THE UCR-EPA ENVIRONMENTAL CHAMBER

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Outline

- Background and Objectives
- Facility Descriptions
- Characterization Results
- Representative Gas-Phase Results
- Current and Anticipated Projects

IMPORTANCE OF ENVIRONMENTAL CHAMBERS TO AIR POLLUTION MODELS

- **Chemical mechanisms** are critical components of models for predictions of secondary pollutants such as O_3 and PM
- Mechanisms in current pollution models have many uncertain estimates, simplifications and approximations
- **Environmental chambers**, simulating atmospheric reactions under controlled conditions, are essential to:
  - Developing predictive mechanisms when basic mechanistic data insufficient, e.g., for aromatics
  - Testing approximations and estimates for almost all VOCs under simulated atmospheric conditions
  - Testing entire mechanisms under varied conditions
- Results of experiments are influenced by chamber effects, so developing an appropriate chamber effects model is important

NEED FOR IMPROVED CHAMBER FACILITY FOR REDUCING CHEMICAL MECHANISM UNCERTAINTY

- Chamber effects and analytical limitations make most previous chambers unsuitable for simulating low ambient pollutant levels
- Large volume chambers are needed to reduce chamber effects, for studies of low volatility VOCs and PM, and to permit use of equipment with high sampling rates
- Largest current chambers are outdoors. But outdoor chambers are difficult to control and characterize for model testing
- Need to test predictions on how temperature affects O_3 and PM formation. Current chambers not suitable for this.
- Most U.S. chambers lack the analytical instrumentation needed to monitor many important trace species
- **The new UCR U.S. EPA Chamber was funded and constructed to address these needs**

DESIGN CHARACTERISTICS OF NEW CHAMBER FACILITY

- 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^{o}C in ~5^{o}C to ~50^{o}C range.
- Improved array of analytical instrumentation and provision for additional instrumentation in the future

