SOA Formation: Chamber Study and Model Development

William P. L. Carter
College of Engineering Center for Environmental Research
and Technology (CE-CERT)
University of California, Riverside, CA
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Outline

- Background and Objectives

- Approach: Overall and Current Phase

- Experimental Methods and Results

- Mechanism Updates, Development and Evaluation Results

- Discussion and Recommendations

Problem Statement

- Fine particle (PM) formation is a major air quality problem

- Secondary Organic Aerosol (SOA), formed from emitted VOCs reacting in air in sunlight, is an important component of PM

- Development of effective control strategies for PM requires an ability to **predictively model** how SOA formation depends on

  - Chemical composition and reactivity of the emitted VOCs

  - Other pollutants such as NO_x, other VOCs and PM sources

  - Conditions such as temperature, humidity and dilution

- SOA formation is complex, incompletely understood, and expected to be highly dependent on atmospheric conditions

- Current models predict SOA using simplified parameterized models based on limited data and unverified assumptions

- Available laboratory and environmental chamber data are insufficient to develop and evaluate predictive SOA models

Background

- SOA yields have been measured for a number of VOCs and analyzed assuming a simple equilibrium partitioning model

"Two Product" Model

$$Y = PM \left(\frac{\alpha_1 K_{p1}}{1 + K_{p1} PM} + \frac{\alpha_2 K_{p2}}{1 + K_{p2} PM} \right)$$

Y = yield (SOA/VOC reacted)

PM = mass of organic PM present

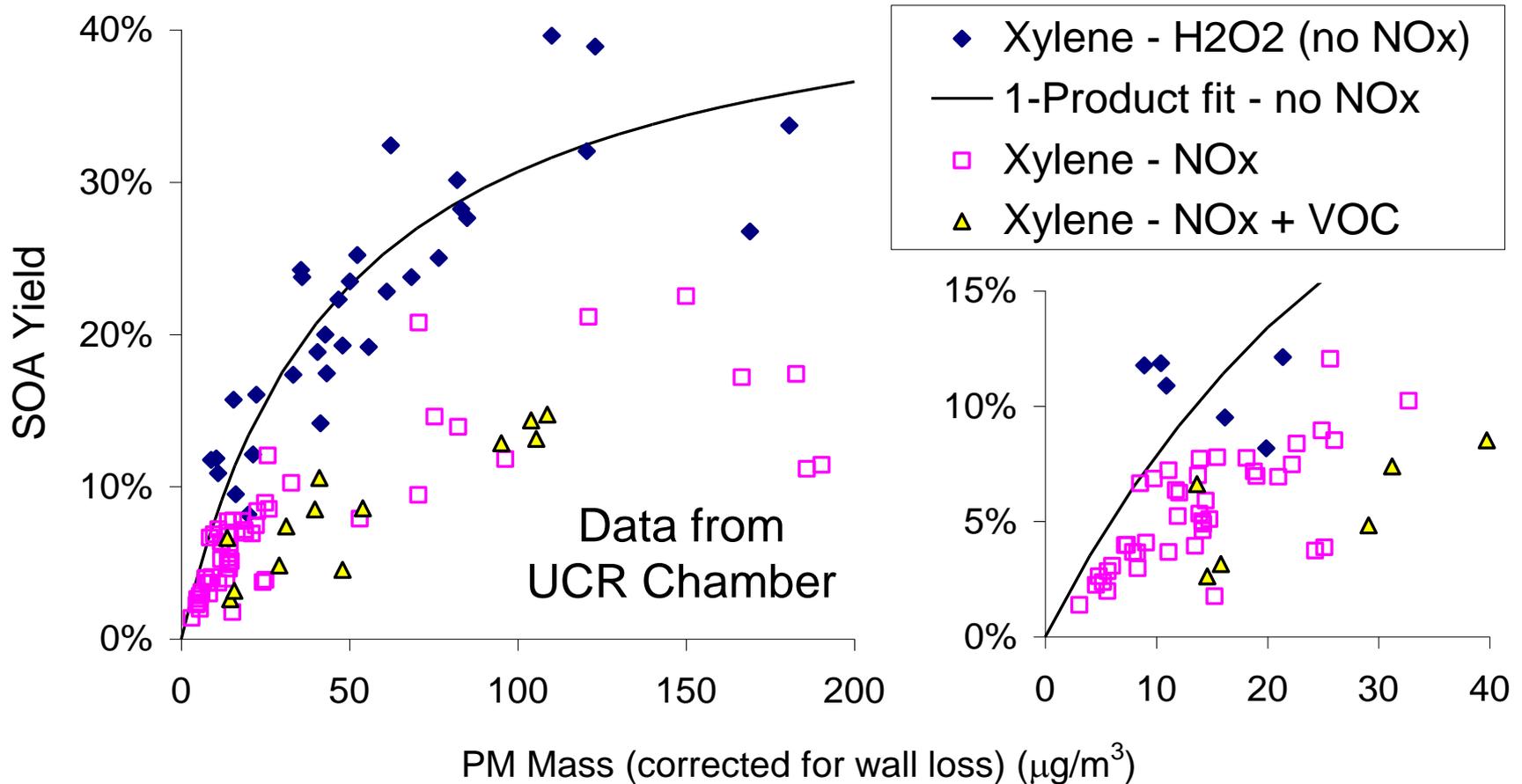α = SOA precursor yield

K_p = equilibrium partitioning

- The α, K_p's adjusted to fit SOA yields in chamber experiments
- Two product model is generally used, though in many cases the data are insufficient to support deriving 4 parameters
- The α's are assumed to be independent of reaction conditions
- The PM values are adjusted for PM wall loss
- Limited data available on temperature dependence of the K_p's

Example of Published SOA Yield Data for Aromatics

From Odum et al (1996)
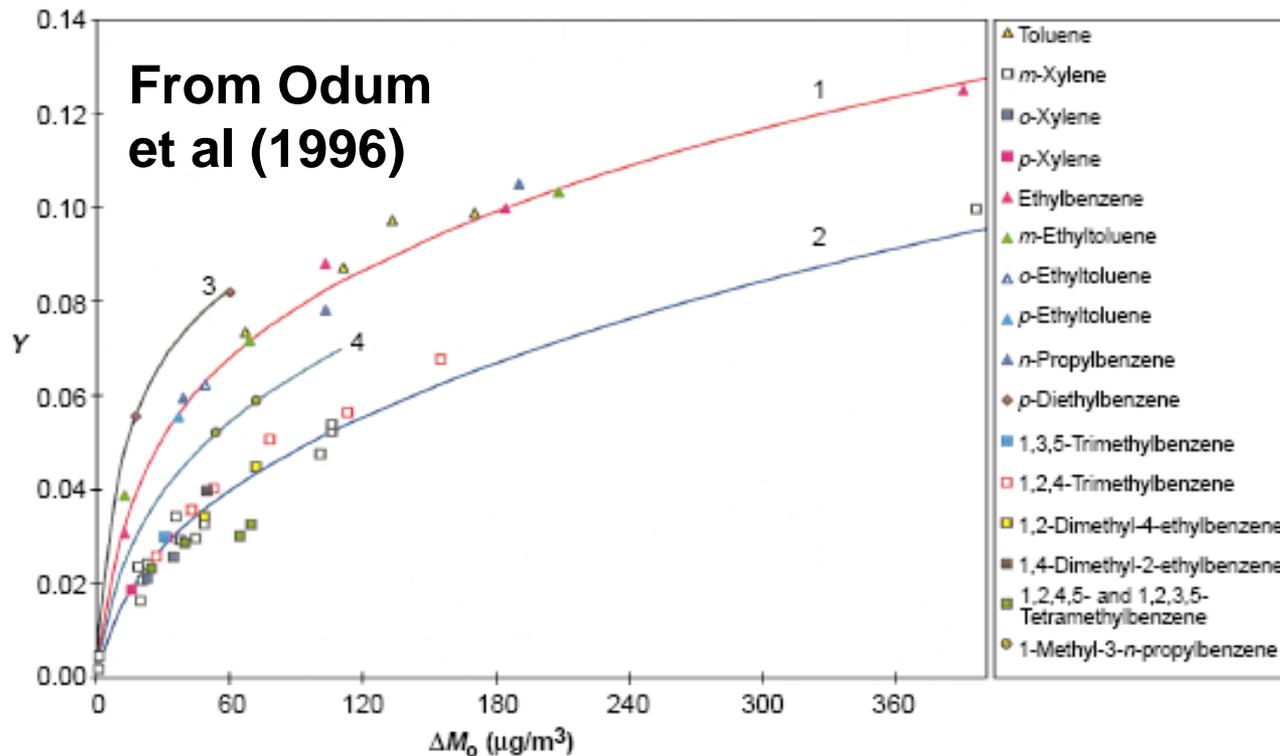
- Significant SOA formation from aromatics, but varies with compound
- Data are fit assuming condensable product yields (α_1, α_2) are independent of reaction conditions.

SOA Yields from m-Xylene
Under A Wider Range of Conditions

Data from UCR Chamber

Legend:
- ◆ Xylene - H2O2 (no NOx)
- — 1-Product fit - no NOx
- ☐ Xylene - NOx
- △ Xylene - NOx + VOC

X-axis: PM Mass (corrected for wall loss) ($\mu g/m^3$)

Y-axis: SOA Yield

- Data indicate SOA yields depend on NO_x and other conditions

Overall Objective

- Develop and evaluate process-based mechanisms for SOA formation for more reliable PM predictions in regulatory models.

Overall Approach

- Add SOA prediction capability to the SAPRC mechanism
- Use results of *well-characterized* environmental chamber experiments to develop and evaluate mechanism
    - Review and utilize existing available chamber data with sufficient characterization information
    - Conduct new experiments in the UCR EPA chamber most needed for model development and evaluation
- Initial focus on aromatics, believed to be the largest source of *anthropogenic* SOA.

Summary of Previous Work at UCR

- A number of chamber experiments have been conducted in the UCR chamber assessing SOA from aromatics
  - Focus has been on m-xylene but experiments with other aromatics and a few aromatic products were conducted
  - The results indicated that current models do not predict how aromatic SOA yields vary with chemical conditions
- A preliminary PM-SAPRC-07 mechanism was developed for m-xylene. The results indicated that more work was needed
  - No single adjusted model fit all the data
  - Data needed to assess role of cresol products
  - Data needed for other aromatic compounds
- This preliminary database and modeling effort served as the starting point for the work for this project.

