CURRENT STATUS OF THE UCR-EPA ENVIRONMENTAL CHAMBER PROJECT

By

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Outline

- Background, Description and Timeline
- Characterization Results
- Current Projects
- Summary of Experiments and Results to Date
- New and Upcoming Programs and Funding
- Potential future research directions

BACKGROUND

Chemical mechanisms used to predict VOC reactivity have many uncertain estimates and approximations

Environmental chambers are essential evaluating the predictive capabilities of mechanisms

The existing chambers had limitations affecting utility and range of conditions for mechanism evaluation

The **UCR EPA Chamber** was developed to address these limitations. Major design features include:

- Indoor chamber for best control, & characterization
- Large volume to minimize background and for best sampling capability (two ~100,000-L reactors)
- Arc light used simulates sunlight intensity and spectrum. (Blacklights also installed)
- Replaceable Teflon reactors in a “clean room” to further minimize background effects
- Temperature control range is ~5^o to ~50^{o}C ($\pm$1^{o}C)
- Array of analytical instrumentation for gas-phase species and PM
- Chamber conditions characterized to reduce uncertainties for mechanism evaluation

DIAGRAM OF CHAMBER AND ENCLOSURE

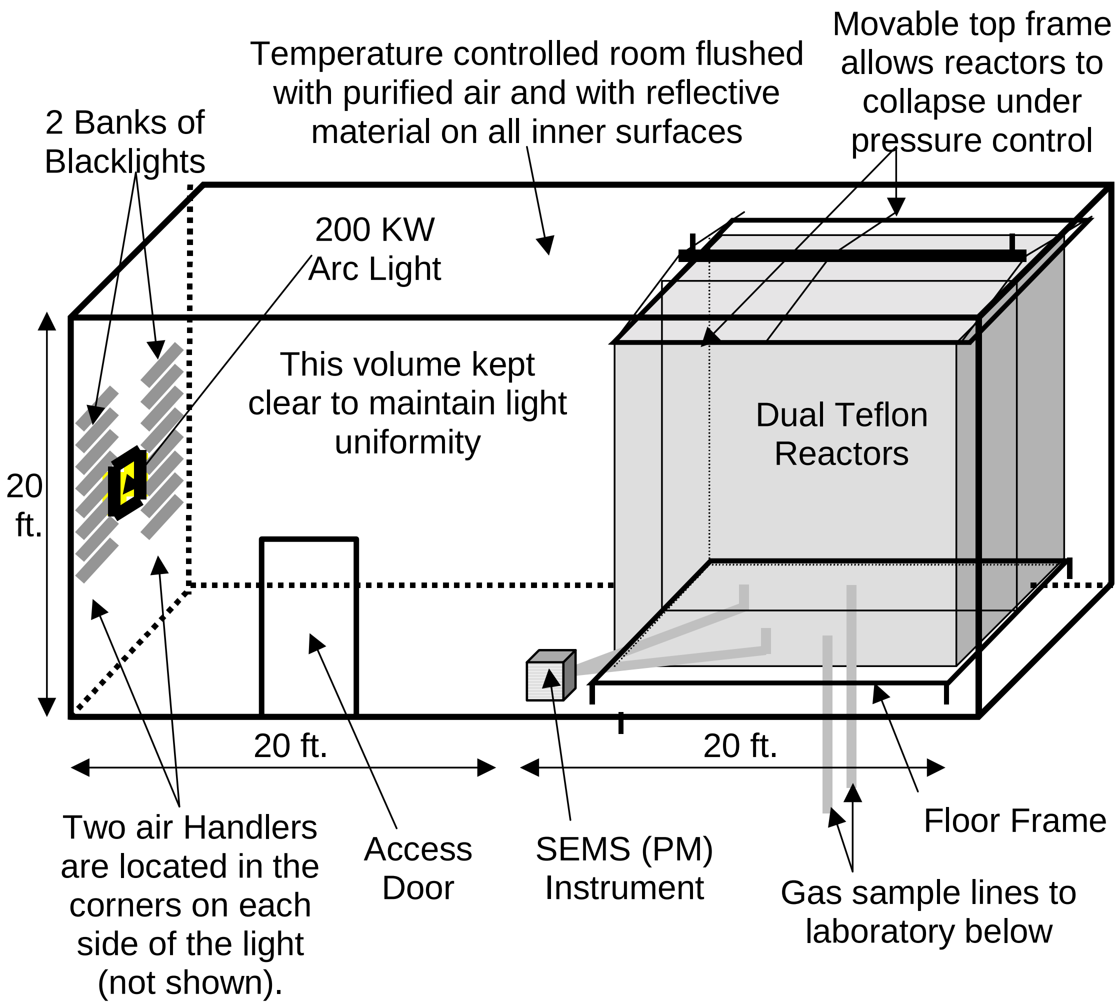
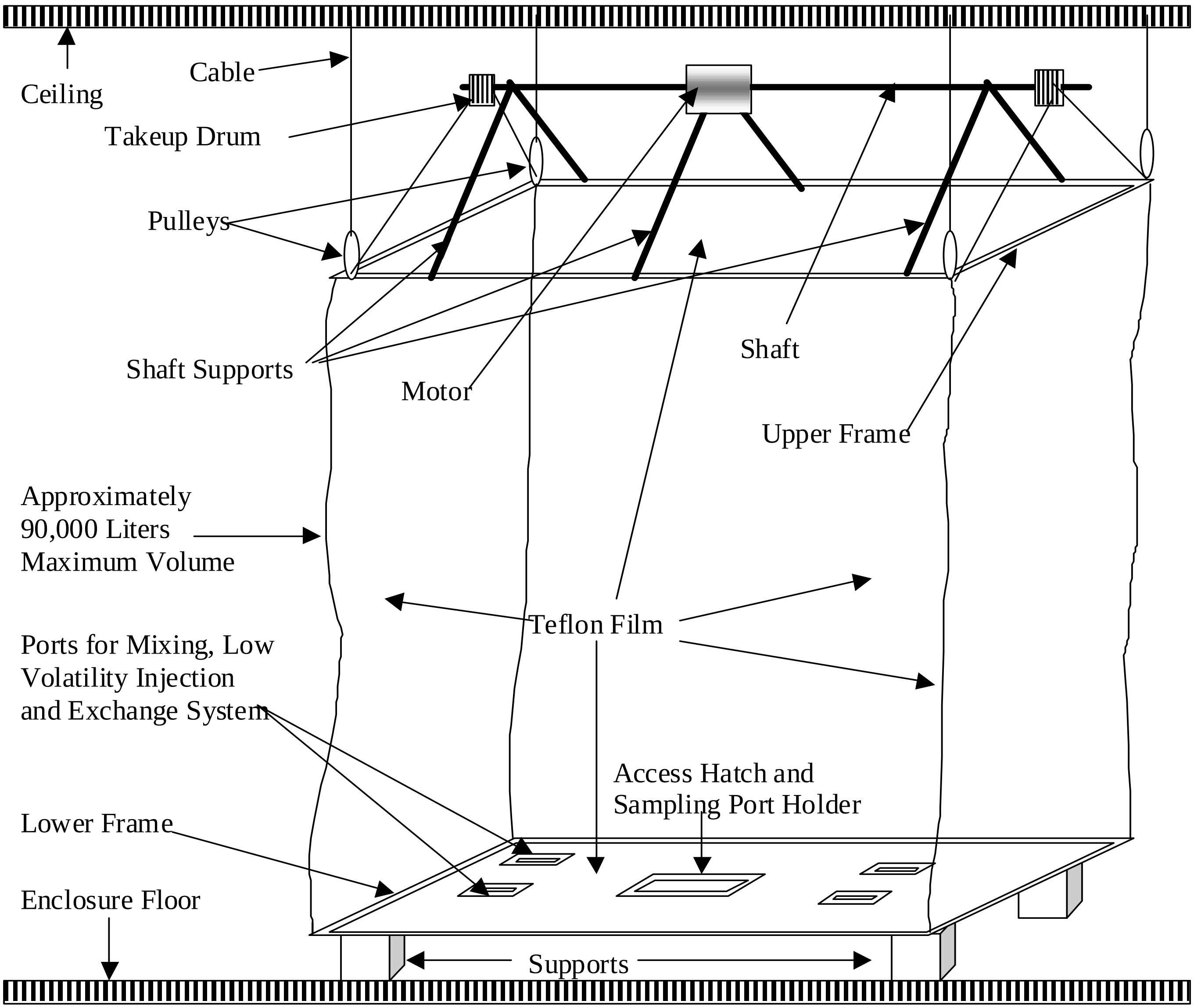
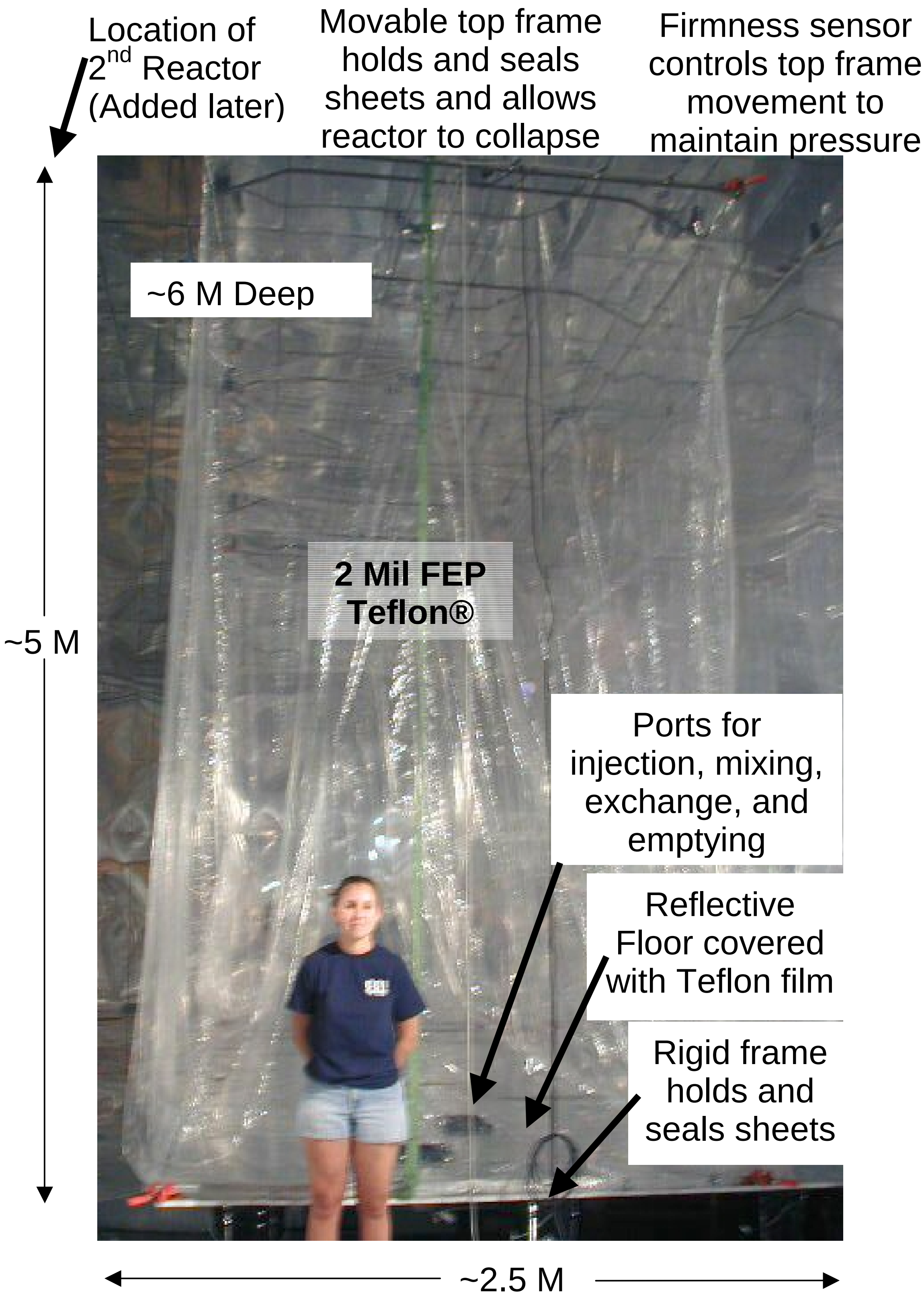


