The UCR Environmental Chamber Database for Mechanism Evaluation

William P. L. Carter
CE-CERT, University of California, Riverside
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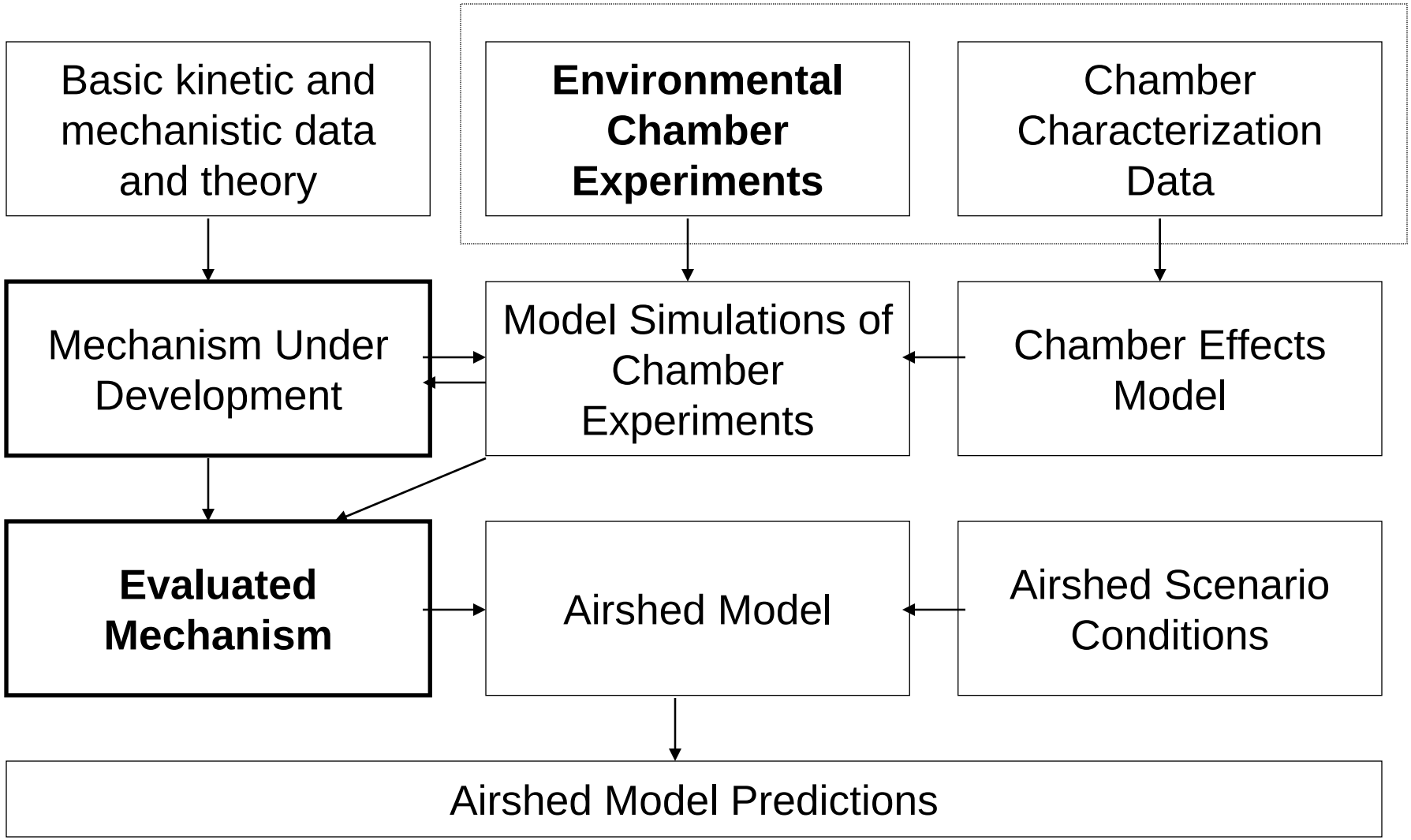
Outline

- Database used in SAPRC-99 evaluation and Current database
- New UCR-EPA chamber
- Examples of SAPRC and CB4 mechanism performance
- Issues regarding evaluating condensed mechanisms and mechanisms for secondary reactions of products
- Examples of PM measurements in the new UCR EPA chamber
- Summary and Recommendations

Relationship Between Mechanisms, Chamber Data and Airshed Models



UCR Chamber Data Base Used when Developing the SAPRC-99 Mechanism

Type of Experiment	No. of Runs	No. of VOCs	NO_x Range (ppb)
Chamber Characterization	73[1]		0 - 660
Simple VOC - NO_x (a few with added CO or alkane)	490	39	90- 1100
Incremental Reactivity (effect of adding VOC to Surrogate - NO_x)	435	81	180 - 610
Ambient Surrogate - NO_x	645		75 - 1200
Other Mixture - NO_x	29		50 - 2000

[1] Radical Source and NOx offgasing characterization experiments only

UCR Chamber Data Base Available for Current Mechanism Evaluation

Type of Experiment	No. of Runs	No. of VOCs	NO_x Range (ppb)
Chamber Characterization	227[1]		0 - 660
Simple VOC - NO_x (a few with added CO or alkane)	611	40	4 - 1100
Incremental Reactivity (effect of adding VOC to Surrogate - NO_x)	479	88	5 - 610
Ambient Surrogate - NO_x	834		2 - 1200
Other Mixture - NO_x	29		50 - 2000

[1] Radical Source and NOx offgasing characterization experiments only

UCR Chambers whose Data were Used for SAPRC-99 Mechanism Development

Chamber	Walls	Lights	Vol (m^3)	NO_x (ppb)	Runs
ITC	Teflon Film	Blacklights	6	75 - 1200	130
ETC, DTC	Teflon Film	Blacklights	3 - (2 x 6)*	80 - 990	1027
XTC, CTC	Teflon Film	Xenon Arc	2.5 - 5	90 - 650	292
EC	Teflon Coated Al., Quartz	Xenon Arc	6.4	90 - 2000	98
OTC	Teflon Film	Solar	2 x 20*	200 - 630	36

* Two reactors

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OTC	Teflon Film	Solar	2 x 20*	200 - 630	36
UCR EPA	Teflon Film	Argon Arc, Blacklights	2 x 100*	2 - 711	403

