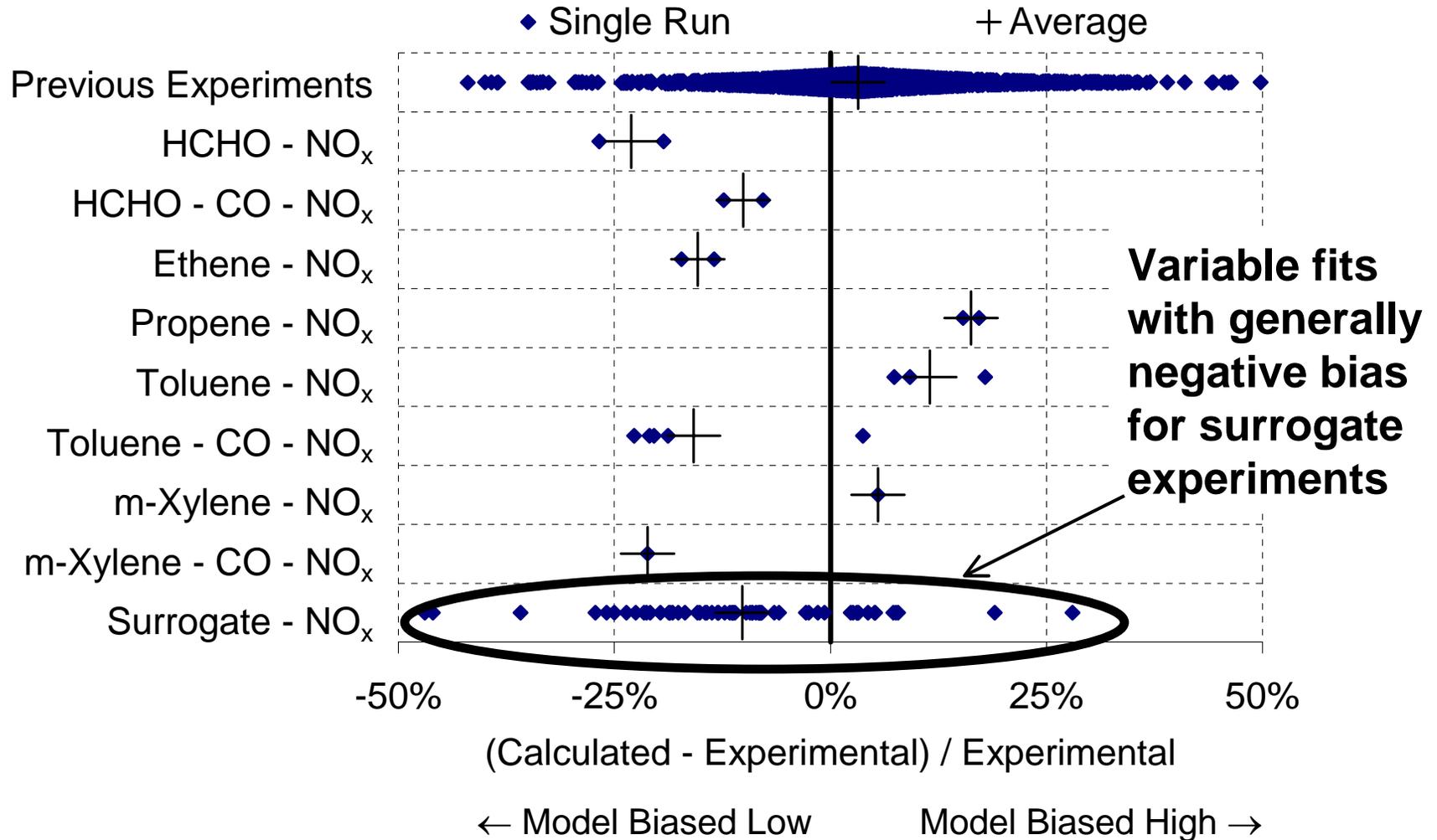
♦ Single Run   + Average

Previous Experiments
HCHO - NO_x
HCHO - CO - NO_x
Ethene - NO_x
Propene - NO_x
Toluene - NO_x
Toluene - CO - NO_x
m-Xylene - NO_x
m-Xylene - CO - NO_x
Surrogate - NO_x

Variable fits with generally negative bias for surrogate experiments

-50%   -25%   0%   25%   50%

(Calculated - Experimental) / Experimental

← Model Biased Low   Model Biased High →

Model Underprediction Errors for Surrogate - NO$_x$ Experiments

◆ SAPRC-99 (Range gives low and high Walls->HONO)

Model Underprediction Errors for Surrogate - NO$_x$ Experiments

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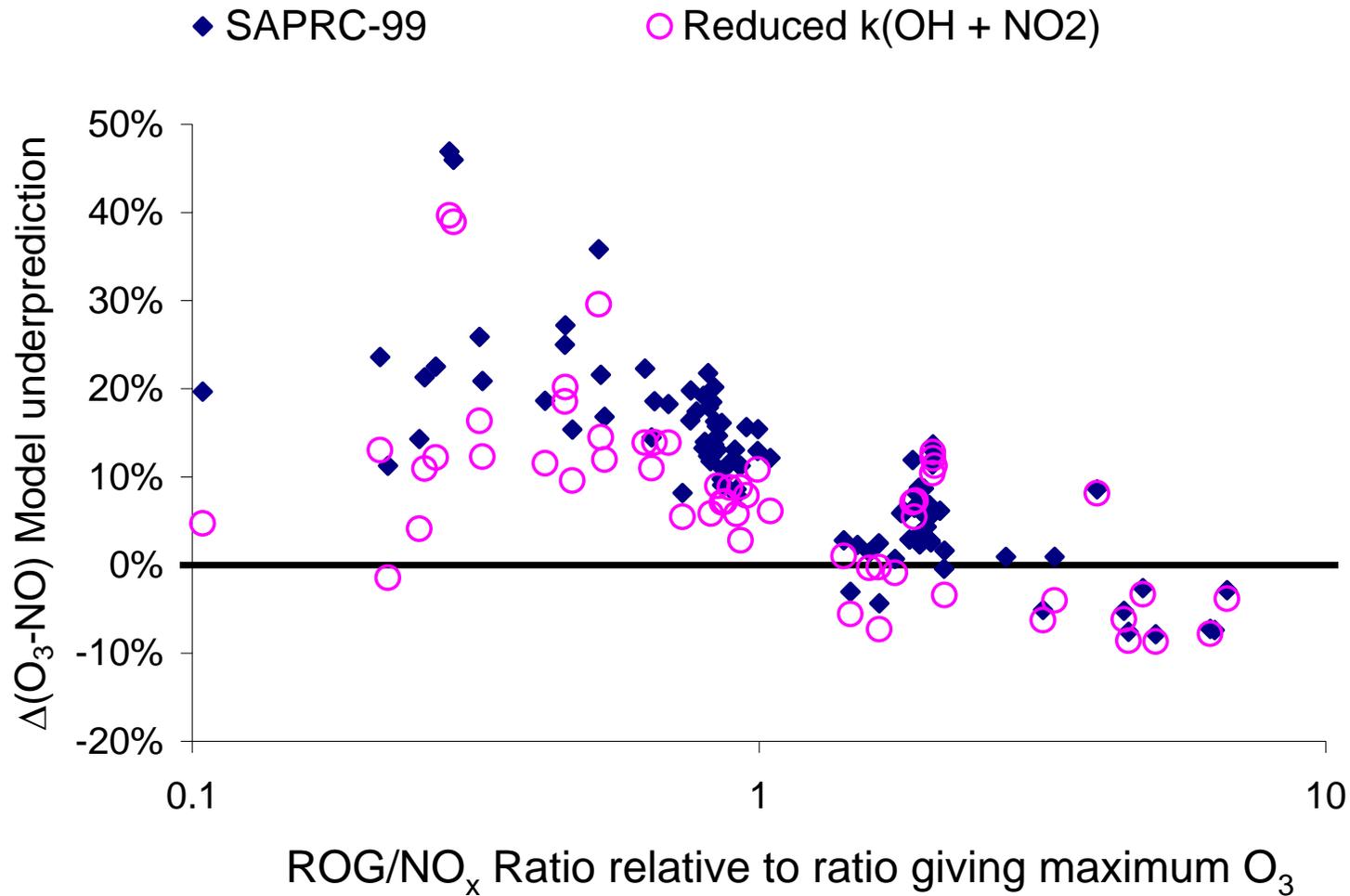
Model Underprediction Errors for Surrogate - NO$_x$ Experiments: SAPRC-99 vs Carbon Bond 4
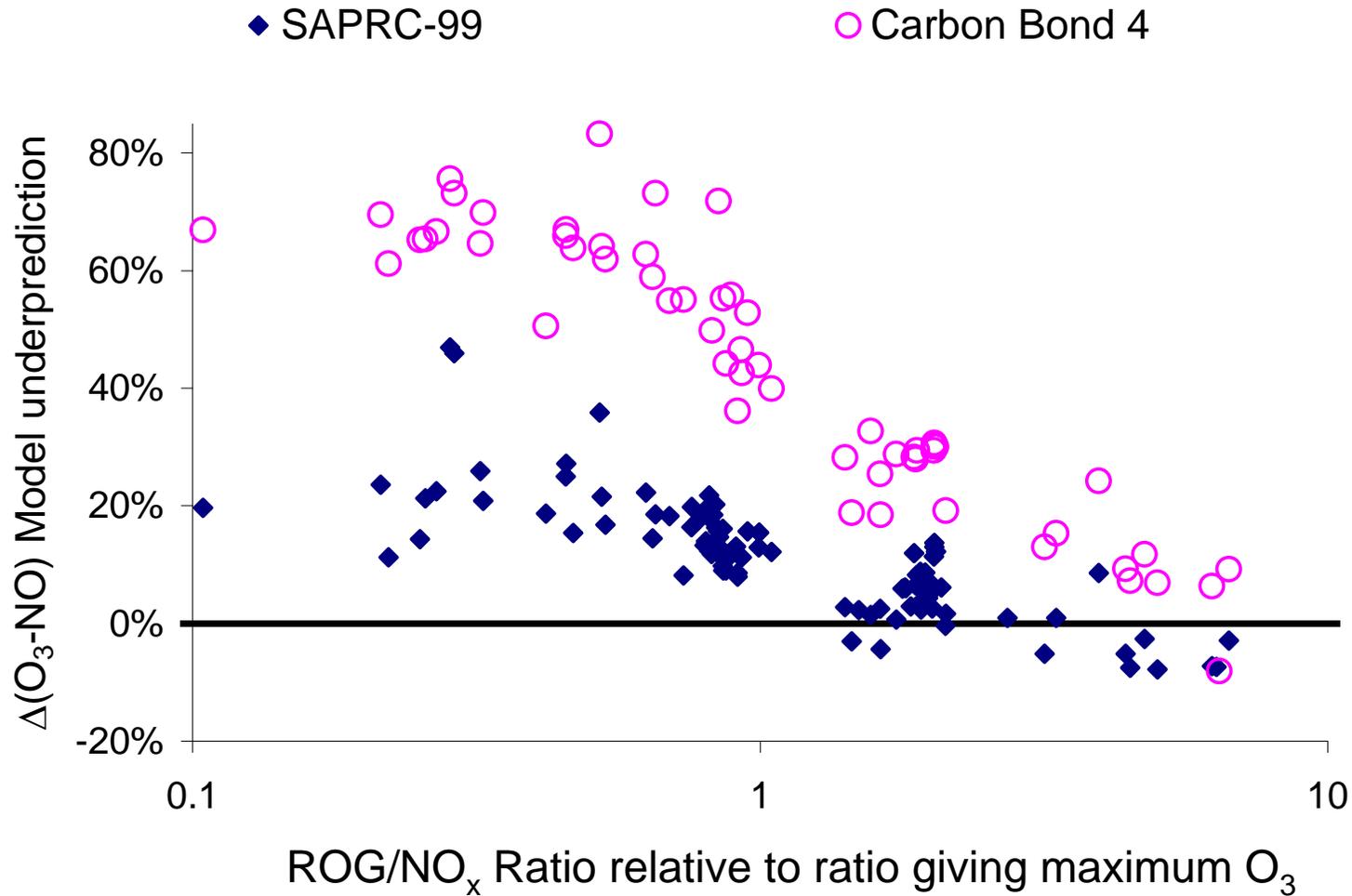
SAPRC-99 Model Underprediction Errors for Mixture and Surrogate - NO$_x$ Experiments

