DEVELOPMENT OF A NEXT-GENERATION ENVIRONMENTAL CHAMBER FACILITY FOR CHEMICAL MECHANISM EVALUATION

<u>OUTLINE</u>

NEED FOR ENVIRONMENTAL CHAMBER DATA TO EVALUATE MECHANISMS

LIMITATIONS OF EXISTING CHAMBER DATA BASE

OBJECTIVES

OVERALL APPROACH

- DESIGN AND INITIAL EVALUATION PHASE
- CONSTRUCTION PHASE
- EVALUATION PHASE
- EXPERIMENTAL PHASE
- INSTRUMENTATION

SCHEDULE

NEED FOR ENVIRONMENTAL CHAMBER DATA TO EVALUATE MECHANISMS

POLLUTANTS FORMED WHEN EMITTED VOCs REACT ARE OF CONCERN:

- OZONE
- SECONDARY PM
- TOXIC OR PERSISTENT OXIDATION PRODUCTS

VOC REACTIONS ARE COMPLEX

- MOST VOCs ENHANCE O_3 AT HIGHER NO_x BUT MANY REDUCE O_3 AT LOW NO_x
- VOCs THAT ENHANCE O_3 NOT ALWAYS THOSE THAT ENHANCE PM
- VOC OXIDATION PRODUCTS DIFFERENT WHEN NO_x VERY LOW

MODELS PROVIDE THE ONLY PRACTICAL MEANS TO ASSESS ALL VOC EFFECTS

MODELS HAVE ESTIMATES AND SIMPLIFIED OR PARAMETERIZED REPRESENTATIONS OF POORLY UNDERSTOOD REACTIONS.

CHAMBER DATA PROVIDE ONLY PRACTICAL MEANS TO TEST PREDICTIVE CAPABILITIES OF MECHANISMS USED IN THE MODELS.

LIMITATIONS OF AVAILABLE CHAMBER DATA BASE

UNCERTAINTIES IN CHARACTERIZATION OF CHAMBER CONDITIONS

LIMITED MEASUREMENTS OF IMPORTANT INTERMEDIATES AND PRODUCTS

LIMITED MECHANISM EVALUATION DATA UNDER LOW NO_x CONDITIONS

LIMITED DATA ON TEMPERATURE EFFECTS ON O_3 FORMATION AND NO_x AND VOC OXIDATION

LIMITED DATA ON TEMPERATURE AND HUMIDITY EFFECTS ON PM FORMATION

NO DATA TO EXPERIMENTALLY EVALUATE ESTIMATED MECHANISMS FOR MANY VOCs

OBJECTIVES

DEVELOP ENVIRONMENTAL CHAMBER FACILITY WITH FOLLOWING CAPABILITIES

- CHAMBER WALL EFFECTS MINIMIZED, REPRODUCIBLE, WELL CHARACTERIZED
- CAN CONDUCT USEFUL EXPERIMENTS WITH NO_x LEVELS BELOW 1 PPB
- CAN CONDUCT EXPERIMENTS AT VARYING TEMPERATURES
- CAN QUANTITATIVELY MONITOR MAJOR REACTIVE SPECIES AND PRODUCTS
- ABILITY TO MONITOR PM FORMATION AND SIZE DISTRIBUTIONS
- CAN OBTAIN DATA FOR EVALUATING NO_Y AND RADICAL BUDGETS
- INDOOR LIGHT SOURCE WITH SPECTRUM SIMULATING SUNLIGHT

USE THE FACILITY TO OBTAIN DATA NEEDED FOR MODEL EVALUATION AND CONTROL STRATEGY DEVELOPMENT

OBJECTIVES
(CONTINUED)