* Two reactors

UCR EPA Chamber

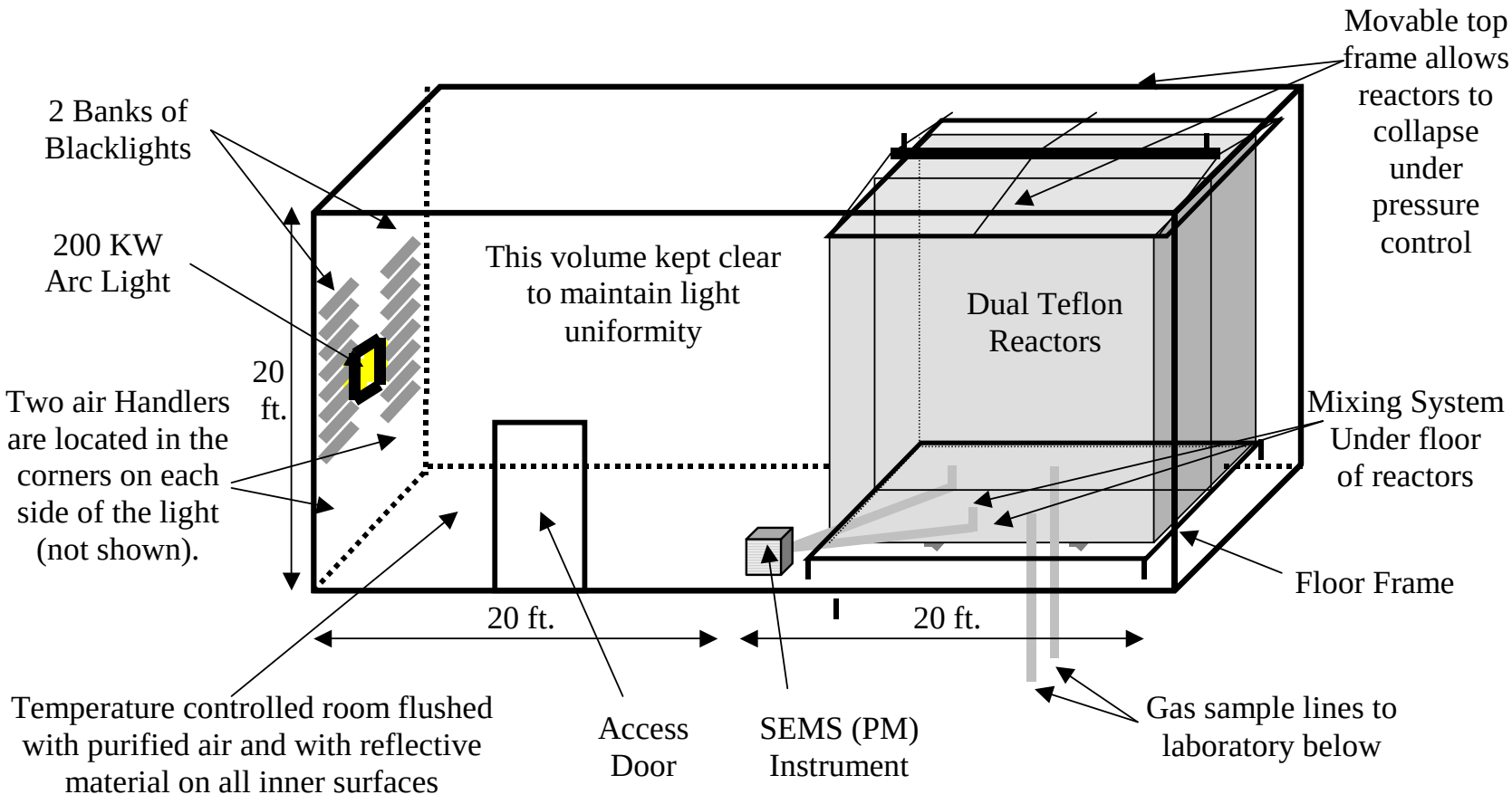
Major Objectives

- Reduce background effects to permit well-characterized mechanism evaluation experiments at lower pollutant levels
- Provide well-characterized data for PM mechanism evaluation

Characteristics

- Indoor chamber for maximum control and characterization
- Largest practical volume for indoors (two ~100,000-L reactors)
- 200 KW filtered argon arc solar simulator (also blacklights)
- “Clean room” design and positive pressure reactor volume control to minimize dilution and contamination
- Temperature controlled to ±1^{o}C in ~5^{o}C to ~50^{o}C range.
- Improved array of instrumentation, including PM measurements

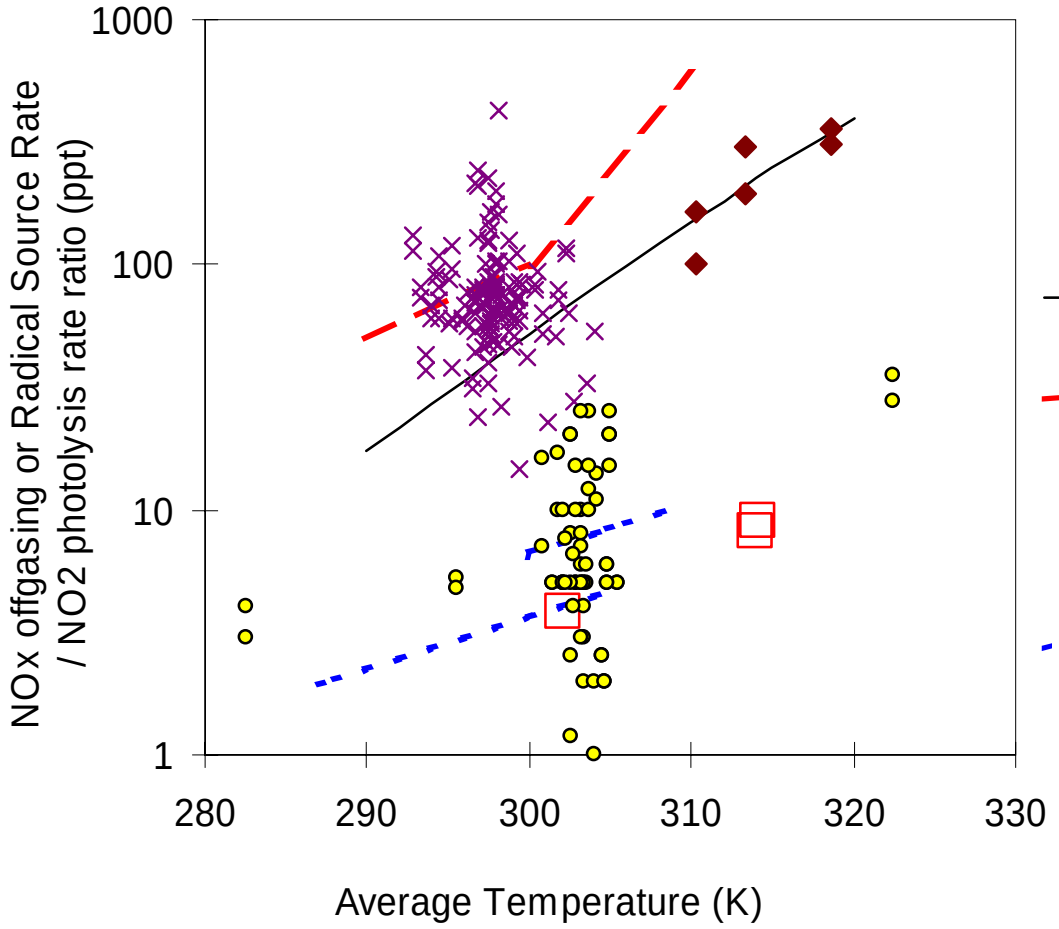
Diagram of UCR EPA Chamber



Summary of UCR EPA 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, but reproducible results obtained when >10 $\mu g/m^3$ PM formed.