DIAGRAM OF UCR EPA CHAMBER

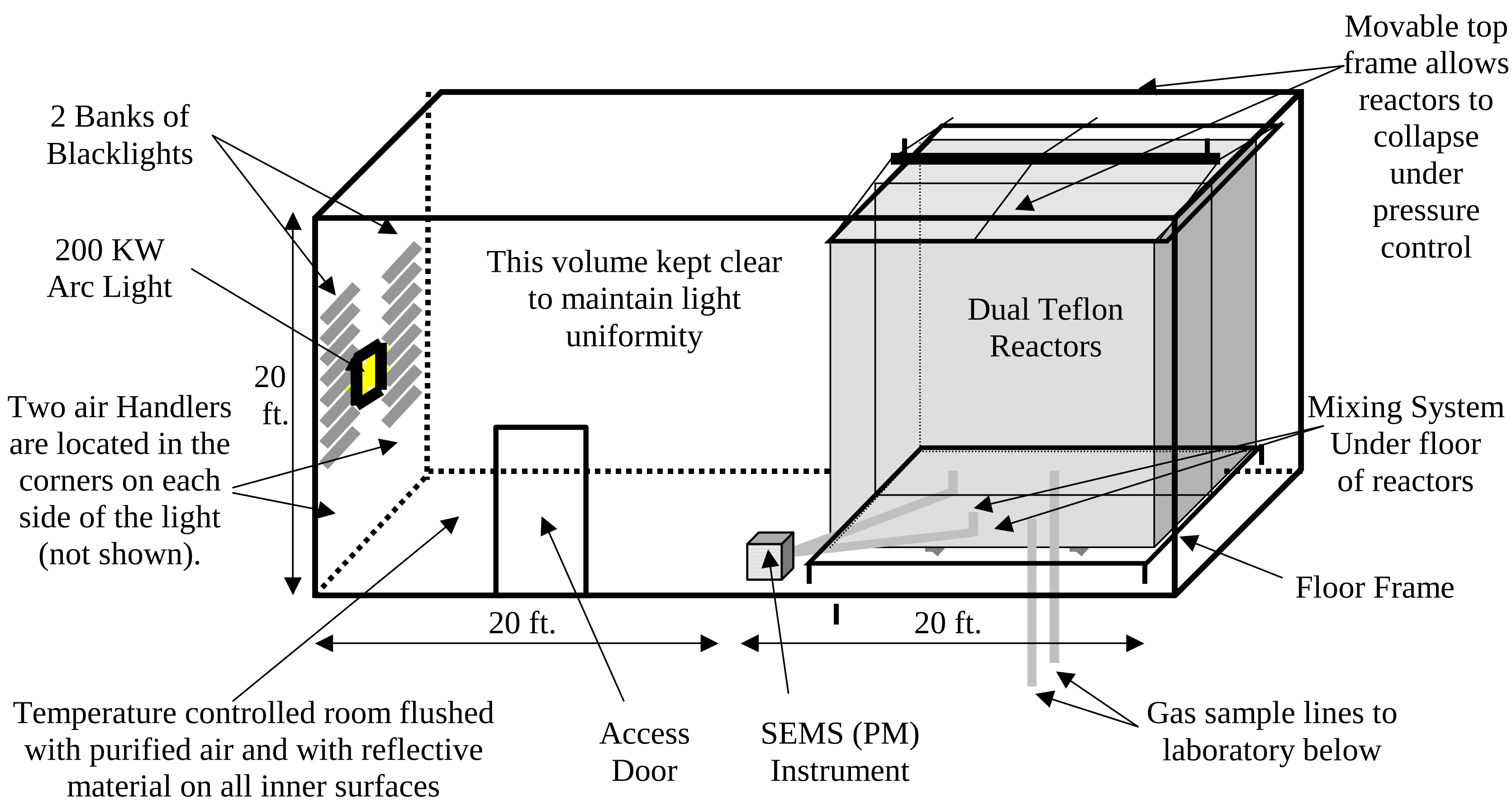
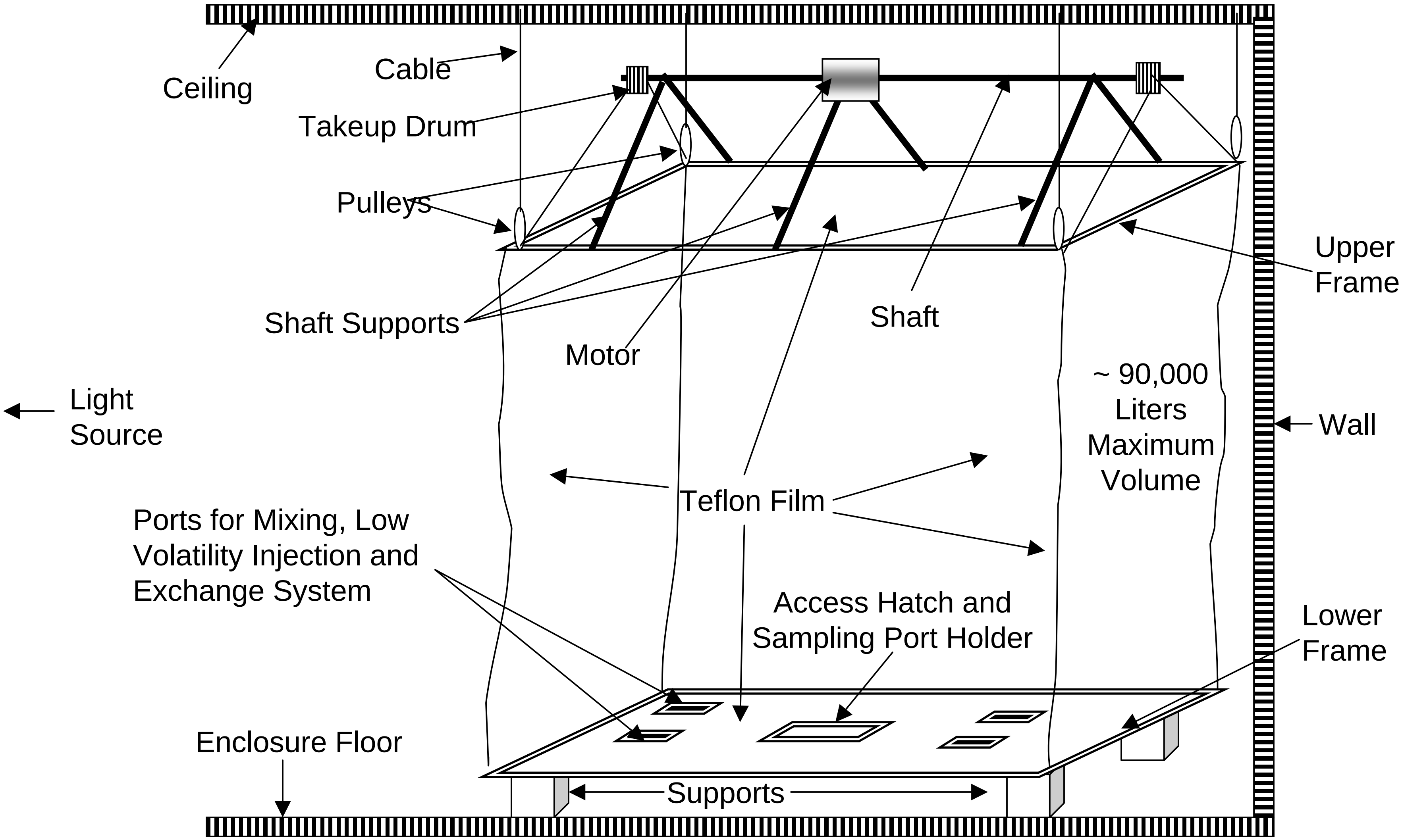


DIAGRAM OF REACTOR AND FRAMEWORK (One of Two)