Long Term Approach for SOA Modeling

- Obtain mechanism evaluation data for representative individual SOA precursors under a wide variety of conditions

- Use results to develop and evaluate mechanistic models for each VOC studied representing the important processes

- Test the mechanisms for mixtures under a variety of reactant, temperature, humidity, and PM conditions

- Use the results to derive scientifically-based lumped mechanisms for ambient modeling

- **Not possible to do all this properly in one 3-year project**

  - A large number of experiments are needed to obtain data on effects of varying conditions for the many compounds

  - Aromatic reactivity varies significantly with compound, so a full variety of compounds need to be studied

  - Other types of compounds besides aromatics (e.g., terpenes, other high heavy VOCs) need to be studied.

Phased Approach to Developing Predictive SOA Mechanisms

- First Phase (this project)

  - Focus on studying how aromatic SOA depends on compound and reactant concentrations

  - Obtain data on all C_6 through C_9 alkylbenzene isomers to assess how SOA reactivity depends on structure

  - Obtain data on phenols, major oxidation products known to be important contributors to aromatic SOA

  - Obtain comprehensive data on reactant levels (no NO_x and NO_x varied, varied VOC, lights, and added VOCs

  - Focus on single temperature (~300K) and dry conditions in this phase to allow for comprehensive data on reactants. *Also simplifies characterization*

- Subsequent phases would focus on other types of VOCs and effects of temperature, humidity, PM, and mixtures

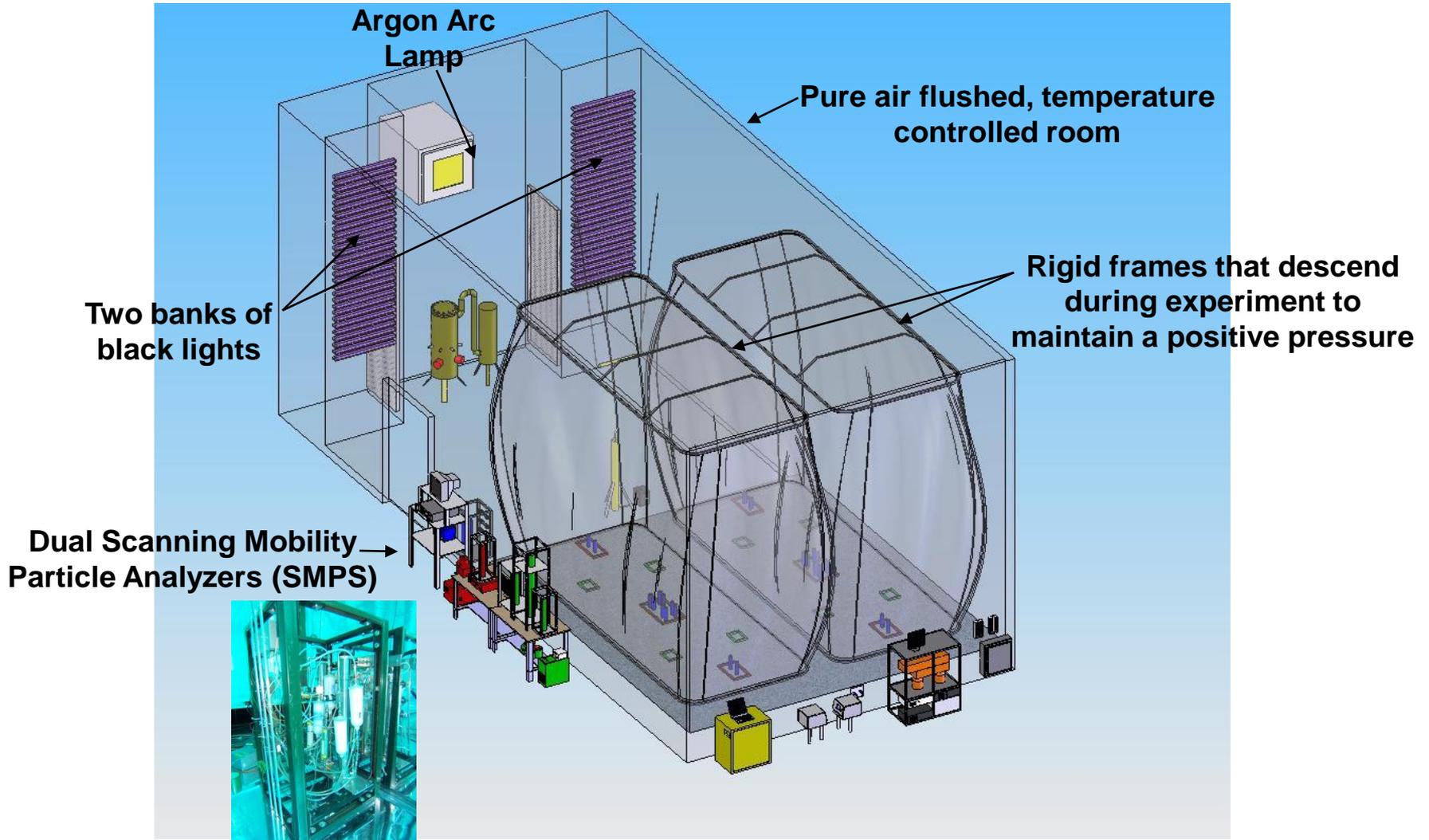- Final phase would focus on developing lumped mechanisms

Experiments Carried Out and Modeled

- Total of 316 mixture irradiations (158 dual reactor experiments) carried out in the UCR chamber for this project, of which 40 were used for characterization and 215 judged suitable for modeling
  - All carried out with blacklights (NO_2 photolysis rate varied from 0.13 to 0.4 min^{-1}). UCR Arc light no longer functional
- Total of 98 UCR chamber irradiations from previous projects (mostly with m-xylene) were also judged suitable for modeling
  - 22 used arc lights, rest used blacklights
- 313 irradiations used for mechanism evaluation
  - 40% were aromatic - H_2O_2
  - 52% were aromatic - NO_x (NO_x = ~10 – 500 ppb)
  - 8% were aromatic - NO_x with added CO or other VOC
  - All modeled experiments were dry and with T≈300K.
  - Runs with characterization problems or questionable PM data were excluded

Numbers of Aromatic SOA Irradiations Judged Suitable for Modeling

Aromatic Compound	VOC - NO_x	VOC - H_2O_2	2nd Cmpd
Benzene	10	6	1
Toluene	11	5	4
Ethyl Benzene	4	4	-
m-Xylene	50	33	20
Other Xylenes (2)	15	11	-
Propyl Benzenes (2)	6	10	-
Ethyl Toluenes (3)	29	18	-
Trimethyl Benzenes (3)	25	10	-
Phenol	4	5	-
o-Cresol	6	5	-
Other Cresols (2)	-	7	-
2,4-Dimethyl Phenol	4	5	-
Other Xylenols (2)	-	5	-

Diagram of the UCR EPA Chamber

Argon Arc Lamp

Pure air flushed, temperature controlled room

Two banks of black lights

Rigid frames that descend during experiment to maintain a positive pressure

Dual Scanning Mobility Particle Analyzers (SMPS)

Measurement Data Used

- Measurements used for gas-phase mechanism evaluation

  - Ozone, NO, NO_y, CO -- commercial instrumentation

  - Reacting VOCs – commercial GC-FID instruments

  - Temperature sensors – attached to data acquisition system

  - NO_2 actinometry in and out of reactors – quartz tube method

  - Dilution tracer (C_6F_{14}) measured by GC-FID

- Scanning Mobility Particle Spectrometer (SMPS) used to measure PM volume and number

  - Information on size distribution in 28-720 nm range. Size distributions used to derive total PM number and volume

  - Density of 1.4 gm/cm^3 assumed based on previous studies

Other PM chemical characterization measurements were made during most experiments, but results not used in this work. These data were analyzed for other projects and are available for future modeling efforts

Characterization Data Used

- Same characterization standards as used for gas-phase evaluations, with additional characterization for PM

- NO_2 actinometry experiments used to measure light intensity

- CO – air and CO – NO_x irradiations used to derive apparent HONO offgasing rates (background radical and NO_x sources)

- PM ($\sim$0.1 - 2 $\mu m^3/cm^3$) formed in most pure air irradiations. No PM in dark or when OH low. Background PM attributed to:

$$\text{Walls} + h\nu \rightarrow \text{PM precursor}$$
$$\text{PM precursor} + \text{OH} \rightarrow \text{Low Volatility material} \quad \text{(fast reaction)}$$
$$\text{Low Volatility material} \rightarrow \text{PM} \quad \text{(high } K_p \text{ assumed)}$$

- Wall losses of PM derived for each experiment to fit loss rates of PM numbers once nucleation ended.