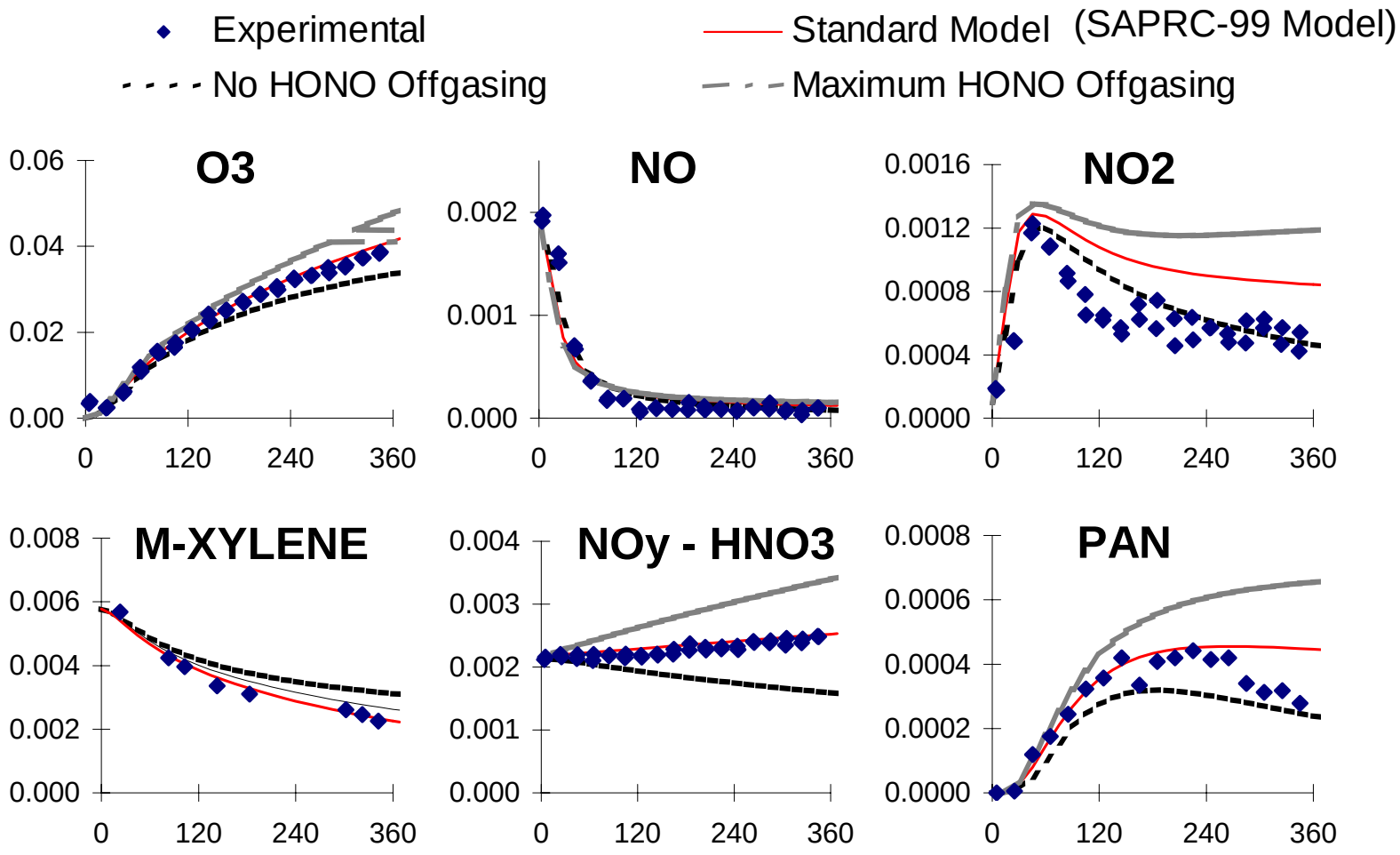
Radical or NO_x Offgasing Rates Derived for Various Chambers



Previous UCR Indoor
Previous UCR Outdoor
Previous UCR Default Model
Used for Modeling UNC Outdoor
TVA Indoor (NOx offgasing)
UCR EPA Chamber
SAPHIR HONO offgasing (dry)

Modeled data derived using the SAPRC-99 mechanism

Lowest NO_x Surrogate Experiment
(ROG surrogate = 300 ppbC, NO_x = 2 ppb)



Concentration (ppm) vs Time (minutes)

Types of VOCs for which Data are Available

Type of Compound or Mix	Number of Types	Number of Runs	
		Simple	React'y
Common organic products	5	49	41
Alkanes	16	-	94
Alkenes (incl. Styrene)	13	232	48
Aromatic Hydrocarbons	12	135	29
Alkynes (Acetylene)	1	5	7
Alcohols, ethers, esters, etc.	31	-	152
Aromatic oxygenates, furans	9	7	2
Other aldehydes, ketones	6	24	18
Misc. heteroatom-containing	12	-	41
Complex hydrocarbon mixes	11	-	12

Types of Measurement Data Available

- All runs*: O_3, NO, NO_y, CO, added VOCs, temperature
- All indoor chamber runs: Sufficient light intensity and spectral distribution data to assign photolysis rates
- All runs: Sufficient characterization data to assign parameters for modeling radical source, NO_x offgasing, dilution and humidity
- Many but not all runs: Data for formaldehyde, PAN, a few other oxygenated products in some cases (data quality varies)
- Most EPA chamber runs: PM number and size data from SEMS
- Some EPA chamber runs: NO_2 and HNO_3 data from TDLAS. H_2O_2, OH, and other radical data available for a few runs.

* Refers to experiments suitable for modeling

Note: Data on organic oxidation products are highly limited except for some earlier EC runs. Data are mainly suitable for evaluating predictions of O_3, overall oxidation rates, and (in some cases) PM number and volume.

Examples of Mechanism Evaluations

Mechanisms

- SAPRC-99 (Both detailed and “fixed parameter” condensed)
- Preliminary Updated SAPRC-99
- Carbon Bond 4 (CB4)
- Updated CB4 (CB 05) (May not be the final version)

Types of Experiments

- Propene - NO_x
- m-Xylene - NO_x
- Ambient Surrogate - NO_x in UCR EPA chamber with arc light
  - Initial ROG surrogate and NO_x varied over a wide range
  - Surrogate is mixture of n-butane, n-octane, ethene, propene, trans-2-butene, toluene, m-xylene and formaldehyde (one compound for each model species in lumped mechanisms)