◆ Full Surrogate (includes m-xylene and toluene)

○ Non-Aromatic Surrogate (Range gives low, high Walls->HONO)

Y-axis: $\Delta(O_3\text{-}NO)$ Model underprediction

X-axis: ROG/NO$_x$ Ratio relative to ratio giving maximum O$_3$
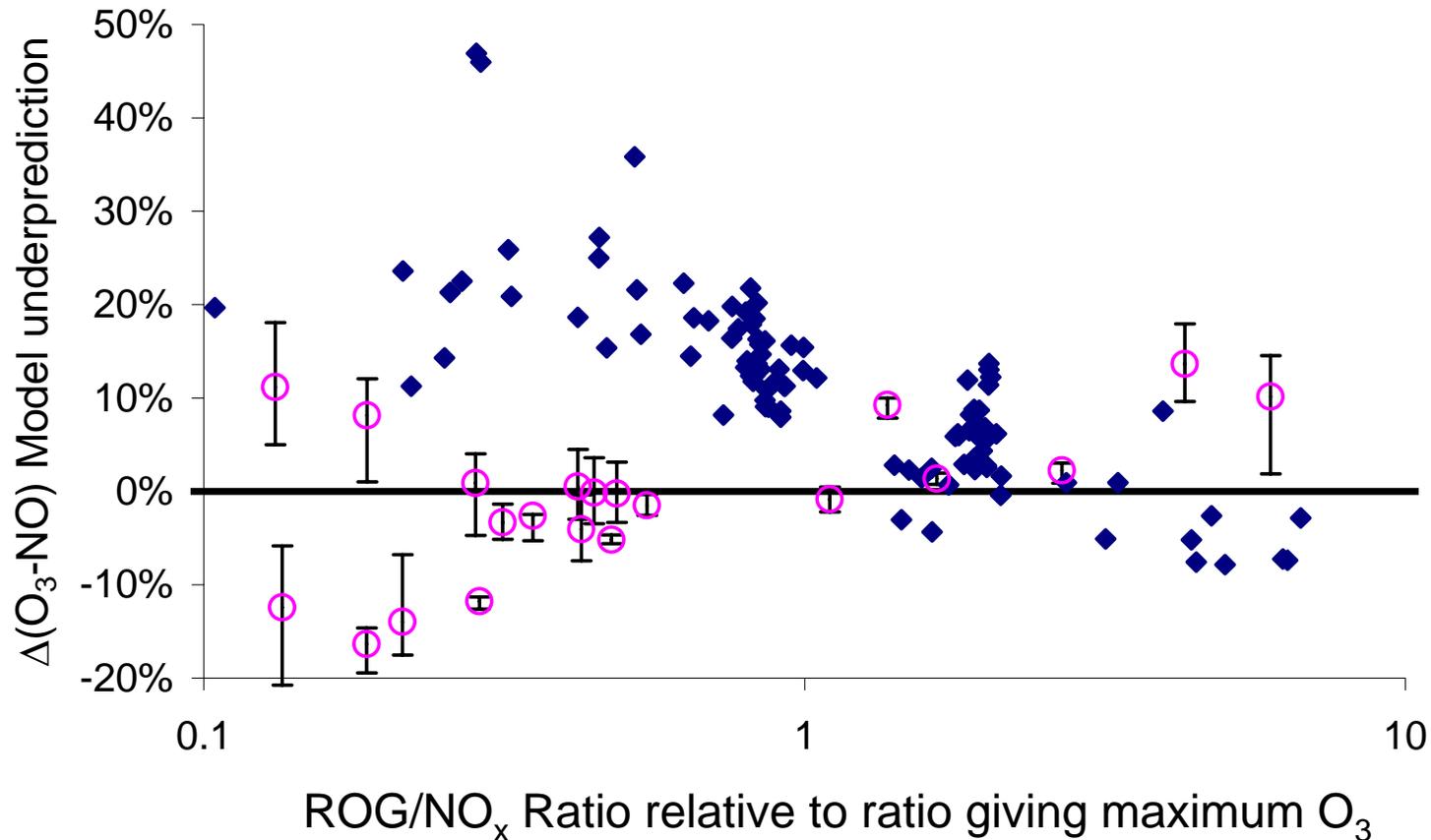
Uncertainties in Aromatics Mechanisms

- Major atmospheric reactions of aromatics involve OH adding to the ring, followed by various ring fragmentation processes

- Despite considerable study, details of ring fragmentation process is unknown. Less than half of the product mass has been identified and quantified

- In order for model to simulate chamber data, it is necessary to derive parameterized mechanisms with following characteristics:
  - Some uncharacterized products are highly photoreactive
  - Photoreactive product yields and photolysis rates adjusted for model to predict O_3 in aromatics - NO_x experiments

- Evidence for compensating errors between numbers of NO to NO_2 conversions and radical input rates

Measurement of Direct Reactivity

- Direct reactivity is the number of NO to NO2 conversions caused by a VOC's reactions

- A HONO + VOC photolysis flow system was developed to give a measurement sensitive to direct reactivity

- Initial experiments indicate SAPRC-99 overpredicts direct reactivities of aromatics by up to a factor of 2