- Side equivalency and reproducibility tests conducted
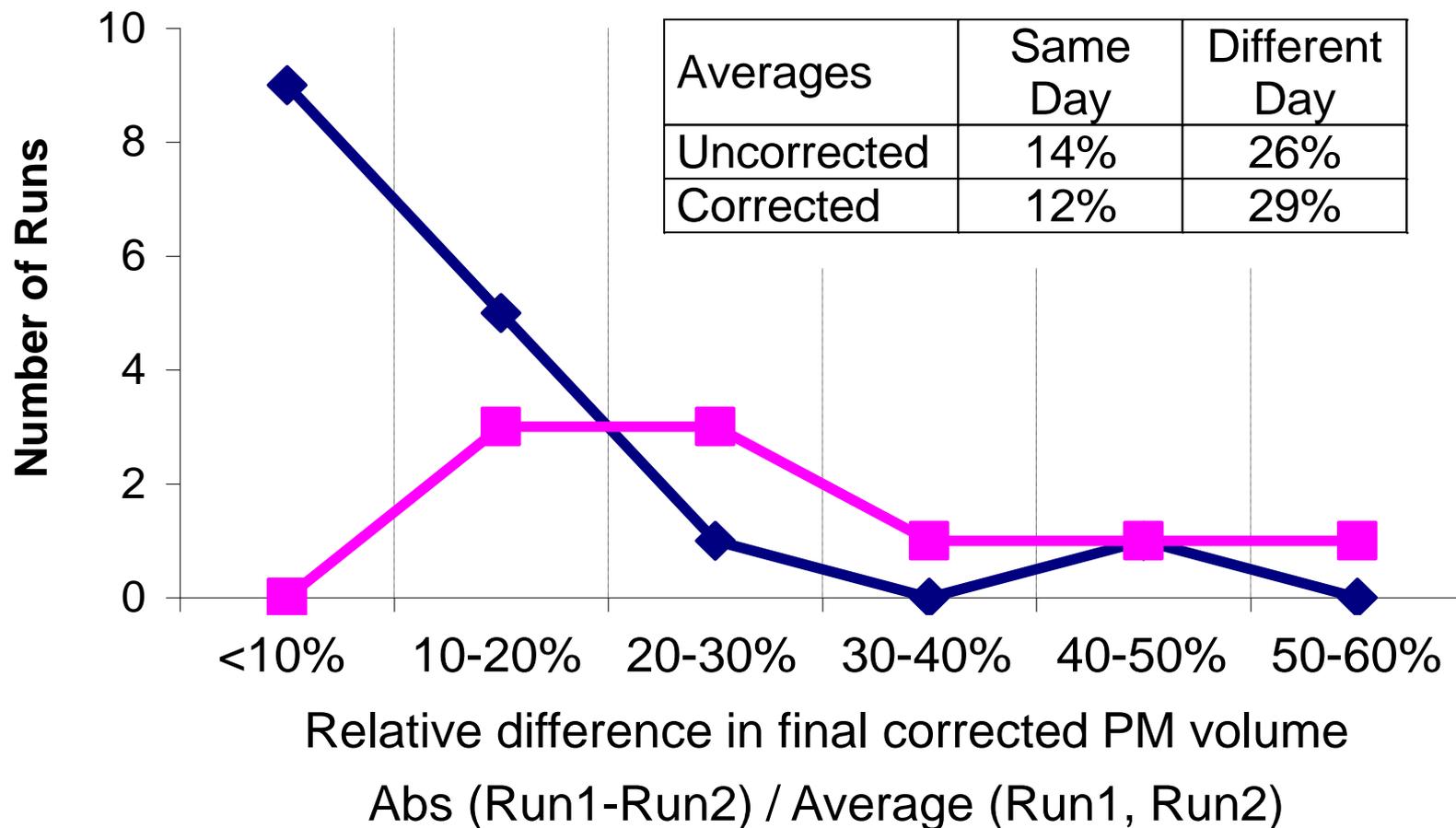
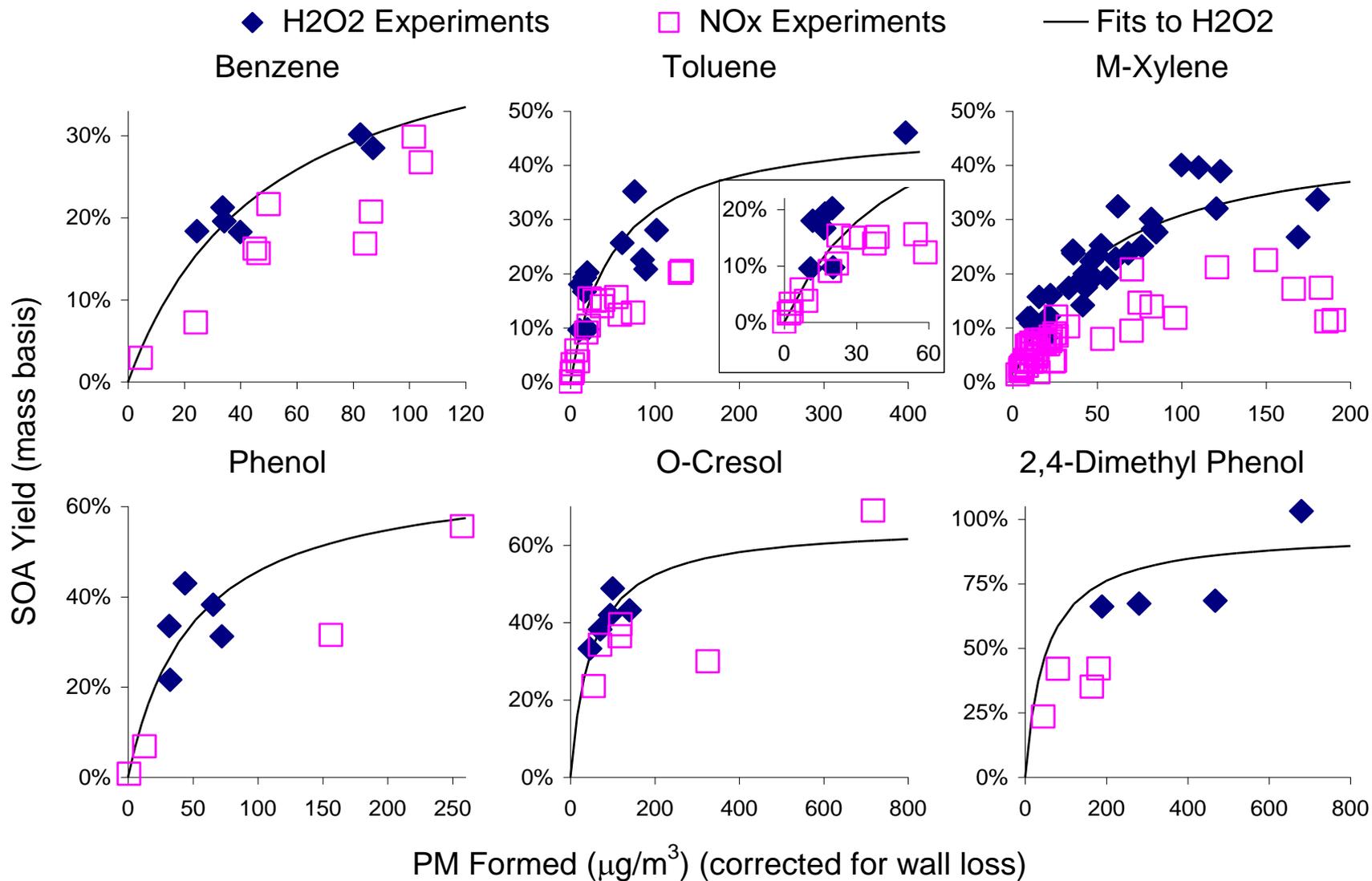# Variability of PM Wall Loss Rates in UCR Chamber
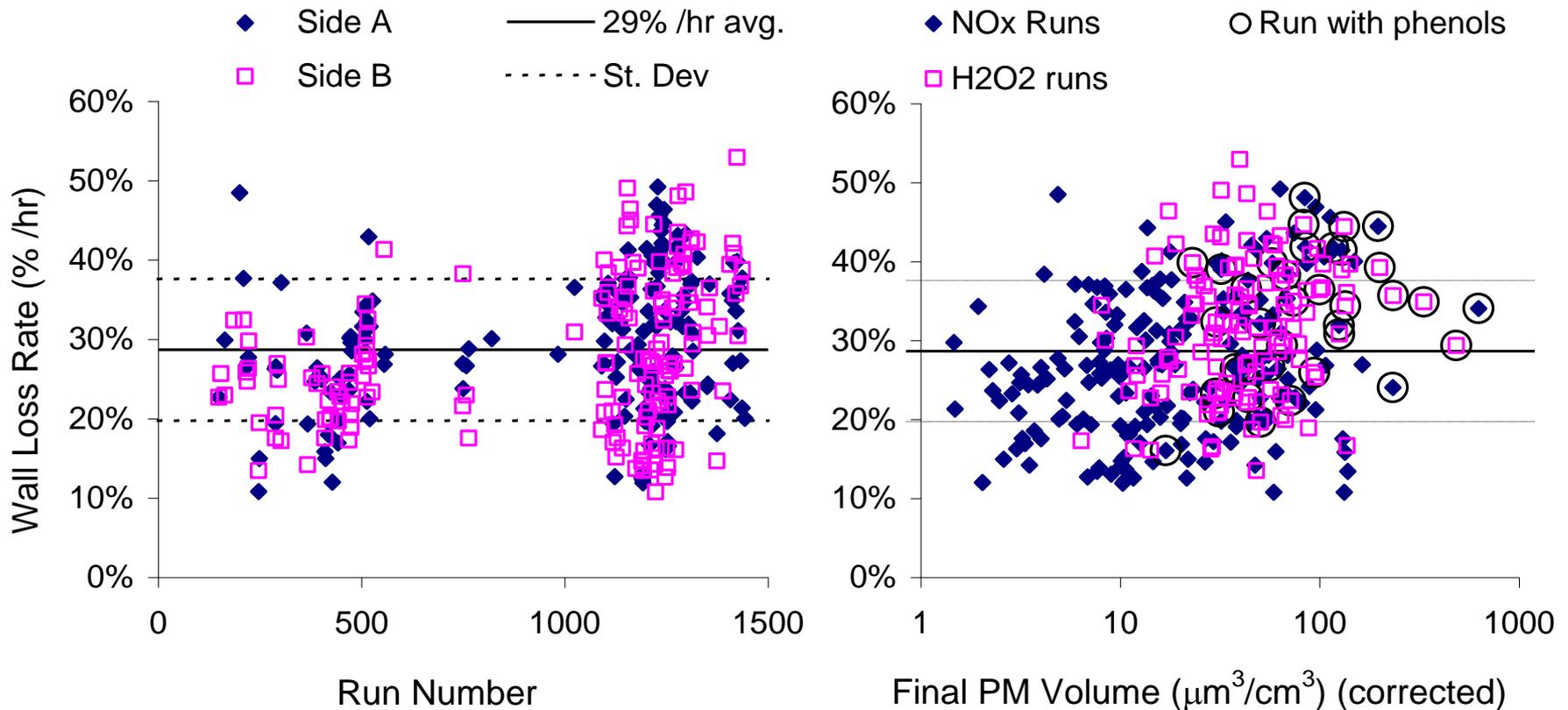
- Large variability from run to run
- May be slightly higher for more recent runs
- May be slightly lower with low PM levels
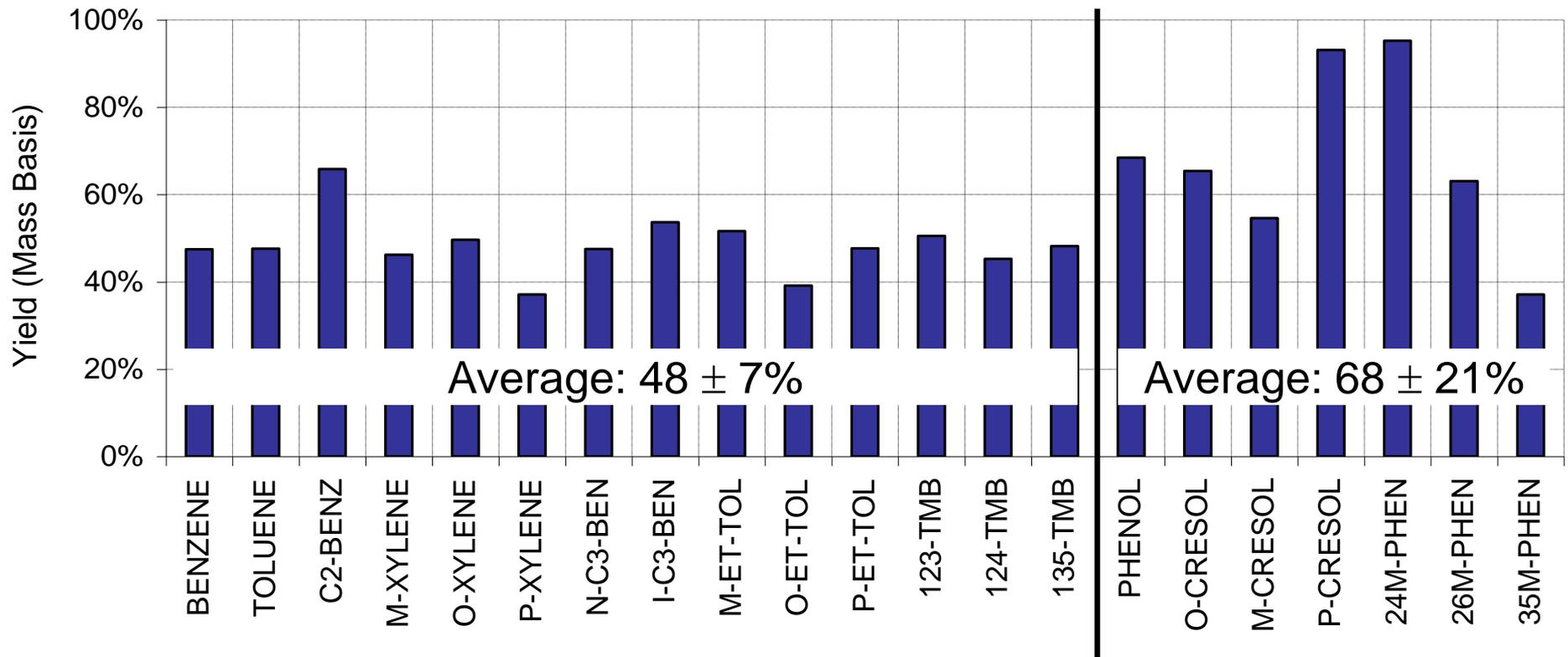
Reproducibility of Replicate Runs