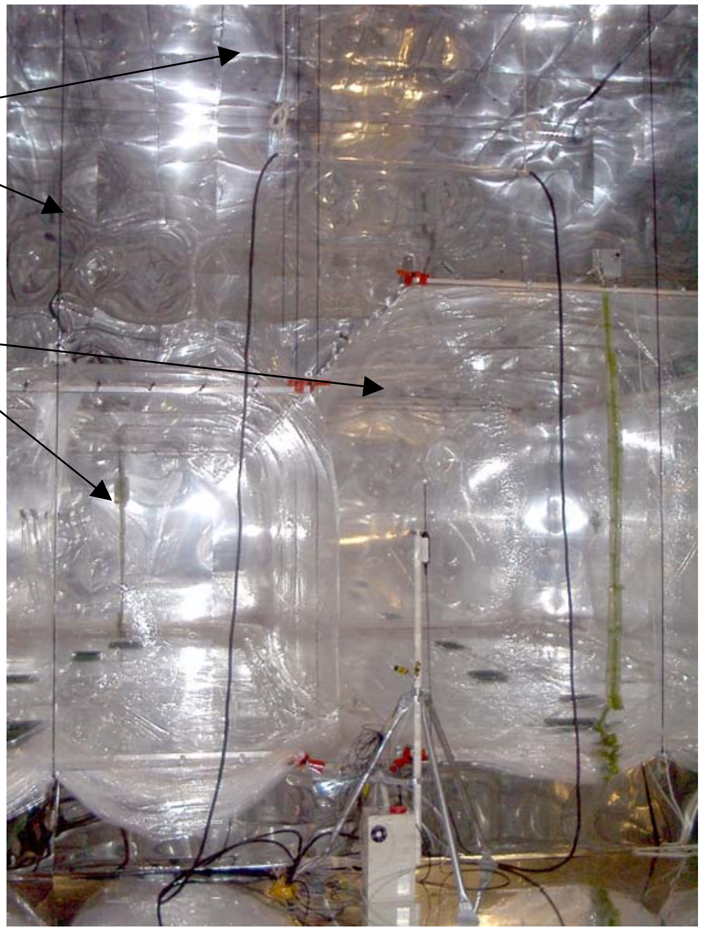


PHOTOGRAPHS OF CHAMBER AND LIGHTS

Looking Towards Reactors (from light)