Direct Reactivity Measurement / kOH
(Relative to Ethane = 2)
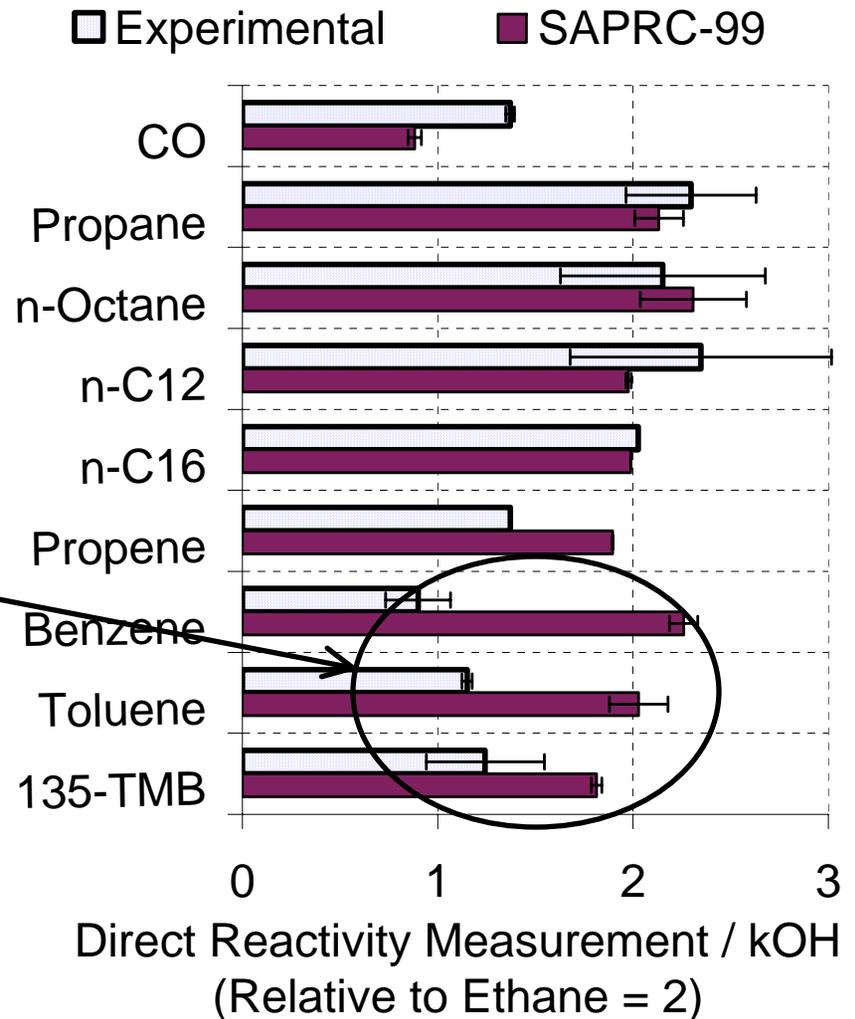
Effect of CO in Aromatic - NO$_x$ Runs

Toluene

Ozone

Ozone Change (effect of CO)

EPA077 (~25 ppb NOx)

m-Xylene

Ozone

Ozone Change (effect of CO)

EPA067 (~20 ppb NOx)

EPA066 (~5 ppb NOx)

□ **Aromatic - NOx experiment**

◆ **Aromatic - CO - NOx experiment**

- - - **Aromatic - NOx model**

—— **Aromatic - CO - NOx model**
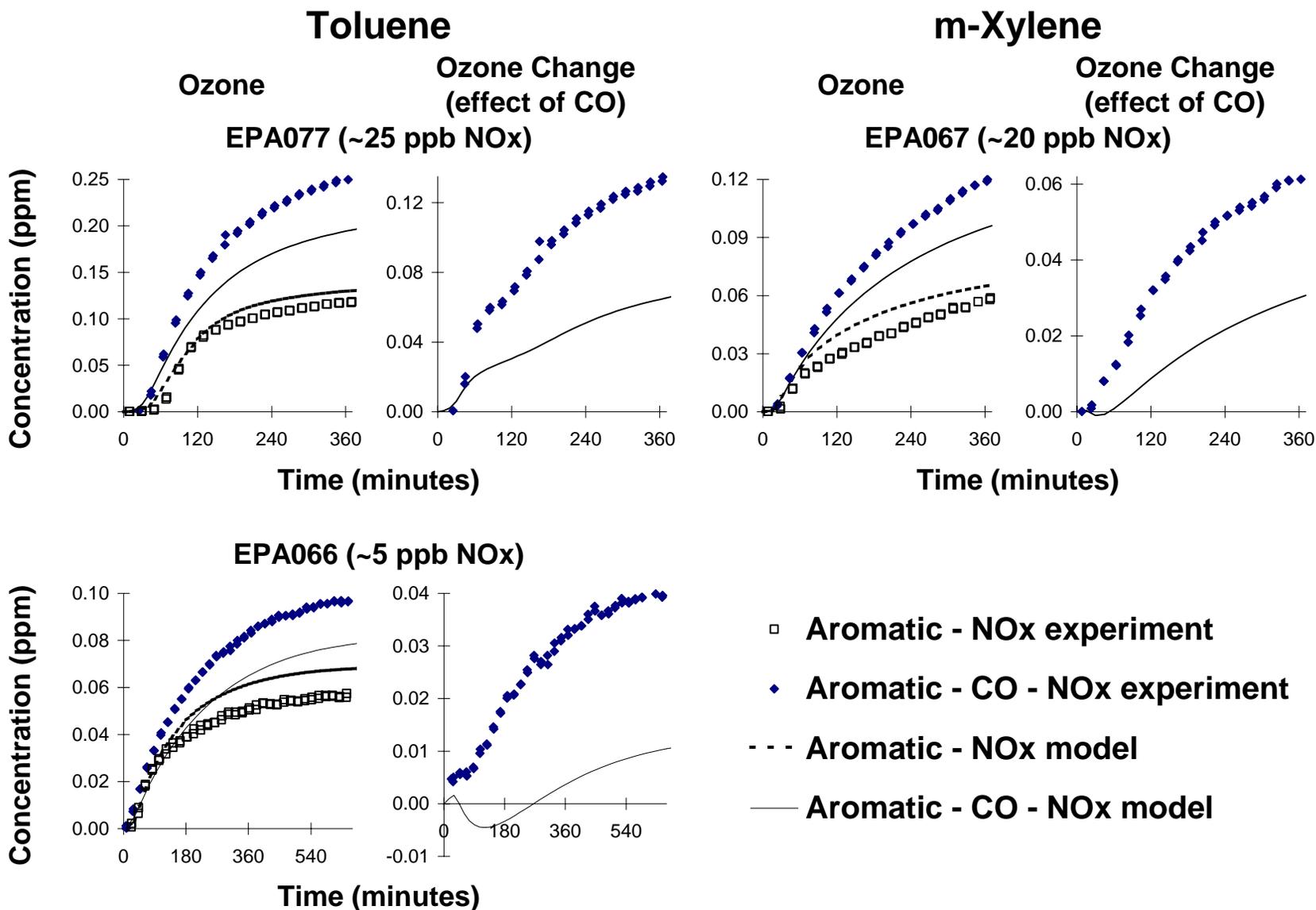
Effects Of Adjustments to Parameterized Toluene Mechanism

