

**DEVELOPMENT OF A NEXT-GENERATION  
ENVIRONMENTAL CHAMBER FACILITY FOR  
CHEMICAL MECHANISM AND VOC  
REACTIVITY RESEARCH**

**SUMMARY OF PROGRESS AND  
DRAFT RESEARCH PLAN**

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FOR PRESENTATION TO THE  
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## **NEED FOR IMPROVED CHAMBER FACILITY FOR REDUCING CHEMICAL MECHANISM UNCERTAINTY**

MANY VOCs ARE REPRESENTED IN MODELS USING  
PARAMETERIZED MODELS ADJUSTED TO FIT  
RELATIVELY HIGH CONCENTRATION CHAMBER DATA.

NONLINEAR CHEMISTRY MAY NOT ALWAYS  
EXTRAPOLATE TO LOWER CONCENTRATIONS.

LOWER URBAN POLLUTANT LEVELS ARE BECOMING  
MORE COMMON AS CONTROLS ARE IMPLEMENTED.

CONCERN THAT COSTLY REGULATIONS BASED ON  
REDUCING O<sub>3</sub> AT HIGH URBAN NO<sub>x</sub> LEVELS MAY NOT  
BE IMPROVING AIR QUALITY IN OTHER AREAS.

MOST CHAMBERS NOT SUITABLE FOR EVALUATING  
VOC IMPACTS OTHER THAN ON O<sub>3</sub>.

INFORMATION IS NEEDED ON HOW TEMPERATURE  
AND HUMIDITY AFFECTS VOC IMPACTS.

# **NEW U.C. RIVERSIDE CHAMBER FACILITY**

## **MAJOR OBJECTIVES**

- DETERMINE WHETHER PREDICTIONS OF EFFECTS OF VOC AND NO<sub>x</sub> ON O<sub>3</sub> AND AEROSOLS ARE APPLICABLE AT LOWER POLLUTANT LEVELS.
- ASSESS O<sub>3</sub>, AEROSOL, AND OTHER IMPACTS OF VOCs UNDER LOW NO<sub>x</sub> AND OTHER CONDITIONS.
- EVALUATE MECHANISMS FOR PREDICTIONS OF KEY SPECIES (E.G., H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>, "TRUE" NO<sub>2</sub>) FOR WHICH CHAMBER DATA HAVE BEEN LIMITED.
- DETERMINE EFFECTS OF TEMPERATURE ON VOC REACTIVITY, AEROSOL FORMATION AND OTHER IMPACTS.
- EVALUATE USEFULNESS OF INDICATOR SPECIES FOR ASSESSING RESPONSES OF AMBIENT ATMOSPHERES TO EMISSIONS CHANGES.
- PROVIDE A WAY TO TEST AMBIENT MONITORING EQUIPMENT UNDER WELL CHARACTERIZED BUT REALISTIC CONDITIONS.