Lumped Model Species Used for Propene and m-Xylene

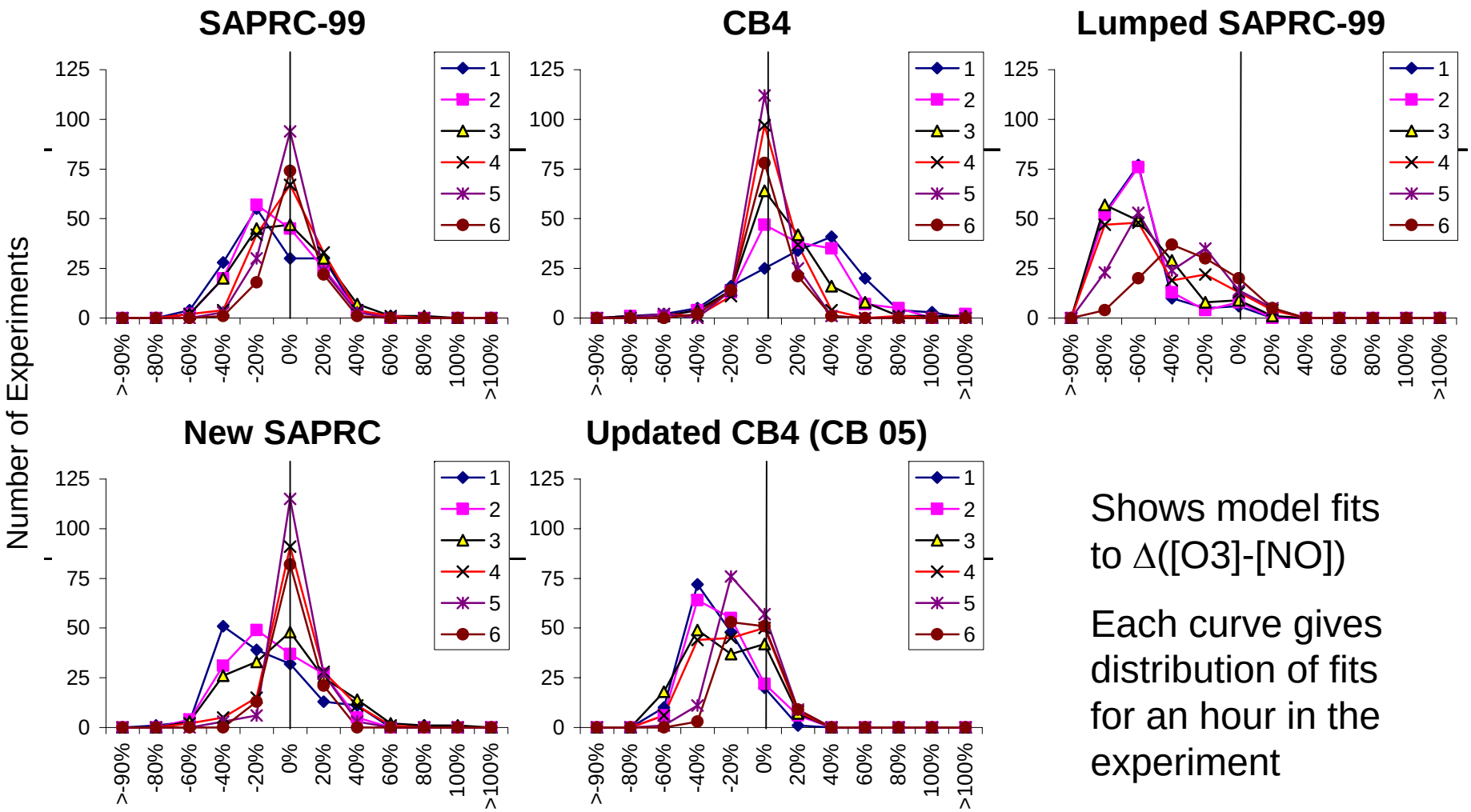
Propene and Other Terminal Alkenes

Mechanism	Species	Mechanism Based On
CB4, CB05	OLE + PAR	Propene
Lumped SAPRC-99	OLE1	29% Propene; 24% 1-Hexene; 12% 1-Butene; 35% Other 1-alkenes

m-Xylene and Other Higher Reactivity Aromatics

Mechanism	Species	Mechanism Based On
CB4, CB05	XYL	Xylenes (probably primarily o-xylene)
Lumped SAPRC-99	ARO2	23% p-Xylene; 20% o-Xylene; 20% m-Xylene; 37% Trimethylbenzenes

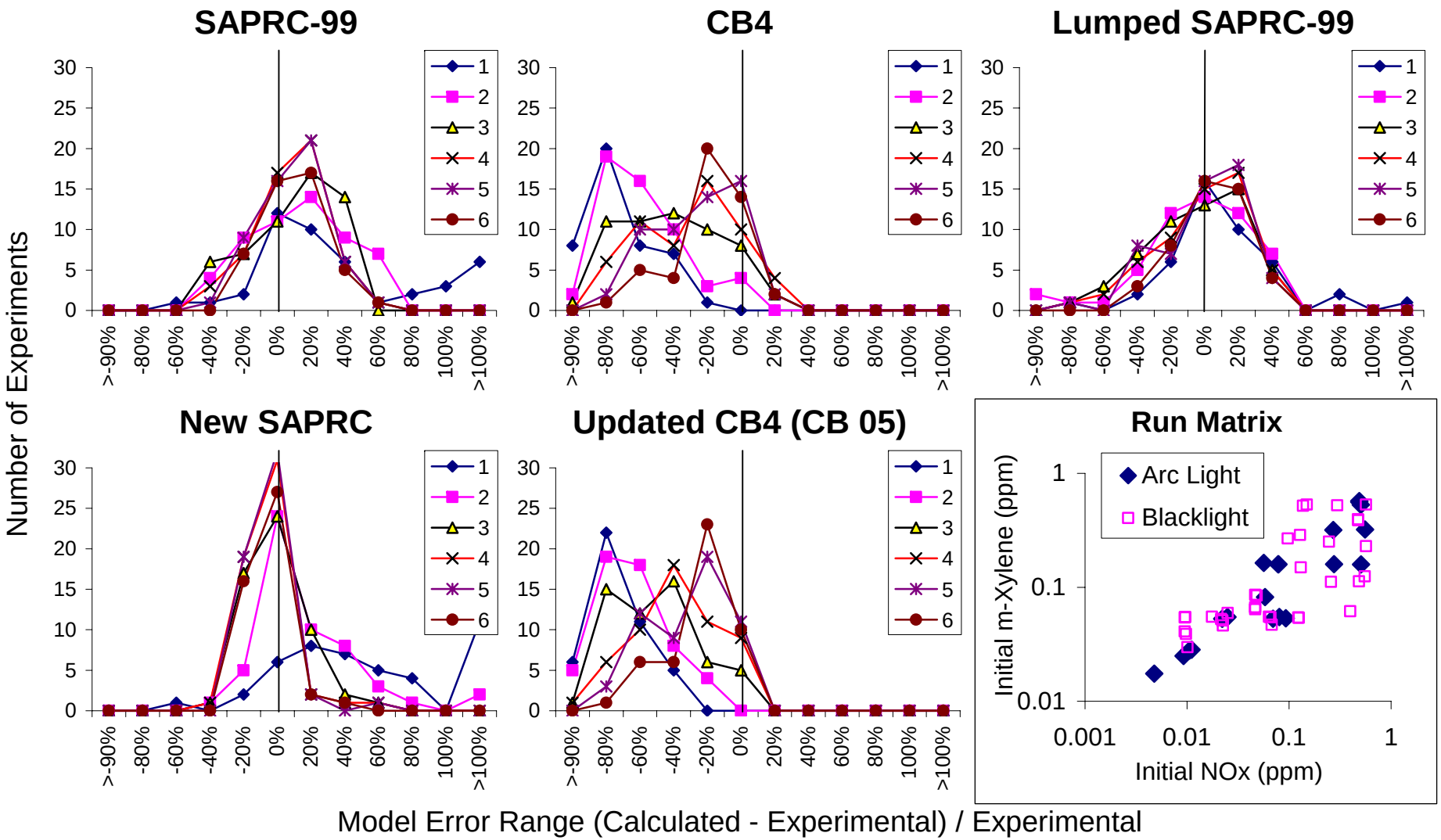
Model Error for Propene Experiments



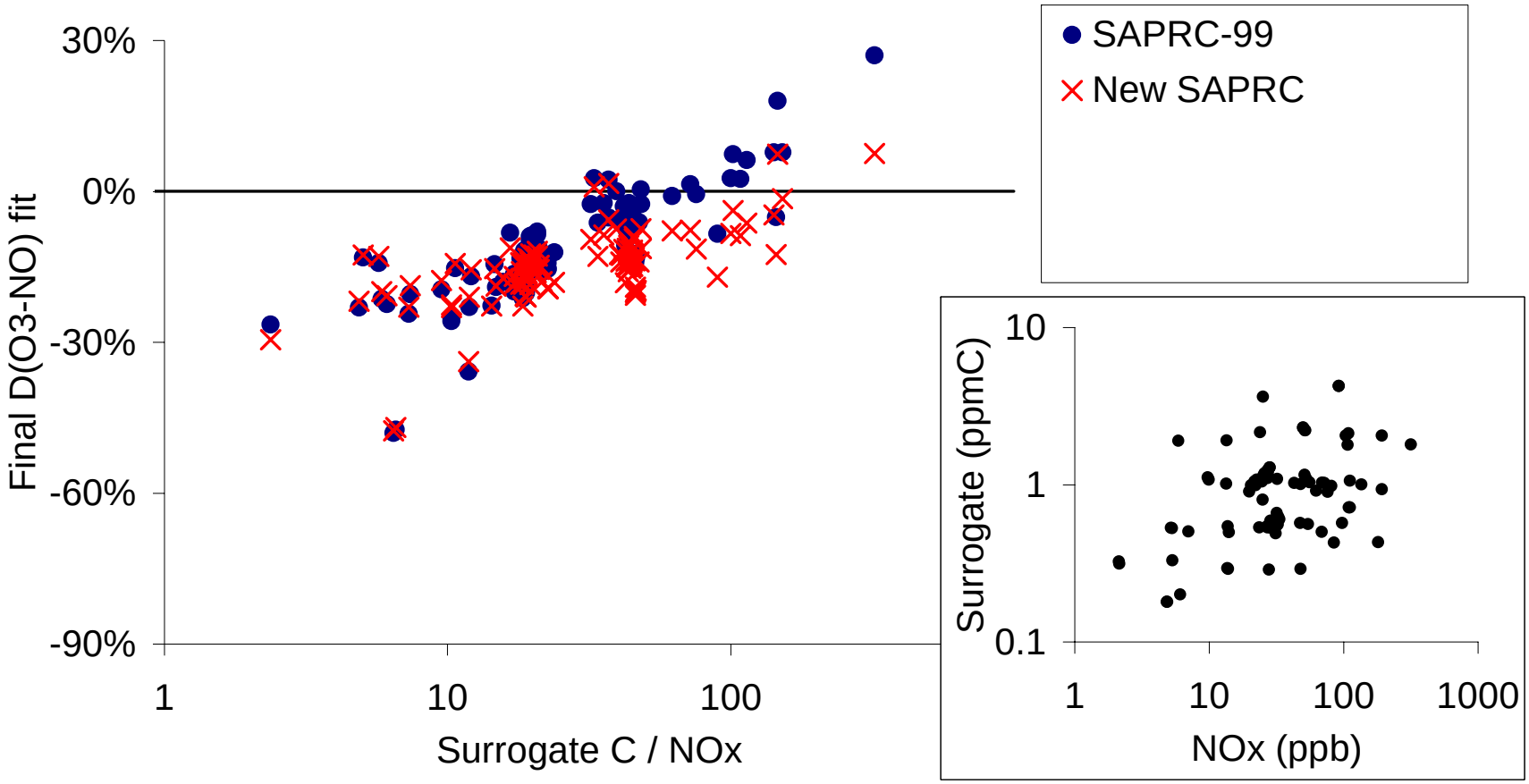
Shows model fits to Δ([O3]-[NO])