Reflective walls and Ceiling

Partially Filled Reactors



Looking Towards Lights and Air Inlet

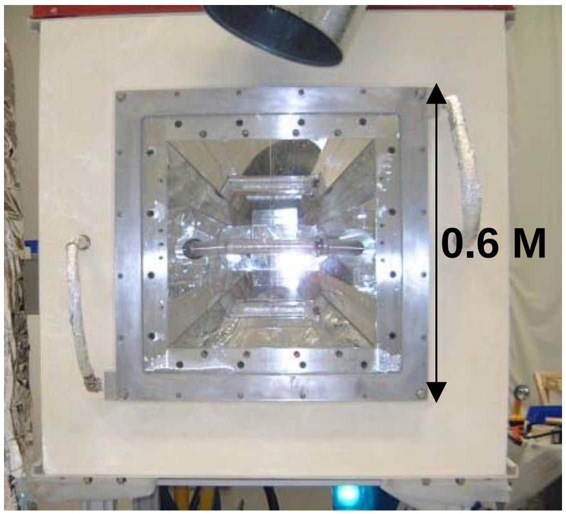
Black Lights

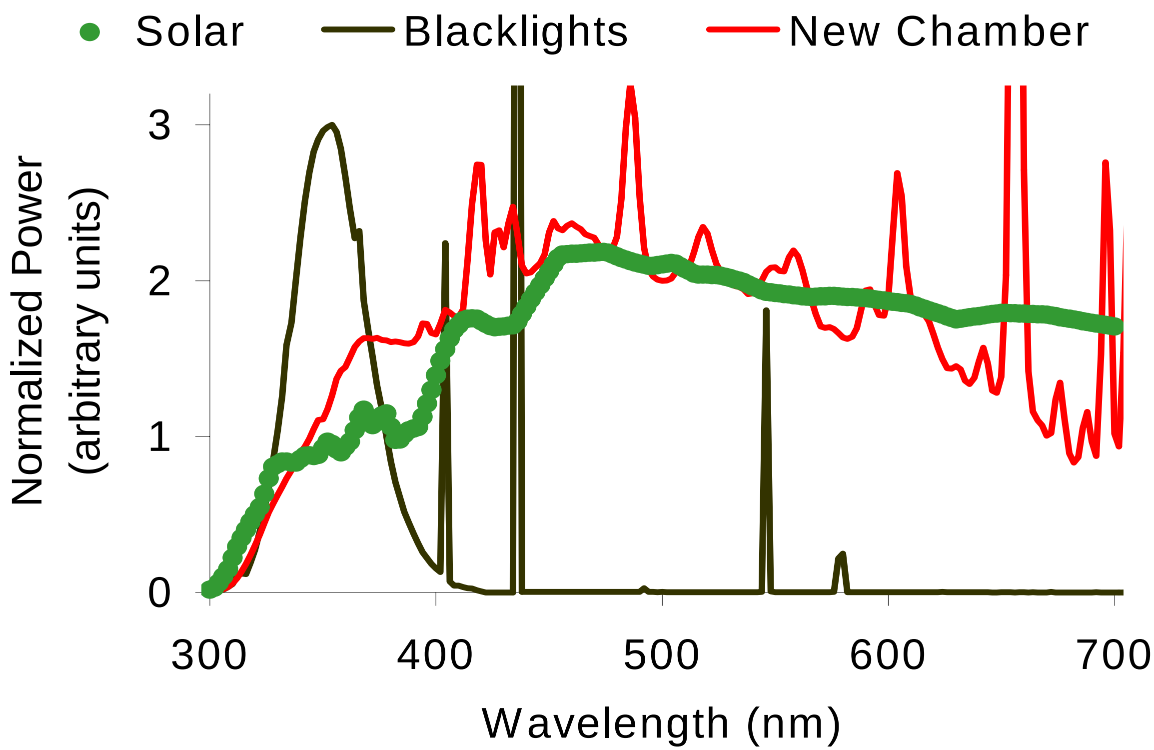
Air Intake

Arc Light

Reflective walls

LIGHT SOURCE AND SPECTRUM





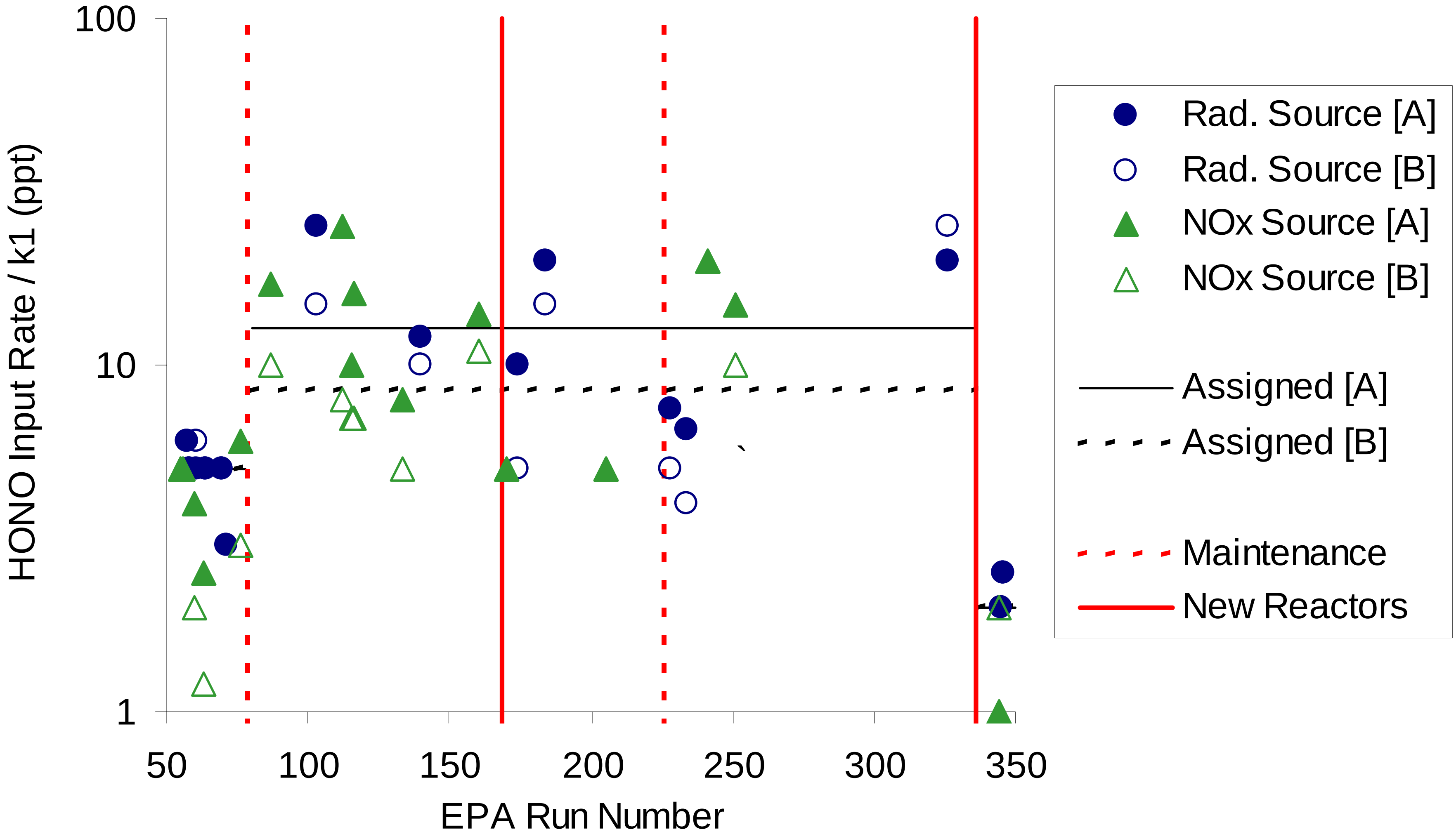
SUMMARY OF CHARACTERIZATION RESULTS

- 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
- Both chamber radical source and NO_2 offgasing can be represented by HONO offgasing at rates comparable to those observed in the SAPHIR chamber
- 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)