## **U.C. RIVERSIDE CHAMBER FACILITY PROGRESS AND CURRENT STATUS**

INTERNATIONAL WORKSHOP ON ATMOSPHERIC  
CHEMISTRY AND ENVIRONMENTAL CHAMBER  
RESEARCH HELD IN OCTOBER, 1999

CHAMBER AND LIGHT SOURCE FACILITY DESIGNED  
AND CONSTRUCTED

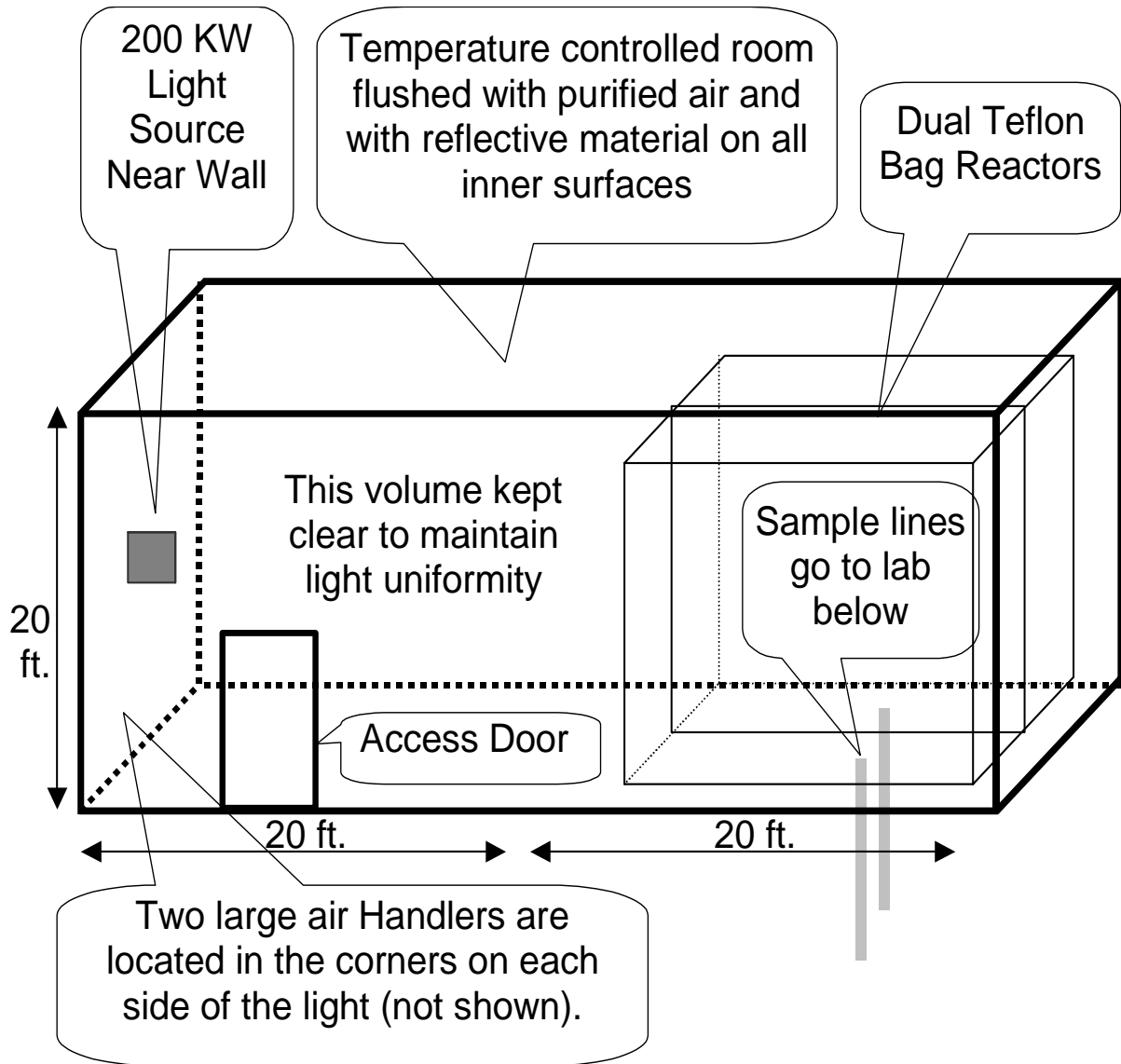
- NEW BUILDING CONSTRUCTED TO HOUSE FACILITY. TOOK OCCUPANCY LATE JULY 2001
- DUAL 80-100 M<sup>3</sup> TEFLON BAG REACTORS WILL BE IN "CLEAN ROOM" FLUSHED WITH PURE AIR
- 200 KW ARGON ARC LIGHT WILL SIMULATE SUNLIGHT SPECTRUM AND INTENSITY
- TEMPERATURE CONTROL FROM 4 - 50°C (40 - 120°F) TO ±1°C (±2°F)
- EXPECTED TO BE OPERATIONAL IN EARLY 2002