Each curve gives distribution of fits for an hour in the experiment

Model Error for m-Xylene Experiments



Model Error for UCR EPA Standard Surrogate Experiments (Arc Light)



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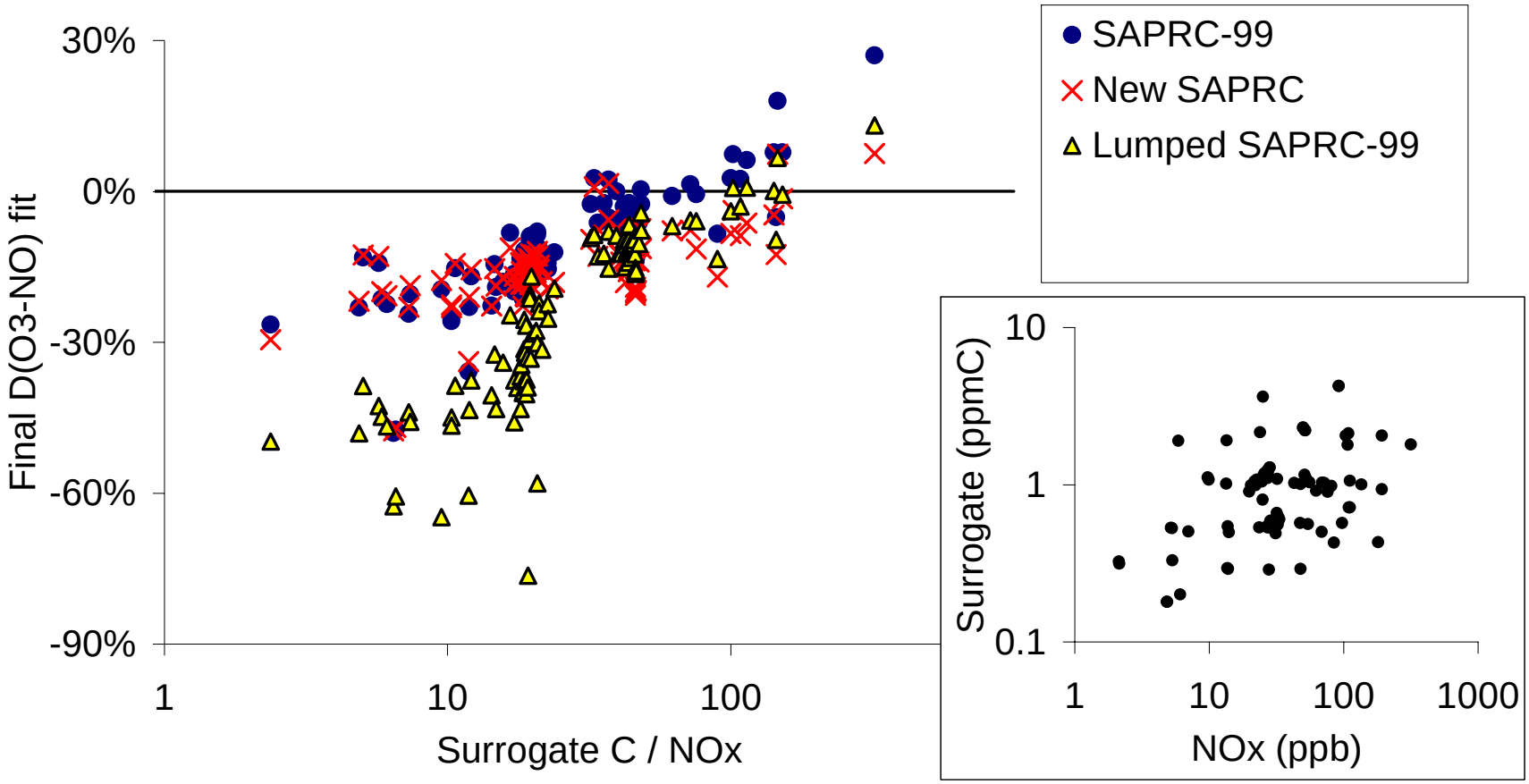

