Current Status of SAPRC Mechanism Development

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Outline

- Mechanism development objectives
- Evaluating predictive capability
- SAPRC mechanisms: description, recent updates, plans
- Recommendations

Mechanism Development Objectives

- **Predictive capability**
  - First priority for mechanisms for regulatory models.
  - Requires evaluation of predictions against measurement data representing environments to be modeled
- **Consistency with accepted laboratory data and theories**
  - Necessary for scientific credibility. First priority for many research mechanisms
  - Reduces chance of compensating errors
  - *Sometimes consistency with accepted data is in conflict with predictive capability*
- **Appropriate condensation for the modeling application**
  - Too much condensation limits utility and accuracy
  - Too much detail wastes resources and may not increase accuracy

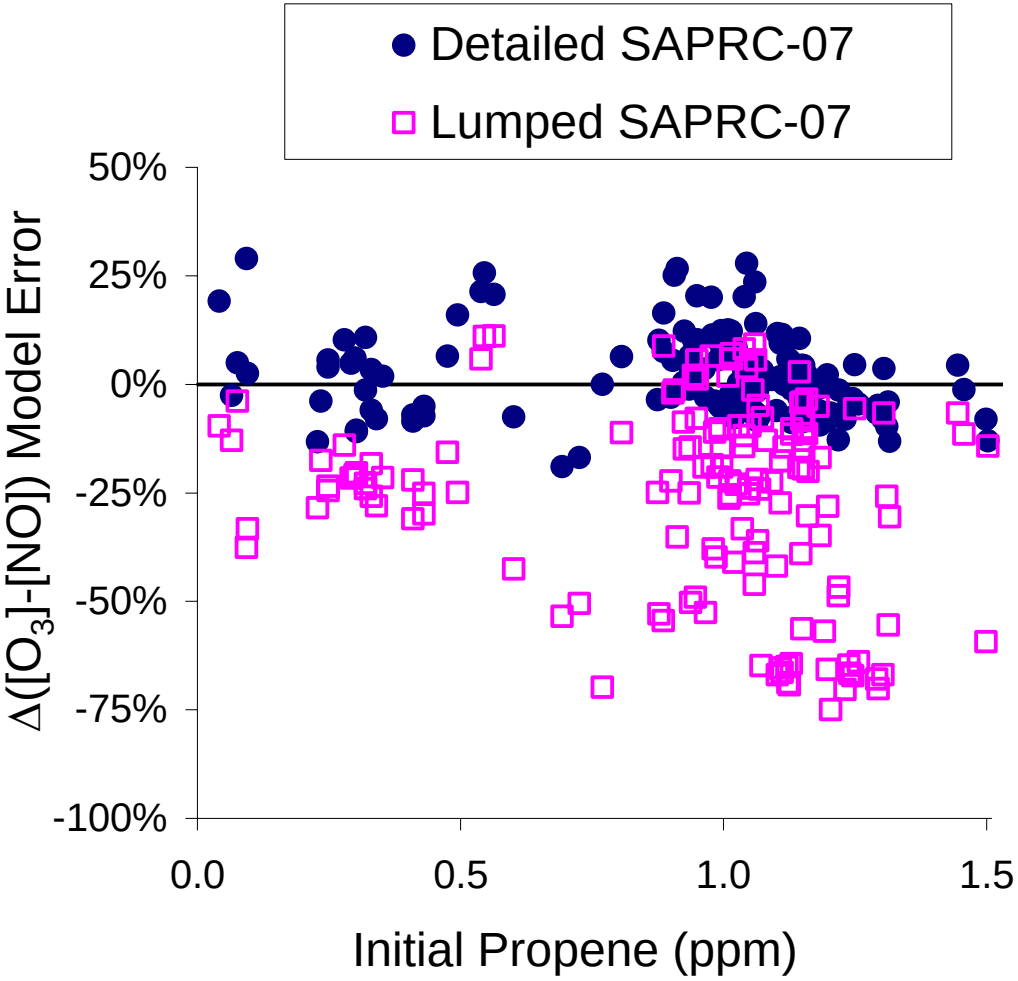
Evaluating Predictive Capability

- Conditions used to derive the evaluation data must be less uncertain than the mechanism being evaluated
- Environmental chamber data provide the most practical test of mechanisms without emissions and meteorological uncertainties
  - Has uncertainties and disadvantages: uncertain chamber effects, artificial conditions, etc.
  - Important uncertain parameters in many current mechanisms have to be adjusted to fit chamber data
  - *SAPRC mechanism development has always been closely linked to conducting and using chamber experiments*
- Ambient measurements provide an important and necessary test to predictive capability
  - But uncertainties in ambient conditions limit utility for mechanism *development* and *adjustment*

Problems with Evaluating Condensed Mechanisms Against Experimental Data

- Lumped model species (e.g., OLE1, PAR) do not really exist, so we cannot conduct experiments with them.
- Fits to data with representative compounds do not test how well the lumped model fits data for ambient mixtures
- Experiments with mixtures can evaluate condensed mechanisms. But such evaluations have problems
  - Cause of problems unclear if the fits are poor
  - Good fits may be due to compensating errors or low sensitivity to errors for components
  - May not be relevant when ambient mixtures are different
- Evaluations against experimental data do not separately test for effects of condensation and errors in the chemistry

Effects of VOC Lumping on Simulations of Ozone Formation Rates in Propene – NO_x Chamber Experiments



Compounds used to derive OLE1 mechanism

Mole %	Compound
29%	Propene
24%	1-Hexene
12%	1-Butene
11%	1-Pentene
11%	1-Heptene
10%	C_9-C_{12} 1-alkenes
3%	3-Methyl-1-Butene

From ambient mixture used to derive reactivity scales

What is SAPRC?

- The SAPRC mechanisms are a series of gas-phase atmospheric chemical mechanisms developed primarily by W.P.L. Carter
- SAPRC stands for (California) Statewide Air Pollution Research Center, a research center at UCR where the mechanism was first developed in the 1980's
- Research center name changed to APRC in 1990's. Now SAPRC is just a name, and doesn't mean anything else (like "NARSTO")

History of the SAPRC Mechanisms

1979-1980	First papers by Carter et al. on mechanisms
1985	Paper on mechanism generation for alkanes published
1987	Reports to EPA, USAF and CARB on multi-VOC mechanisms that served as basis for subsequent detailed SAPRC
1990	SAPRC-90 detailed mechanism developed and published
1991	Condensed SAPRC-90 for airshed models developed
1994	Paper on MIR and other reactivity scales using SAPRC-90
1999-2000	Reports on SAPRC-99 mechanisms. Current SAPRC mechanism generation system first developed
2008-2010	Reports and papers on SAPRC-07 detailed and condensed mechanisms. Mechanism generation system updated
2011-2012	SAPRC-11 for aromatics and aromatic SOA developed
2013-2014	Updates to gas-phase SAPRC planned. SOA uncertain
2015	Carter plans to be *really* retired. Future of SAPRC uncertain

Versions of the SAPRC Mechanisms: Mechanism Generation System

- Mechanism type: semi-explicit
  - Mechanism generation software used
  - Uses measured rate constants and branching where available, estimation methods where not
  - Reaction pathways <1% for single steps are ignored
  - Because of limitations, not currently used to generate complete mechanisms for models (but could in principle)
- Major limitations:
  - Not used for aromatics and cannot estimate reactions with radicals whose heats of formation cannot be estimated
  - Does not understand steric factors
  - Currently limited to generating mechanisms in presence of NO_x (peroxy + peroxy mechanisms not generated)

Versions of the SAPRC Mechanisms: Mechanism Generation System (cont'd)

- Utility
  - Full capability: alkane and alkene hydrocarbons, compounds with -O-, -OH, -CO-, -CHO, & $-ONO_2$ groups, simple amines
  - Partial capability: cyclic compounds, dialkenes, alkynes, compounds with -Cl and -F groups
  - Generates reactions with: OH, O_3, NO_3, hν (carbonyls), Cl (limited capability for alkenes)
- Used to derive SAPRC-07 mechanisms for >600 VOCs
  - Derives overall process for reactions in presence of NO_x, eliminating most intermediate organic radicals
  - "Lumping Rules" used to derive lumped model species for each predicted products
- Documentation at http://www.cert.ucr.edu/~carter/SAPRC
- Now available online at http://mechgen.cert.ucr.edu