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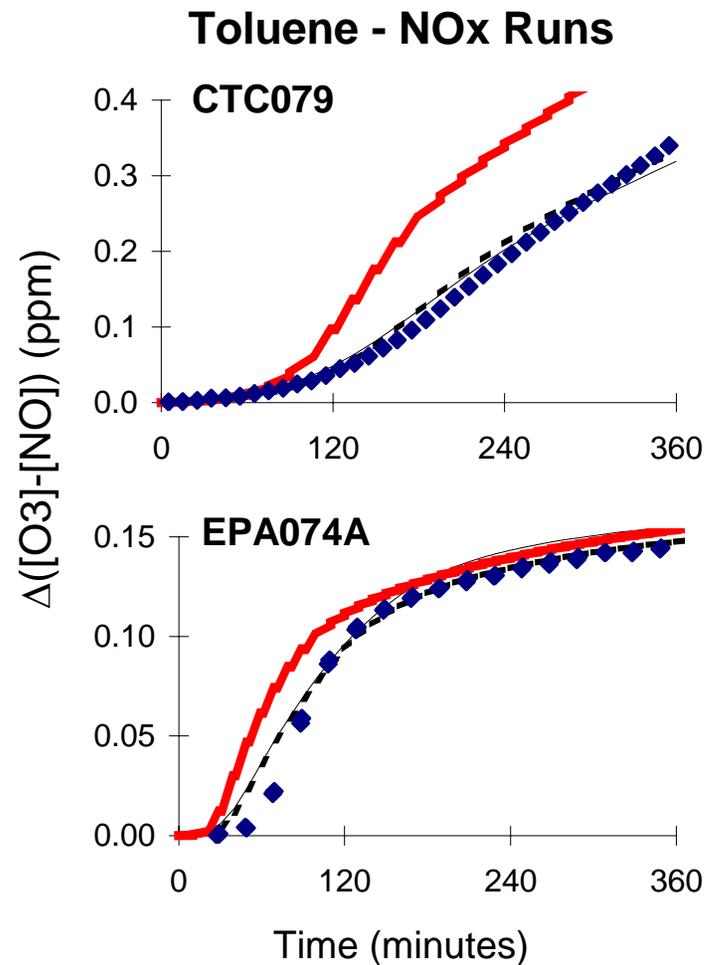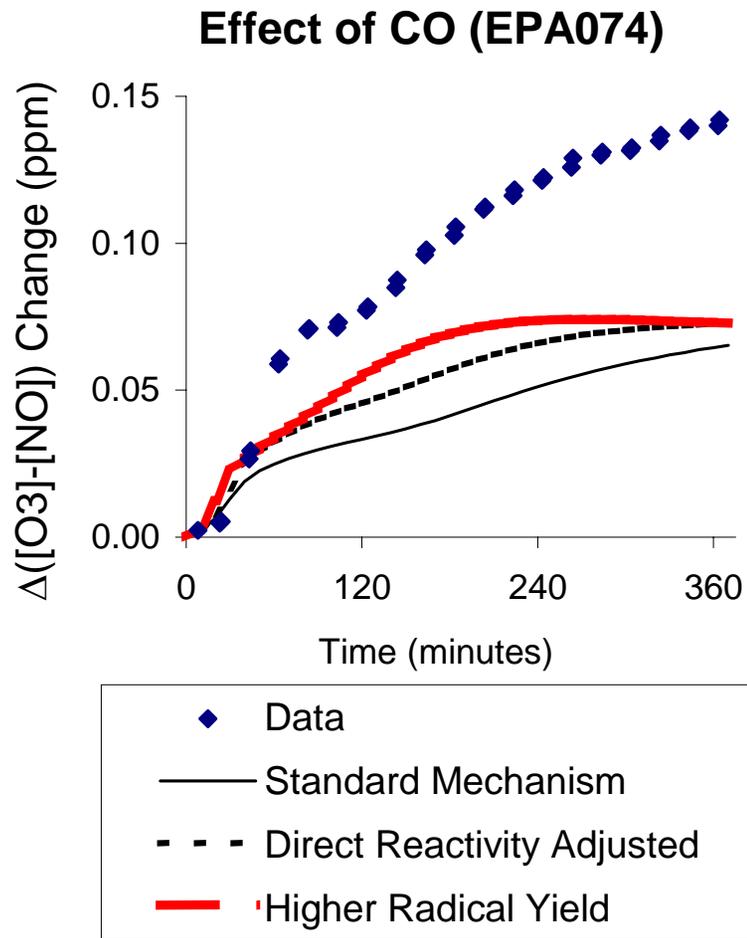
Ongoing Mechanism Development Work

- SAPRC mechanism is being updated as part of a contract for the California ARB. Due to be completed by the end of 2006

- Significant work on the European Master Mechanism is underway. Current version does not perform well for aromatics

- Improving the aromatics mechanism is a high priority.
  - New chamber experiments conducted to evaluate models for aromatics products
  - New laboratory data are available
  - A more explicit aromatics mechanisms is being developed, but simulations of data no better than SAPRC-99.

- The California ARB is sponsoring an international conference on the future of mechanism development in December, 2006. See http://www.cert.ucr.edu/~carter/Mechanism_Conference

PM Measurements in the UCR EPA Chamber

- PM Measurements are being made in conjunction with most UCR EPA chamber experiments. PM alternately sampled from each of the two reactors, switching every 10 minutes

- Number densities of particles in 71 size ranges (28 - 730 nm) measured using a a Scanning Electrical Mobility Spectrometer. Data used to compute particle number and volume densities

- Background PM formation now less than 0.5 $\mu g/m^3$. (Was up to 2 $\mu g/m^3$ in Reactor A before it was replaced)

- PM measurements made during incremental reactivity experiments with representative architectural coatings VOCs.

- A number of experiments were conducted to determine effects of varying initial concentrations on secondary PM from m-xylene

- Most experiments to date are unhumidified with no seed aerosol

Representative PM Data

Volume · — Corected Volume · Number — Corrected Number

Pure Air Irradiation

CO - Air Irradiation

m-Xylene - NOx

Surrogate - NOx

PM Volume (µg/m³)

PM Number (1000/cm³)

Hours of Irradiation

Side B Data
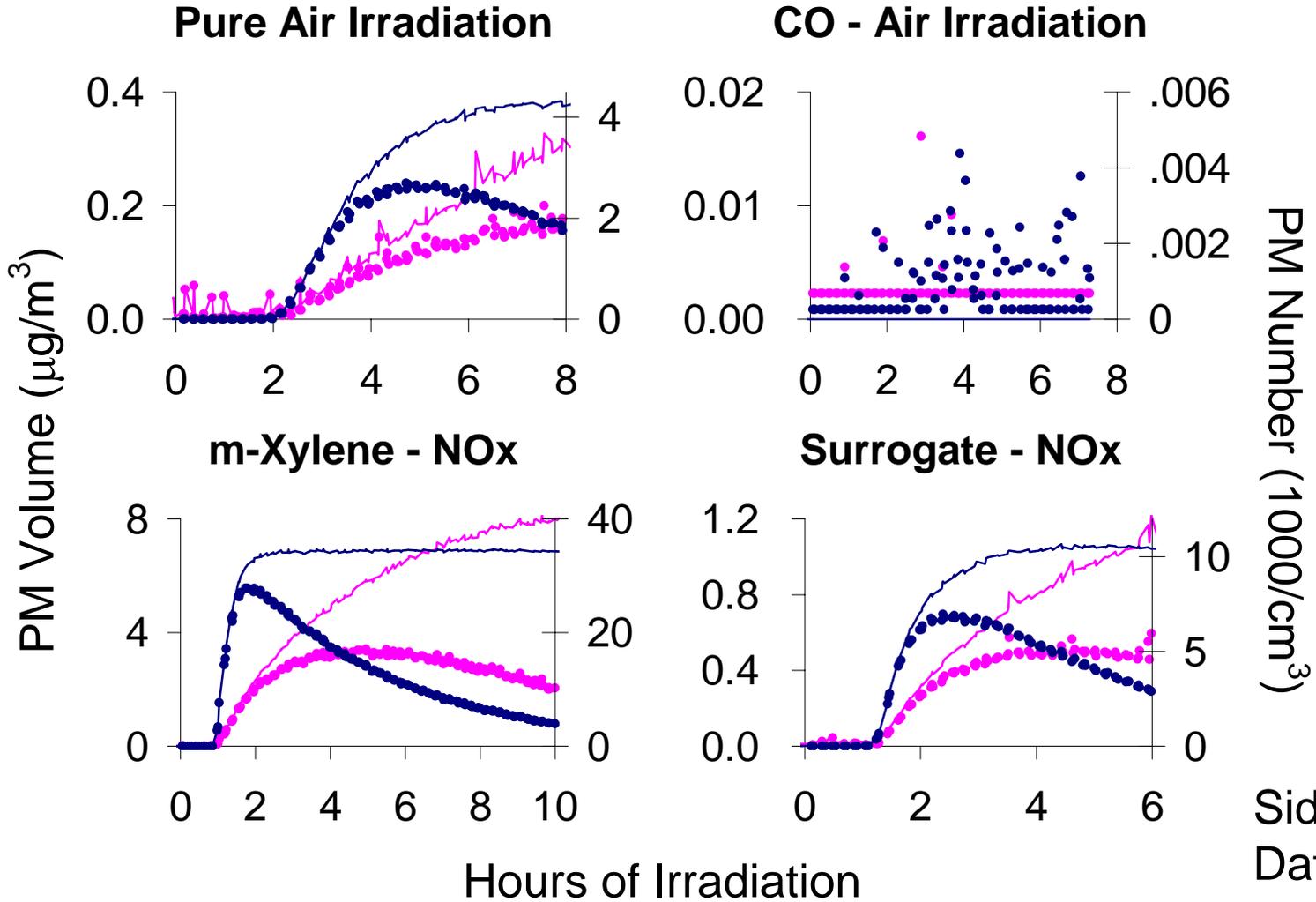
# Matrix of m-Xylene - NOx Experiments to Study Effect of Reactant Levels on PM
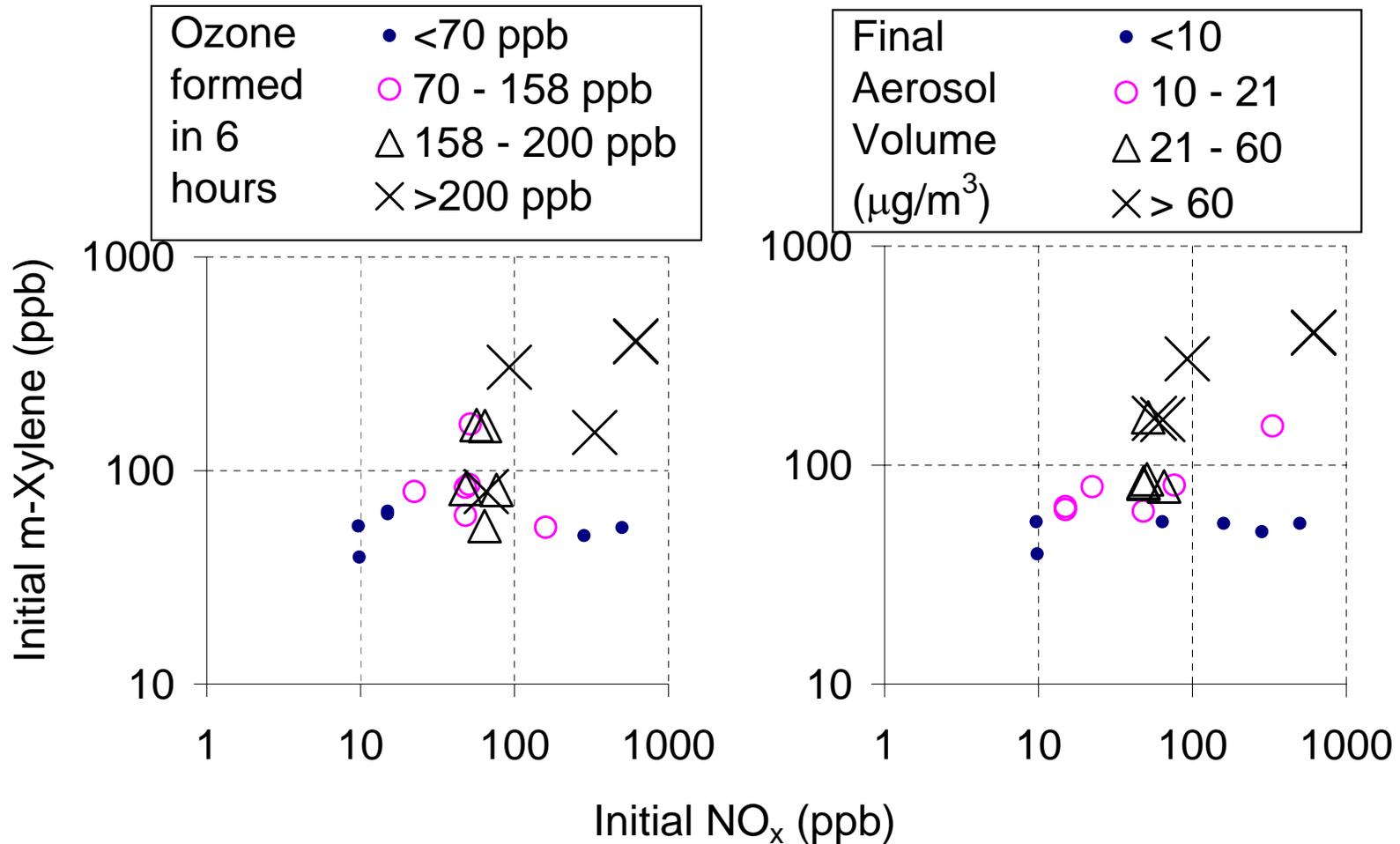
Equilibrium Model for PM in Experiments