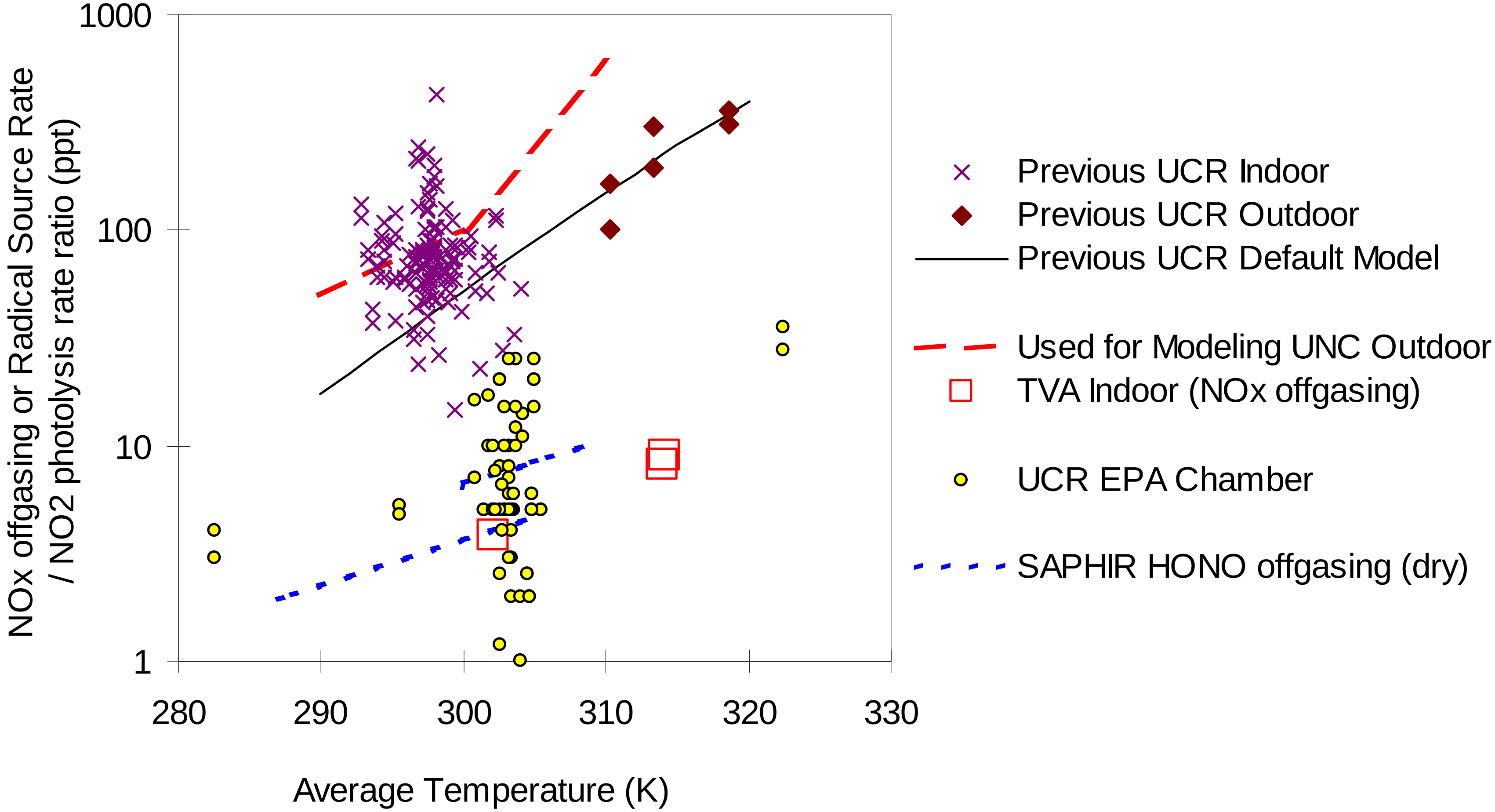
DERIVATION AND VALUES OF MAJOR CHAMBER CHARACTERIZATION PARAMETERS

Parameter	Derivation	Values
Continuous Radical source (Represented as HONO offgasing)	Model CO – NO_x and n–butane – NO_x runs	S_{HONO} / J_{NO2} = Runs 55-80: 5 ppt Runs 81-168: •Side A: 8.5 ppt •Side B: 12.5 ppt
NO_x Offgasing (Also Represented as HONO offgasing)	Model pure air and CO – air runs	
Formaldehyde offgasing	Model HCHO in runs without HCHO source	S_{HCHO} / J_{NO2} = 10 ppt
Initial HONO	Model char. runs sensitive to initial HONO	0 - 0.05 ppb
O_3 Decay	O_3 dark decay runs	Loss = 1.1% /hour

HONO OFFGASING PARAMETER VS. RUN NO.



COMPARISONS OF RADICAL SOURCE PARAMETER VALUES FOR VARIOUS CHAMBERS



SUMMARY OF CHAMBER PROJECTS TO DATE

“Development of a Next-Generation Environmental Chamber Facility …”

- Funded by U.S. EPA
- Funded chamber construction and initial characterization
- Initial exploratory experiments:
  - Low NO_x experiments with selected VOCs
  - Reactive organic gas (ROG) surrogate – NO_x experiments at varying ROG and NO_x levels
  - Incremental reactivity of m-xylene and n-octane at varying ROG and NO_x levels
- Status: complete. Report in preparation

SUMMARY OF CHAMBER PROJECTS TO DATE

“Development and Evaluation of a Gas-Phase Atmospheric Reaction Mechanism for Low NOx Conditions”

- Funded by the California Air Resources Board
- Primary objective is to evaluate the SAPRC-99 mechanism using previous and new low NO_x environmental chamber data
- A limited number of low NO_x ROG surrogate runs carried out for this project
- Data from the CSIRO and TVA chambers also used in this evaluation
- Project completed. Reporte available at http://www.cert.ucr.edu/~carter/absts.htm#lnoxrpt

SUMMARY OF CHAMBER PROJECTS TO DATE
(continued)

"Experimental Evaluation of Observational Based Methods for Evaluating the Sensitivity of O_3 to VOCs and NO_x"