From Generated Mechanism to SAPRC-07: Lump Reactions, but Keep Chemical Detail

90%	**$CH_3CH_2OH + OH \rightarrow$** $H_2O + CH_3CH(\cdot)OH$
5%	$CH_3CH_2OH + OH \rightarrow H_2O + CH_3CH_2O\cdot$
5%	$CH_3CH_2OH + OH \rightarrow H_2O + .CH_2CH_2OH$
90%	$CH_3CH(\cdot)OH + O_2 \rightarrow$ **$CH_3CHO + HO_2\cdot$**
5%	$CH_3CH_2O\cdot + O_2 \rightarrow$ **$CH_3CHO + HO_2\cdot$**
5%	$.CH_2CH_2OH + O_2 \rightarrow .OOCH_2CH_2OH$
5%	$.OOCH_2CH_2OH +$ **$NO \rightarrow NO_2$** $+ .OCH_2CH_2OH$
1%	$.OCH_2CH_2OH + O_2 \rightarrow$ **$HOCH_2CHO + HO_2\cdot$**
4%	$.OCH_2CH_2OH \rightarrow$ **$HCHO$** $+ .CH_2OH$
4%	$.CH_2OH + O_2 \rightarrow$ **$HCHO + HO_2\cdot$**

Generated mechanism (NO_x reactions)

Explicit Product SAPRC-07 (lumped peroxy)

$CH_3CH_2OH + OH \rightarrow 0.95\ \{HO_2 + CH_3CHO\} + 0.08\ xHCHO + 0.01\ xHOCH_2CHO + 0.05\ \{xHO_2 + RO2C + yROOH\}$

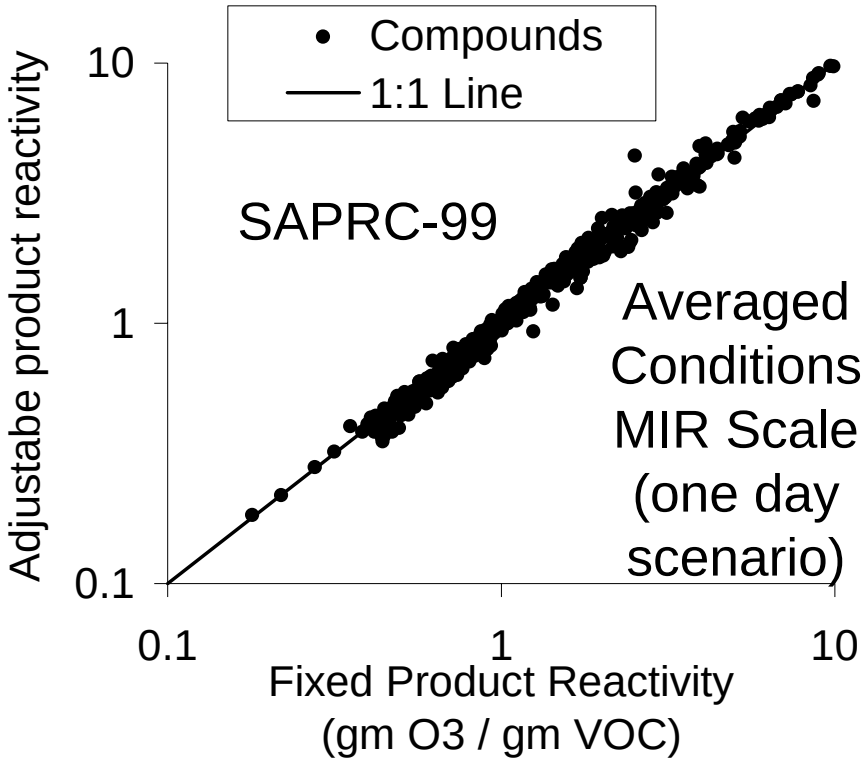
Versions of the SAPRC Mechanisms: Adjusted Product "Detailed" Mechanisms

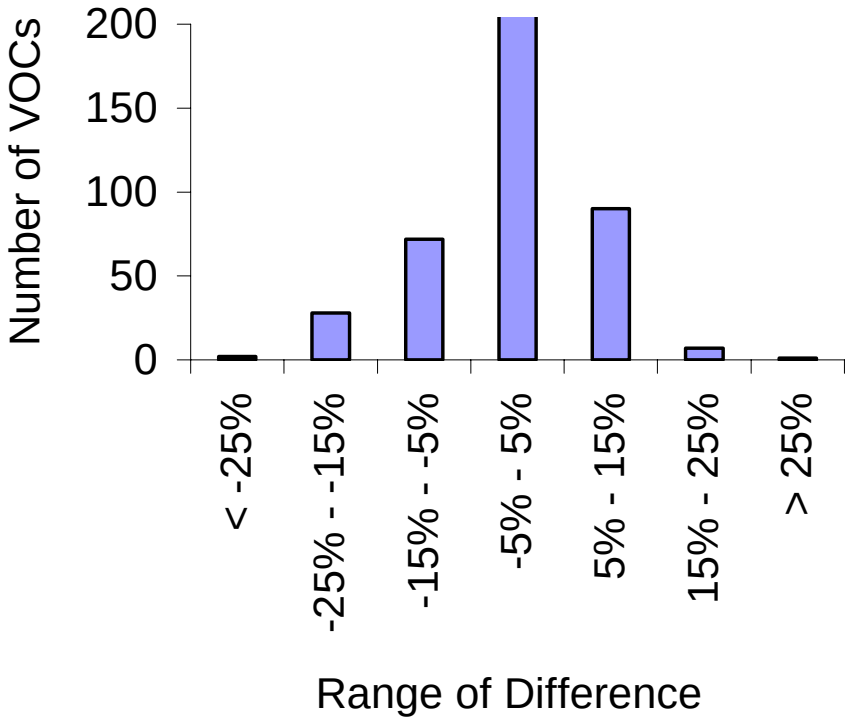
- Mechanism type: detailed VOC, semi-explicit + lumped products
  - Mechanisms for reactive product lumped model species derived based on mechanisms for products they represent
  - Used for VOCs whose primary and reactive product mechanisms could be derived by mechanism generation
  - Lower reactivity or lower yield (<5%) products represented using lumped product model species
- Used for reactivity scale calculations if this method changed the SAPRC-99 "averaged conditions" MIR by >8% (134 VOCs)
- Not currently used for other purposes, but could potentially be the basis for deriving an explicit product version of SAPRC (comparable in size or larger than MCM)

Versions of the SAPRC Mechanisms: Lumped Product "Detailed" Mechanism

- Mechanism type: explicit VOC, lumped products
  - Used in reactivity calculations (in conjunction with a lumped VOC version that represents the base ROG mixture)
  - Mechanisms for >600 VOCs from mechanism generation
  - Mechanisms for ~130 others estimated using other means
  - 31 model species used to represent organic products
- Ozone predictions extensively evaluated against chamber data
  - >2500 experiments, 11 chambers, 4 laboratories
  - $\Delta([O_3]\text{-}[NO])$ generally simulated within $\pm$ 30%
- Used to calculate MIR and other VOC reactivity scales
  - 774 calculated explicitly, 407 others based on explicit VOCs
  - "Adjusted product" version used for 134 VOCs (next slide)
- **Used to derive the lumped VOC versions of SAPRC-07**

Differences Between Adjusted Product and Lumped Product Ozone Reactivity Values





- SAPRC-07 Results should be similar
- Differences may be greater for multi-day scenarios