OBTAINING AND EVALUATING INSTRUMENTATION  
MOST NEEDED FOR ASSESSING LOW NO<sub>x</sub> EFFECTS

EXPERIMENTS CONDUCTED TO INVESTIGATE AND  
MINIMIZE BACKGROUND EFFECTS USING SMALLER  
(~3000-LITER) REACTORS

QUALITY ASSURANCE PLAN IN PREPARATION AND  
WILL BE SUBMITTED LATE JANUARY, 2002

# DIAGRAM OF ENVIRONMENTAL CHAMBER AND TEMPERATURE-CONTROLLED ENCLOSURE



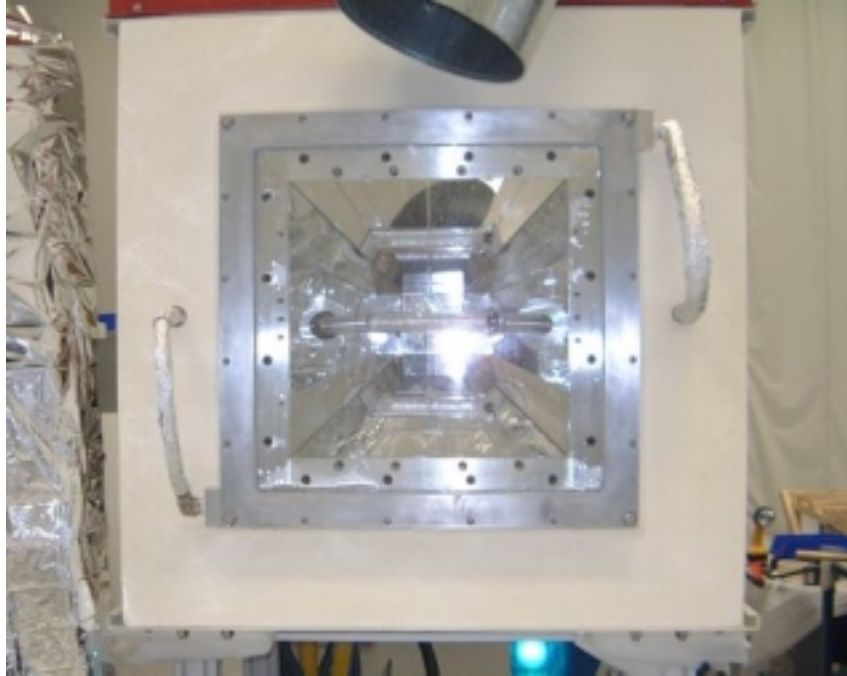
## CHAMBER BUILDING AND LABORATORY



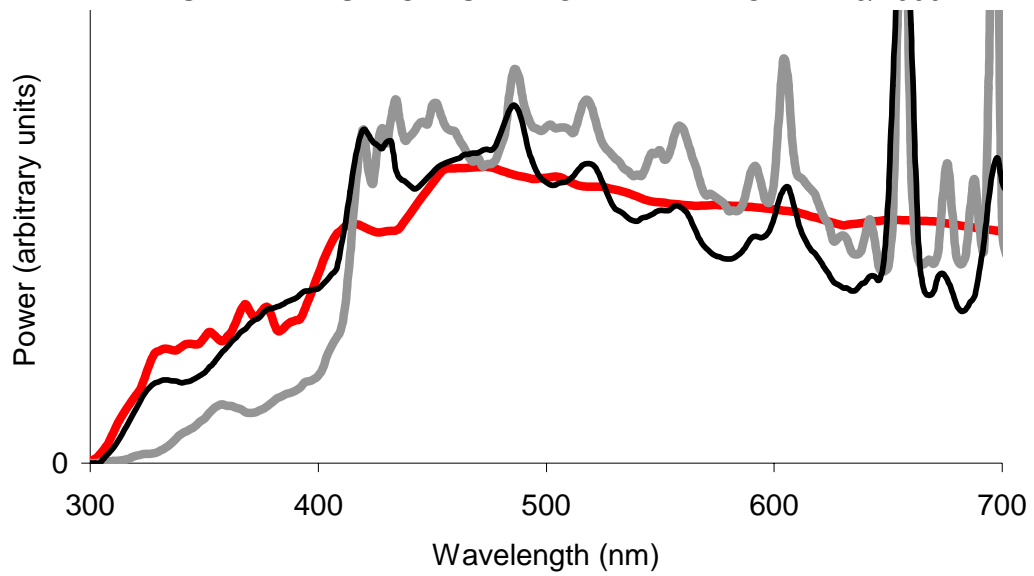
## CHAMBER ENCLOSURE AS OF 8/01



# LIGHT SOURCE AND SPECTRUM



- REPRESENTATIVE SOLAR SPECTRUM
- LAMP AS INSTALLED 9/2001
- ESTIMATED SPECTRUM PROVIDED BY VORTEK 9/2000



## RESULTS OF INITIAL EVALUATION EXPERIMENTS

PURE AIR AND OTHER CHARACTERIZATION  