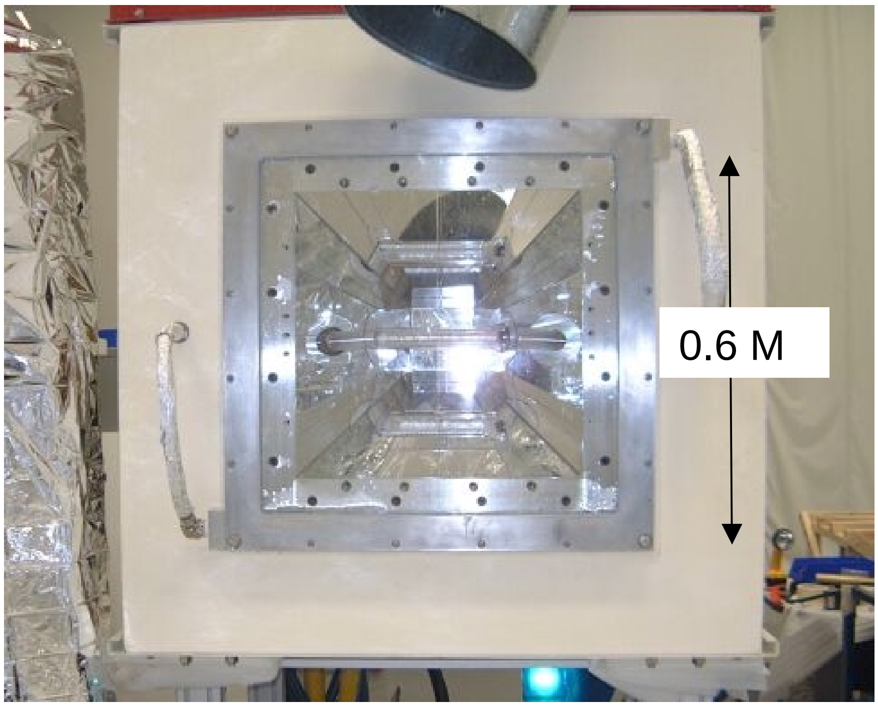
DIAGRAM OF REACTOR AND FRAMEWORK
(One of Two)