Averages	Same Day	Different Day
Uncorrected	14%	26%
Corrected	12%	29%

Runs on the same day (side equivalency tests)

Runs on different days with simlar reactant levels

Relative difference in final corrected PM volume

Abs (Run1-Run2) / Average (Run1, Run2)

Examples of SOA Yield Data

SOA Yield (mass basis)

PM Formed (μg/m^3) (corrected for wall loss)

Plots of High PM Limit SOA Yields for Aromatic - H_2O_2 Runs

- Data fit using one-product equilibrium partitioning model with K_p = 0.02 $m^3/\mu g$ (best fit in most cases)

- Two-product model does not give better fits to the data

Summary of Mechanism Development

Gas-Phase Mechanism Development (PTSD Project)

- SAPRC-07 detailed mechanism used as the starting point
  - Individual VOCs explicit, most organic products lumped
- SAPRC-11 aromatics mechanism developed
  - Same lumping approach as detailed SAPRC-07
  - Base and non-aromatic VOC mechanisms mostly unchanged
  - Aromatics mechanisms revised to better fit new gas-phase chamber data, including data from this project.
  - Documented in separate report to CARB, paper in preparation

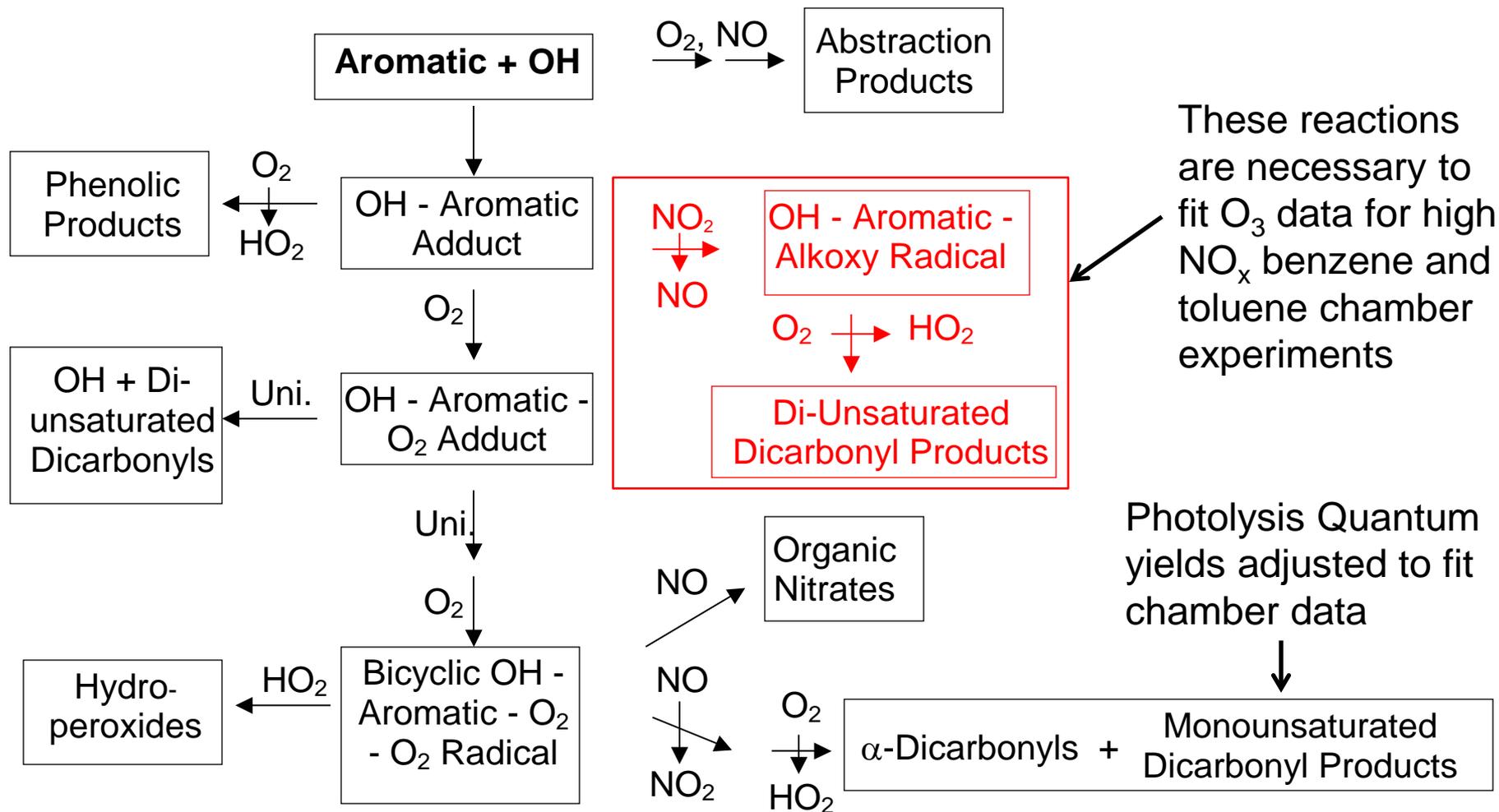**Aromatic SOA Mechanism Development (RD Project)**

- Lumped SOA precursor model species added to SAPRC-11 as needed to predict how SOA affected by reaction conditions
- Derived and adjusted using UCR chamber data from this project

Overview of SAPRC-11
Gas-Phase Aromatics Mechanism

- Minor corrections to reactions of acetylene and glyoxal, and reactions of acyl peroxy radicals with HO_2

- Aromatic mechanisms revised, but same general approach (lumped unknown products, parameters adjusted to fit data)

  - Rate constants, known product yields updated

  - New parameterized mechanisms for phenol, cresols, and xylenols derived to fit new chamber data for this project

  - Much better fits to results of many new aromatic – NOx experiments, especially at lower concentrations

- Most inconsistencies and problems with SAPRC-07 remain

  - OH radical levels still significantly underpredicted

  - Chamber data for benzene and toluene have greater dependence on NO_x than indicated by product studies

- Lumped SAPRC-11 for airshed models not yet developed
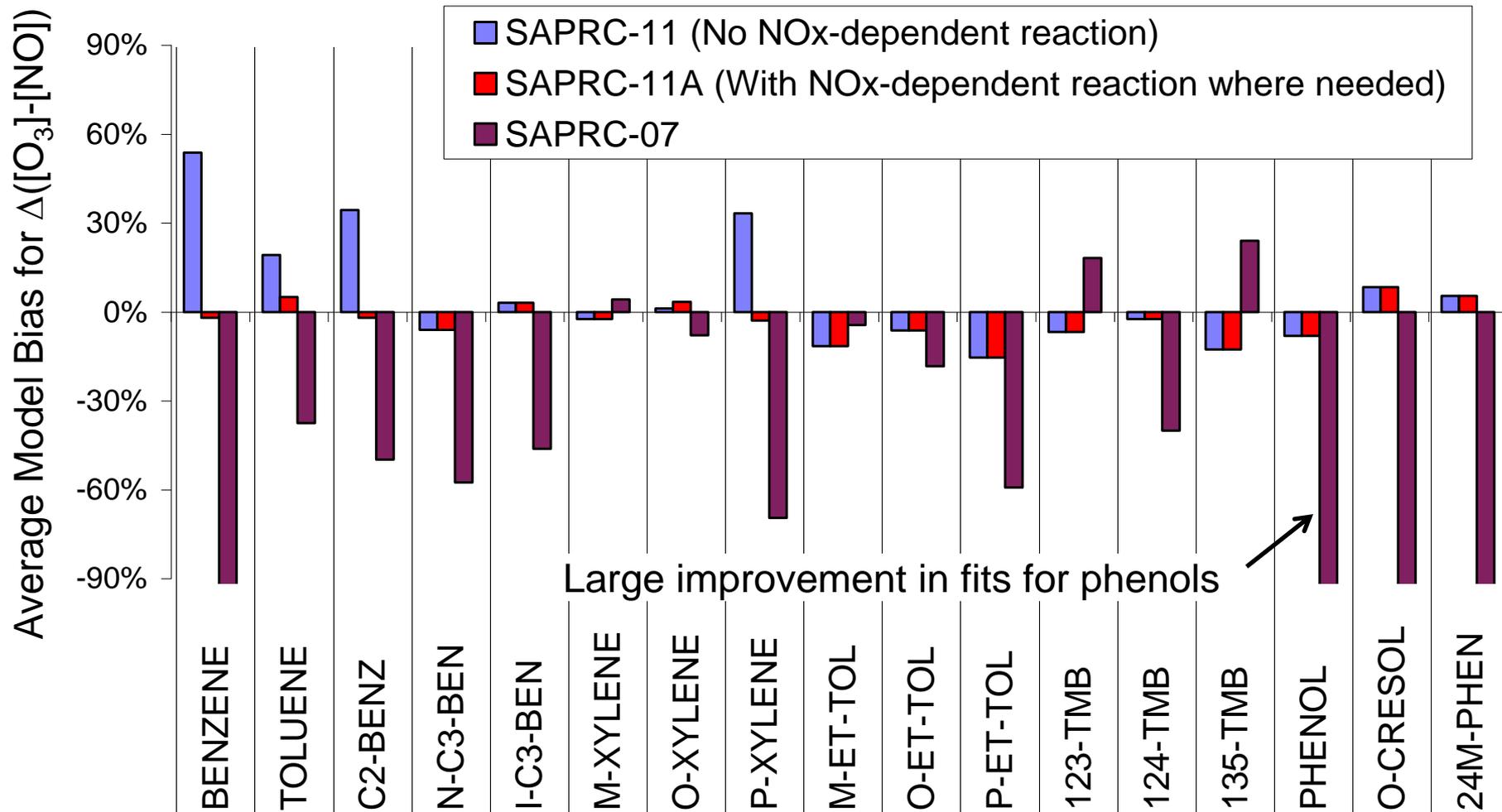
Features of SAPRC-11 Aromatic Reactions