Versions of the SAPRC Mechanisms: SAPRC-07 Lumped VOC Mechanisms

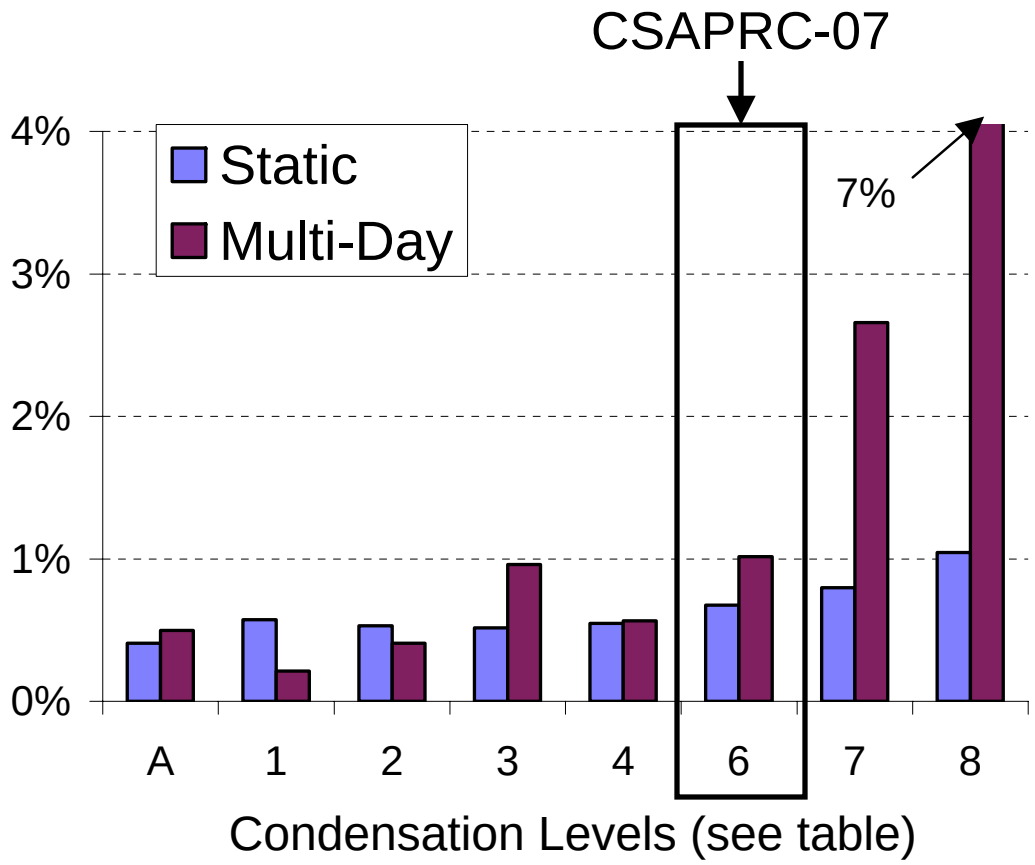
- Mechanism type: lumped VOC
  - Developed for use in airshed models.
  - Same inorganic and lumped product mechanisms as detailed
  - 10 Lumped VOC species: ALK1-5, OLE1-2, ARO1-2, TERP
  - Currently two versions:
    - Standard version: methane, ethene, benzene, isoprene, acetylene explicit (total of 15 VOC species)
    - "Toxics" version: these + 11 other selected VOCs explicit
- *Derived from explicit VOC, lumped product mechanisms*, with lumped VOC reactions based on the compounds they represent
  - Weighting factors from base ROG mixture used in reactivity scales. (But ambient mixture needs updating)
- Used to represent base case when calculating reactivity scales

Versions of the SAPRC Mechanisms: CSAPRC-07 Condensed Mechanisms

- Mechanism type: lumped VOC
  - Developed for give almost same O_3 in airshed calculations as standard lumped SAPRC-07 with fewer model species.
  - Number of organic product model species reduced from 30 to 13, VOCs species reduced from 15 to 10.
- Derived from standard lumped SAPRC-07
  - Test calculations used to examine incrementally increasing lumping effects on O_3, NO_x, H_2O_2, OH and total PANs.
    - Static, dynamic, multi-day ambient simulations
    - Static simulations with individual types of VOCs
  - Most extensive condensations that did not significantly affect O_3 results were adopted for CSAPRC07

Ozone Changes Caused by Condensations

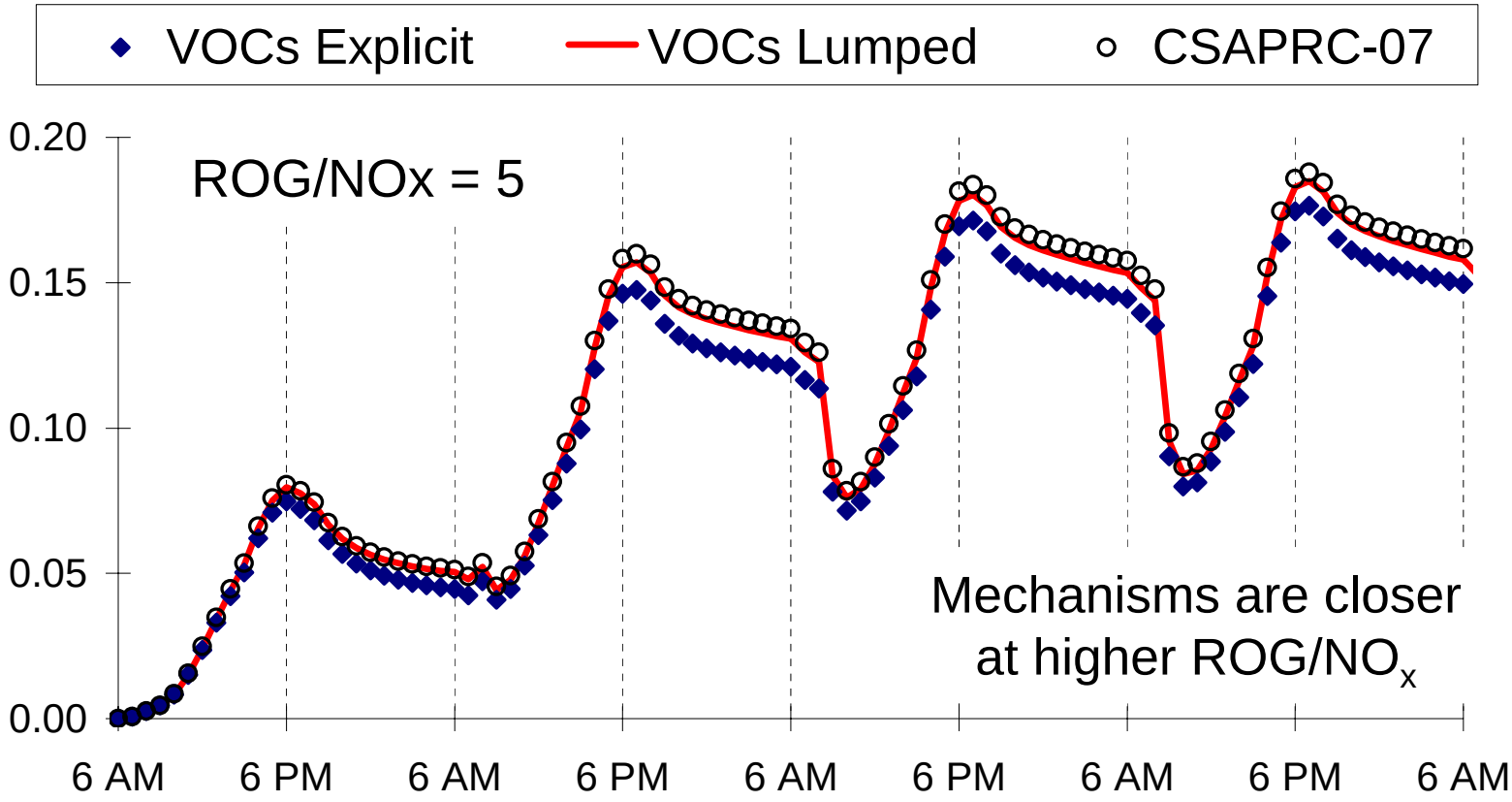
Average of absolute change in O_3 for scenarios at various ROG and NO_x levels, relative to uncondensed SAPRC-07