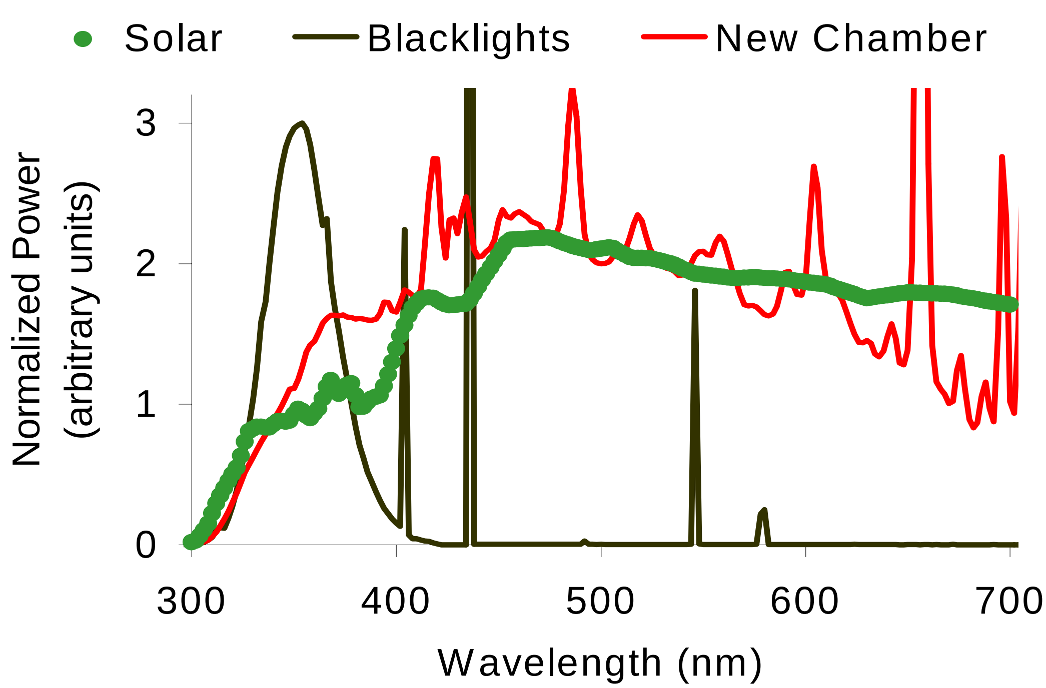


PICTURE OF SINGLE REACTOR



ARC LIGHT SOURCE AND SPECTRUM





TIMELINE

Time	Activity
1999	Project Started. International chamber workshop held in Riverside
2000	Design work and small reactor evaluation experiments.
2001	Construction
2002	Component, chamber, instrument testing, problem resolution, general debugging, initial evaluation experiments
Jan ‘03	First experiment in current configuration
Jan-Mar ‘03	Characterization runs and low NO_x runs on simple chemical systems
Feb ’03 - present	PM Instrumentation on line. Begin blacklight experiments for PM evaluation
Mar ‘03	Initial characterization for dry, single temperature conditions complete
Mar-Jun ‘03	Surrogate evaluation runs for low NO_x and to support reactivity studies.
Jun ’03 - present	Coatings component reactivity experiments underway

CHARACTERIZATION RESULTS

Contamination or dilution of reactors by enclosure air is negligible when run on positive pressure control

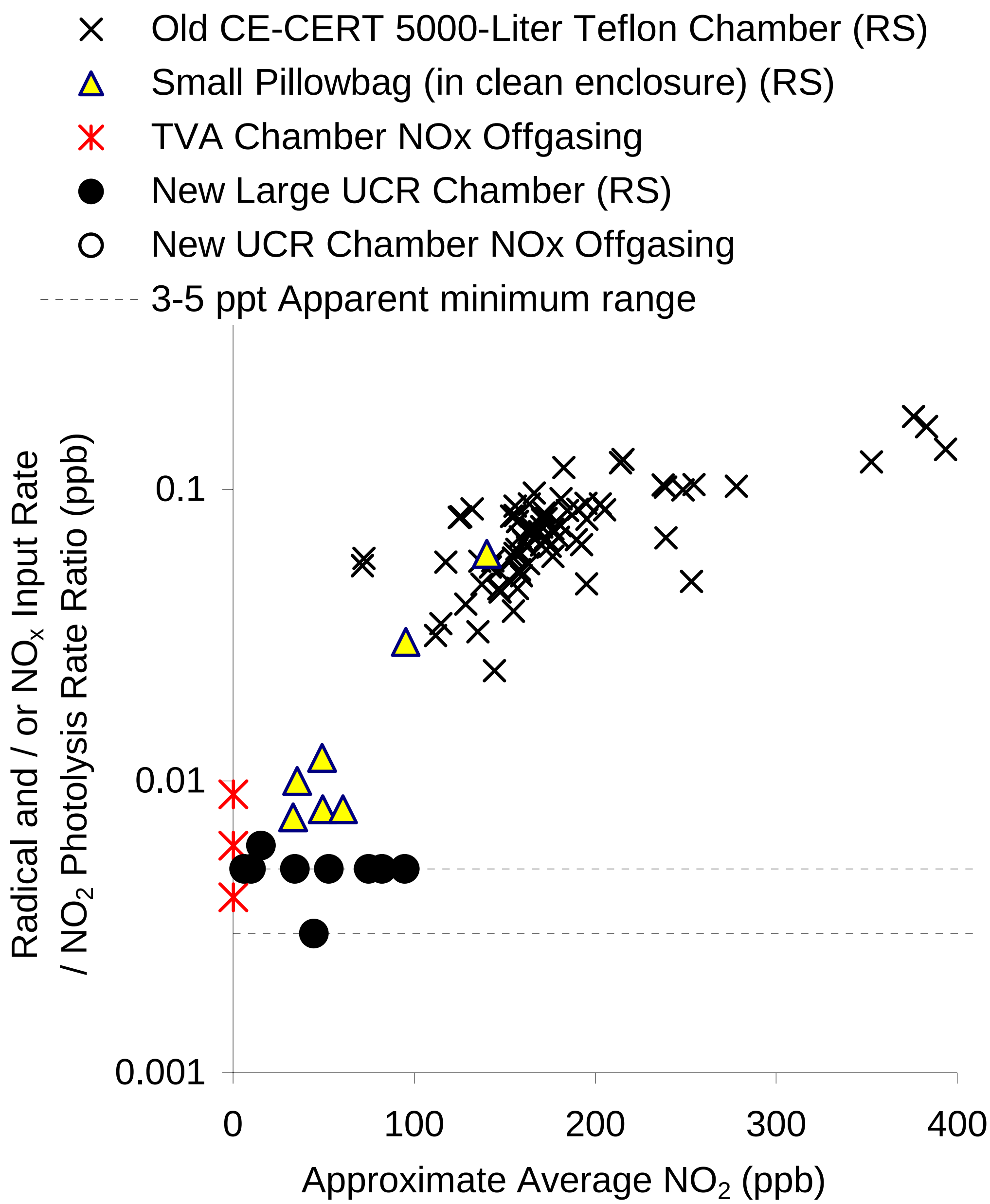
Light intensity with lamp at 80% recommended maximum gives NO_2 photolysis rate of 0.25 min^{-1}

Characterization results indicate chamber effects are probably as low as can be obtained in Teflon film chambers

- O_3 wall loss rate is 0.8%/hour, comparable to that in other Teflon film reactors
- Apparent HCHO offgasing rate is ~160 ppt/hour. (This is not measured in most other chambers because of inadequate sensitivity for HCHO)
- Apparent NO_x offgasing rate, determined by modeling in CO - air runs, is ~40 - 80 ppt/hour
- Apparent “chamber radical source” and minimum NO_x offgasing rates are ~40 - 80 ppt/hour

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

COMPARISON OF RADICAL SOURCE AND NO_x OFFGASING RATES IN VARIOUS CHAMBERS



CURRENT PROGRAMS AND TYPES OF CHAMBER WORK COVERED

Current EPA Chamber Program

- Construction and evaluation of chamber performance
- Experiments with simple chemical systems for testing
- Begin surrogate evaluation for reactivity studies
- Begin evaluating utility for PM studies
- Funds now exhausted.