- Measured PM yield is the ratio of aerosol mass formed (corrected for wall loss) to mass of VOC reacted

- From equilibrium gas-particle absorptive partitioning theory, assuming no initial PM and all PM is secondary organic aerosol:

$$\text{PM Yield} = \frac{PM_{tot}}{\Delta VOC} \approx PM_{tot} \sum_i \frac{\alpha_i \, K^{part}_i}{1 + K^{part}_i \, PM_{tot}}$$

Where: α_i = Yield of condensable product i in VOC reactions

K^{part}_i = Gas-particle partitioning constant for product i

PM_{tot} = Total organic PM mass formed in experiment

ΔVOC = Mass of VOC reacting in experiment

- Standard parameterization for chamber experiments assumes:
  - Stoichiometric yields, α_I, are constant for a given VOC
  - Maximum of 2 products (i = 1,2) sufficient to fit data

# Standard Equilibrium Model Yield Curves
for the m-Xylene Experiments
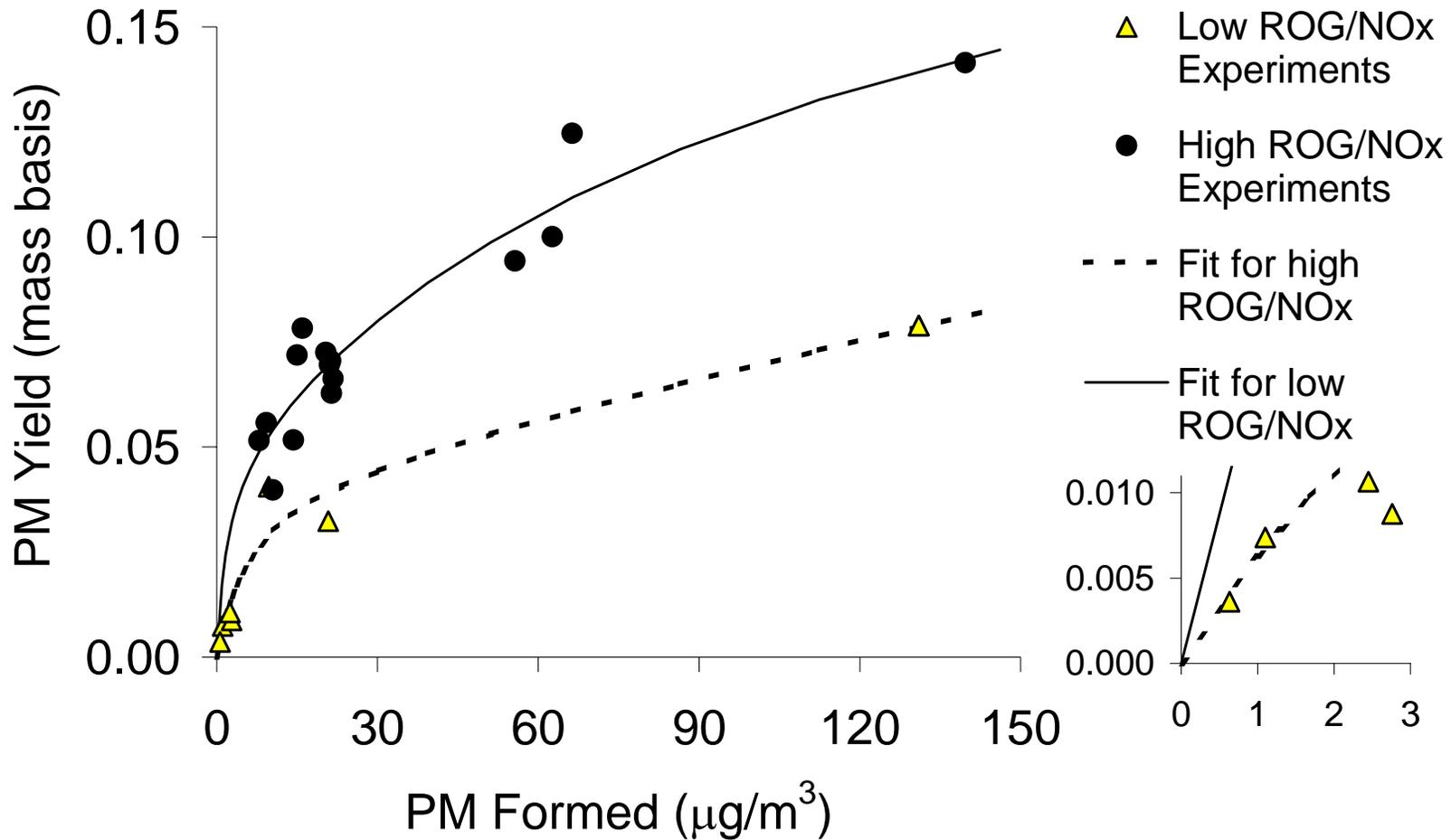
NO$_x$-Dependent Yield Model

- Assume that of formation yield of PM precursor, α_i, is NO$_x$-dependent, as suggested by:

  $$\boxed{\begin{array}{l} \text{Xylene + OH} \rightarrow \text{Intermediate} \\[6pt] \text{Intermediate} \xrightarrow{k_1} \alpha' \ \underline{\text{PM Precursor}} \\[6pt] \text{Intermediate + NO}_x \xrightarrow{k_2} \text{other products} \end{array}}$$
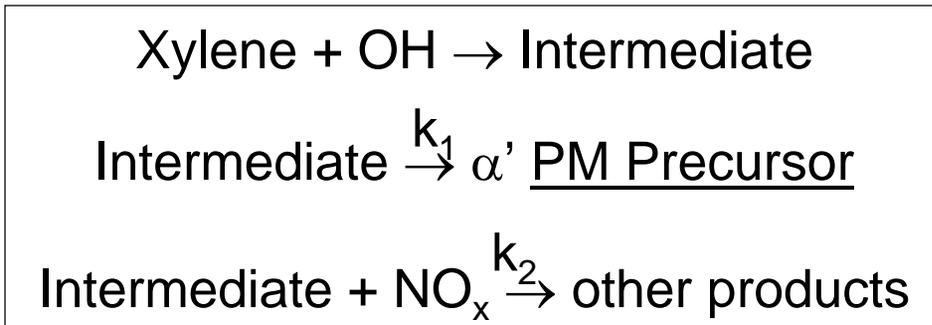
- Adjust α', K^{part}, and k_1/k_2 to fit data

- Single product model (i=1) is sufficient to fit data

- Fits better using NO$_x$ to xylene ratio rather than total NO$_x$.

