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
REACTIVITY RESEARCH WORKING GROUP

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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_3 AT HIGH URBAN NO_x LEVELS MAY NOT BE IMPROVING AIR QUALITY IN OTHER AREAS.

MOST CHAMBERS NOT SUITABLE FOR EVALUATING VOC IMPACTS OTHER THAN ON O_3.

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_x ON O_3 AND AEROSOLS ARE APPLICABLE AT LOWER POLLUTANT LEVELS.
- ASSESS O_3, AEROSOL, AND OTHER IMPACTS OF VOCs UNDER LOW NO_x AND OTHER CONDITIONS.
- EVALUATE MECHANISMS FOR PREDICTIONS OF KEY SPECIES (E.G., H_2O_2, HNO_3, "TRUE" NO_2) 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

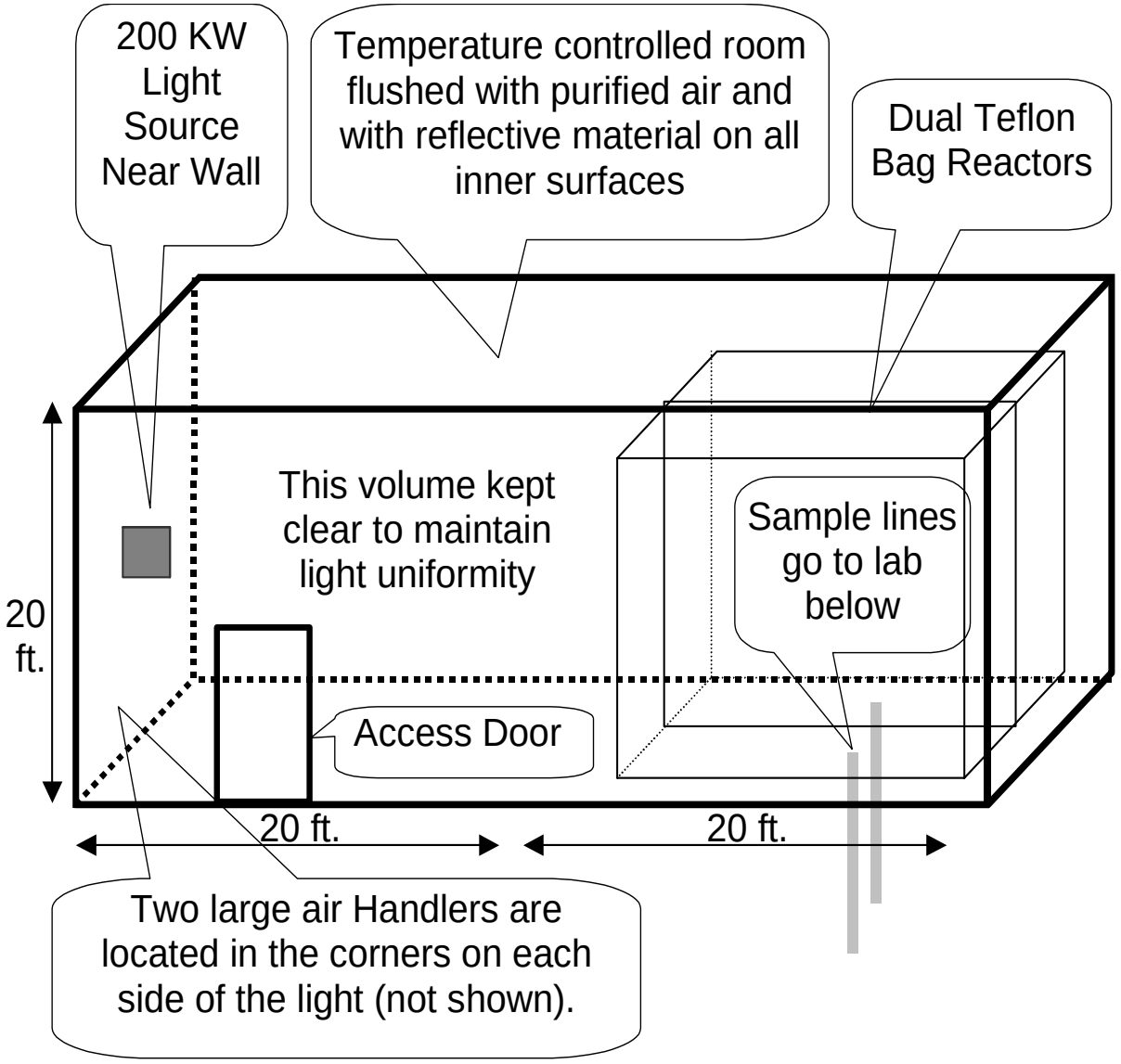
- NEW BUILDING CONSTRUCTED TO HOUSE FACILITY. TOOK OCCUPANCY LATE JULY 2001
- DUAL 80-100 M^3 TEFLON BAG REACTORS WILL BE IN "CLEAN ROOM" FLUSHED WITH PURE AIR
- 200 KW ARGON ARC LIGHT WILL SIMULATE SUNLIGHT SPECTRUM AND INTENSITY
- TEMPERATURE CONTROL FROM 4 - 50^{o}C (40 - 120^{o}F) TO $\pm$1^{o}C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