CARB LOW NO_x Mechanism Evaluation

- Primarily surrogate - NO_x experiments at NO_x Levels
- Funding limited to relatively few experiments

CARB Coatings Reactivity

- Reactivity experiments with Texanol® and selected petroleum distillates
- Petroleum distillate experiments now underway

NSF Grant and Startup Funds (D. Cocker, PI)

- Limited support to blacklight runs for PM studies
- Experiments for comparison with previous PM yield studies with aromatics now underway (when chamber not needed for CARB projects)

CHAMBER EXPERIMENTS CONDUCTED 6/16/03

(Excluding Characterization)

Type of Experiment	No.
Simple Chemical Systems	
Formaldehyde – NO_x (with & w/o added CO)	4
Acetaldehyde – NO_x (with & w/o added CO)	2
Ethene and Propene – NO_x	4
Toluene – NO_x or Toluene – NO_x + CO	8
m-Xylene – NO_x + or m-Xylene – NO_x + CO	2
Surrogate Evaluation Experiments	
Surrogate - NO_x (Various ROG and NO_x)	12
n-Octane reactivity	5
m-Xylene reactivity	7
Coatings Reactivity	
Petroleum Distillate Reactivity – MIR Conditions	1
Petroleum Distillate Reactivity – Low NO_x	2
Blacklight Aerosol Yield Experiments	
Toluene - NO_x	9
m-Xylene - NO_x	12

SUMMARY OF NEW MECHANISM EVALUATION RESULTS TO DATE

Low NO_x Mechanism Evaluation

No apparent low NO_x mechanism performance problems for following systems:

- Formaldehyde - CO - NO_x (NO_x down to ~15 ppb)
- Toluene and m-xylene - NO_x (NO_x down to ~5 ppb)
- Ethene - NO_x (NO_x down to ~10 ppb)
- **Ambient Surrogate Runs (NO_x down to ~2 ppb)**

Aromatic Mechanism Evaluation

Satisfactory simulations of single aromatic - NO_x and aromatic reactivity experiments (as with previous data)

BUT new data indicate **aromatic mechanism problems**: Probable compensating errors.

- Model underestimates effect of adding CO to aromatic - NO_x runs. (Sensitive to radical initiation)
- Direct reactivity measurement overpredicted

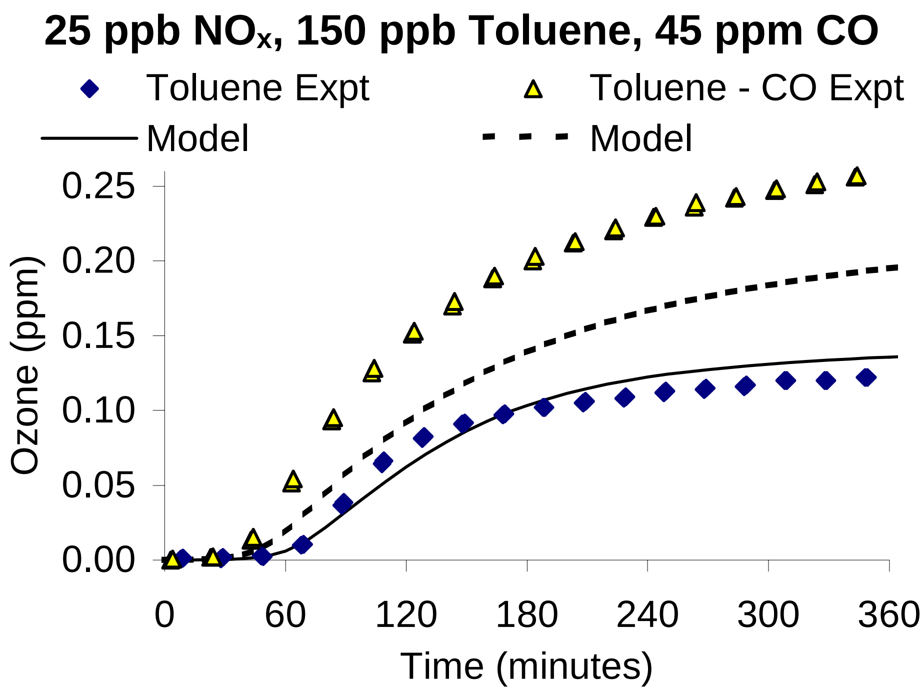
Surrogate Evaluation

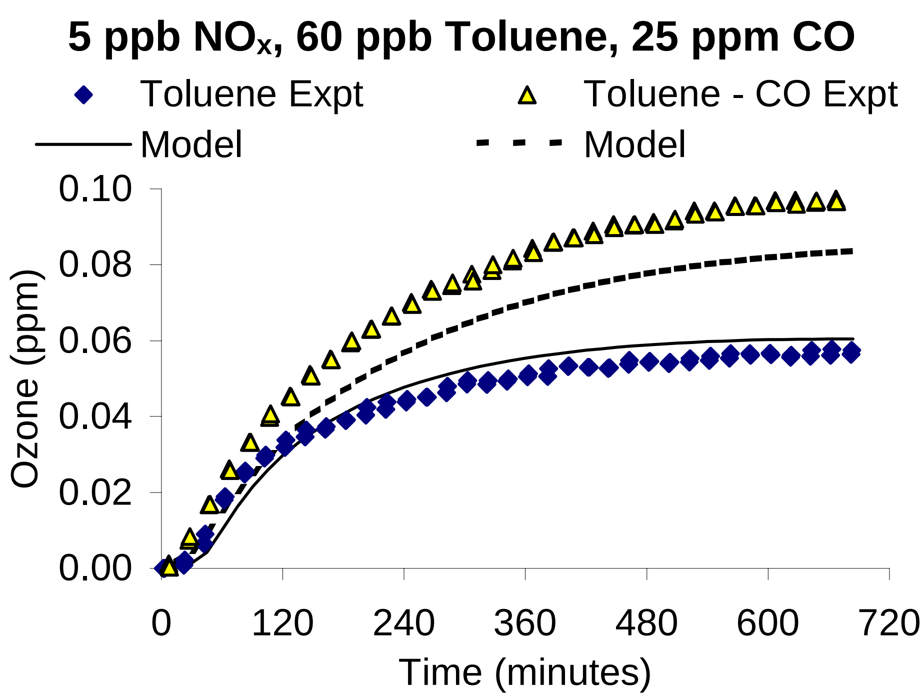
Good simulations with MOIR or higher ROG/NO_x levels