- Model and best-fit K^{part}, and k_1/k_2 values can be used to derive precursor yields, α, for individual experiments

△ Low ROG/NOx Experiments
● High ROG/NOx Experiments
── 1:1 Line

Experimental PM Yield

Predicted PM Yield (mass basis)
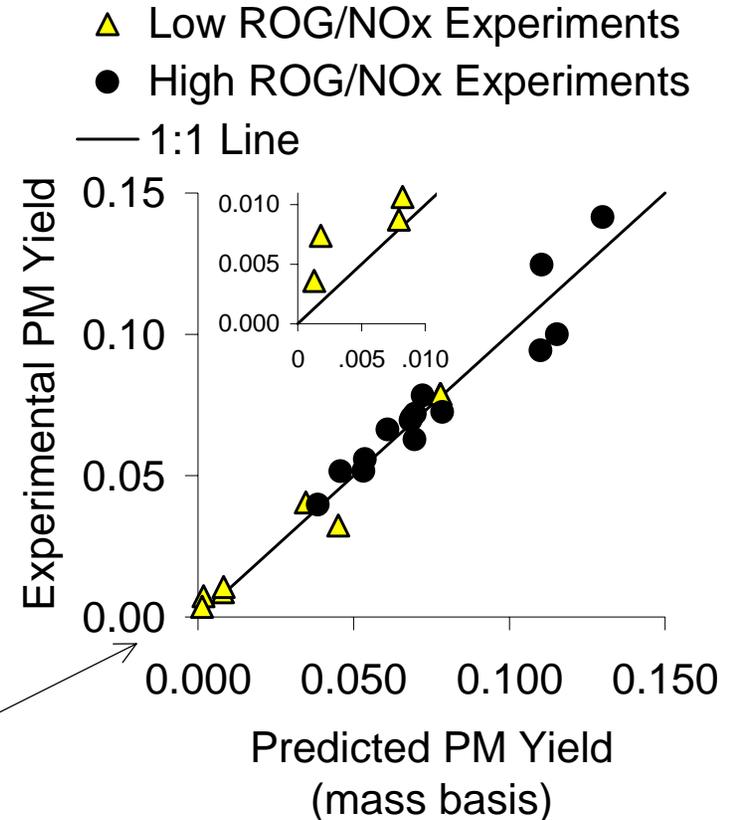
Dependence of Derived PM Precursor Yields on NO_x/ROG, O_3, and Extent of Reaction

- PM precursor yields (molar) derived from data for a run
— Predicted dependence on NOx/xylene ratio by NOx-dependent yield model

Initial NOx / m-Xylene Ratio

6-Hour Ozone (ppb)

Fraction Xylene Reacted
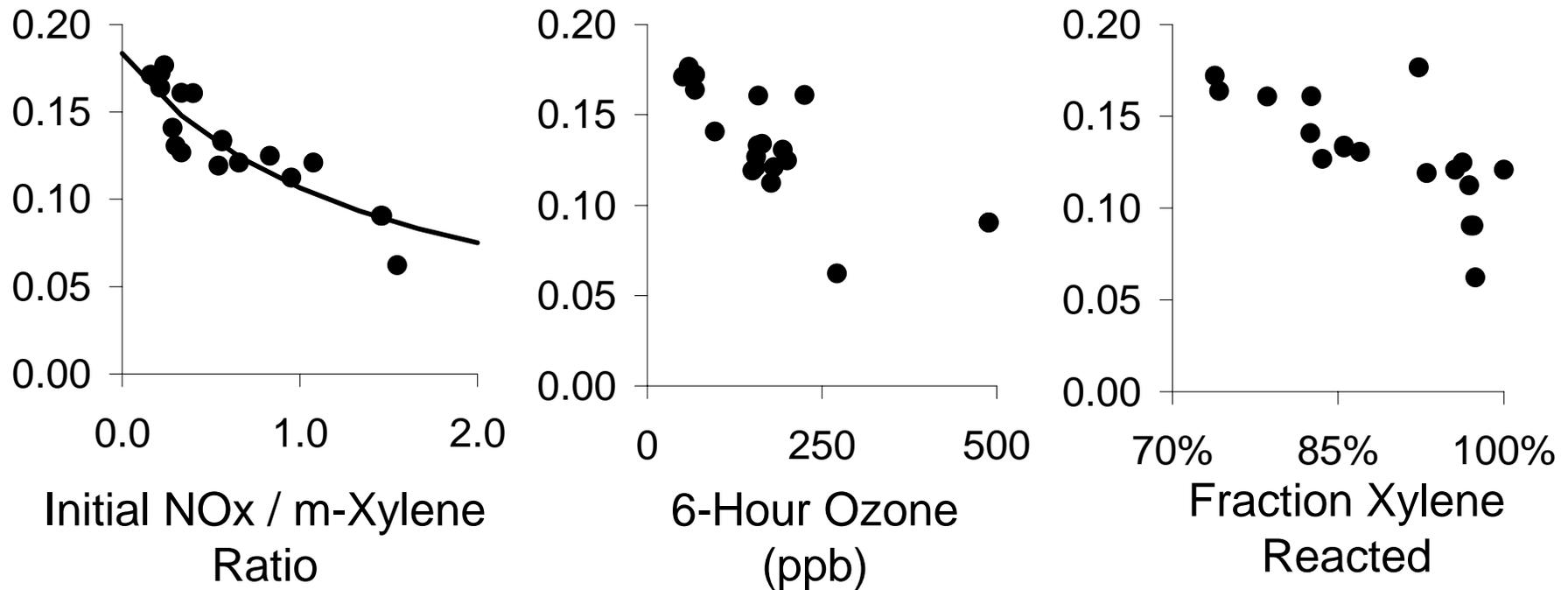
PM Yields from Zero NOx
(m-Xylene – H_2O_2) Experiments
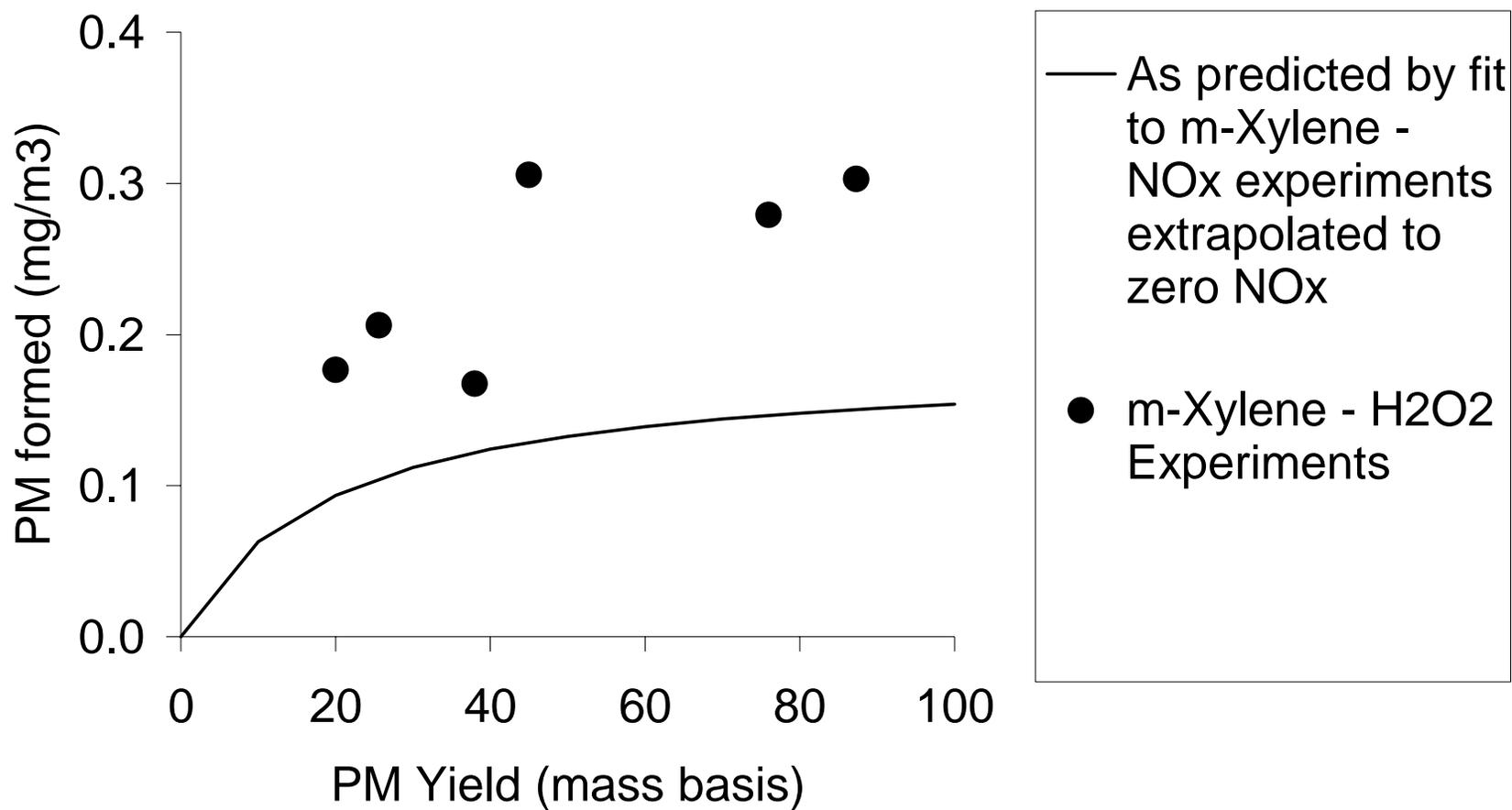
Partial Mechanism for m-Xylene Reactions