OBTAINING AND EVALUATING INSTRUMENTATION MOST NEEDED FOR ASSESSING LOW NO_x 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

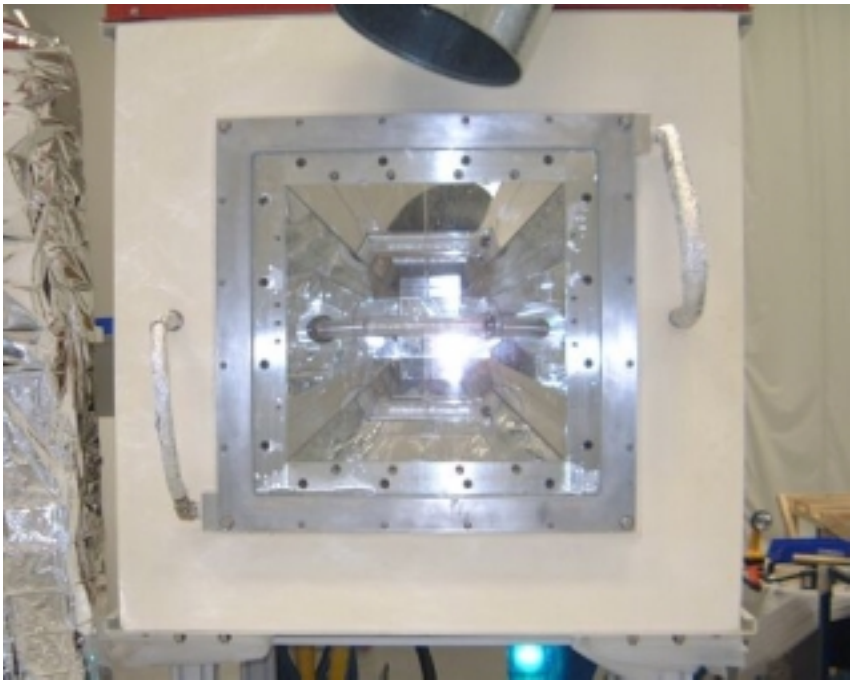
DIAGRAM OF ENVIRONMENTAL CHAMBER AND TEMPERATURE-CONTROLLED ENCLOSURE

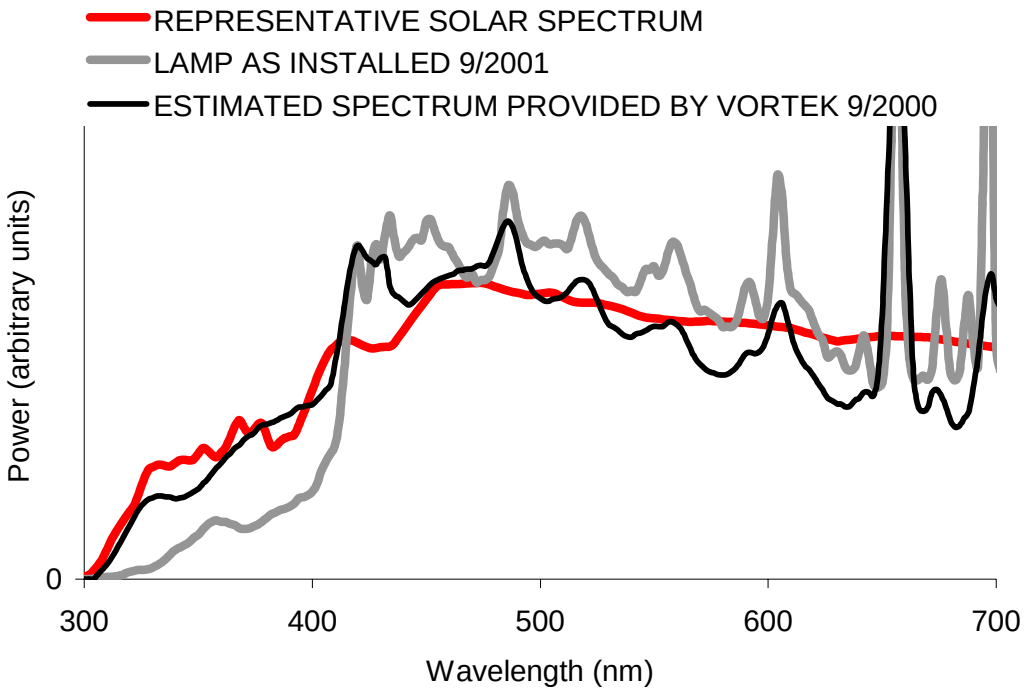


CHAMBER BUILDING AND LABORATORY

CHAMBER ENCLOSURE AS OF 8/01