EXPERIMENTS CONDUCTED TO MEASURE NO<sub>x</sub>  
OFFGASING AND OTHER BACKGROUND EFFECTS

DIFFERENT TEFLON® WALL MATERIALS TESTED AND  
WALL TREATMENT METHODS EVALUATED.

- TESTS CONDUCTED USING SMALL (~3000-LITER)  
“PILLOWBAG” REACTORS WITH BLACKLIGHTS
- NO ALTERNATIVES SIGNIFICANTLY BETTER  
THAN FEP TEFLON® FILM
- BACKGROUND EFFECTS DECLINE AFTER  
REPEATED PURE AIR IRRADIATIONS
- PERMEATION THROUGH 0.2 MIL TEFLON® FILM  
NON-NEGLIGIBLE.

DATA INDICATE MINIMUM NO<sub>x</sub> OFFGASING RATES OF  
≥ 0.5 PPB/DAY IN THE “PILLOWBAG” REACTORS

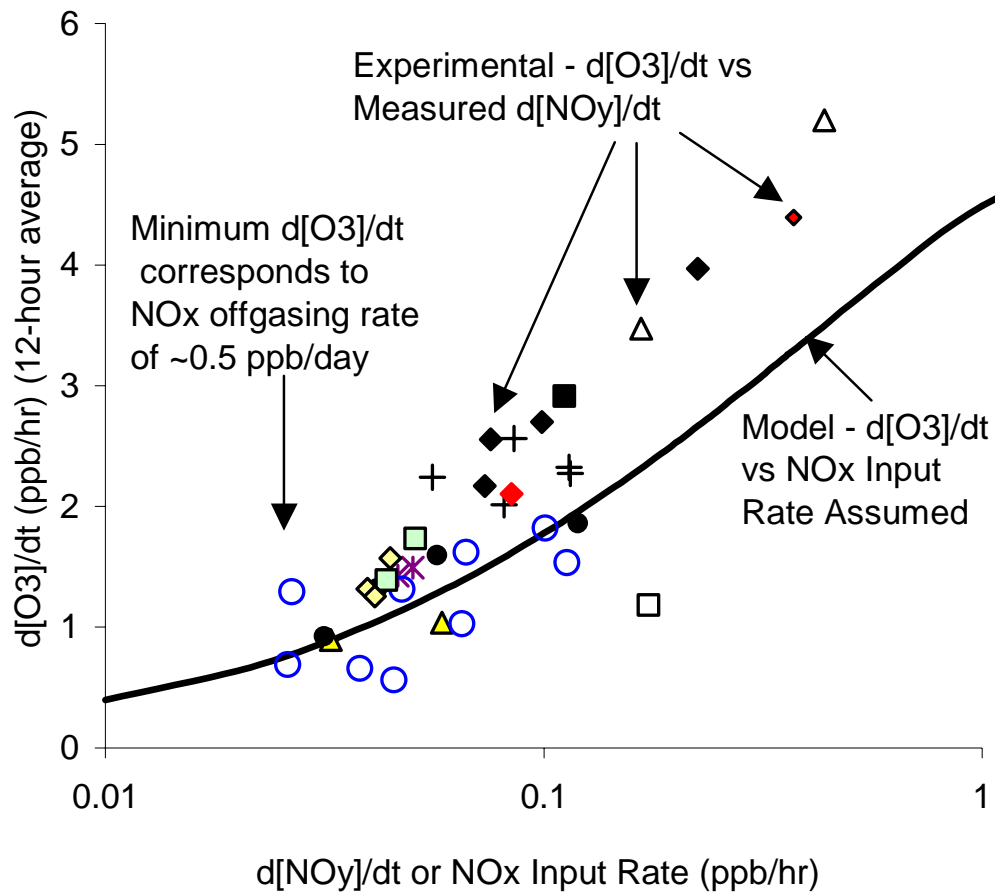
- MECHANISM EVALUATION FEASIBLE AT ≥ ~5 PPB  
NO<sub>x</sub> OR LOWER WITH LARGER REACTORS