Model underpredicts O_3 formation rates with MIR or lower ROG/NO_x levels

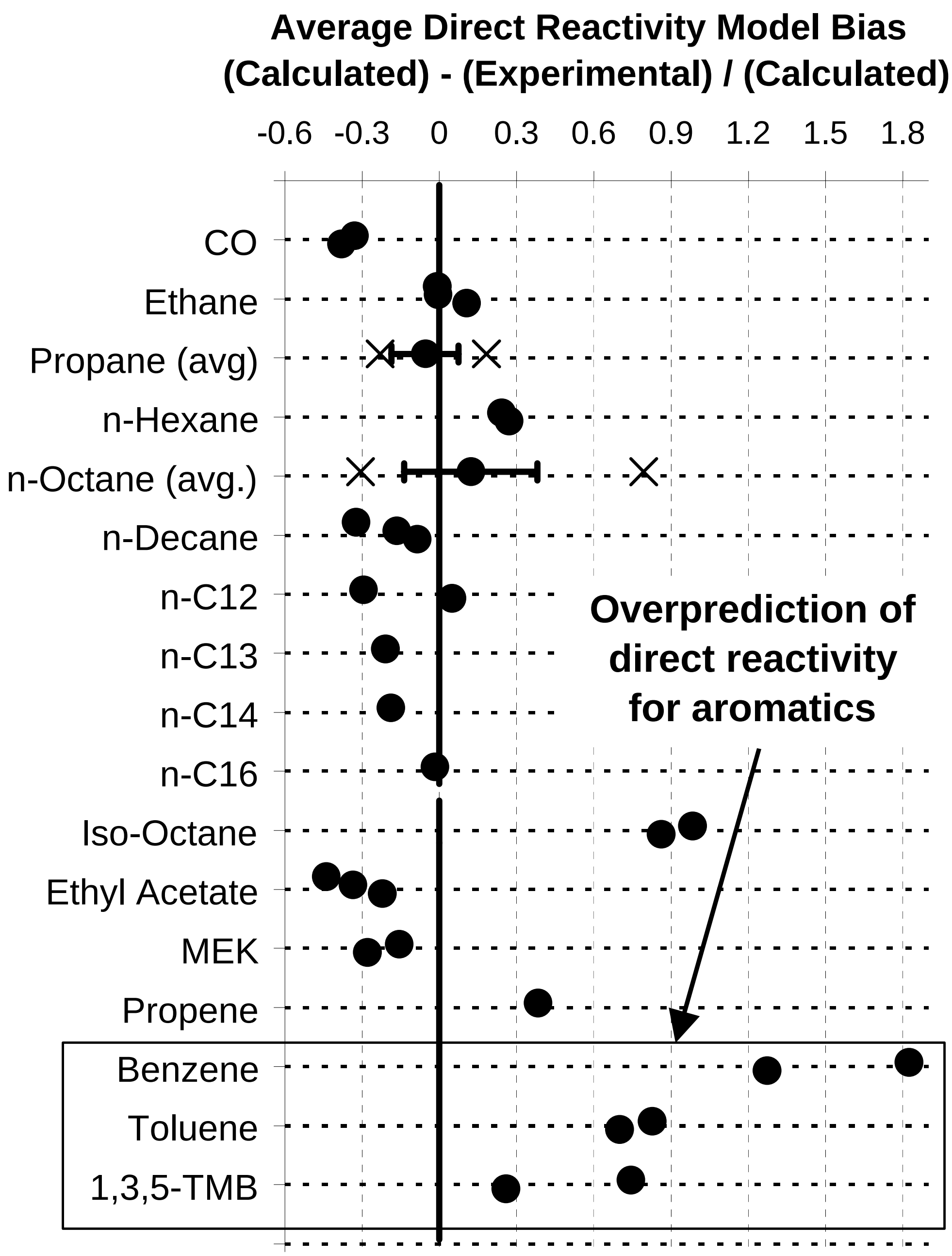
n-Octane reactivity data reasonably well simulated in runs where base case well simulated.

TOLUENE & TOLUENE – CO - NO_x RUNS

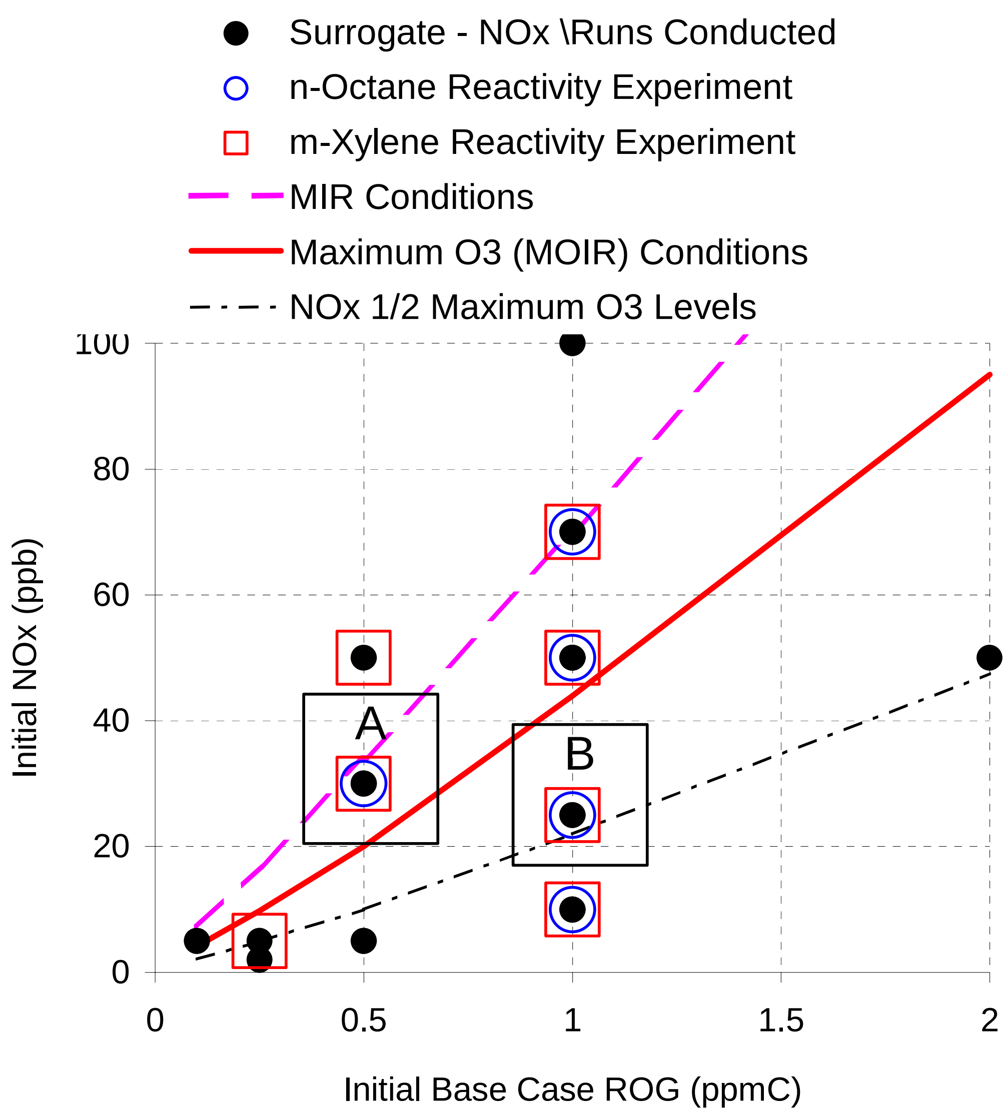




MODEL PERFORMANCE IN SIMULATING DIRECT REACTICITY DATA (HONO +VOC FLOW TUBE EXPERIMENTS)