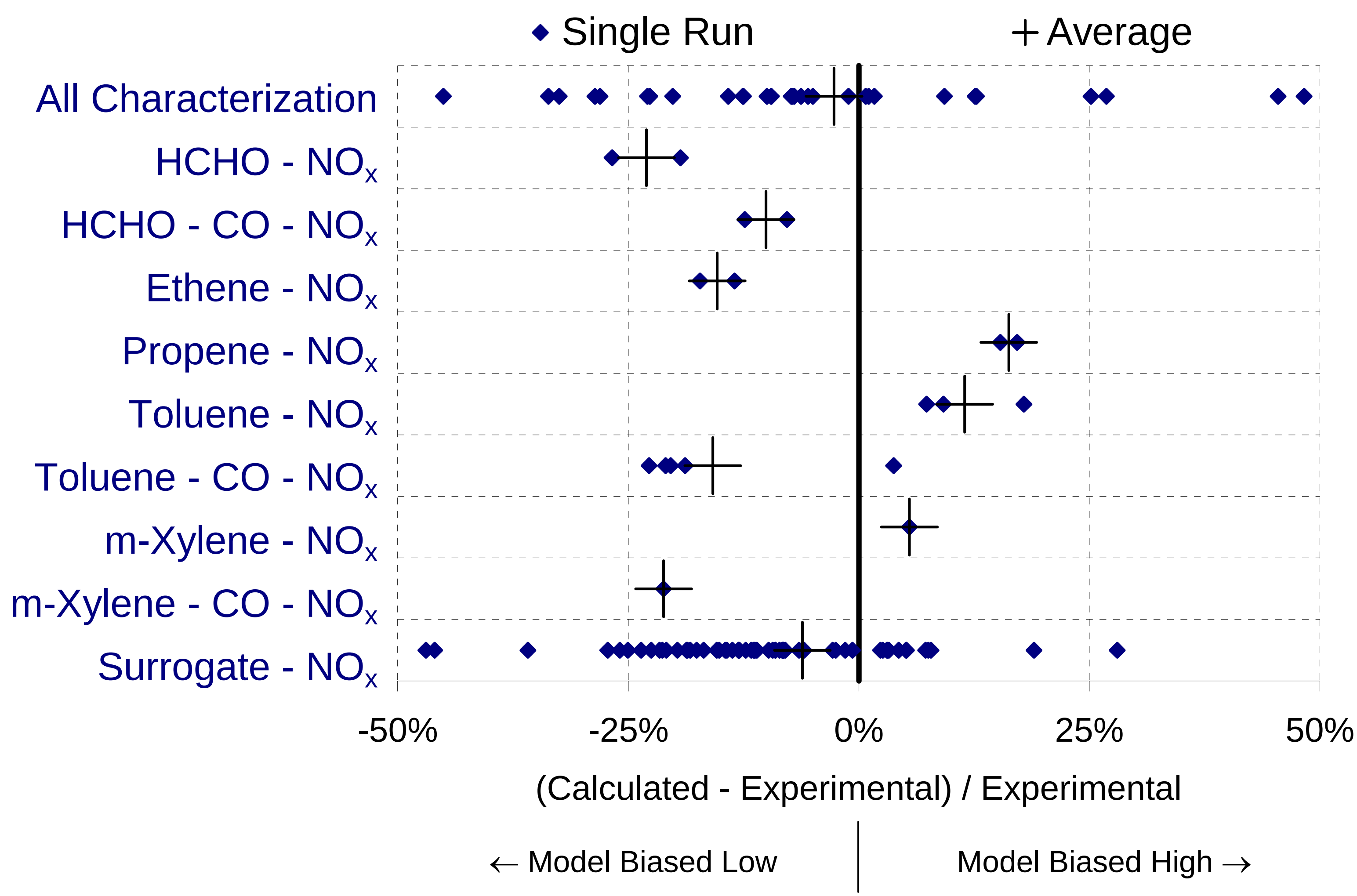
- Funded by U.S. EPA
- Objective is to provide data to evaluate OBMs using well-characterized chamber data
- ROG Surrogate – NO_x experiments at varying ROG and NO_x with measurements of key radical and "indicator" species
- Collaborated with Bill Brune of Penn State University to provide OH, HO_2, and "OH reactivity" measurements using LIF
- Successfully completed 20 dual-chamber surrogate experiments with radical measurements; 40 separate ROG/NO_x irradiations
- Report and journal articles in preparation