CHAMBER RADICAL SOURCE IN TEFLON® FILM LOW  
AT LOW NO<sub>x</sub> LIMIT, INCREASES WITH NO<sub>2</sub>

# EXPERIMENTAL AND CALCULATED RELATIONSHIPS BETWEEN O<sub>3</sub> FORMATION AND NO<sub>x</sub> OFFGASING IN PURE AIR EXPERIMENTS

Symbols indicate different experimental reactors or conditions

- ◆ F2x   ◆ F2   □ F3   ▲ K1   ✖ P1   ● F4   △ F4a
- + F5   ○ F6   ■ F7x   ◆ F8x   □ F7   ◇ F8



## **MAJOR ANALYTICAL EQUIPMENT**

### **GAS-PHASE INSTRUMENTATION ACQUIRED**

- STANDARD O<sub>3</sub>, NO<sub>x</sub>, CO, GC-FID AND OTHER ANALYZERS (MOST FROM PREVIOUS PROJECTS)
- TDLAS #1: NO<sub>2</sub> AND HNO<sub>3</sub> (~0.5-1 ppb sensitivity)
- TDLAS #2: FORMALDEHYDE AND H<sub>2</sub>O<sub>2</sub> (Sub-ppb sensitivity for HCHO, H<sub>2</sub>O<sub>2</sub> not yet evaluated)
- GC-LUMINOL FOR NO<sub>2</sub> AND PAN (Highly sensitive but needs further evaluation of reliability and interferences)
- HIGH SENSITIVITY NO ANALYZER (NO ≥ 0.05 PPB)

### **AEROSOL INSTRUMENTATION** (being fabricated)

- TWO SCANNING ELECTRICAL MOBILITY SPECTROMETERS (Measures size and number distributions)
- TANDEM DIFFERENTIAL MOBILITY ANALYZER (Measures responses to changes in RH or temperature)

### **GAS-PHASE INSTRUMENTS NOT ACQUIRED**

- GC-MS (Product identification de-emphasized in current research plan. May be obtained from other funding)
- FTIR (Insufficient sensitivity for chamber studies)
- DOAS (Need and priority not yet determined)
- RADICAL MEASUREMENT INSTRUMENTATION (Very useful for evaluation but insufficient funds in this project)

## **RESEARCH NEEDS CONSIDERED IN DEVELOPMENT OF DRAFT RESEARCH PLAN**

ADEQUATELY CHARACTERIZE PERFORMANCE OF FACILITY (LIGHT, T-CONTROL, MIXING, ETC.)

ADEQUATELY CHARACTERIZE CHAMBER EFFECTS AS FUNCTION OF T, RH, NO<sub>x</sub> LEVELS, CONDITIONING

EVALUATE NEW MEASUREMENT METHODS AND POSSIBLE SAMPLING AND WALL ARTIFACTS, PARTICULARLY FOR H<sub>2</sub>O<sub>2</sub> AND HNO<sub>3</sub>.