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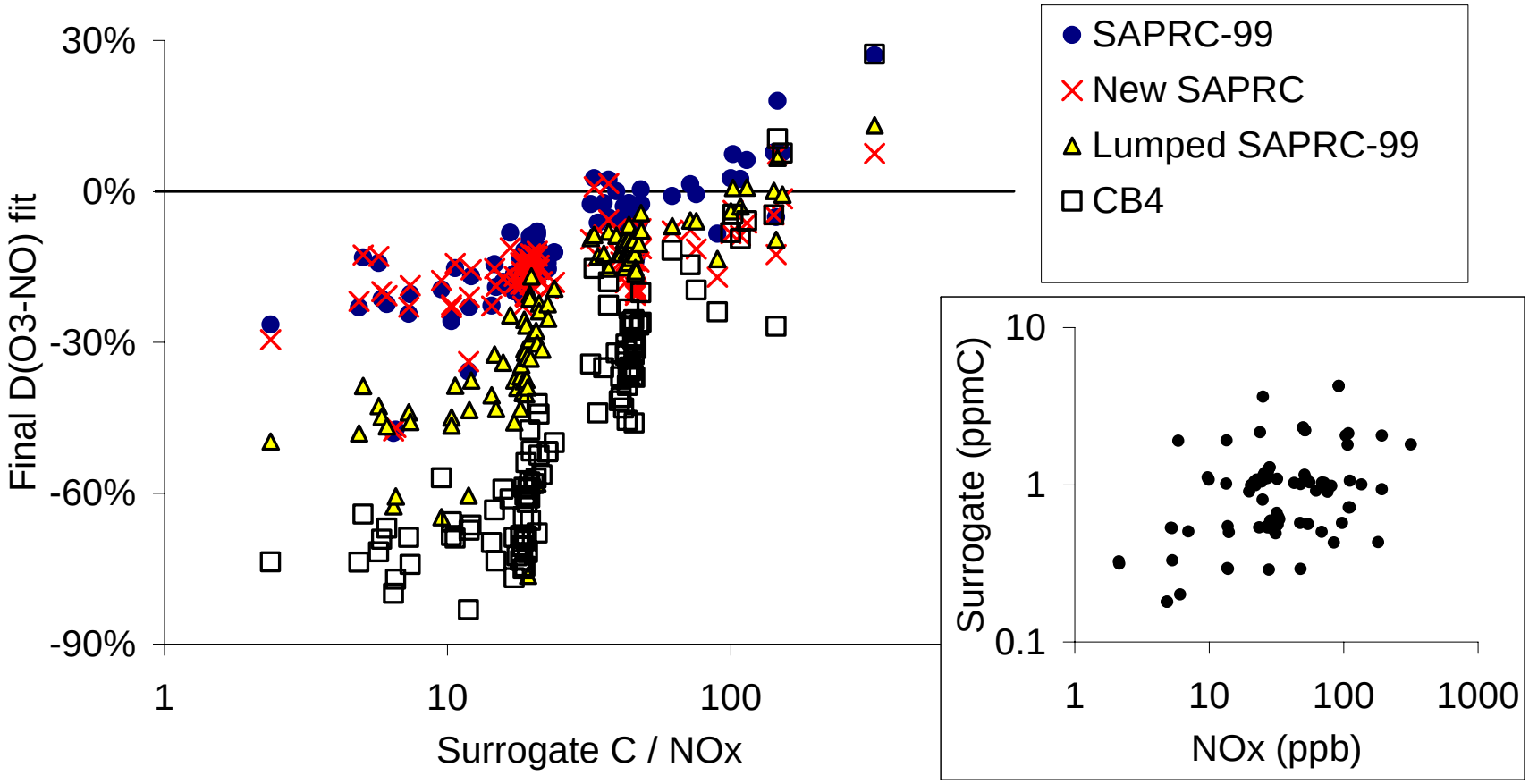

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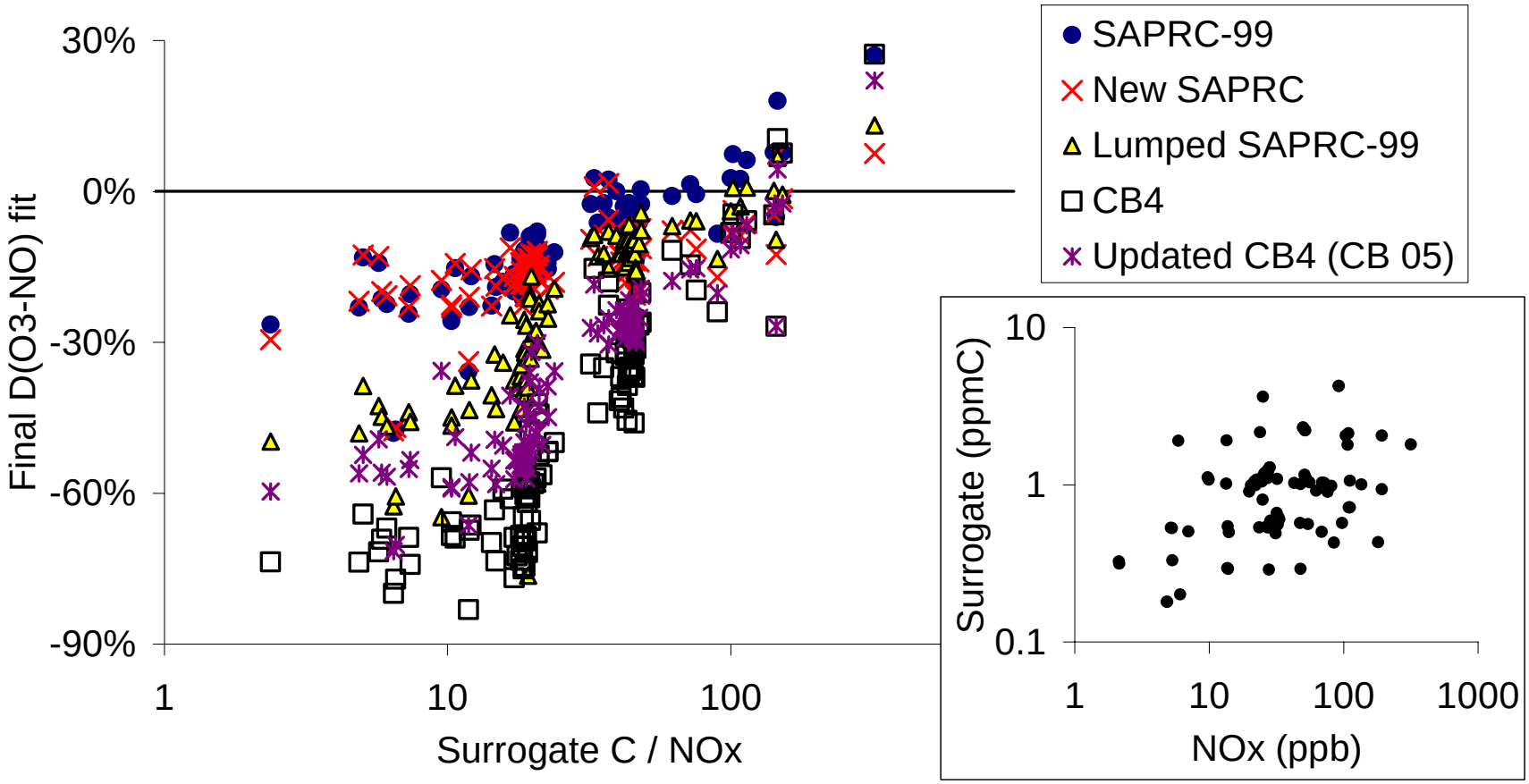
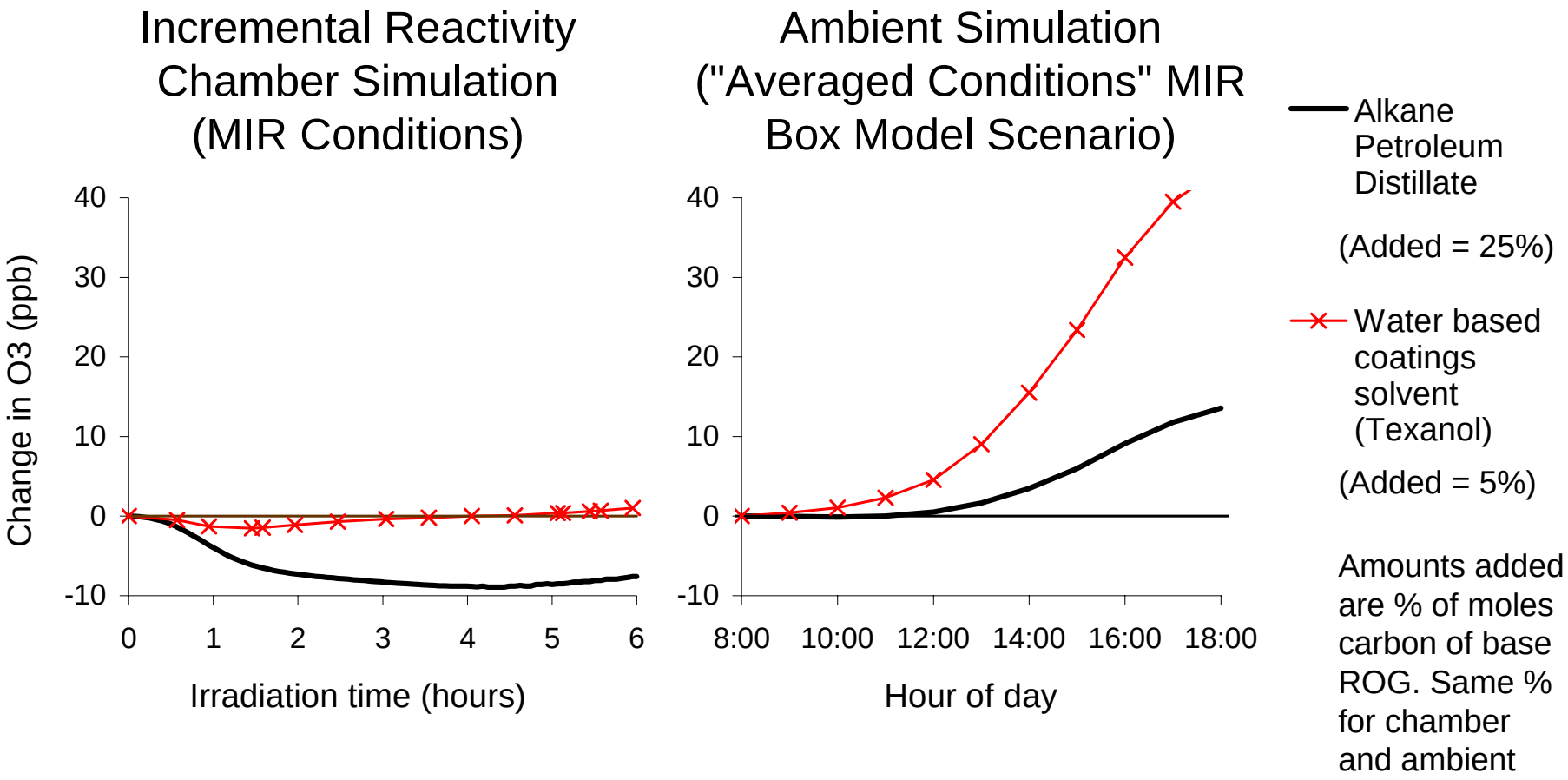