MATRIX OF SURROGATE EXPERIMENTS

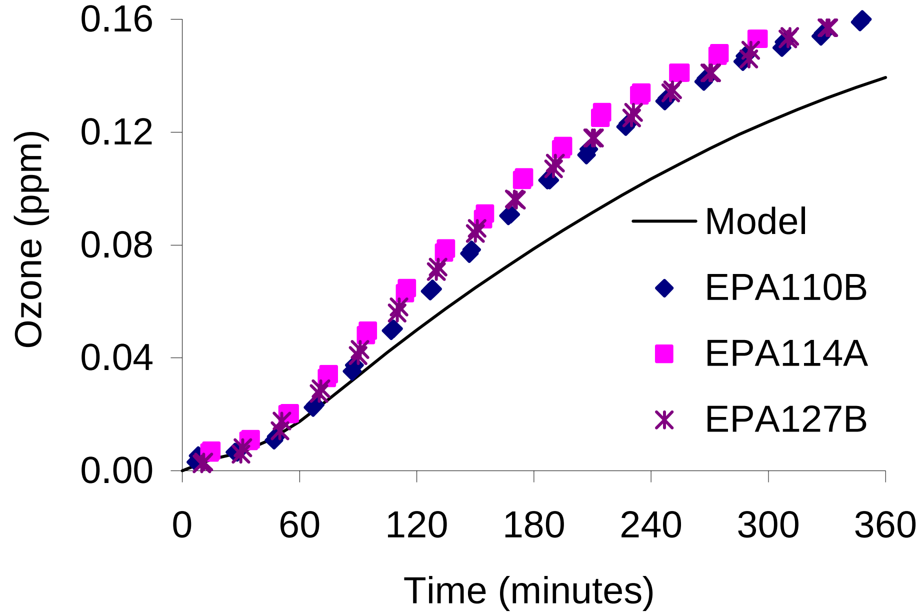


Base case conditions chosen for initial reactivity assessment experiments

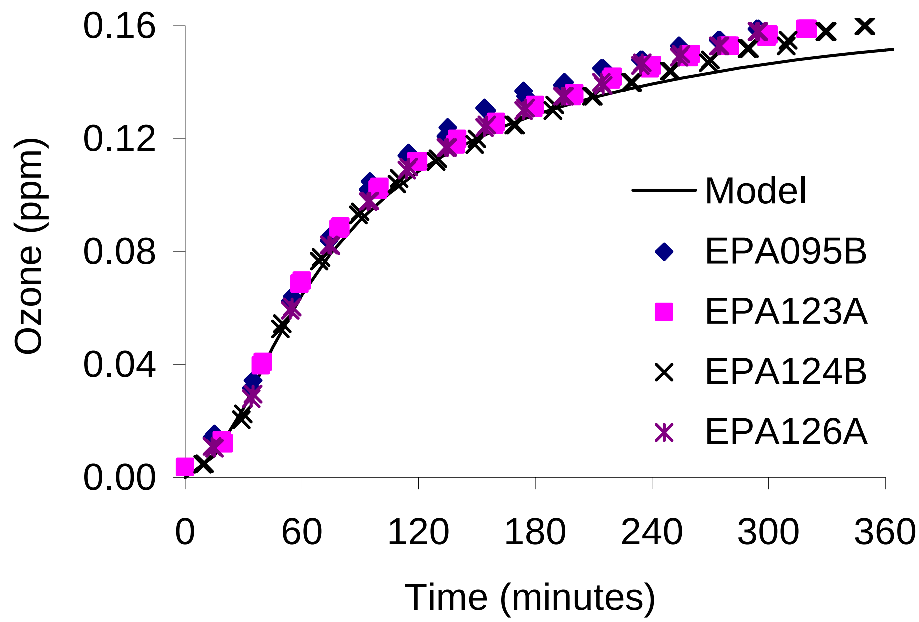
- A.....MIR Conditions (Higher NO_x / VOC)
- B.....Lower NO_x / VOC; $NO_x \approx$1/2 MOIR Level

BASE CASE SURROGATE EXAMPLES

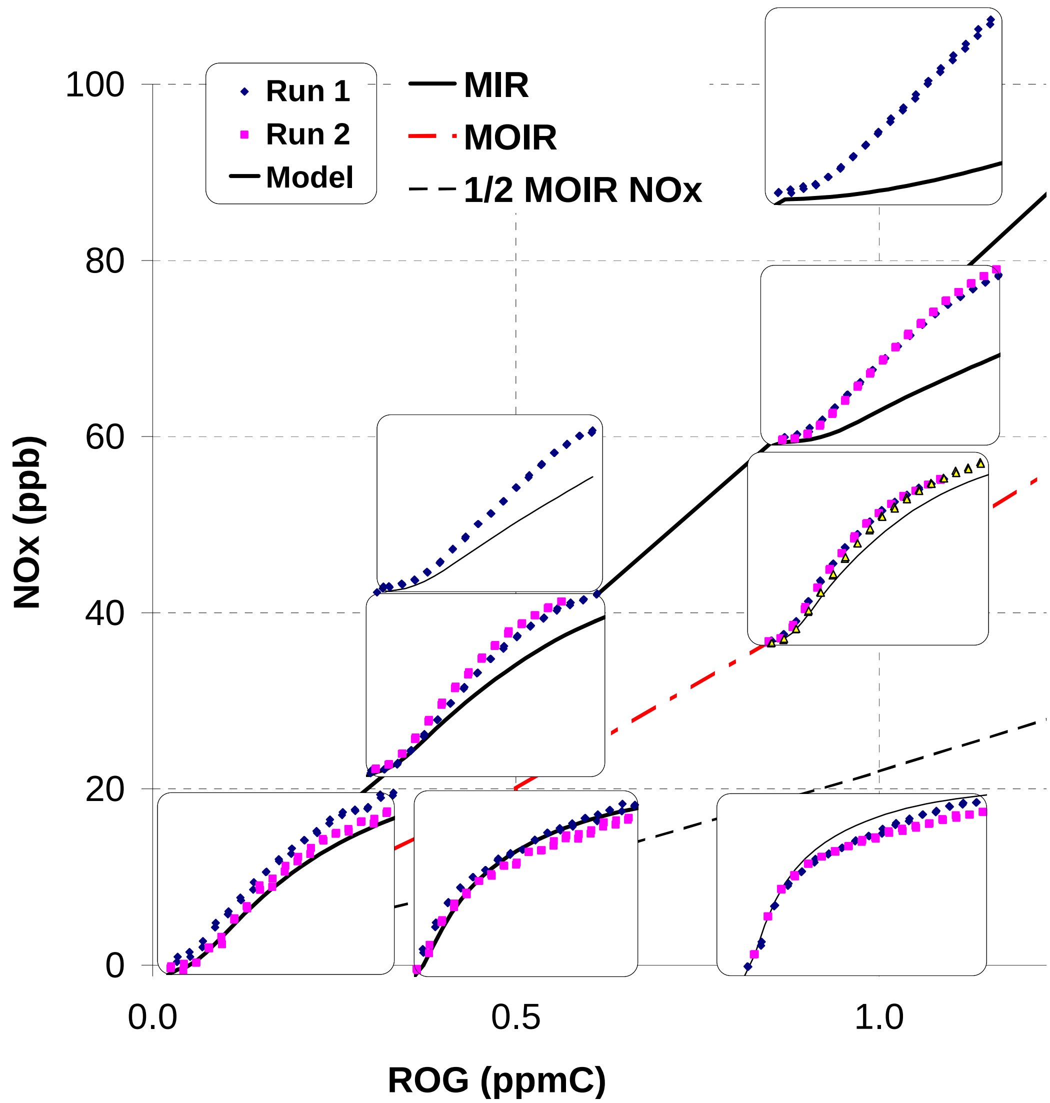
MIR Conditions (NO_x=30,ROG=0.5)