Aromatic + OH $\xrightarrow{\quad O_2, NO \quad}$ Abstraction Products

Phenolic Products $\xleftarrow{\begin{array}{c} O_2 \\ HO_2 \end{array}}$ OH - Aromatic Adduct

OH - Aromatic Adduct $\xrightarrow{O_2}$ OH - Aromatic - O_2 Adduct

OH + Di-unsaturated Dicarbonyls $\xleftarrow{\text{Uni.}}$ OH - Aromatic - O_2 Adduct

OH - Aromatic - O_2 Adduct $\xrightarrow{\text{Uni.}}$ O_2 $\downarrow$

Hydro-peroxides $\xleftarrow{HO_2}$ Bicyclic OH - Aromatic - O_2 - O_2 Radical

$\begin{array}{c} NO_2 \\ \xrightarrow{\quad} \\ NO \end{array}$ OH - Aromatic - Alkoxy Radical

$O_2 \xrightarrow{\quad} HO_2$

Di-Unsaturated Dicarbonyl Products

These reactions are necessary to fit O_3 data for high NO_x benzene and toluene chamber experiments

Bicyclic OH - Aromatic - O_2 - O_2 Radical $\xrightarrow{NO}$ Organic Nitrates

NO / NO → NO_2 / HO_2

α-Dicarbonyls + Monounsaturated Dicarbonyl Products

Photolysis Quantum yields adjusted to fit chamber data

Problem with NO$_2$ Dependences on Benzene and Toluene Model Fits

- Benzene and toluene models adjusted for runs with NO$_x$<100 ppb overpredict O$_3$ formation rates at higher NO$_x$

- Data can be fit if the OH-aromatic adduct reacts with NO or NO$_2$ to form less reactive products than the adduct + O$_2$ reaction.

- The NO$_x$ levels where the NO$_x$ reaction compete with the O$_2$ reaction are not consistent with laboratory product yield data.
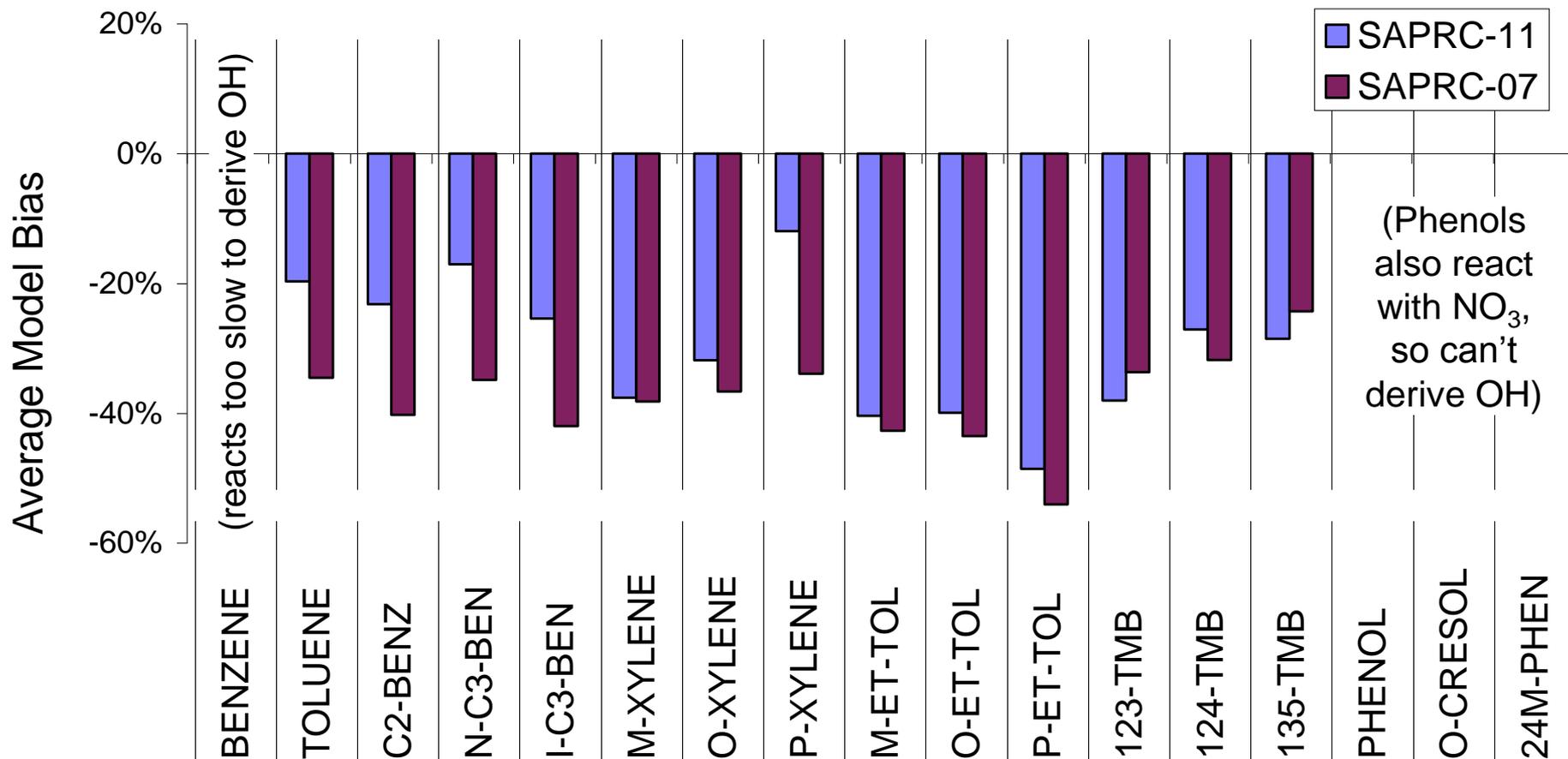
Compound(s)	Fits Chamber Data	Derived from Lab Studies
Benzene	~ 10 ppb NO$_2$	~ 1 ppm NO$_2$
Toluene	~ 200 ppb NO$_2$	~ 3 ppm NO$_2$
Most others	(Reaction not needed)	Higher NO$_2$

- NO$_x$-dependent reaction is not included in standard SAPRC-11. Parameters adjusted using only experiments with NO$_x$ < 90 ppb

  - Appropriate for current ambient NO$_x$ conditions

Average Model Biases for Compounds: Ozone Formation and NO Oxidation Rates

Average Model Bias for $\Delta([O_3]-[NO])$

Legend:
- ■ SAPRC-11 (No NOx-dependent reaction)
- ■ SAPRC-11A (With NOx-dependent reaction where needed)
- ■ SAPRC-07

Large improvement in fits for phenols

Compounds: BENZENE, TOLUENE, C2-BENZ, N-C3-BEN, I-C3-BEN, M-XYLENE, O-XYLENE, P-XYLENE, M-ET-TOL, O-ET-TOL, P-ET-TOL, 123-TMB, 124-TMB, 135-TMB, PHENOL, O-CRESOL, 24M-PHEN

Average Model Biases for Compounds: Integrated OH Levels

Average Model Bias

20%

0%

-20%

-40%

-60%

(reacts too slow to derive OH)

SAPRC-11
SAPRC-07

(Phenols also react with NO_3, so can't derive OH)

BENZENE
TOLUENE
C2-BENZ
N-C3-BEN
I-C3-BEN
M-XYLENE
O-XYLENE
P-XYLENE
M-ET-TOL
O-ET-TOL
P-ET-TOL
123-TMB
124-TMB
135-TMB
PHENOL
O-CRESOL
24M-PHEN

Problem with underprediction of OH persists

Photoreactive Dicarbonyls:
Yields and Adjusted Quantum Yields

OH Adjustments for SOA Modeling

- Gas-phase aromatics mechanisms consistently underpredict OH radical levels and amounts of aromatic reacted

- OH underprediction bias probably less important in ambient simulations because of more varied ambient OH sources

- This will lead to biases when adjusting yield parameters to fit SOA data (adjusted model may overpredict ambient SOA)

- Therefore, OH levels are adjusted to force model to fit amounts of aromatic hydrocarbon reacted when modeling SOA formation

- These adjustments are necessary for almost all aromatic– NO_x experiments but not for most aromatic – H_2O_2 runs

- These adjustments are not possible for phenolic – NO_x experiments because of loss of phenolic by reaction with NO_3
  - But generally the model gives reasonably good fits to amounts of phenolic compound reacted in such runs