OBJECTIVES FOR MECHANISM AND CONTROL STRATEGY EVALUATION

- ASSESS EFFECTS OF VOCs AND NO_x ON O_3 AND PM AT VARYING VOC AND NOx LEVELS, RH, AND TEMPERATURES
- EVALUATE MECHANISMS AND VOC REACTIVITY IN MULTI-DAY SIMULATIONS
- DETERMINE HOW OXIDATION PRODUCTS AND PM FORMED FROM VOCs DIFFER WHEN NOx IS REDUCED
- OBTAIN DATA TO EVALUATE INDICATORS OF O3 SENSITIVITY TO PRECURSOR EMISSIONS
- TEST EQUIPMENT FOR MONITORING TRACE POLLUTANTS IN AMBIENT AIR UNDER CONTROLLED CONDITIONS

OVERALL APPROACH: DESIGN PHASE

REVIEW AVAILABLE INFORMATION CONCERNING CHAMBER EFFECTS

CONDUCT INITIAL EVALUATION EXPERIMENTS ON CHAMBER EFFECTS

EVALUATE ALTERNATIVE CHAMBER WALL MATERIALS AND CLEANING TREATMENTS

DEVELOP SPECIFICATIONS AND EVALUATE OPTIONS FOR FACILITY COMPONENTS

- LIGHT SOURCE
- TEMPERATURE CONTROL
- AIR PURIFICATION SYSTEM

ACQUIRE ANALYTICAL INSTRUMENTS MOST NEEDED FOR CHAMBER EFFECTS EVALUATION

DETERMINE PRIORITIES FOR EQUIPMENT FOR EXPERIMENTAL PHASE

DESIGN PHASE:
INITIAL CHARACTERIZATION TESTS

PERMEATION TESTS

- DETERMINE RATES OF PERMEATION OF MATERIALS THROUGH CHAMBER WALLS

CHAMBER EFFECTS CHARACTERIZATION

- DETERMINE EFFECTS OF VARYING:
  - TEMPERATURE
  - HUMIDITY
  - SURFACE MATERIAL
  - EXPOSURE TO NO_x, HNO_3
  - SURFACE TREATMENTS OR CLEANING PROCEDURES.
  - EXPOSURE TO REACTANTS IN PREVIOUS EXPERIMENTS
- MONITOR NO, NO_2, HONO, HNO_3, CO, VOC REACTANTS AND PRODUCTS, AS APPLICABLE

AEROSOL LIFETIME EXPERIMENTS

EXAMPLES OF WALL EFFECTS CHARACTERIZATION RUNS

EXPERIMENT	SENSITIVE TO
PURE AIR (DARK)	• OFFGASING OF NO_x OR OTHER SPECIES
PURE AIR (LIGHT)	• NO_x OFFGASING • RADICAL SOURCE • BACKGROUND VOCs
CO - AIR	• NO_x OFFGASING • RADICAL SOURCE
ALDEHYDE - AIR	• NO_x OFFGASING
N-BUTANE OR CO - NO_x	• CHAMBER RADICAL SOURCE
O_3 DECAY	• O_3 WALL LOSS
NO_2 DARK	• DARK HONO FORMATION
HNO_3 DARK	• WALL ABSORPTION • WALL REACTIONS
HNO_3 LIGHT	• LIGHT-INDUCED WALL PROCESSES
N_2O_5 DARK	• N_2O_5 HYDROLYSIS

APPROACHES BEING CONSIDERED TO REDUCE NO_x OFFGASING

ALTERNATIVE MATERIALS

- NON-HEAT SEALABLE TEFLON MAY BE MORE INERT
- PREVIOUS CHARACTERIZATION STUDIES SHOWED THAT GLASS OR TEFLON COATED ALUMINUM HAVE HIGHER RADICAL SOURCE
- DUPONT CO. IS PROVIDING ASSISTANCE ON TEFLON

TREATMENT OPTIONS

- WATER WASHING
- FLUSHING WITH LIGHTS ON (REDUCES NO_x OFFGASING ONLY SLOWLY)
- FLUSHING AT HIGH TEMPERATURE
- TREATMENT WITH F_2
- HEATING IN A VACUUM (PROBABLY TOO EXPENSIVE TO IMPLEMENT)
- REPLACING TEFLON AFTER USE (PROBABLY TOO EXPENSIVE)

