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

SUMMARY OF PROGRESS AND DRAFT RESEARCH PLAN

BY
WILLIAM P. L. CARTER

COLLEGE OF ENGINEERING CENTER FOR ENVIRONMENTAL RESEARCH AND TECHNOLOGY UNIVERSITY OF CALIFORNIA RIVERSIDE, CALIFORNIA

FOR PRESENTATION TO THE REACTIVITY RESEARCH WORKING GROUP

JANUARY 16-17, 2001
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 O₃ AT HIGH URBAN NOₓ LEVELS MAY NOT BE IMPROVING AIR QUALITY IN OTHER AREAS.

MOST CHAMBERS NOT SUITABLE FOR EVALUATING VOC IMPACTS OTHER THAN ON O₃.

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\textsubscript{X} ON O\textsubscript{3} AND AEROSOLS ARE APPLICABLE AT LOWER POLLUTANT LEVELS.

- ASSESS O\textsubscript{3}, AEROSOL, AND OTHER IMPACTS OF VOCs UNDER LOW NO\textsubscript{X} AND OTHER CONDITIONS.

- EVALUATE MECHANISMS FOR PREDICTIONS OF KEY SPECIES (E.G., H\textsubscript{2}O\textsubscript{2}, HNO\textsubscript{3}, “TRUE” NO\textsubscript{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 M³ TEFLOM 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 NOₓ 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

- 200 KW Light Source Near Wall
- Temperature controlled room flushed with purified air and with reflective material on all inner surfaces
- Dual Teflon Bag Reactors
- Access Door
- Sample lines go to lab below
- This volume kept clear to maintain light uniformity
- Two large air Handlers are located in the corners on each side of the light (not shown).
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\textsubscript{x} OFFGASING AND OTHER BACKGROUND EFFECTS

DIFFERENT TEFLO\textregistered{} WALL MATERIALS TESTED AND WALL TREATMENT METHODS EVALUATED.

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

DATA INDICATE MINIMUM NO\textsubscript{x} OFFGASING RATES OF ≥ 0.5 PPB/DAY IN THE “PILLOWBAG” REACTORS

- MECHANISM EVALUATION FEASIBLE AT ≥ ~5 PPB NO\textsubscript{x} OR LOWER WITH LARGER REACTORS

CHAMBER RADICAL SOURCE IN TEFLO\textregistered{} FILM LOW AT LOW NO\textsubscript{x} LIMIT, INCREASES WITH NO\textsubscript{2}
EXPERIMENTAL AND CALCULATED RELATIONSHIPS BETWEEN O₃ FORMATION AND NOₓ 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

Minimum d[O3]/dt corresponds to NOx offgasing rate of ~0.5 ppb/day.

Experimental - d[O3]/dt vs Measured d[NOy]/dt

Model - d[O3]/dt vs NOx Input Rate Assumed
MAJOR ANALYTICAL EQUIPMENT

GAS-PHASE INSTRUMENTATION ACQUIRED

- STANDARD O₃, NOₓ, CO, GC-FID AND OTHER ANALYZERS (MOST FROM PREVIOUS PROJECTS)
- TDLAS #1: NO₂ AND HNO₃ (~0.5-1 ppb sensitivity)
- TDLAS #2: FORMALDEHYDE AND H₂O₂ (Sub-ppb sensitivity for HCHO, H₂O₂ not yet evaluated)
- GC-LUMINOL FOR NO₂ 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_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 NOₓ 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

<table>
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<tr>
<th>DESCRIPTION</th>
<th>RUNS</th>
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<td>AEROSOL CHARACTERIZATION - MINIMAL VARIABLE TEMPERATURE AND RH</td>
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<td>MECHANISM EVALUATION – SIMPLE SYSTEMS</td>
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<td>H$_2$O$_2$, HNO$_3$, HCHO TESTS</td>
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<td>TOLUENE</td>
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<td>ISOPRENE</td>
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<tr>
<td>REACTIVITY EXPERIMENTS – MAJOR VOCs</td>
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<tr>
<td>FORMALDEHYDE, ACETALDEHYDE, N-OCTANE, PROPENE, ISOPRENE</td>
<td>16</td>
</tr>
<tr>
<td>TOLUENE, M-XYLENE (AT DIFFERENT T’S)</td>
<td>12</td>
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<tr>
<td>CARB PROJECT REACTIVITY EXPERIMENTS</td>
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<tr>
<td>TEXANOL®</td>
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<td>PETROLEUM DISTILLATES</td>
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<tr>
<td>OTHER COATINGS VOCs</td>
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<td>TOTAL</td>
<td>230</td>
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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