Condensation Levels

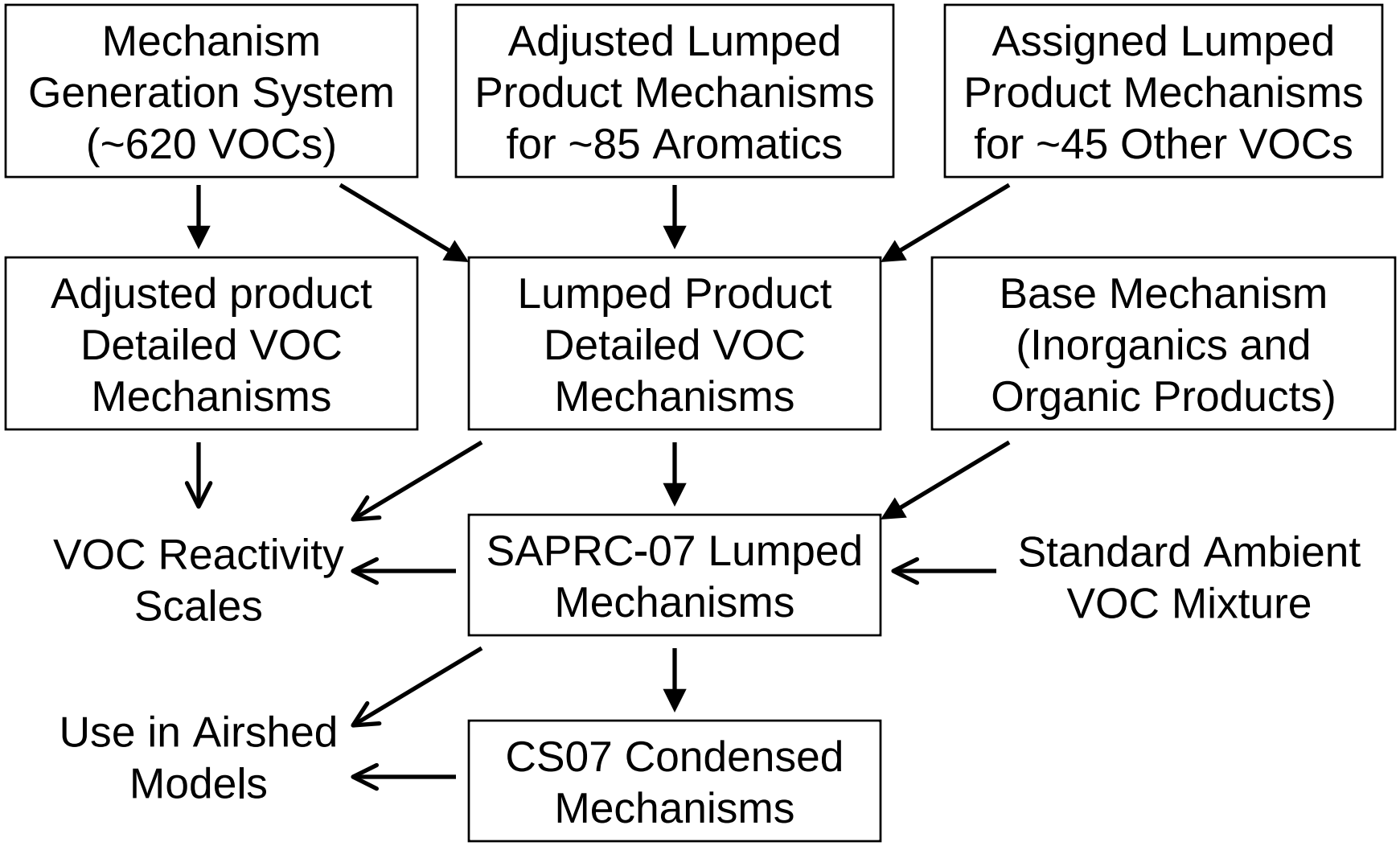
A	SAPRC-99 Peroxy lumping
1	(A) + Low reactivity product compounds lumped
2	(1) + Higher PANs lumped with PAN2
3	(2) + 1-Product isoprene mechanism
4	(3) + Aromatics mechanism simplified
6	(4) + Fewer lumped species for alkanes (CSAPRC-07)
7	(6) PAN lumped with PAN2 (Change too great, not used)
8	(7) + Acetaldehyde lumped with RCHO (Not used)

Effects of Lumping on SAPRC-07 Ozone Predictions for a Multi-Day Scenario



- 5-Day simulations with Continuous emissions
- Same ambient mixture as used to derive the lumped mechanism

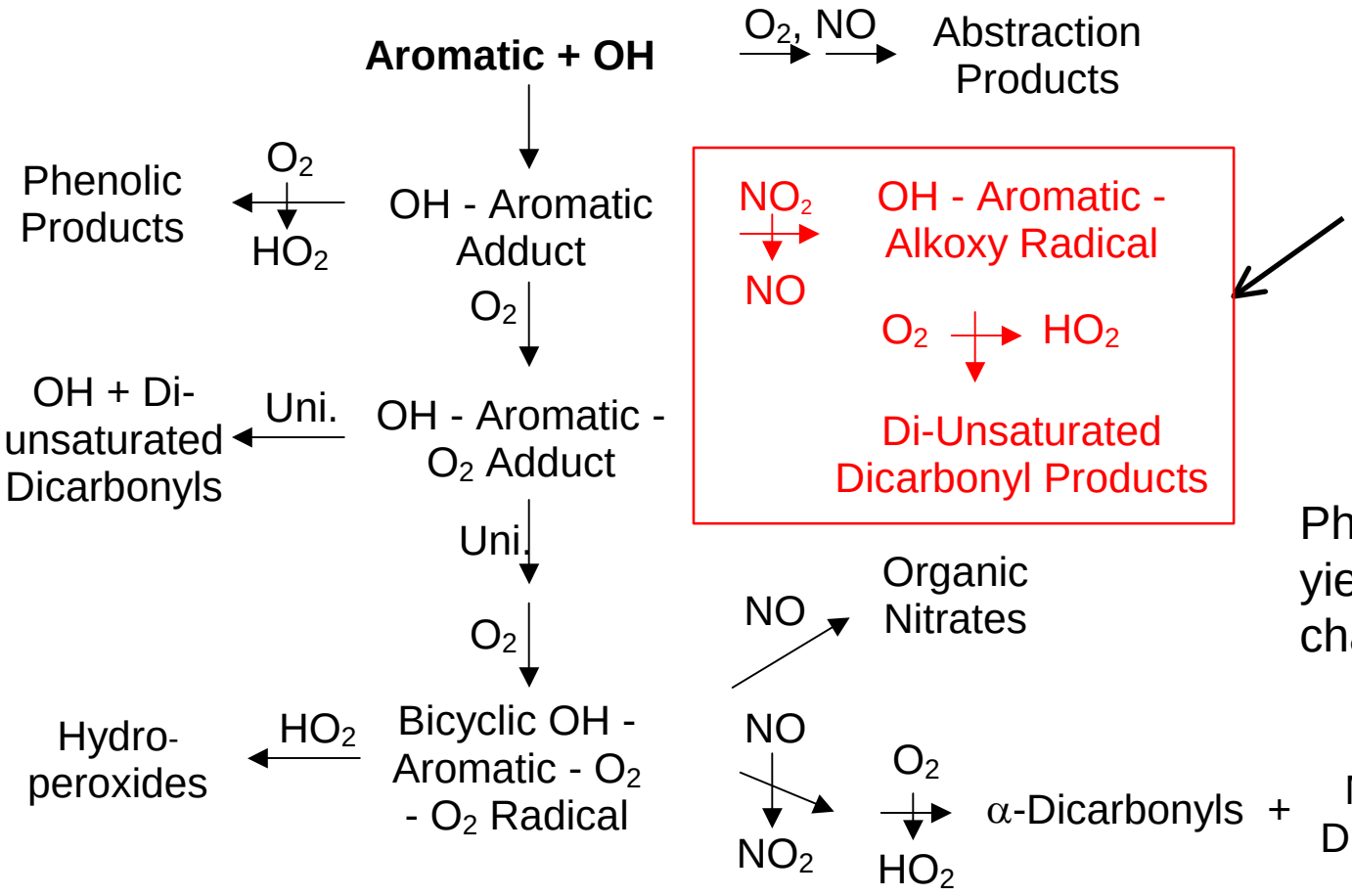
Relationships Between Current Versions of the SAPRC-07 Mechanisms



Updates to SAPRC-07: SAPRC-11 Gas-Phase Aromatics Mechanism

- Mechanism type: Explicit VOC, lumped products
- Same base mechanism as SAPRC-07, with minor corrections
- Aromatic mechanisms revised, but same general approach
  - Much better fits to results of many new aromatic – NOx experiments, especially at lower concentrations
  - Rate constants, known product yields updated
  - Data and mechanisms for additional compounds
  - Much more reactive mechanisms for phenols
- Most inconsistencies and problems with SAPRC-07 remain
  - Chamber data for benzene and toluene have greater dependence on NO_x than indicated by product studies
  - OH radical levels are still significantly underpredicted
- Lumped versions for airshed models not yet developed