VERIFY COMPARABLE RESULTS WITH PREVIOUS CHAMBER STUDIES, PARTICULARLY AEROSOL DATA

EVALUATE MECHANISMS FOR THE NEW CONDITIONS AND SPECIES USING SIMPLER SYSTEMS

- LEVEL OF EFFORT DEPENDS ON EXTENT TO WHICH UNEXPECTED RESULTS OBTAINED
- EVALUATE LOW NO<sub>x</sub> MECHANISMS FOR BASE CASE VOCs, PARTICULARLY AROMATICS

DETERMINE BEST BASE CASE EXPERIMENTS FOR VOC REACTIVITY (O<sub>3</sub>, PM) ASSESSMENT

STUDY COATINGS VOCs AS REQUIRED IN NEW CARB CONTRACTS

OBTAIN DATA TO EVALUATE INDICATORS OF O<sub>3</sub> SENSITIVITY TO PRECURSORS

## AVAILABLE FUNDING AND TIME CONSIDERATIONS

### FUNDS CURRENTLY AVAILABLE FOR EXPERIMENTS

- REMAINING EPA (APPROXIMATE) \$1,000 K
- RESERVED FOR REMAINING EQUIPMENT AND FACILITY - \$140 K
- CARB COATINGS PROJECTS \$205 K
- CARB LOW NO<sub>x</sub> MECHANISM EVALUATION \$35 K
- TOTAL \$1,100 K

ESTIMATED COST/MONTH: ~\$43K EPA, ~\$38K CARB

AVAILABLE FUNDING WILL LAST UNTIL **MARCH, 2004**

ESTIMATE AT LEAST 8 EXPERIMENTS PER MONTH  
(ONE EVERY 2.5 DAYS) (SOME MAY BE MULTI-DAY)

THEREFORE,  $\geq$  **210 RUNS** CAN BE CONDUCTED  
THROUGH MARCH '04 (STARTING FEB '02)\*

\* (NOTE: ESTIMATE IN DRAFT RESEARCH PLAN OF 230  
EXPERIMENTS BASED ON INCORRECT ESTIMATE OF  
OVERHEAD COSTS)

## SUMMARY OF EXPERIMENTS IN DRAFT RESEARCH PLAN

<b><u>DESCRIPTION</u></b>	<b><u>RUNS</u></b>
CHAMBER CHARACTERIZATION – MINIMAL VARIABLE TEMPERATURE AND RH	26 24
AEROSOL CHARACTERIZATION - MINIMAL VARIABLE TEMPERATURE AND RH	27 13
MECHANISM EVALUATION – SIMPLE SYSTEMS	
H <sub>2</sub> O <sub>2</sub> , HNO <sub>3</sub> , HCHO TESTS	15
TOLUENE	6
ISOPRENE	3
OTHER	17
SURROGATE EVALUATION	24
REACTIVITY EXPERIMENTS – MAJOR VOCs	
FORMALDEHYDE, ACETALDEHYDE, N-OCTANE, PROPENE, ISOPRENE	16
TOLUENE, M-XYLENE (AT DIFFERENT T'S)	12
CARB PROJECT REACTIVITY EXPERIMENTS	
TEXANOL®	5
PETROLEUM DISTILLATES	26
OTHER COATINGS VOCs	16
<b>TOTAL</b>	<b>230</b>

## **EXTERNAL INPUT AND PEER REVIEW**

INPUT ON CARB COATINGS PROJECTS BEING PROVIDED BY CARB'S REACTIVITY RESEARCH ADVISORY COMMITTEE (RRAC)

RECOMMENDED RRWG BE MAIN VEHICLE PROVIDING OVERSIGHT AND INPUT INTO OVERALL PROJECT

- CONSIDER BOTH SCIENCE AND POLICY NEEDS
- FORM SUBGROUP FOR ACTIVE OVERSIGHT
- EPA AND CARB PROJECT OFFICERS PARTICIPATE
- INCLUDE PARTICIPANTS IN CARB'S RRAC

OVERSIGHT GROUP SELECT *PAID* PEER REVIEWERS FOR RESEARCH PLAN AND PERIODIC REPORTS

- CHOSEN FOR TECHNICAL EXPERTISE
- MAKE RECOMMENDATIONS TO OVERSIGHT GROUP AND PI
- REVIEWERS FUNDED BY EPA OR SEPARATE RRWG PROJECTS

PROJECT SHOULD BE REVIEWED AT LEAST BIANNUALLY

EPA WILL REVIEW QA PLAN AND RECOMMEND ADDITIONAL REVIEWERS IF APPROPRIATE