CHAMBER DESIGN

NOT FINALIZED UNTIL WALL MATERIAL AND CLEANING PROCEDURE KNOWN

CURRENT WORKING PROPOSAL

REACTOR

- REPLACEABLE TEFLON FILM.
- PIECES CLAMPED TOGETHER TO REDUCE LEAKAGE, AID REPLACEMENT, CLEANING
- COLLAPSIBLE FOR FASTER FLUSHING

CHAMBER ENCLOSURE:

- 6M X 6M X 12M SPACE FOR TWO ~50,000-LITER REACTORS
- SOLAR SIMULATOR LIGHTS ON CEILING OR OPPOSING WALLS
- REFLECTIVE MATERIAL ON SURFACES
- ENCLOSURE FLUSHED WITH PURE AIR TO MINIMIZE PERMEATION, CONTAMINATION
- HEAT TO 50^{o}C, COOL TO 10^{o}C
- NEW BUILDING PLANNED WITH LABORATORY BELOW CHAMBER ROOM

LIGHT SOURCE

INDOOR CHAMBER USED FOR BETTER CONTROL OF CONDITIONS

SOLAR SIMULATOR (E.G., XENON OR ARGON ARC) SYSTEM WILL BE USED TO PROVIDE A REALISTIC SPECTRUM.

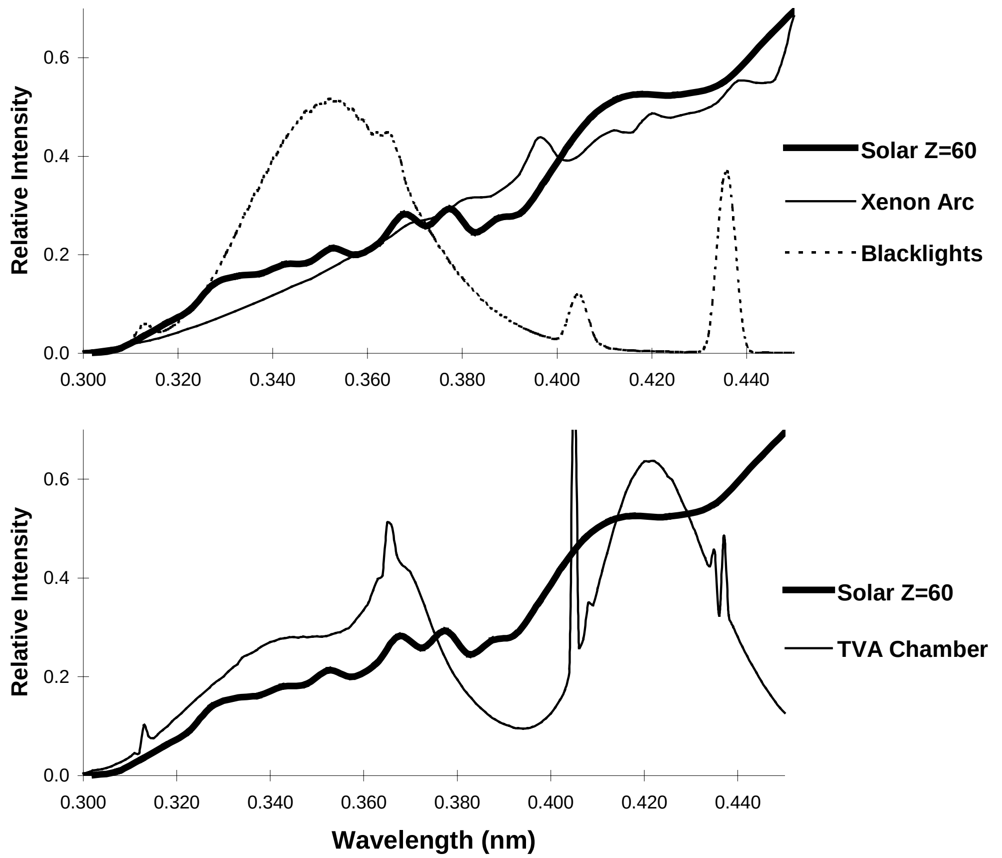
NEED TO IRRADIATE A 6M x 6M x 12 M ROOM WITH UNIFORM INTENSITY.