SUMMARY OF INITIAL EVALUATION EXPERIMENTS

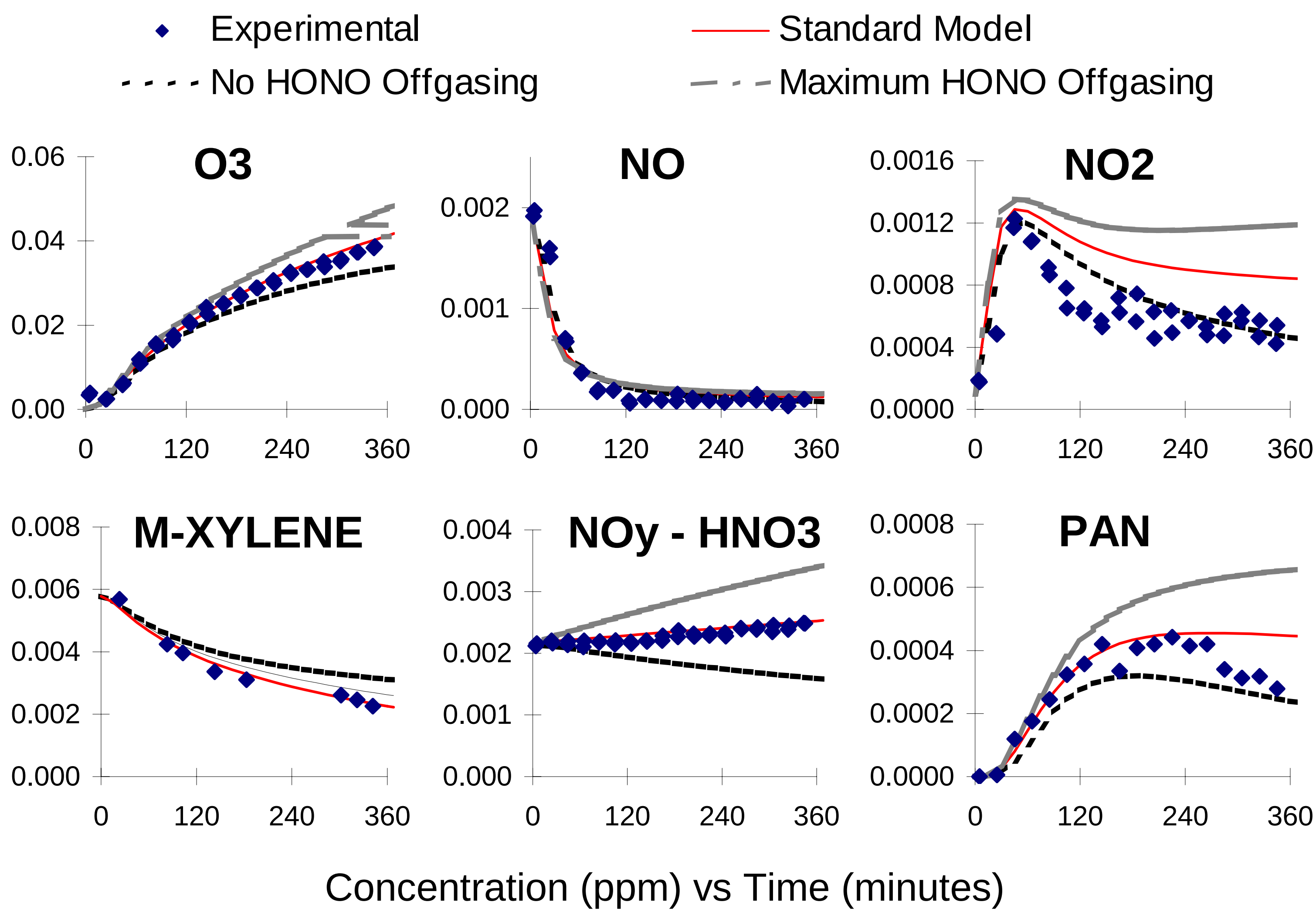
Run Type	Runs	NO_x Range (ppb)	VOC Range (ppm)
Characterization	32	0 - 200	Varied
Formaldehyde - NO_X	2	8 - 25	0.35 – 0.50
Formaldehyde - CO - NO_x	2	15-20	HCHO: 0.4 – 0.5 CO: 15 - 80
Ethene - NO_x	2	10 - 25	~0.6
Propene - NO_x	2	5 - 25	0.4 – 0.5
Toluene or m-Xylene - NO_x	4	5 - 25	Toluene: 0.6 – 0.16 Xylene: 0.18 CO: 25 - 50
Aromatic - NO_x + CO	6	5 - 30	
Ambient Surrogate - NO_x	64*	~0.2 - 315	0.2 – 4.2 ppmC