Fragmentation Products

These hydroperoxides are the probable zero-NOx PM precursors
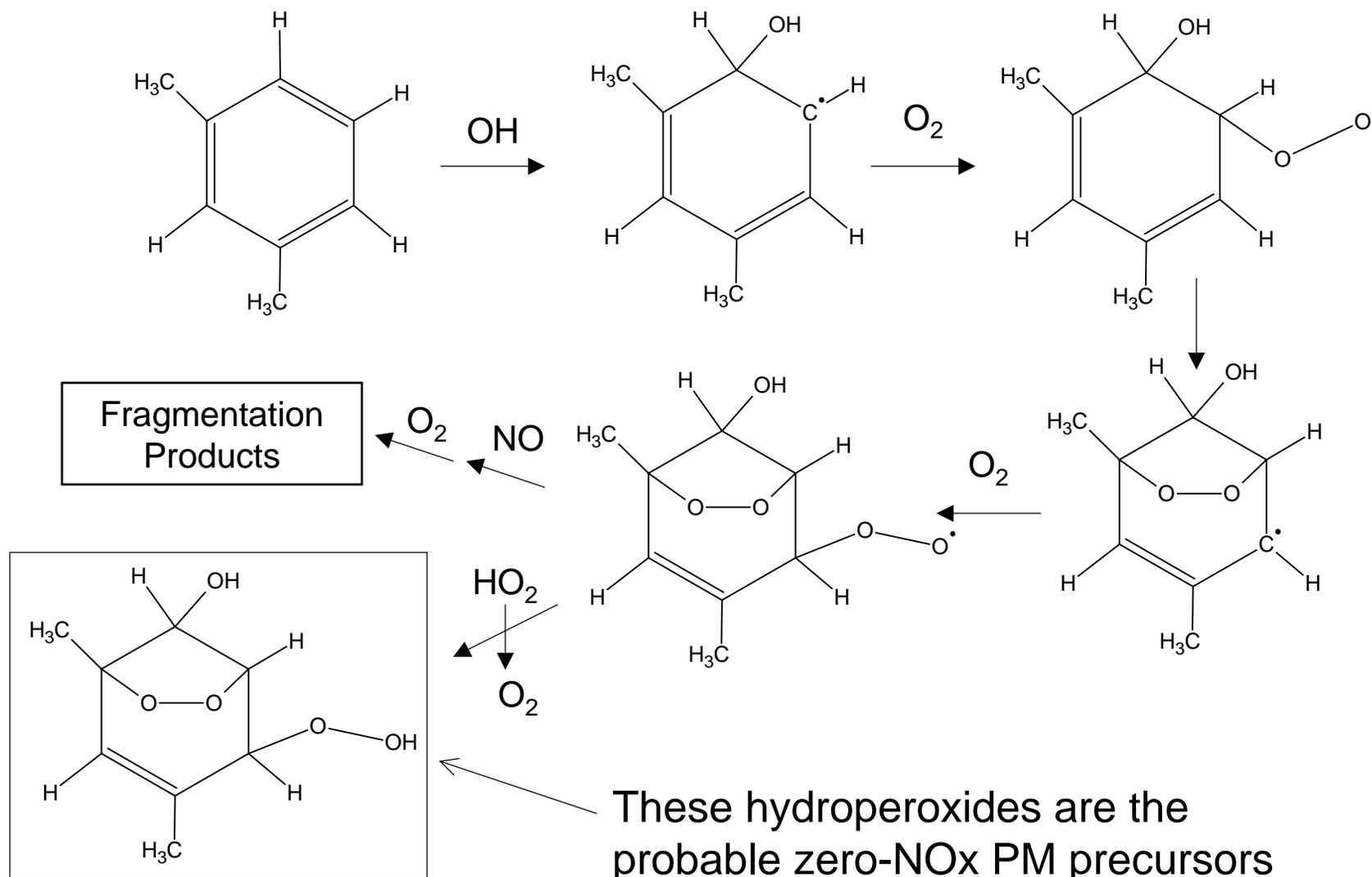
Comparison of Hydroperoxide and Derived PM Precursors Yields <u>vs</u> NO$_x$/Xylene Ratio
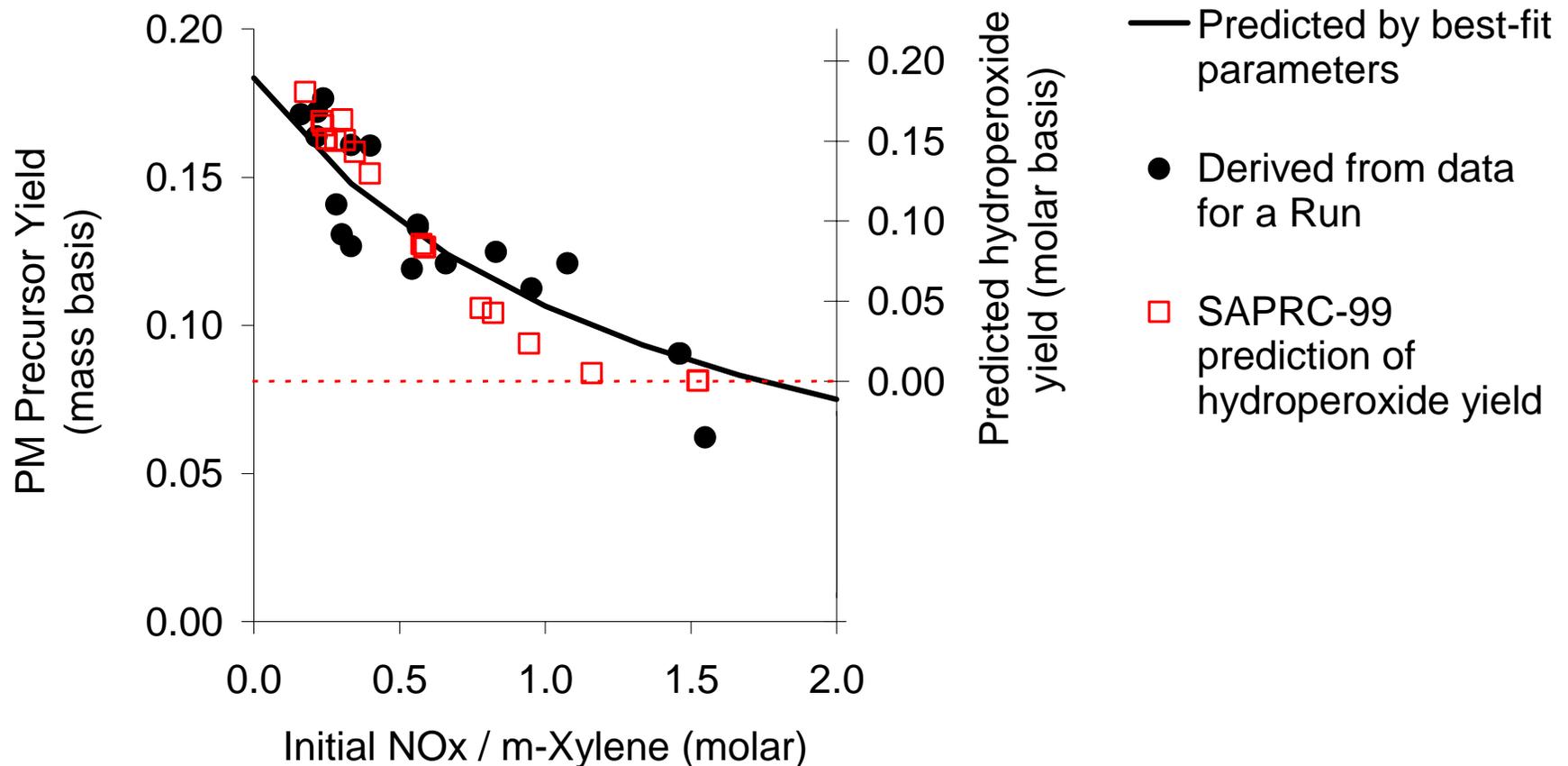
Comparison of Hydroperoxide and Derived PM Precursors Yields <u>vs</u> NO_x/Xylene Ratio
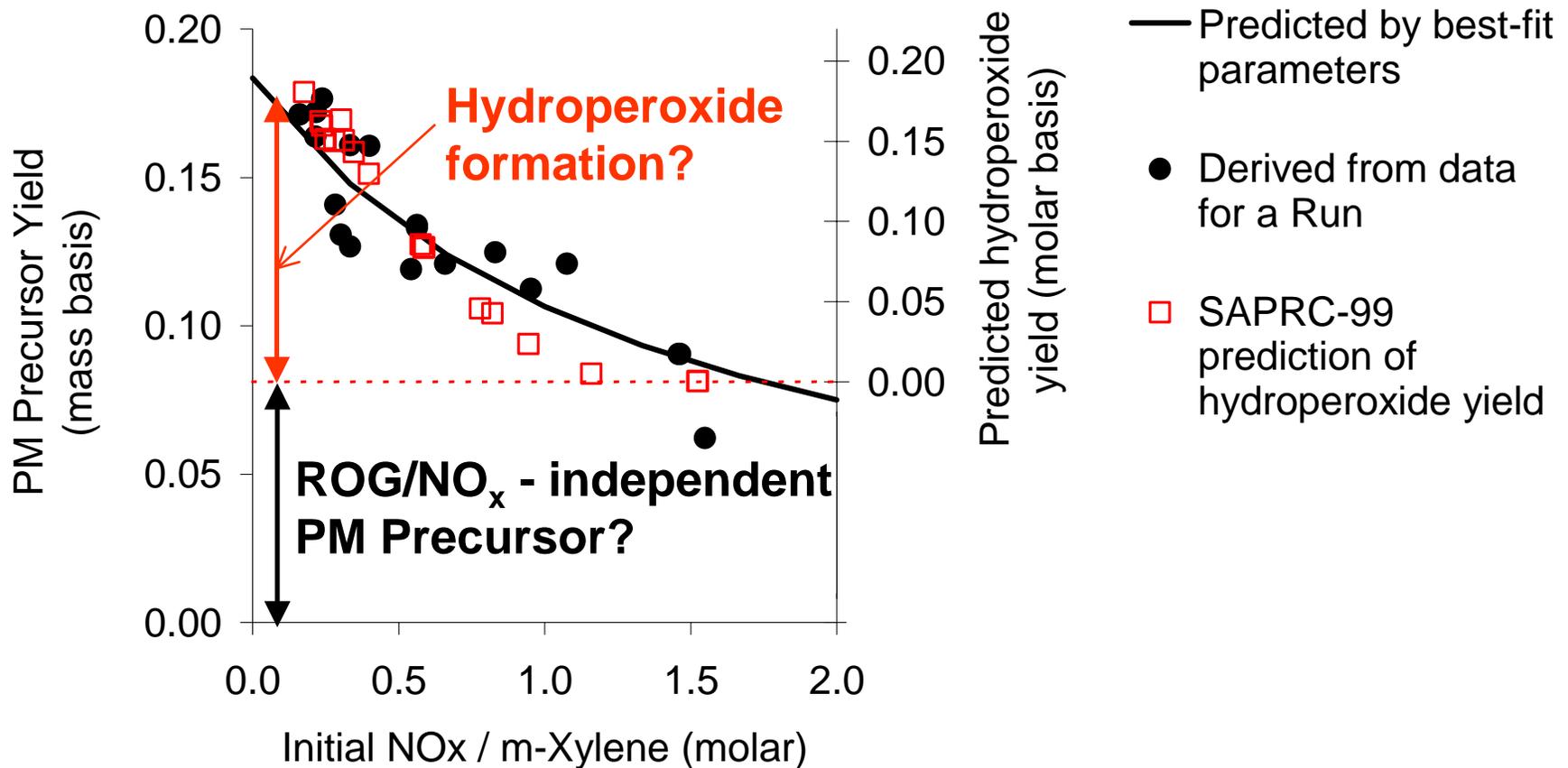
PM Formation in Incremental Reactivity Experiments with Coatings VOCs