Features of SAPRC-11 Aromatic Reactions



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

Photolysis Quantum yields adjusted to fit chamber data

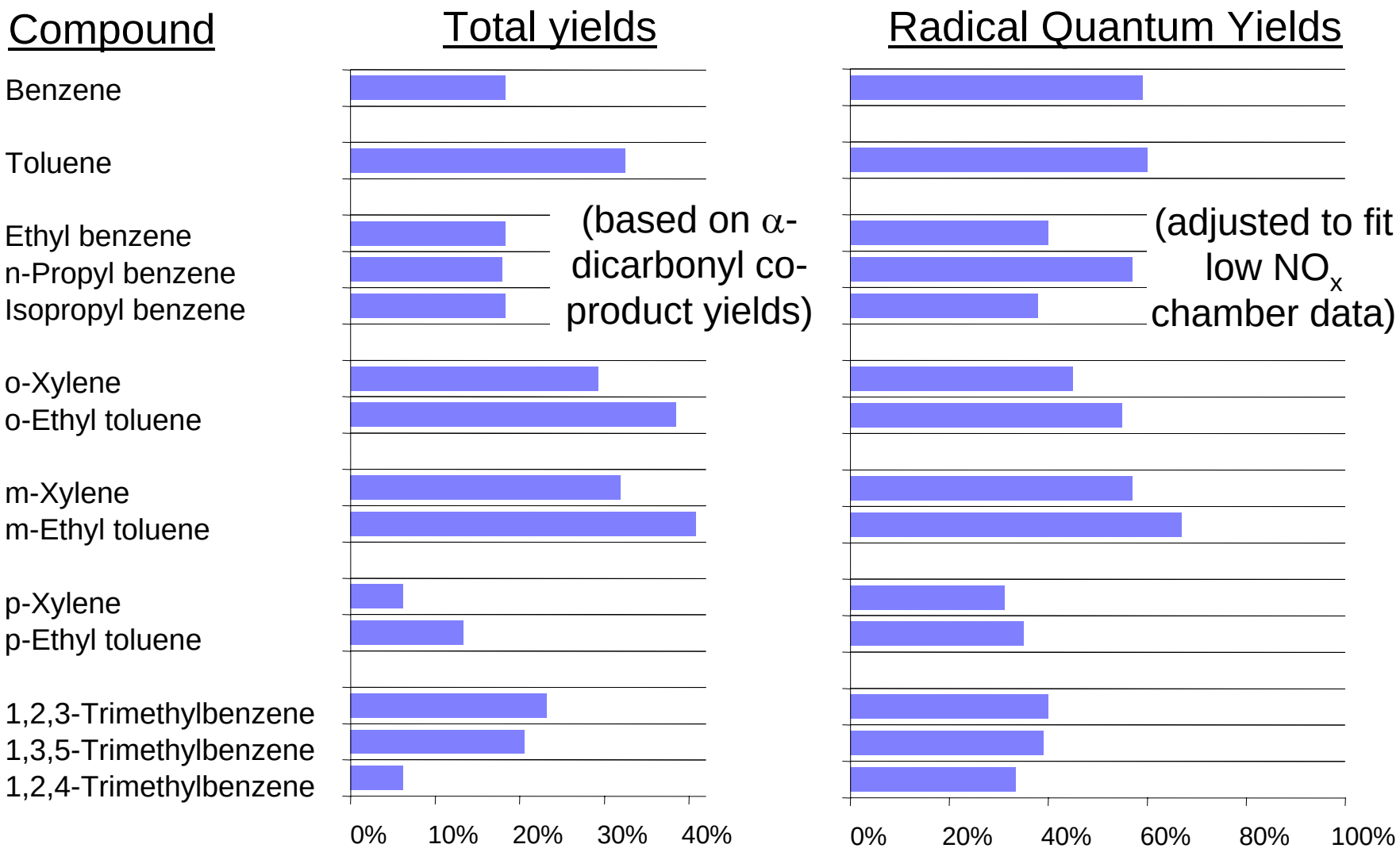
Problem with NO_x Dependences on Benzene and Toluene Model Fits

- 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 a reaction of the OH-aromatic adduct with NO_2, forming lower reactivity products, is added, and $k(O_2) / k(NO_2)$ is adjusted to fit the chamber data
- *The NO_2 levels where the rates of the NO_2 and O_2 reactions are equal are not consistent with laboratory product yield data.*

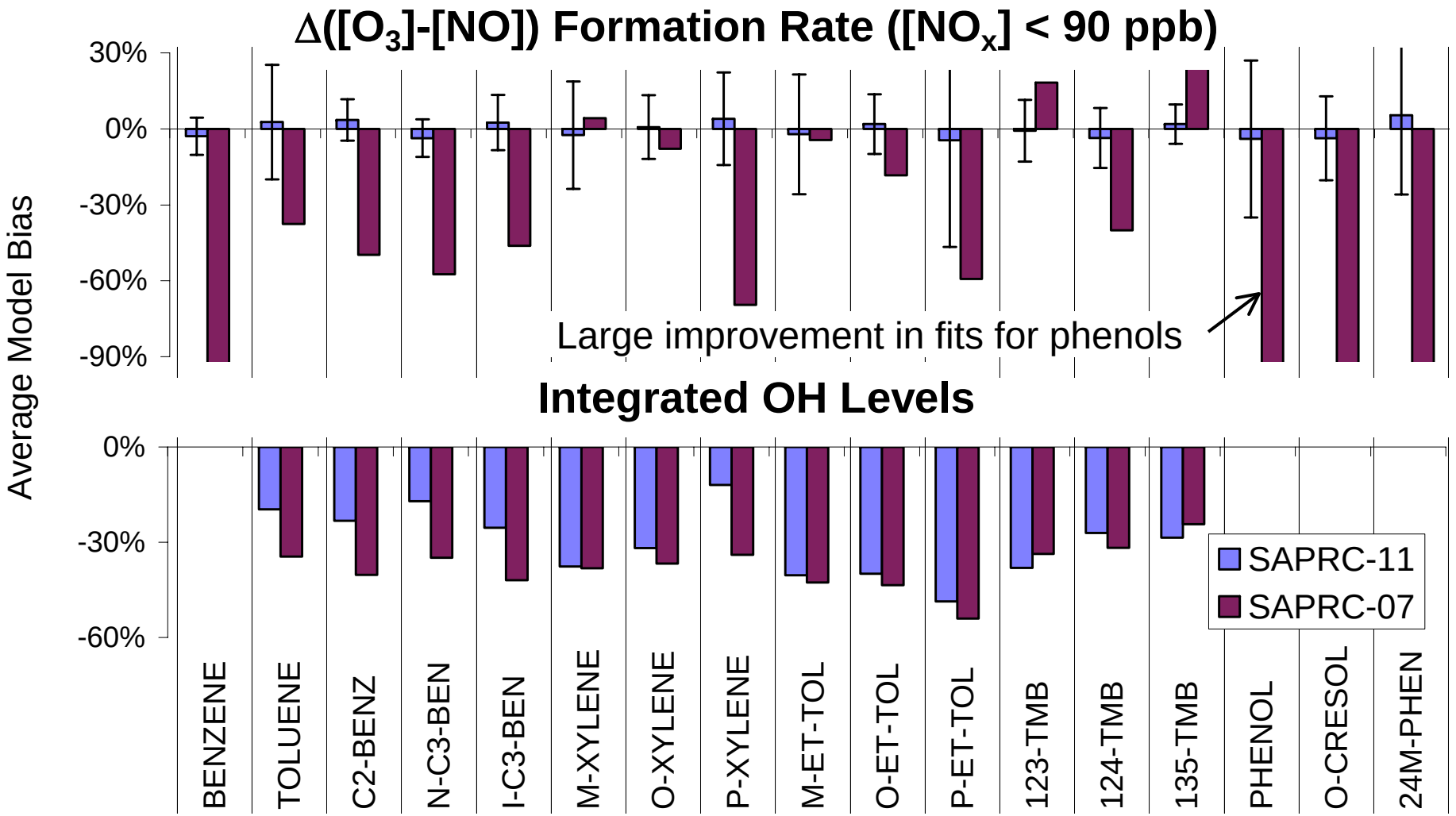
Compound(s)	Fits Chamber Data	Derived from Lab Studies
Benzene	~ 10 ppb NO_2	~ 1 ppm NO_2
Toluene	~ 200 ppb NO_2	~ 3 ppm NO_2
Most others	(Reaction not needed)	Higher NO_2

- **This is a case where apparent predictive capability and accepted laboratory data disagree**