* Includes later experiments carried out for the EPA OBM study

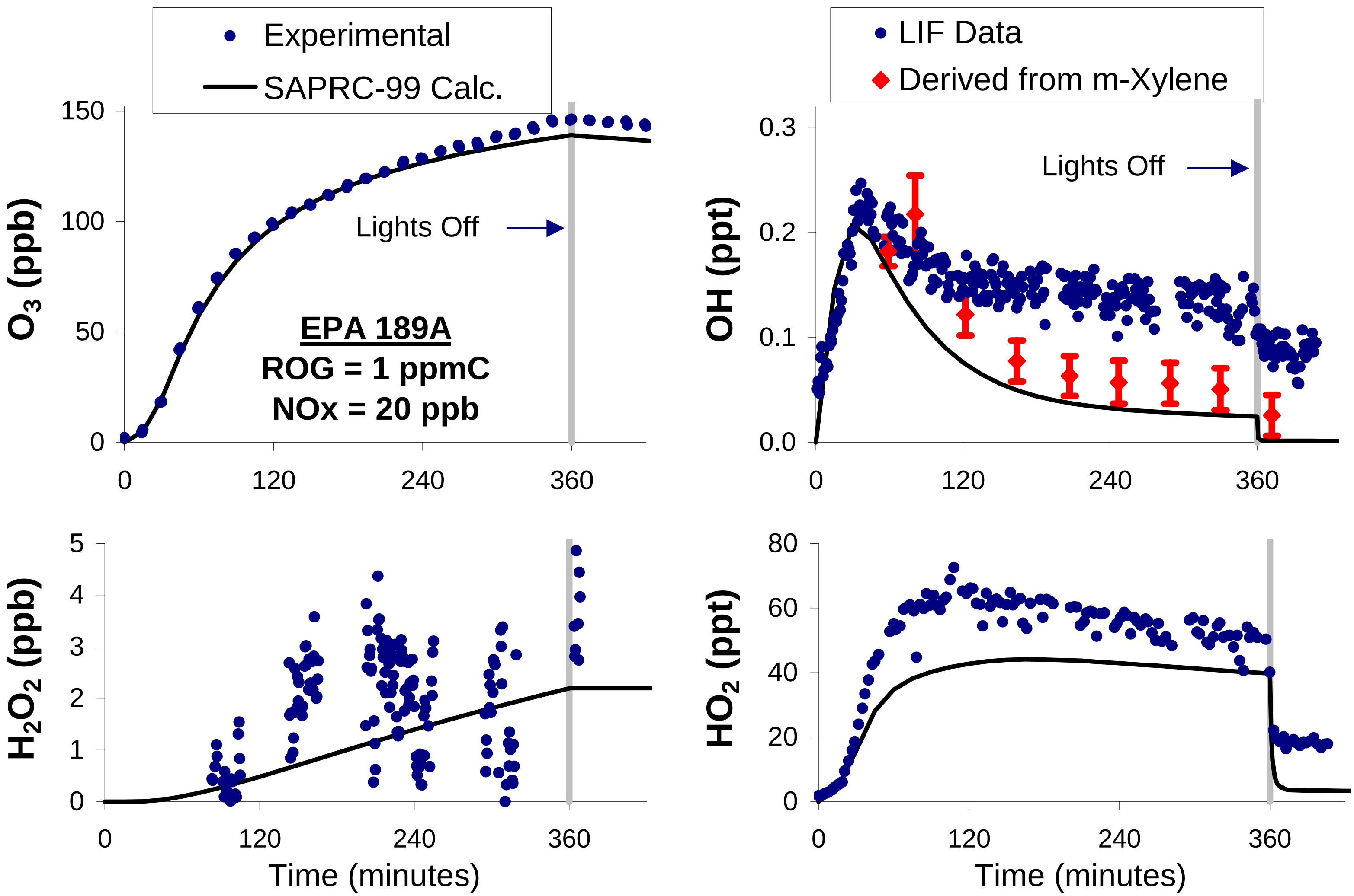
FITS TO Δ([O_3]-[NO]) FOR SAPRC-99 MECHANISM FOR THE INITIAL EVALUATION EXPERIMENTS



LOW NO_x SURROGATE EXPERIMENT
(ROG SURROGATE = 300 PPBC, NOx = 2 PPB)



EXAMPLE DATA FROM AN OBM EXPERIMENT



SUMMARY OF CHAMBER PROJECTS TO DATE
(continued)

"Evaluation of Atmospheric Impacts of Selected Coatings VOC Emissions"

- Funded by the California Air Resources Board
- Objective is to reduce uncertainties in O_3 impact estimates of major types of coatings VOCs where reactivity data needed
- Environmental chamber incremental reactivity experiments being carried out for various types of petroleum distillates, and Texanol®, an important component in water-based coatings
- Experiments carried out at two ROG and NO_x conditions and evaluated using SAPRC-99 mechanism
- Most experiments completed, data now being analyzed

SUMMARY OF CHAMBER PROJECTS TO DATE
(continued)

"Environmental Chamber Studies of VOC Species in Architectural Coatings And Mobile Source Emissions"

- Funded by the South Coast Air Quality Management District
- Primarily supplements CARB architectural coatings reactivity project to allow for additional work:
  - PM measurements during reactivity experiments
  - Incremental reactivity experiments with ethylene and propylene glycols, benzyl alcohol, and butyl carbitol
- Limited experiments to investigate interactions between glycols and aerosols for availability assessment
- Experiments near completion and being analyzed

SUMMARY OF CHAMBER PROJECTS TO DATE
(continued)

"Updated Chemical Mechanisms for Airshed Model Applications"

- Funded by the California Air Resources Board
- Major effort is updating and improving the SAPRC mechanism:
  - Updating to be consistent with current literature
  - Improving performance for aromatics and low ROG/NO_x
  - Developing condensed version for models to replace CB4
- Includes limited funding to support mechanism update effort (primarily for aromatics) (~10 runs)
- Project is now underway

SUMMARY OF CHAMBER PROJECTS TO DATE
(continued)

"Utilization of a Next Generation Environmental Chamber Facility ..."

- To be funded by the U.S. EPA
- Primary objective is to support research utilizing chamber for O_3 and secondary PM mechanism evaluations
- Experiments to be conducted include:
  - Studies of temperature and humidity effects on O_3 and SOA
  - PM and SOA formation characterization experiments
  - Study effects of variable ROG and NOx on and SOA
- Approved for funding. Waiting for contract paperwork

SUMMARY OF CHAMBER PROJECTS TO DATE
(continued)

PM Characterization and Secondary PM Formation Assessment Studies

- Carried out in collaboration with Dr. David Cocker of CE-CERT
- Funded in part by the SCAQMD and EPA projects and in part by other CE-CERT programs
- Experiments include
  - PM characterization and background experiments, and experiments for comparison with data from other chambers
  - Studies of SOA formation from aromatics and the ROG surrogate mixture under various conditions
- Work is underway. Some manuscripts submitted for publication

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