Differences in Incremental Reactivities Between Environmental Chamber and Simulated Atmospheric Conditions



Approximate Contributions of Aspects of Mechanisms to n-Decane Reactivity in Chamber and Atmospheric Simulations

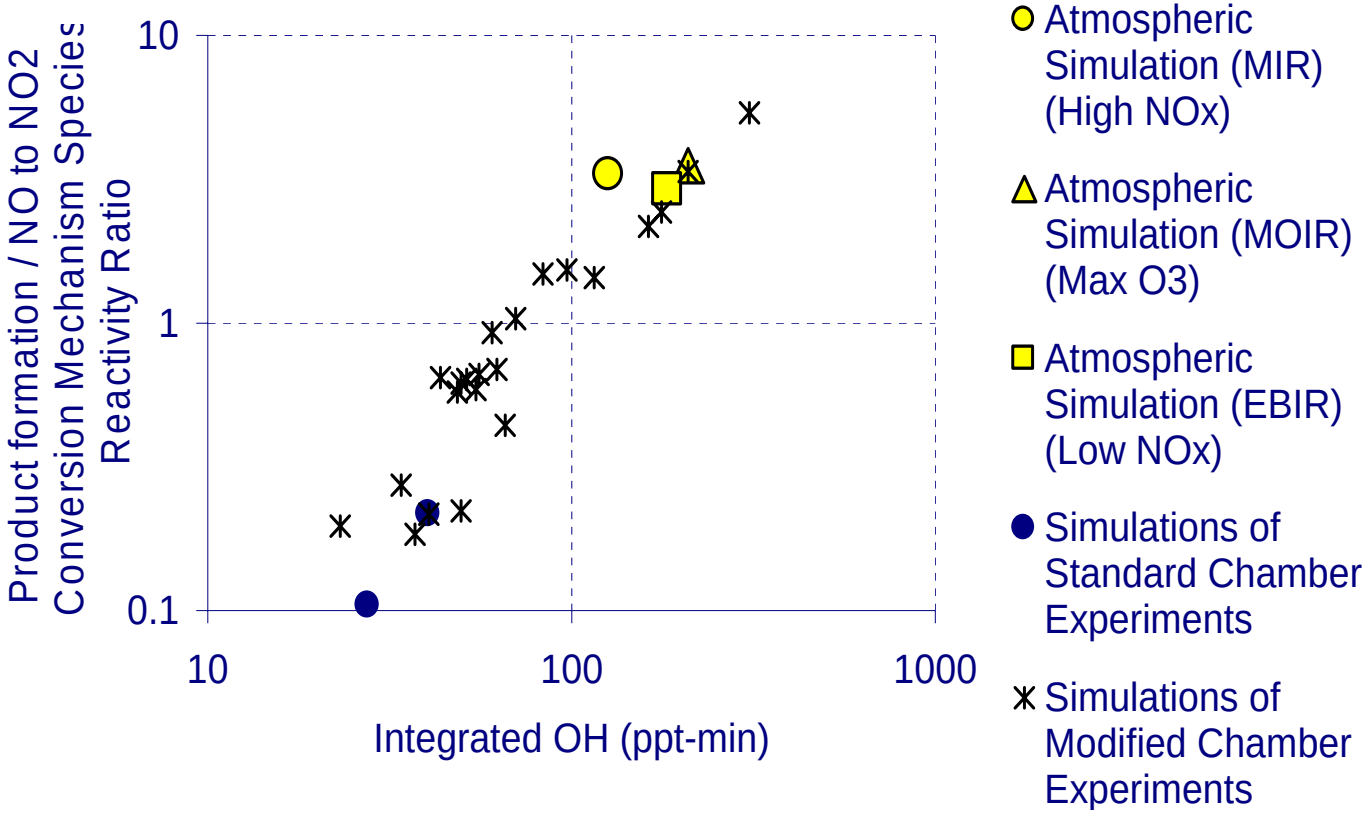
Contributions relative to effect of NO to NO_2 Conversions.

Aspect of Mechanism	Chamber Experiment	Atmospheric Simulation
NO to NO_2 Conversions due to Peroxy + NO	1.0	1.0
Nitrate formation from RO_2 + NO	-0.6	-0.8
Contribution of Product Reactions	0.08	1.0

Calculated using "pure mechanism" model species mechanistic reactivities for kOH = 3 x10^4 ppm^{-1} min^{-1}.