Side B data only

Error Bars are 1-σ standard deviations. No error bar means only one experiment.

Average 5 Hour PM Volume $\mu g/m^3$
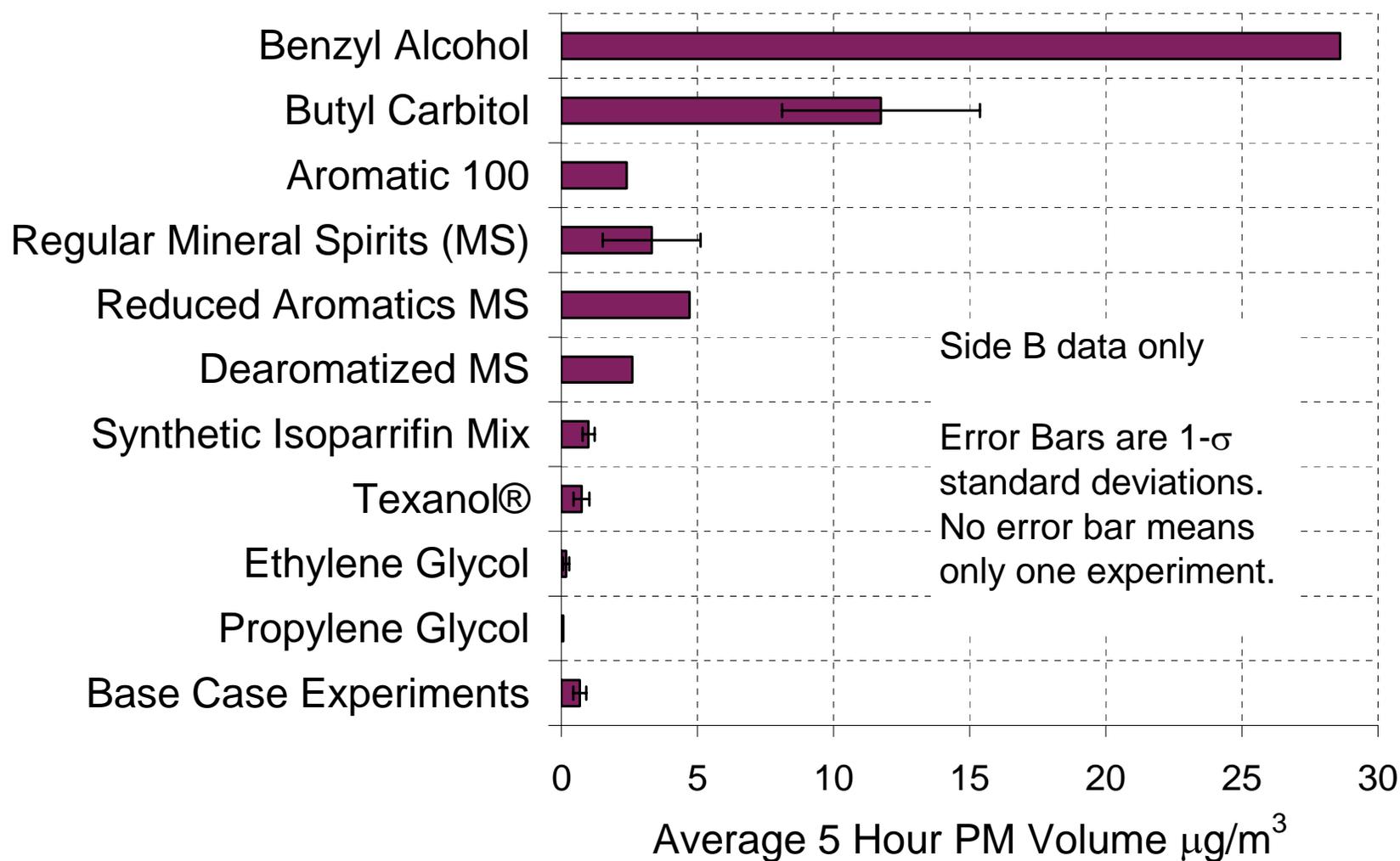
FUTURE RESEARCH DIRECTIONS

- Continue O_3 reactivity and mechanism evaluation experiments as currently underway

- Utilize the capabilities of chamber for well-characterized SOA studies needed for SOA model development and evaluation

- Investigate temperature and humidity effects on O_3 and SOA

- Obtain instrumentation needed for NO_3, N_2O_5, HO_x, and other trace species to improve capabilities and utility of this facility

- Serve as a resource for collaborative studies where environmental chamber measurements under highly controlled and characterized conditions would be useful

- Serve as test bed for instrumentation for ambient monitoring

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  - Major effort in conducting UCR EPA chamber experiments

- **Chen Song**
  - Primarily responsible for m-xylene PM experiments

- **David Cocker**
  - Overall guidance for PM studies

- **Dennis Fitz, Kurt Bumiller, Claudia Sauer, John Pisano, Charles Bufalino, Matthew Smith**
  - Assistance in design and construction of UCR EPA Chamber

- **United States EPA, California Air Resources Board, California South Coast Air Quality Management District**
  - Major funding sources