Example of OH Adjustments
for SOA Modeling

Toluene – NO_x Experiment EPA289B
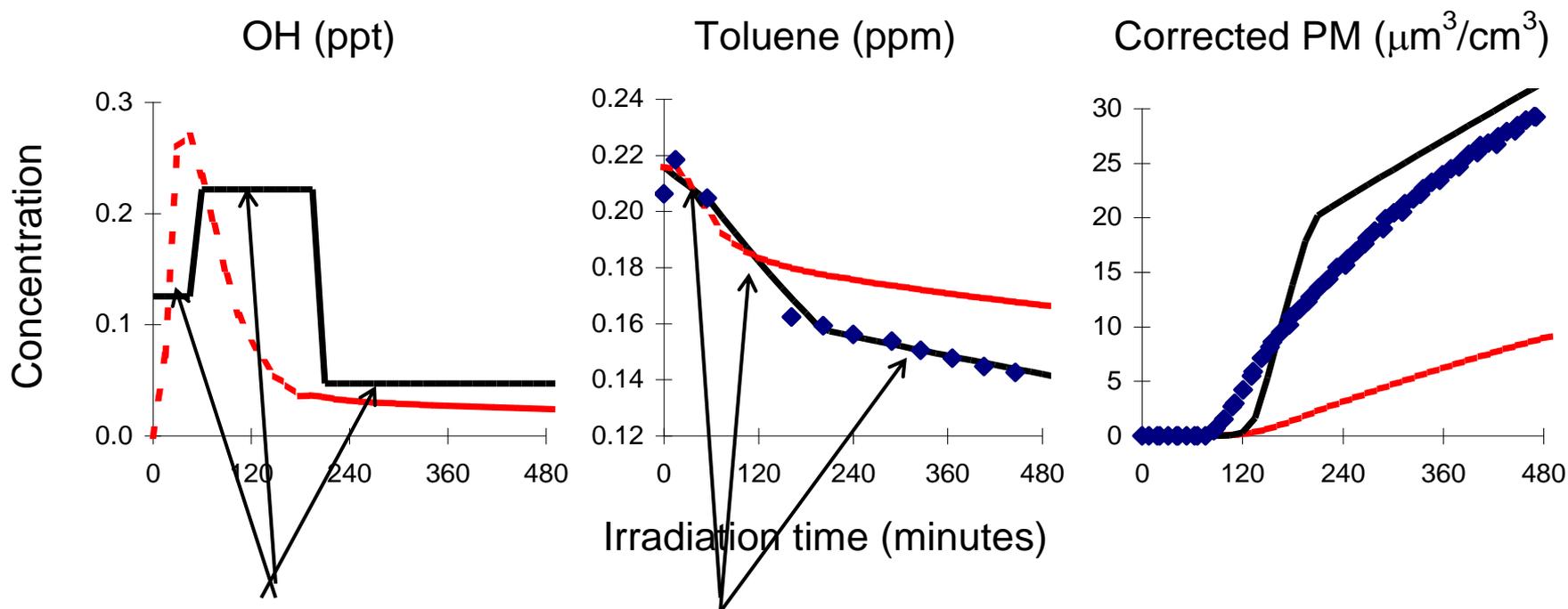
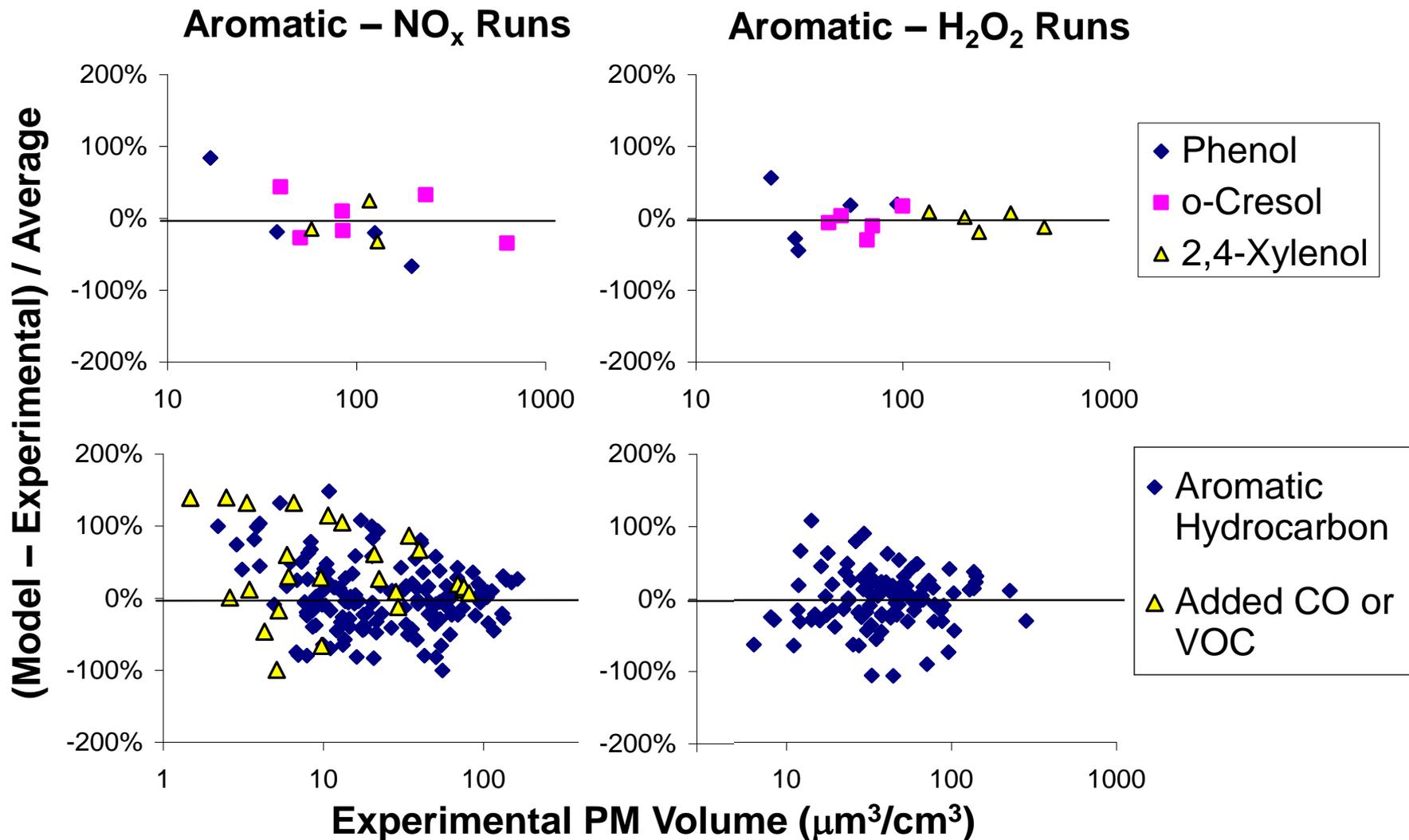
OH adjusted for various time segments
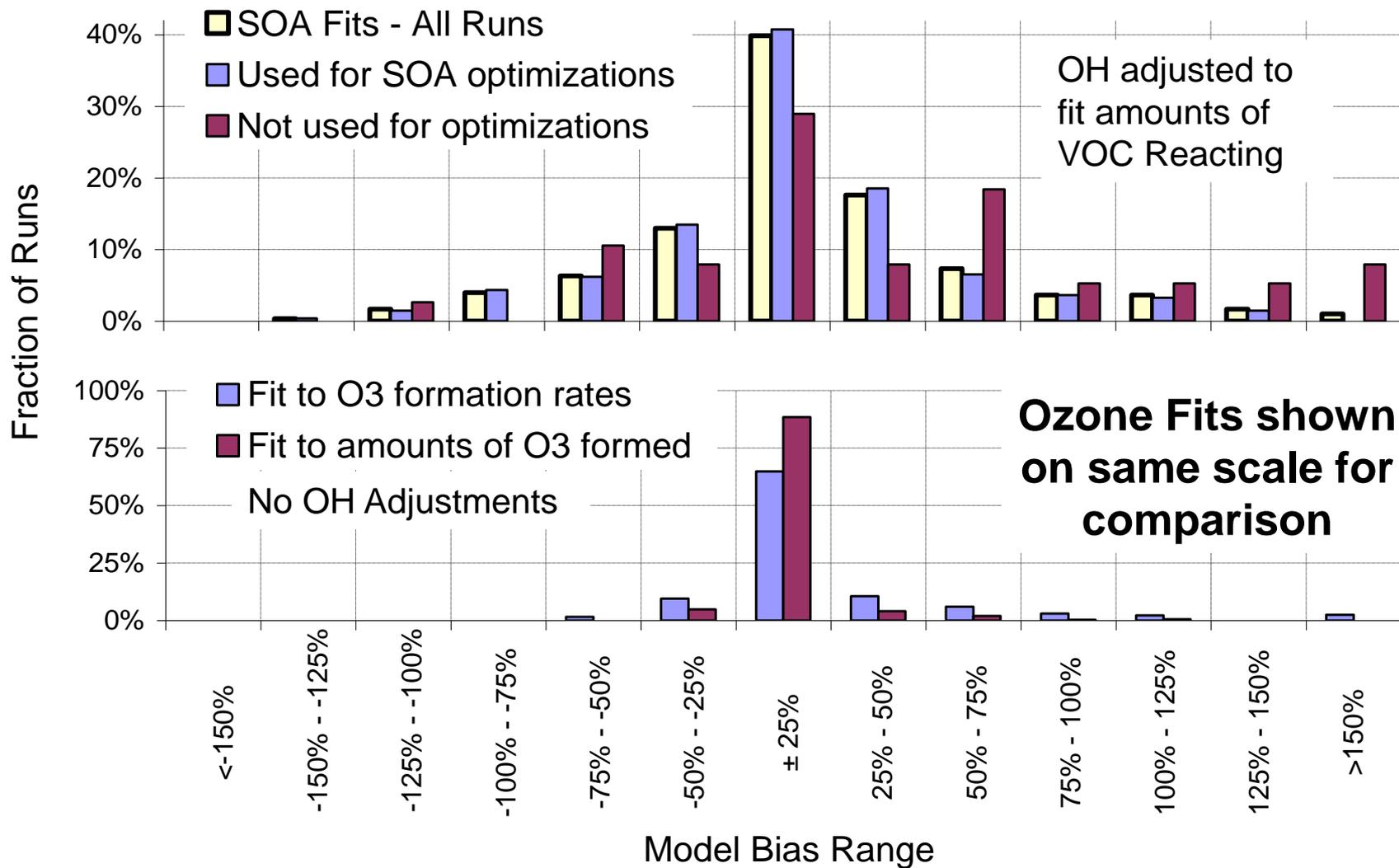to fit rates of toluene consumption

Development of the SAPRC-11 Aromatic SOA Mechanism

- Lumped SOA precursor model species are added as needed to mechanism as to predict how SOA affected by reaction conditions

- No more SOA species added than needed to represent overall processes and fit available data.
  - Insufficient information to support for more detail.