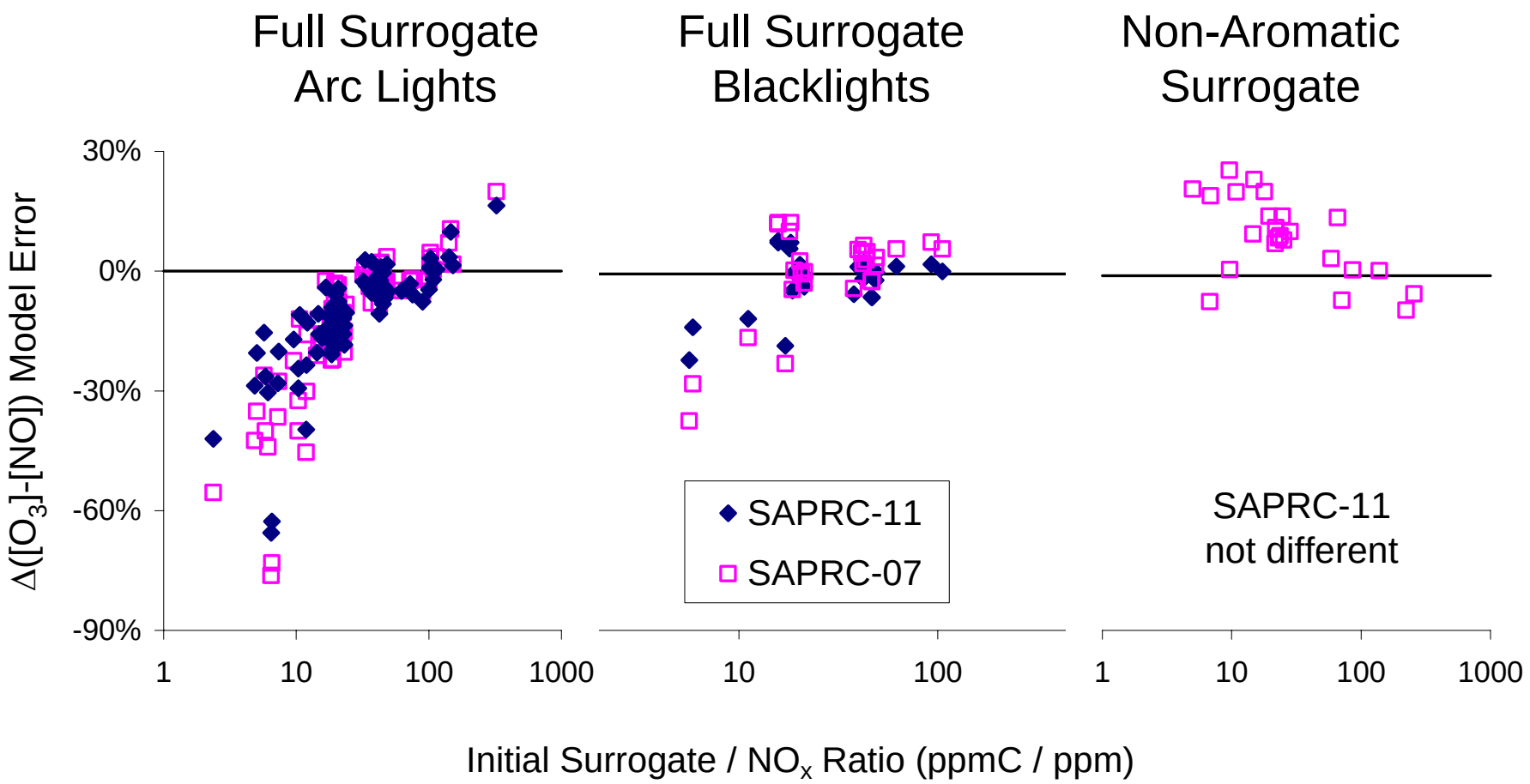
Photoreactive Dicarbonyls: Total Yields and Adjusted Quantum Yields



Average Model Biases for Compounds



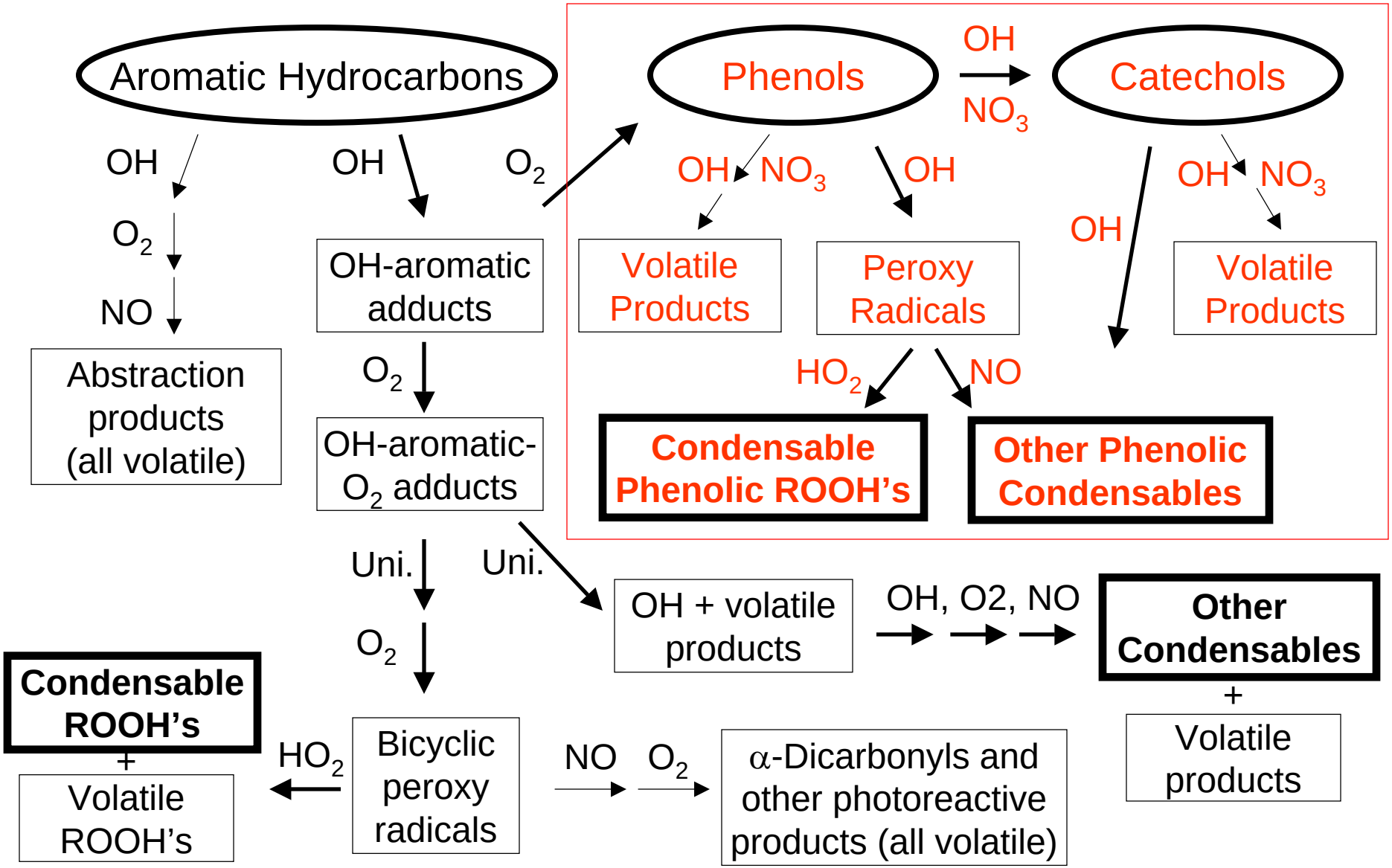
Plots of Δ([O_3]-[NO]) Model Errors against VOC / NO_x for the Surrogate – NO_x Experiments