- Note much lower contributions of product reactions under chamber simulations

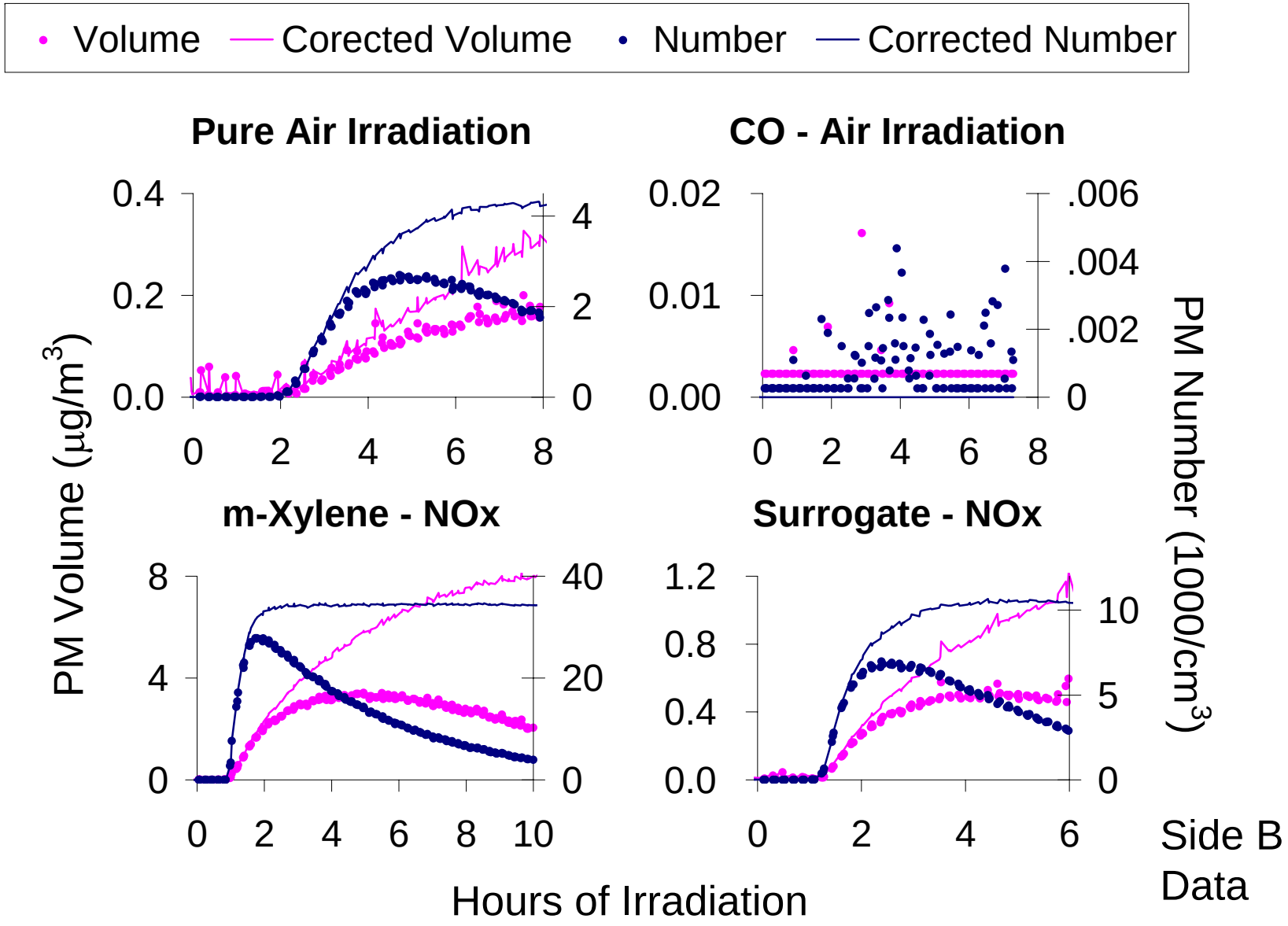
Relative Importance of Product Formation on Reactivity as a Function of Integrated Radical Levels



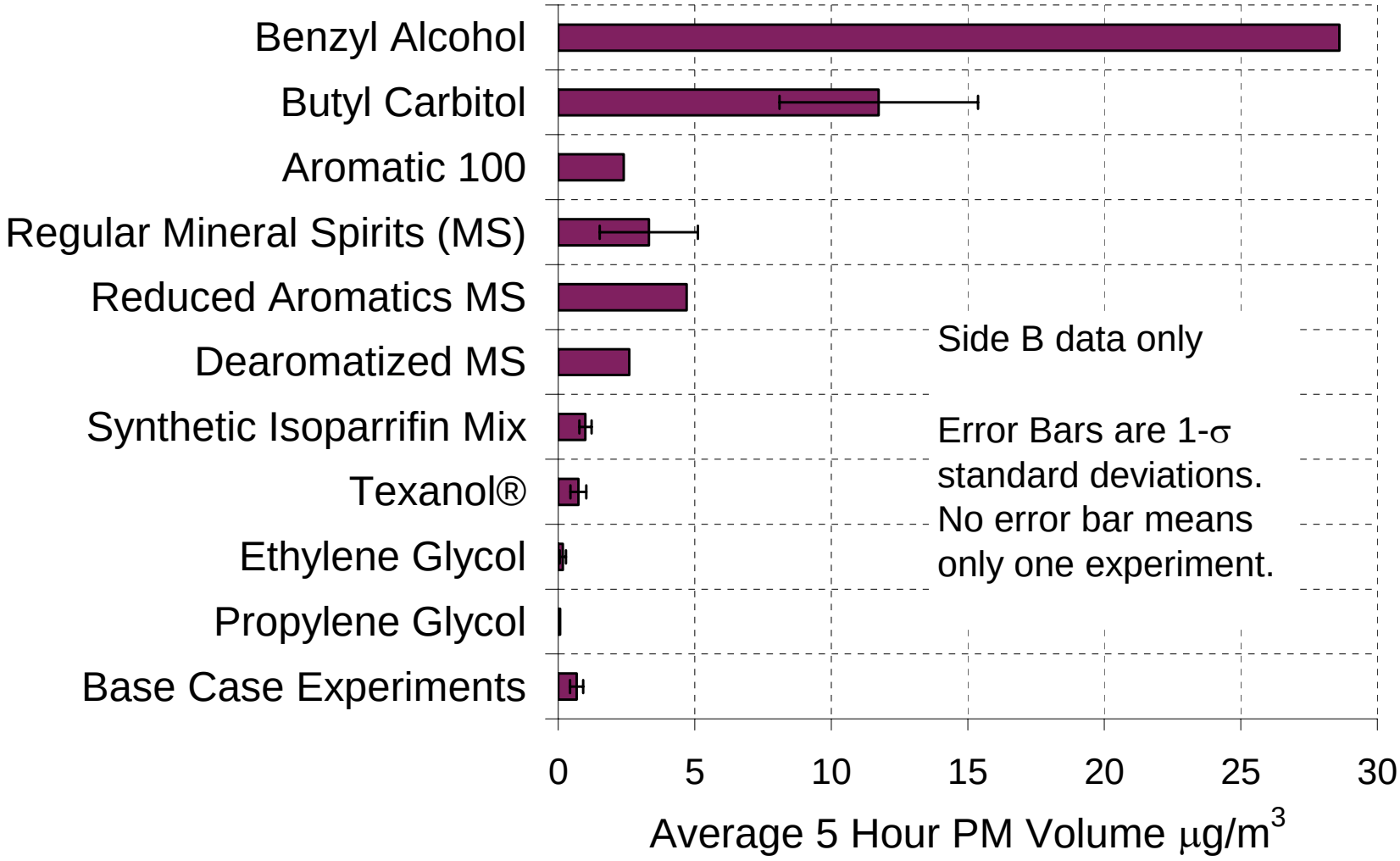
PM Measurements in the UCR EPA Chamber

- 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



PM Formation in Incremental Reactivity Experiments with Coatings VOCs



Summary and Recommendations

- The ability to simulate suitable environmental chamber data is necessary (but not sufficient) to assure mechanism accuracy
- A large database of environmental chamber experiments exists for O_3 mechanism evaluation for a wide variety of VOCs
- The new UCR EPA chamber is providing low NO_x mechanism evaluations and is beginning to provide data for PM impacts
- Current mechanisms differ significantly in their ability to simulate the available chamber database
- Care must be taken when evaluating condensed mechanisms against chamber data. The lumped species may not be designed to represent the compounds in the experiments.
- The present chamber database is not adequate for evaluating contributions of oxidation products to ozone reactivity. Need experiments with higher integrated radical levels.

Availability of Data

- Data for experiments up to 1995 and associated documentation are available at http://www.cert.ucr.edu/~carter/absts.htm#databa
- Partially documented data for more recent experiments are available upon request. Contact

William P. L. Carter
CE-CERT, University of California, Riverside, CA 92521
Phone: (951) 781-5797
Email: carter@cert.ucr.edu
Url: http://www.cert.ucr.edu/~carter

- Additional funding is required to fully compile and document available UCR chamber experiments carried out after 1995

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