LIGHT SOURCE AND SPECTRUM





RESULTS OF INITIAL EVALUATION EXPERIMENTS

PURE AIR AND OTHER CHARACTERIZATION EXPERIMENTS CONDUCTED TO MEASURE NO_x 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.

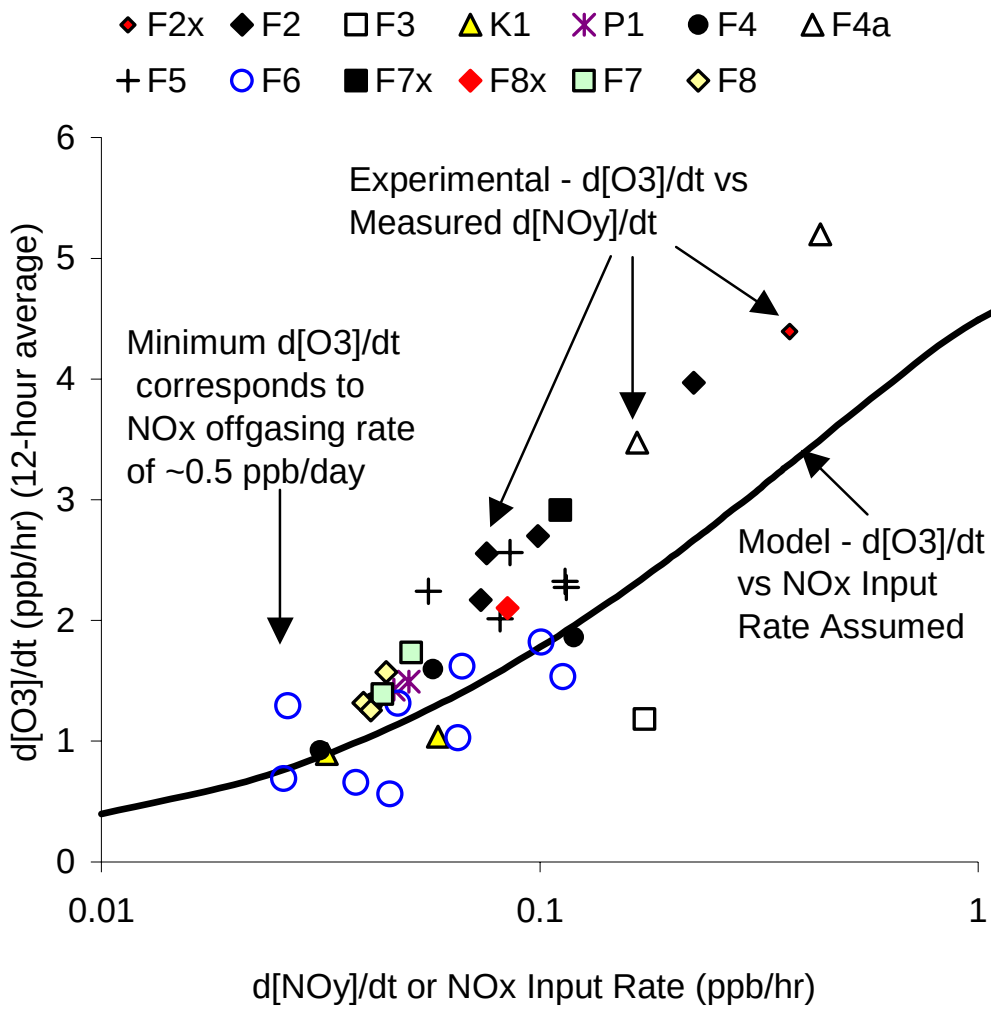
DATA INDICATE MINIMUM NO_x OFFGASING RATES OF $\geq$ 0.5 PPB/DAY IN THE "PILLOWBAG" REACTORS