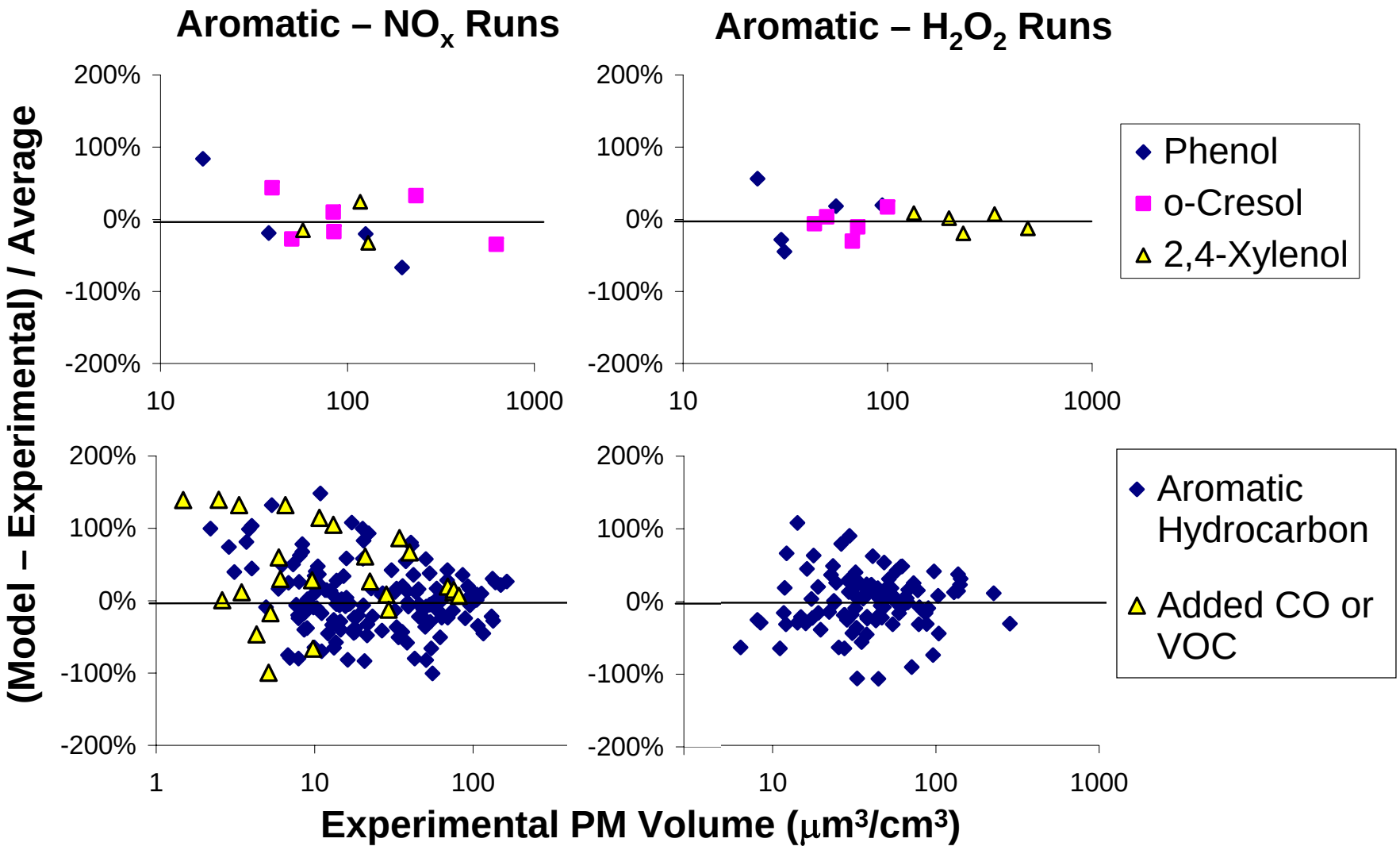
SAPRC-11 Aromatic SOA Mechanism

- Results of 164 aromatic – NO_x and 126 aromatic – H_2O_2 experiments in UCR-EPA chamber used to develop predictive SOA model for 14 aromatic hydrocarbons and 3 phenols
  - Experiments described in presentation by David Cocker
  - Characterized for both gas-phase and PM evaluations
- SAPRC-11 gas-phase mechanism used as the starting point. No changes made that affect gas-phase predictions
- Lumped SOA precursor model species added to mechanism as needed to predict how SOA affected by reaction conditions
  - No more species added than needed. No attempt to identify specific SOA species. Insufficient information for more detail.
  - Yields and partitioning coefficients adjusted to fit data
- Results documented in report to CARB and will be described in a presentation at the CARB on Friday, December 14.

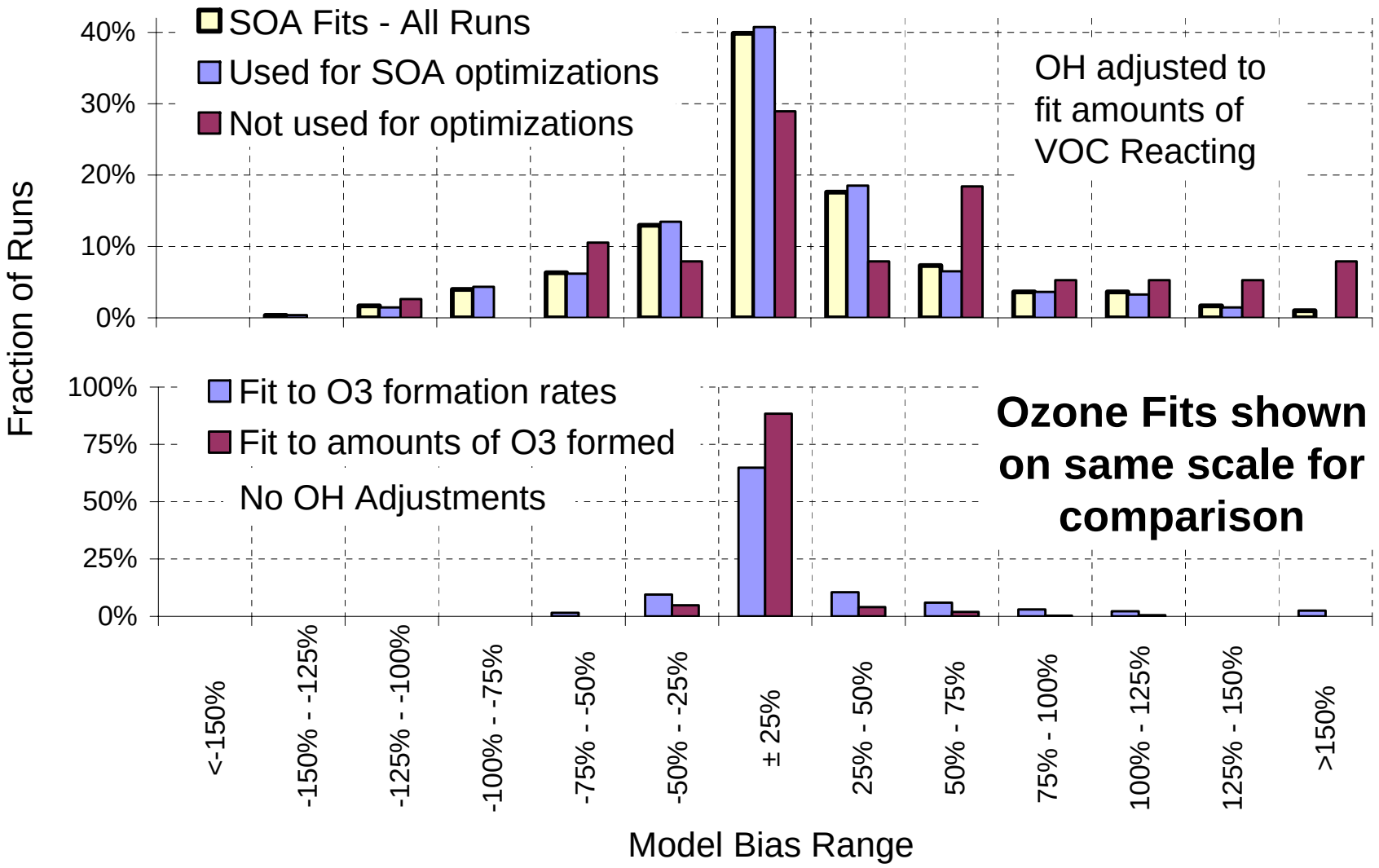
Aromatic SOA Processes Used



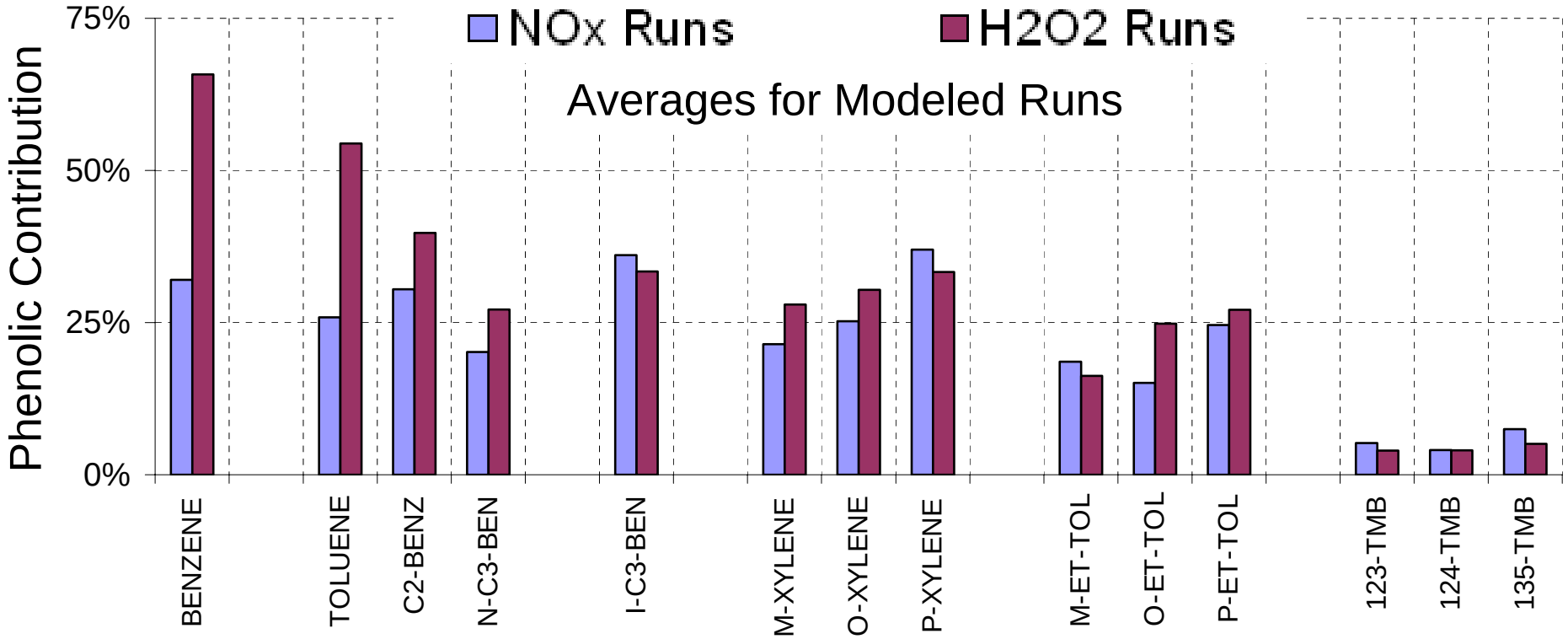
Model Fits for All Experiments used to Derive Aromatic SOA Parameters