- Four SOA species used to represent five types of processes
  - 2 used for SOA from phenolics, 2 for SOA from other products
  - 2 used for hydroperoxides (ROOH's), 2 for other products
  - Other processes either not necessary or did not fit data

- Yields and K_p's of SOA species adjusted to fit chamber data
  - K_p's adjusted to minimize dependences of fits on PM levels
  - Yields adjusted first for phenol, o-cresol, 2,4-xylenol
  - Yields of the non-phenolic SOA species adjusted for each of the 14 C_6-C_9 alkylbenzenes studied

Aromatic SOA Processes Used

Model Fits for All Experiments used to Derive Aromatic SOA Parameters

Aromatic – NO_x Runs

Aromatic – H_2O_2 Runs

W. P. L. Carter   12/10/2012   Chamber and Model Study of SOA Formation   30

Distribution of Bias Ranges in PM Volume Predictions for all Experiments Modeled

Optimized SOA Parameters for Phenols

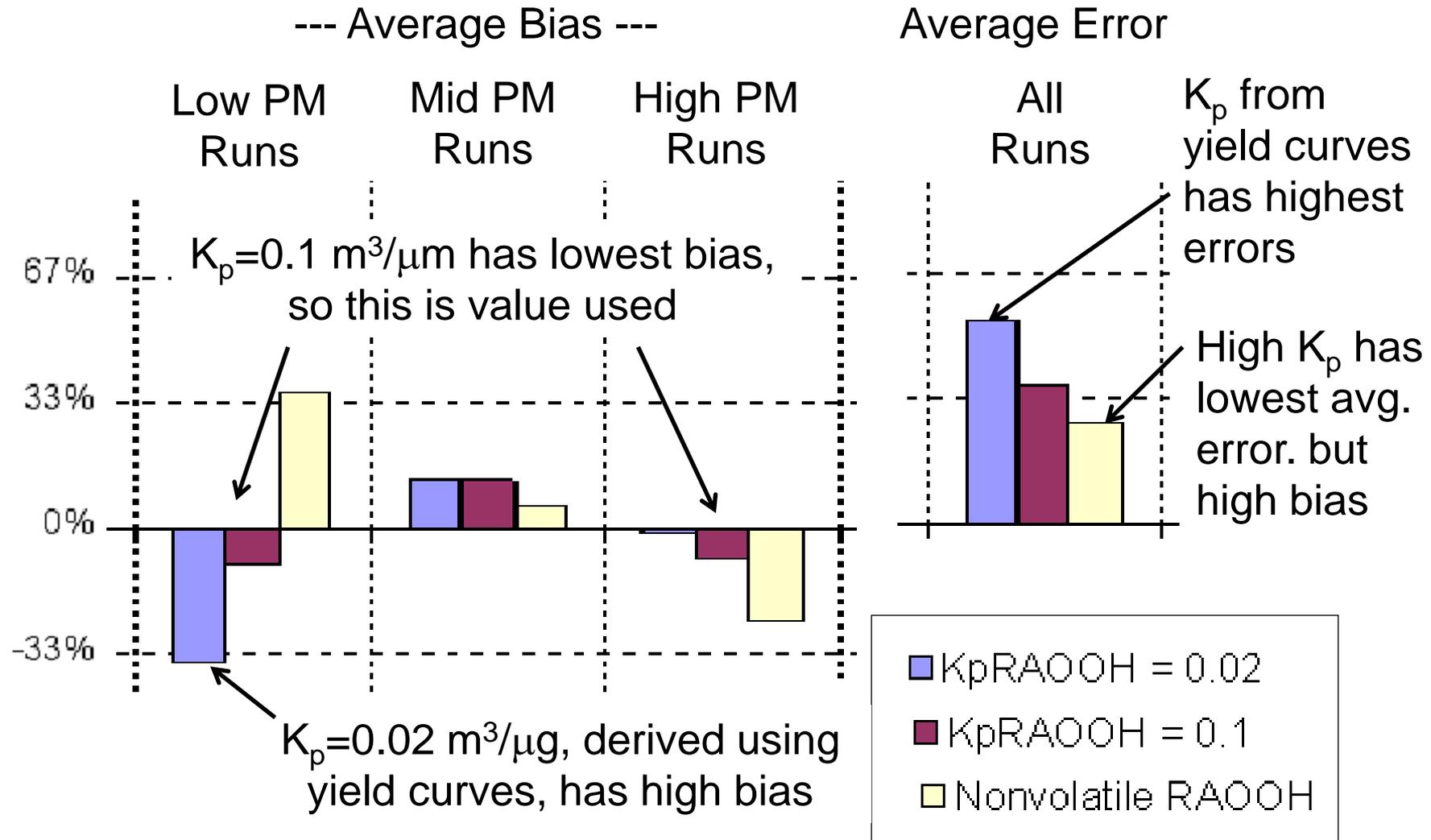| Type of Precursor	From Rxn	K_p $(m^3/\mu g)$	Adjusted Product Yields			
			Phenol	Cresols	Xylenols	Catechols
ROOH	OH	High	2%	4%	21%	-
Other	OH	0.03	~0%	10%	12%	33%
Both	NO_3	-	(Best fit if assumed negligible)			

Average relative contributions of SOA species to experimental PM

Compound	NO_x Runs	H_2O_2 Runs
Phenol	Almost all due to non-ROOH precursors	13%
o-Cresol		18%
2,4-Dimethyl Phenol		47%

■ ROOH Contribution

# Effects of Varying K_p for Hydroperoxide on Average Biases for m-Xylene – H_2O_2 Runs

--- Average Bias ---   Average Error

Low PM Runs   Mid PM Runs   High PM Runs   All Runs K_p from yield curves has highest errors

K_p=0.1 m^3/μm has lowest bias, so this is value used

High K_p has lowest avg. error. but high bias

67%

33%

0%

-33%

K_p=0.02 m^3/μg, derived using yield curves, has high bias

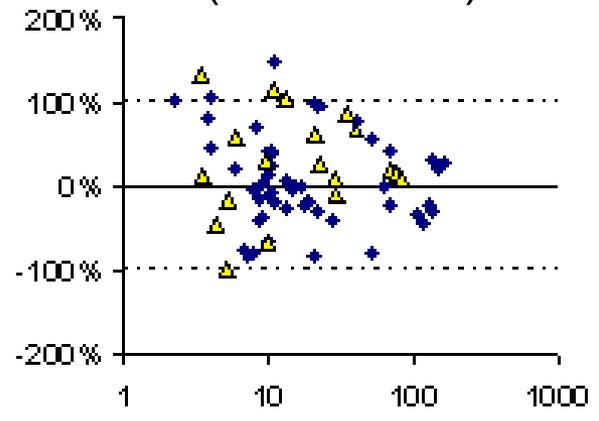□ KpRAOOH = 0.02
■ KpRAOOH = 0.1
□ Nonvolatile RAOOH

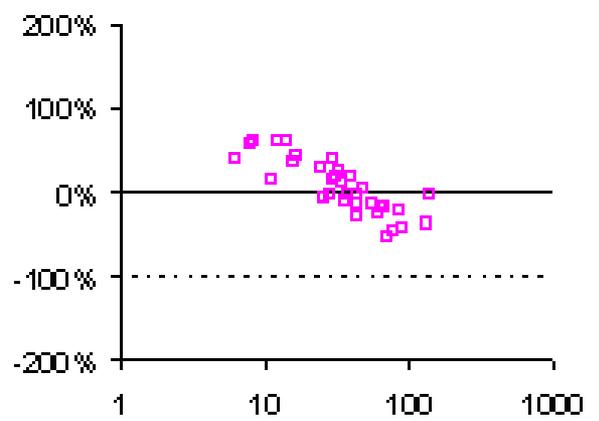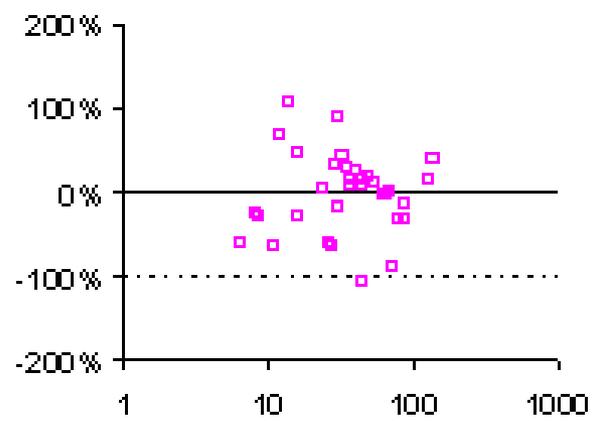# Effects of Varying K_p for Hydroperoxide on Model Fits for m-Xylene Experiments

Kp (ROOH) = 0.1 m³/μg (Least bias)

Non-Volatile ROOH (Least error)

Model Biases for NO$_x$ Runs
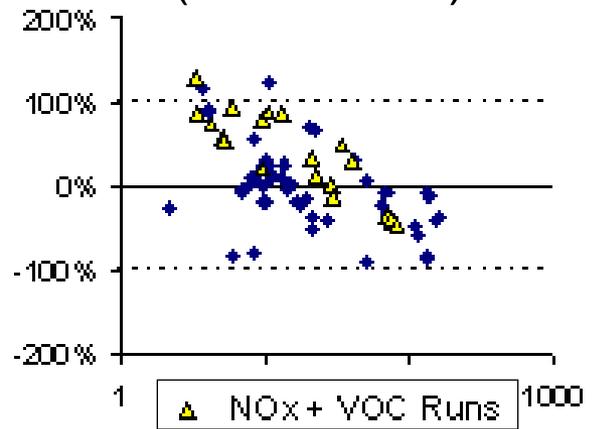
Model Biases for H$_2$O$_2$ Runs

NOx + VOC Runs

Summary of Volatility Partitioning Coefficient Parameters Used

Species Type	Formed From	Mechanism Type	Kp $(m^3/\mu g)$	Derivation
ROOH	HC's	Hydroperoxide	0.02	Yield curve fits to H_2O_2 Runs *
ROOH	HC's	Hydroperoxide	0.1	Model fits to data **
ROOH	Phenols	Hydroperoxide	High	Assumed ***
Other	Non-Phenols	NO_x Product	0.04	Model fits to data **
Other	Phenols	NO_x Product	0.03	Model fits to data **