½ MOIR NOx Conditions (NOx=25,ROG=1)



MODEL PERFORMANCE SIMULATING O_3 AT DIFFERENT ROG AND NO_x LEVELS

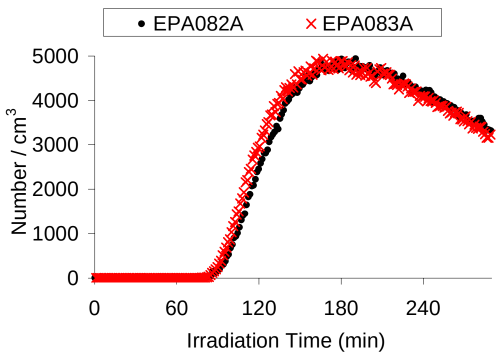


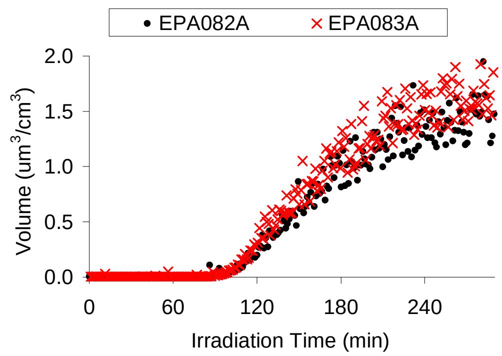
Experimental and Calculated O_3 in
Selected Surrogate - NO_x Experiments

PM REPRODUCIBILITY

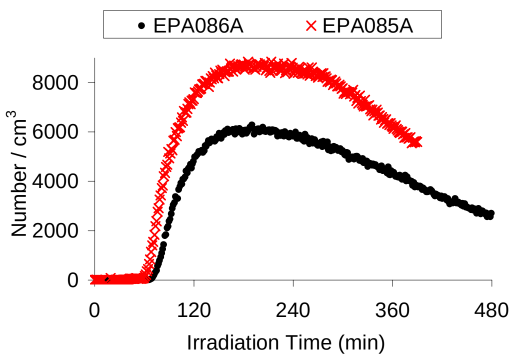
Number (cm^{-3}) vs.time Volume (µg/cm^{-3}) vs. time