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



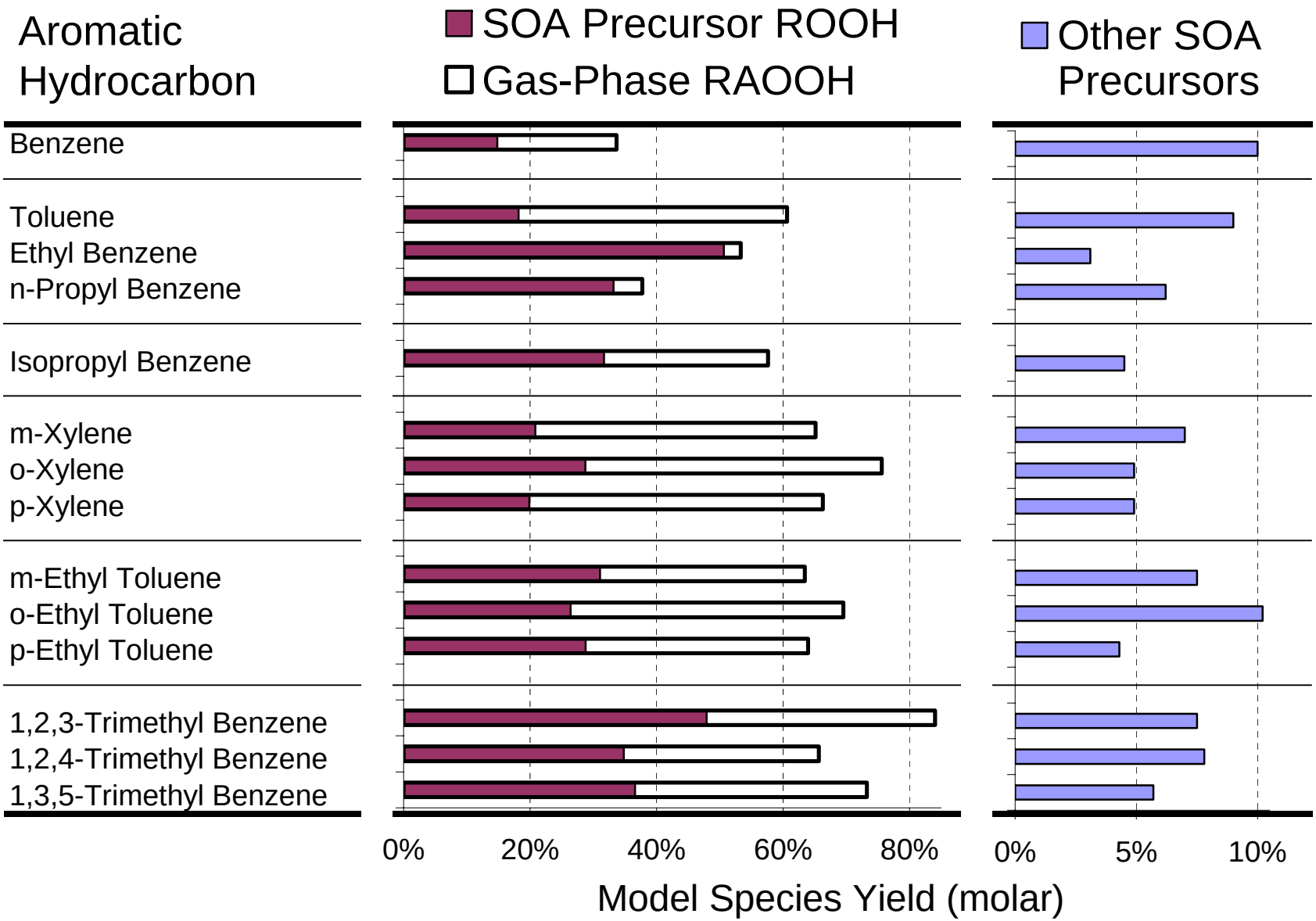
Relative Contributions of Phenolic Products to SOA from Aromatic Hydrocarbons



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



Discussion of Aromatic SOA Mechanism

- Aromatics mechanisms remain highly uncertain and 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

SAPRC Update Projects Currently Underway

- Documentation of SAPRC modeling software and data files
  - Software used for SAPRC mechanism development, evaluation, and use is finally being documented
  - Data files and spreadsheets implementing SAPRC will also be documented and made available for future developers
- Mechanism generation system updates and documentation
  - Estimation methods and assignment database to be updated
  - Publication documenting updated system being prepared
  - Web access being improved (see mechgen.cert.ucr.edu)
- General mechanism updates (detailed and lumped VOC)
  - Complete update of base mechanism
  - Incorporate aromatic and mechanism generation updates
  - Evaluate changes in peroxy and VOC product lumping approaches (implementation mostly for the follow-on project)

SAPRC Update Project Currently Planned

- Develop improved VOC product lumping approach
  - Separate representation of unsaturated PANs and nitrates needed to improve predictions of NO_x recycling
  - Separate representation of higher molecular weight products needed to support process-based SOA modeling
  - Objective is to improve detail for predictive capability, but not more than needed or can be supported by theories and data
- Continue attempting to improve aromatic mechanisms
  - Improve mechanism generation support for aromatics
  - Objectives are to improve
    - Level of detail that is supported by data and theories
    - Consistency with both laboratory and chamber data
- Work on on gas-phase improvements to eventually aid future SOA models being developed by other groups

Proposed SAPRC Updates Not Currently Funded

- Continue steps needed to develop SAPRC SOA mechanism
  - Requires new well-characterized chamber experiments
  - Use results to develop explicit VOC, lumped product mechanisms with enough detail to represent major processes
  - Use the detailed and experimentally evaluated mechanism to develop condensed mechanisms for regulatory models
- Develop near-explicit SAPRC mechanisms that are chemically consistent with existing condensed SAPRC mechanisms
  - Mechanism generation system can be adapted to produce models with any level of detail based on current estimates
  - Allows comprehensive studies of condensation effects
  - Update or alternative to MCM for similar research needs
  - Potential framework for detailed SOA modeling when basic understanding improves

General Recommendations for Mechanism Development

- *Investment in chamber experiments* with high characterization standards is critical to developing predictive mechanisms
  - We would not have reliable models for ozone without the well characterized chamber database developed since the 1970's
  - SOA is more complicated, requires more data, and the availability of suitable data is limited. *This is the main factor limiting predictive SOA model development*
- Start by developing and evaluating the *most chemically detailed mechanism possible* given the available state of knowledge
  - Developing more scientifically valid condensed mechanisms, based on a more detailed understanding, can follow
- *Mechanism generation* is the "wave of the future"
  - Provides a framework to organize theory and data
  - Research in improving estimation methods (including thermochemical) needs to be given higher priority

Acknowledgements

- Roger Atkinson, Helpful discussions on atmospheric chemistry over many years
- Gookyoung Heo: Assistance in ongoing SAPRC mechanism development and evaluation
- David Cocker, UCR: Collaborating on UCR chamber experiments on SOA formation
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- Dennis Fitz, Kurt Bumiller, Chuck Bufalino, other CE-CERT staff: assistance with UCR chamber experiments

- California Air Resources Board: Major funding source for current SAPRC mechanism development