* Derived from 1-product model fits. Not used for kinetic mechanism

** Adjusted to minimize dependence of model bias on PM levels

*** Assumed to be non-volatile because insufficient data available to adjust. K_p for RAOOHp should be higher than for RAOOH.
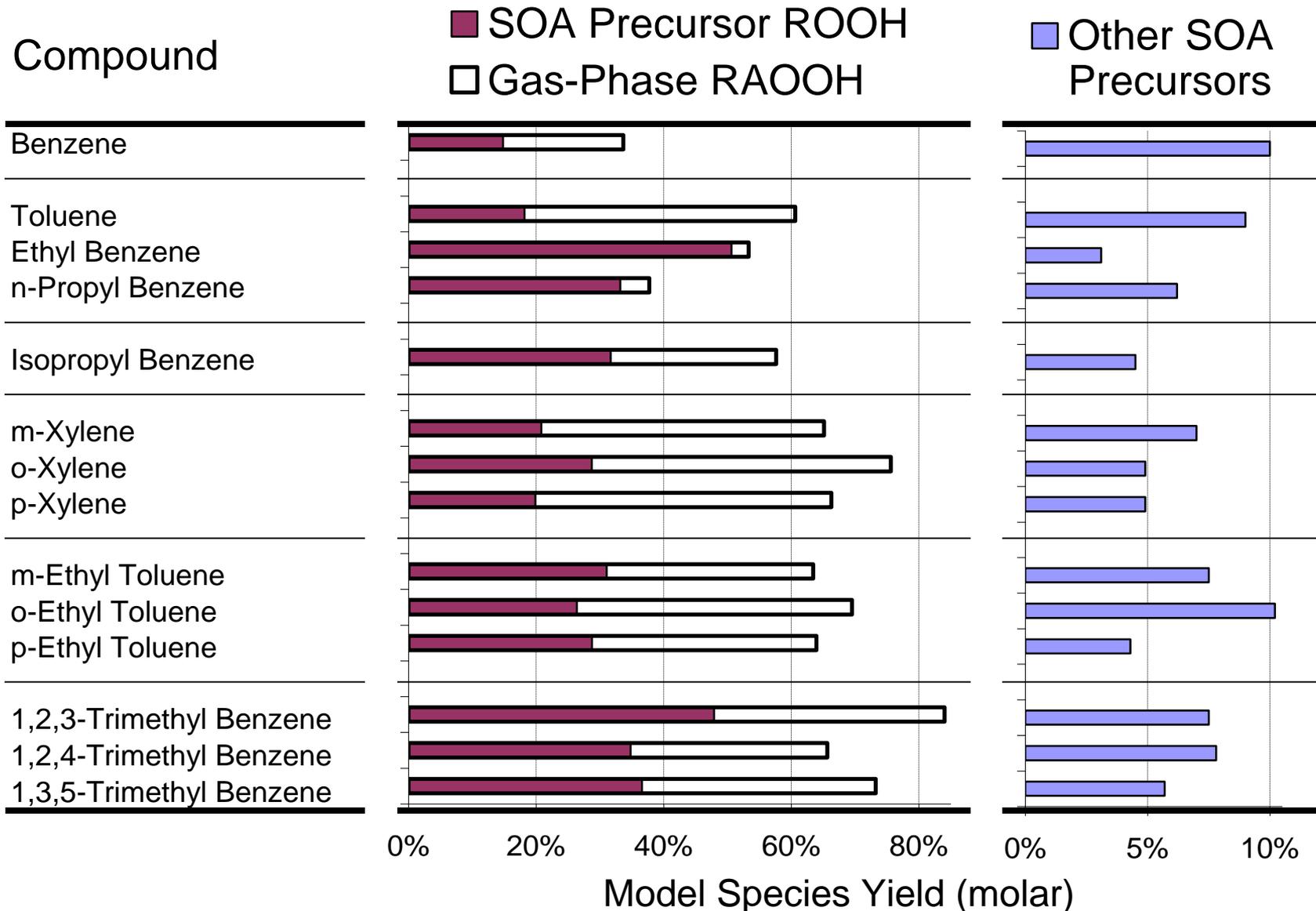
Relative Contributions of Phenolic Products to SOA from Aromatic Hydrocarbons
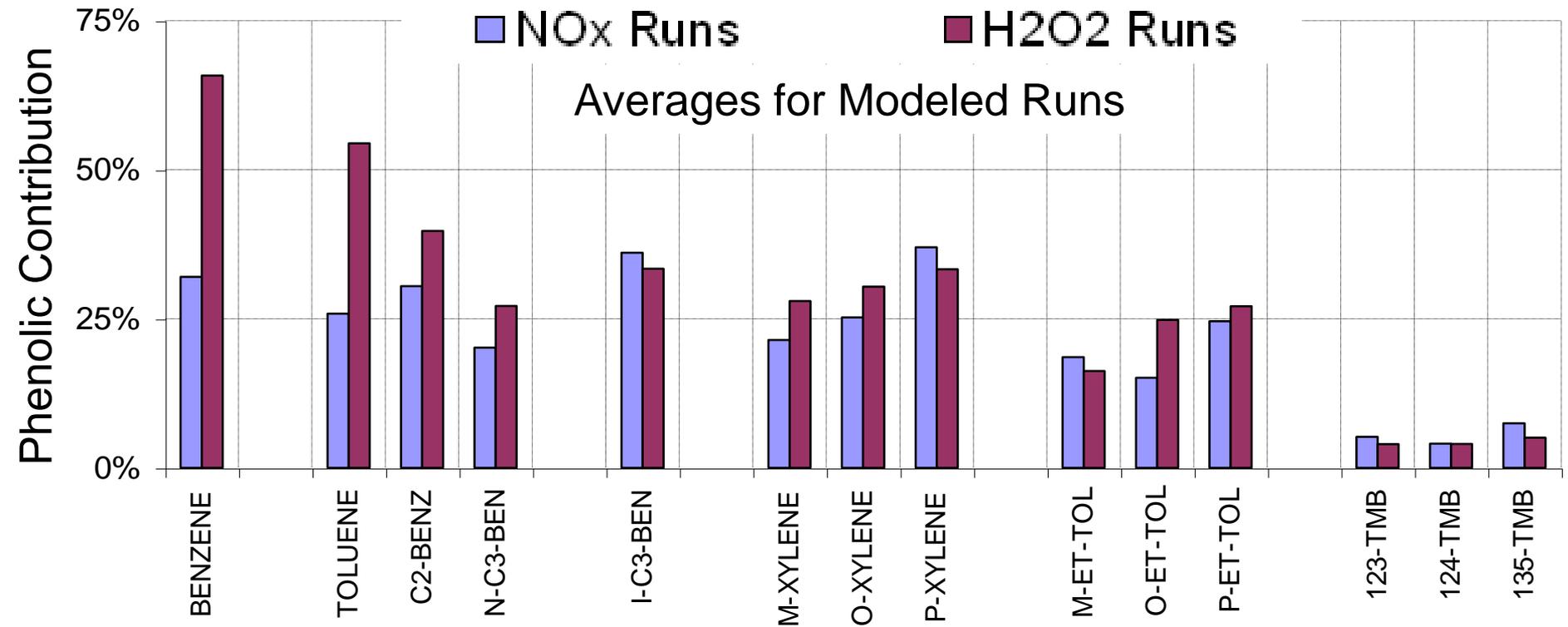
Averages calculated for aromatic - NO_x and Aromatic - H_2O_2 runs

Predicted using parameters adjusted to fit SOA chamber data

Optimized Hydrocarbon SOA Yield Parameters

Chart legend: SOA Precursor ROOH, Gas-Phase RAOOH, Other SOA Precursors

Compound

Benzene
Toluene
Ethyl Benzene
n-Propyl Benzene
Isopropyl Benzene
m-Xylene
o-Xylene
p-Xylene
m-Ethyl Toluene
o-Ethyl Toluene
p-Ethyl Toluene
1,2,3-Trimethyl Benzene
1,2,4-Trimethyl Benzene
1,3,5-Trimethyl Benzene

Model Species Yield (molar)

Summary of results

- Aromatic SOA data are simulated adequately using 4 model species representing 5 overall processes:

  1. Hydroperoxides from OH + alkylbenzene + O_2 + HO_2

  2. SOA precursors from non-phenolic, non-hydroperoxide *secondary* products (data not as well fit if primary product)

  3. Hydroperoxides from cresols and xylenols (not phenol)

  4. Model species representing 2 other processes for phenols

     1. NO_x-dependent SOA precursors from phenols

     2. NO_x-independent SOA precursors from catechols

- Reactions of phenolic products are important sources of aromatic SOA, but usually not the most important

- No clear trends in SOA yield parameters among the 14 C_6-C_9 alkylbenzenes. SOA parameters for monoalkyl benzenes are more variable than those for xylenes and trimethylbenzenes

- Most aromatic SOA relatively volatile ($K_{p, 300K}$ = 0.03 - 0.1 $m^3/\mu g$)

Discussion

- Aromatics mechanisms remain highly uncertain and gas-phase mechanisms are not fully consistent with the data.
  - SOA formation even more complex and uncertain
  - Insufficient knowledge to derive useful explicit mechanisms
- Adjusted lumped product mechanisms can simulate available SOA as well as O_3 chamber data with relatively low biases
  - Generally reasonable representation of overall processes
  - But effects of molecular structure on parameters are unclear
- Parameters from fits to yield curve using equilibrium partitioning models do not fit to the same data using kinetic mechanisms
  - May be due to using finite condensation rates in simulations
- Simulations of SOA in chamber experiments have much more scatter and higher model errors than simulations of ozone
  - Suitable adjustments can give low systematic biases, but model errors remain high. The scatter can hide biases.
  - Cause of scatter is unknown, but is probably experimental

Recommended Next Steps for SOA Mechanism Development

- **SOA mechanism development is limited by data availability**
  - *Projects without a strong experimental component will yield little progress towards a predictive modeling capability*
- Additional experiments needed to expand scope and evaluation of current SOA mechanism. Need *new*, *well characterized* data on:
  - Effects of temperature, humidity and PM from other sources
  - Evaluation data for other types of important SOA precursors
  - Improved characterization and inter-laboratory comparisons
  - Available chamber data from different laboratories should be compiled, characterized, compared, and used if adequate
- Use the data obtained to update and expand the scope of the detailed mechanism to other VOCs and conditions
- Use the evaluated detailed mechanism to develop and evaluate condensed SOA mechanisms for regulatory modeling

Acknowledgements

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- **Robert Griffin**, Rice University: Assistance in reviewing modeling methods and project report

- **California Air Resources Board**: primary funding source for experiments for current project and mechanism development

- **National Science Foundation**: funding source for other UCR chamber experiments modeled for this project.

Thank you