- MECHANISM EVALUATION FEASIBLE AT $\geq$ ~5 PPB NO_x OR LOWER WITH LARGER REACTORS

CHAMBER RADICAL SOURCE IN TEFLON® FILM LOW AT LOW NO_x LIMIT, INCREASES WITH NO_2

EXPERIMENTAL AND CALCULATED RELATIONSHIPS BETWEEN O_3 FORMATION AND NO_x OFFGASING IN PURE AIR EXPERIMENTS

Symbols indicate different experimental reactors or conditions



MAJOR ANALYTICAL EQUIPMENT

GAS-PHASE INSTRUMENTATION ACQUIRED

- STANDARD O_3, NO_x, CO, GC-FID AND OTHER ANALYZERS (MOST FROM PREVIOUS PROJECTS)
- TDLAS #1: NO_2 AND HNO_3 (~0.5-1 ppb sensitivity)
- TDLAS #2: FORMALDEHYDE AND H_2O_2 (Sub-ppb sensitivity for HCHO, H_2O_2 not yet evaluated)
- GC-LUMINOL FOR NO_2 AND PAN (Highly sensitive but needs further evaluation of reliability and interferences)
- HIGH SENSITIVITY NO ANALYZER (NO $\geq$ 0.05 PPB)

AEROSOL INSTRUMENTATION (being fabricated)

- TWO SCANNING ELECTRICAL MOBILITY SPECT-ROMETERS (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_x LEVELS, CONDITIONING

EVALUATE NEW MEASUREMENT METHODS AND POSSIBLE SAMPLING AND WALL ARTIFACTS, PARTICULARLY FOR H_2O_2 AND HNO_3.

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_x MECHANISMS FOR BASE CASE VOCs, PARTICULARLY AROMATICS

DETERMINE BEST BASE CASE EXPERIMENTS FOR VOC REACTIVITY (O_3, PM) ASSESSMENT

STUDY COATINGS VOCs AS REQUIRED IN NEW CARB CONTRACTS

OBTAIN DATA TO EVALUATE INDICATORS OF O_3 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_x 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, ≥ **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

DESCRIPTION	**RUNS**
CHAMBER CHARACTERIZATION – MINIMAL	26
VARIABLE TEMPERATURE AND RH	24
AEROSOL CHARACTERIZATION - MINIMAL	27
VARIABLE TEMPERATURE AND RH	13
MECHANISM EVALUATION – SIMPLE SYSTEMS	
H_2O_2, HNO_3, 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
TOTAL	**230**

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