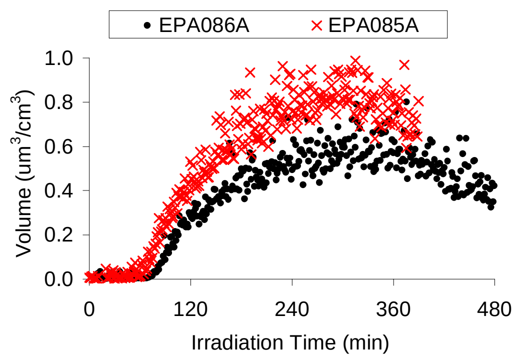
Surrogate - NO_x Runs 82A vs. 83A



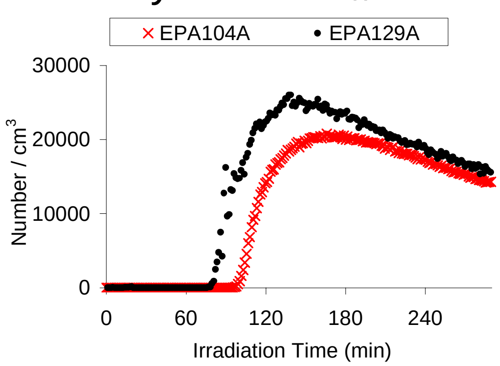


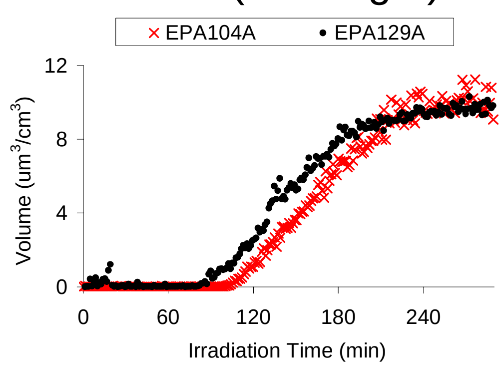
Surrogate - NO_x Runs 85A vs. 86A



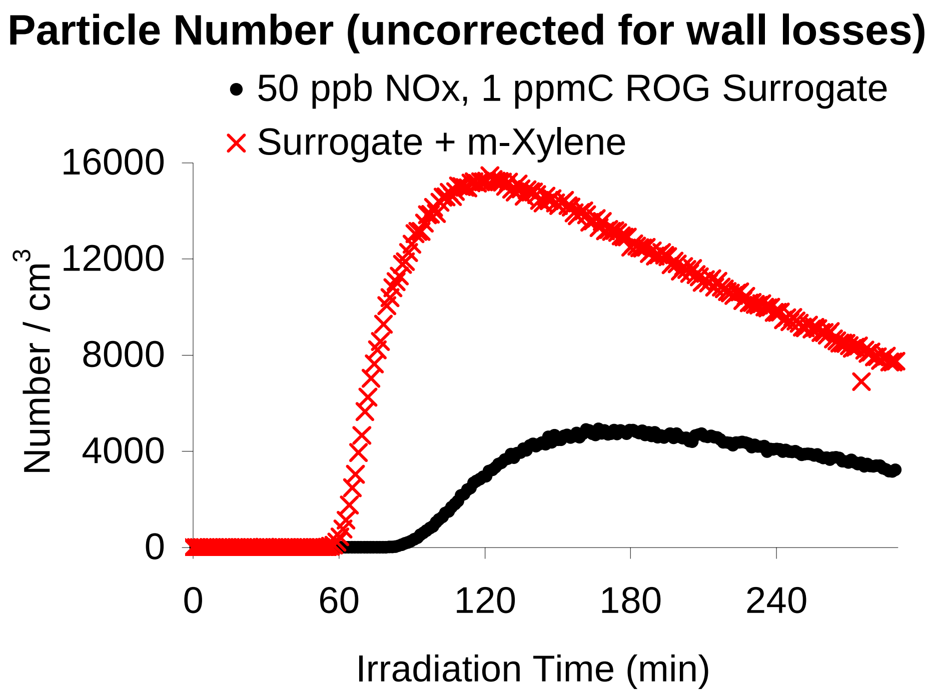


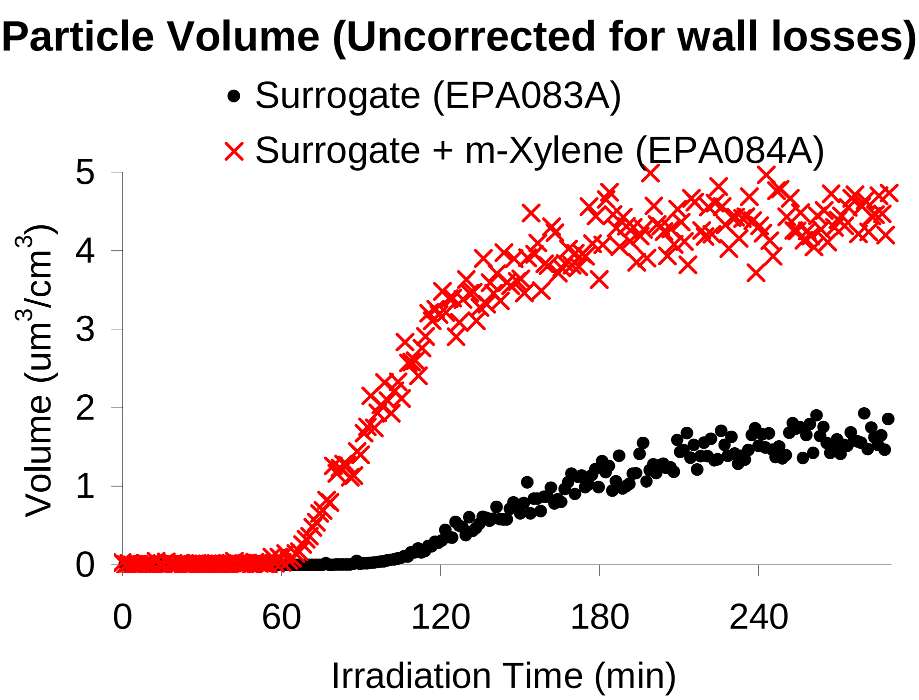
m-Xylene - NO_x Runs 104A vs. 29A (Blacklight)



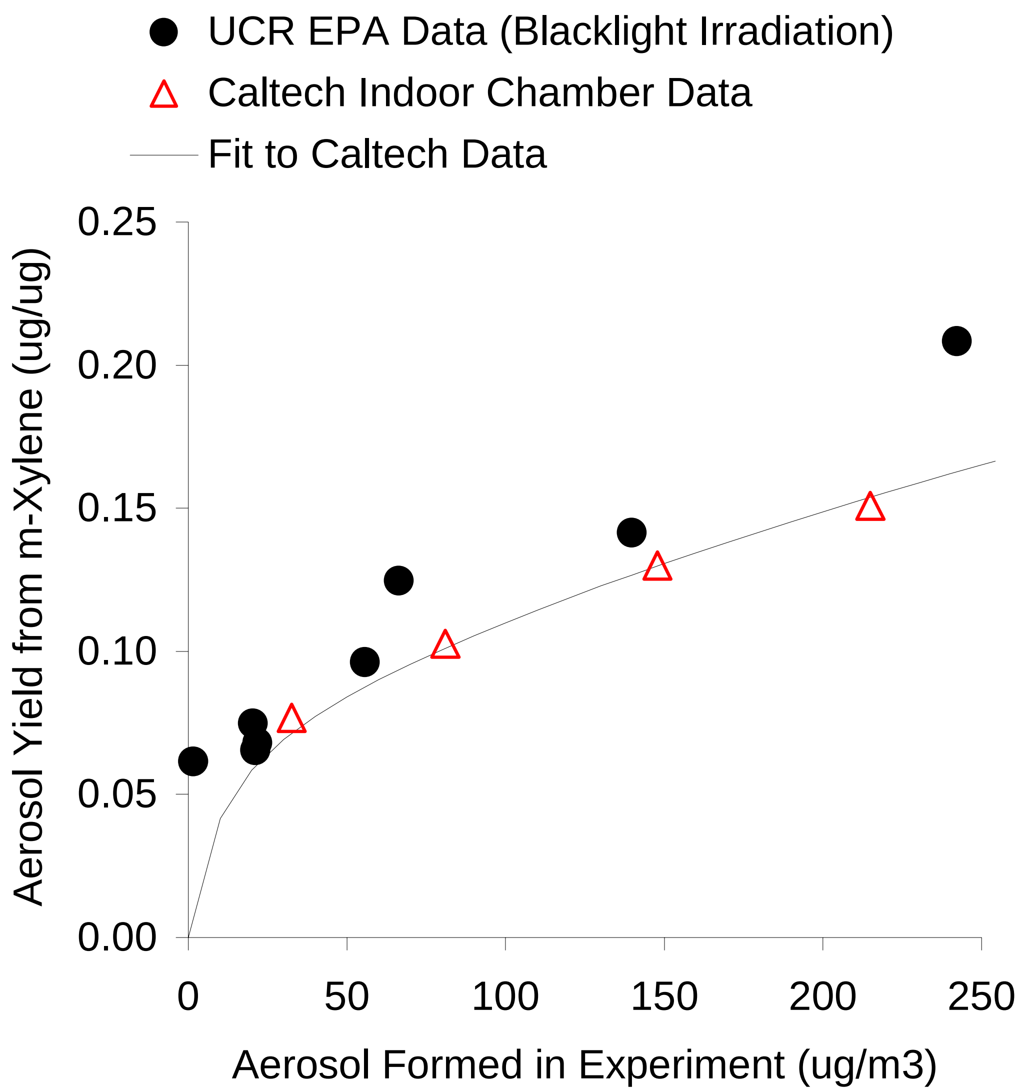


EFFECT OF ADDING m-XYLENE ON PM





COMPARISON OF UCR AND CALTECH CHAMBER RESULTS ON AEROSOL YIELDS FOR M-XYLENE



NEW AND UPCOMING PROGRAMS AND FUNDING

SCAQMD PROGRAM (~$200K)

Support for overall VOC reactivity research of interest to SCAQMD. Includes:

- Base Case Surrogate evaluation
- Experiments with additional coatings VOCs
- Support for PM measurements with CARB and SCAQMD reactivity experiments
- Investigation of utility for availability research

Contract being prepared

EPA OBM PROJECT (~$175K for UCR)

Obtain data to evaluate model predictions of indicator ratios for predicting O_3 sensitivities to emissions.

Subcontract to Bill Brune of Penn State to make radical measurements in UCR chamber for a ~3 month period

Experiments consist of:

- Selected with simple chemical systems to test model and measurements
- Surrogate - NO_x runs at various ROG and NO_x levels (may be in conjunction with reactivity runs)

Most of funding in place, remainder due soon. Radical instruments scheduled to come to UCR in September

NEW AND UPCOMING PROGRAMS AND FUNDING

FY ’03-’04 EPA EARMARK (~$200K)

Provides needed support for

- Improvements and maintenance of facility and instrumentation
- Mechanism evaluation and reactivity assessment at full range of temperature and RH conditions
- Studies of PM formation and gas and aerosol interactions
- Other experiments to advance agenda of original EPA chamber proposal and work plan

To be funded through EPA Ann Arbor as part of a larger earmark for CE-CERT projects. Funding not yet in place

POTENTIAL FUTURE RESEARCH DIRECTIONS

Evaluation of Temperature Effects

- Temperature expected to affect O_3 and PM formation, but existing data highly limited.

Research on Gas and Aerosol Phase Interactions

- Chamber well suited to study effects of PM on gas-phase processes and vise-versa

Research on PM Formation Potentials of Organics

- Organics differ widely in effects on secondary PM.
- Chamber can provide data under more controlled, and atmospherically realistic conditions than previously possible

Development and Evaluation of Models for Secondary PM

- Chamber can provide the well-characterized data most needed for model evaluation.
- Chamber well suited to test models for temperature and humidity effects