K_1 AT LEAST 0.4 MIN^{-1}

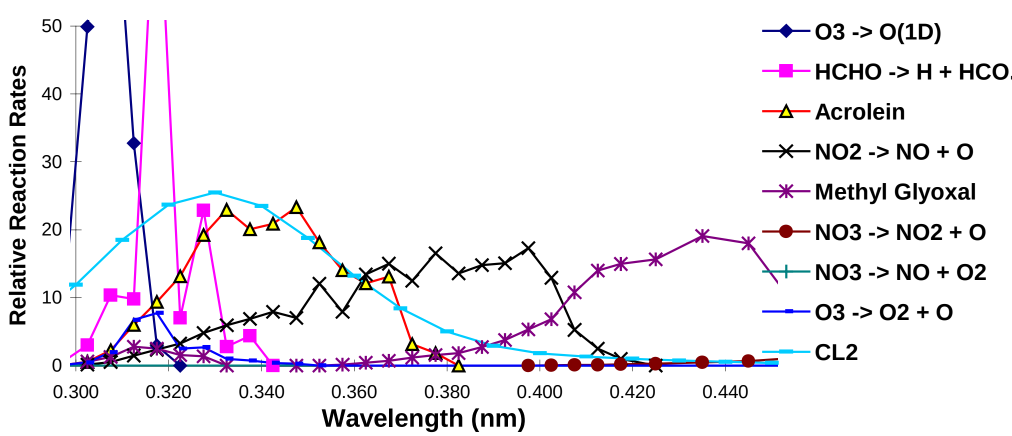
CURRENTLY EVALUATING PROPOSAL FROM VORTEC CO. FOR SYSTEM WITH TWO 50 OR 100 KW ARGON ARC LIGHTS

AN ALTERNATIVE IS TO GET MORE OF THE ATLAS 6 KW XENON ARC LIGHTS WE CURRENTLY USE.

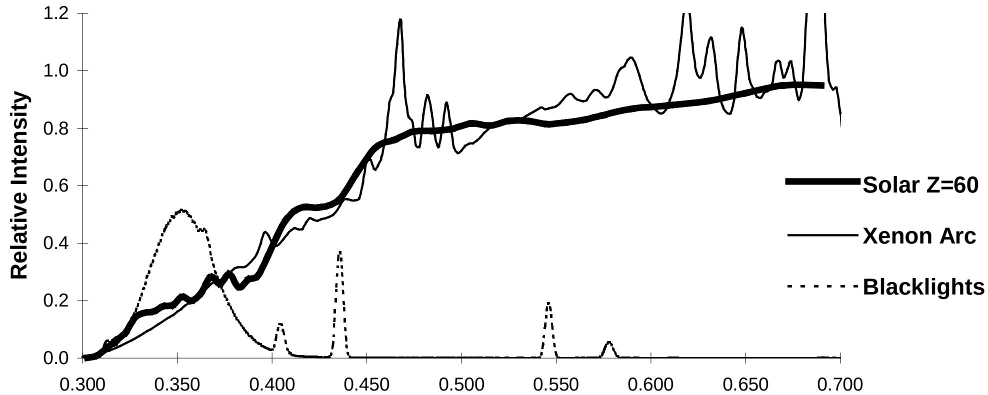
RELATIVE INTENSITY
(Normalized to give same k(NO_2))

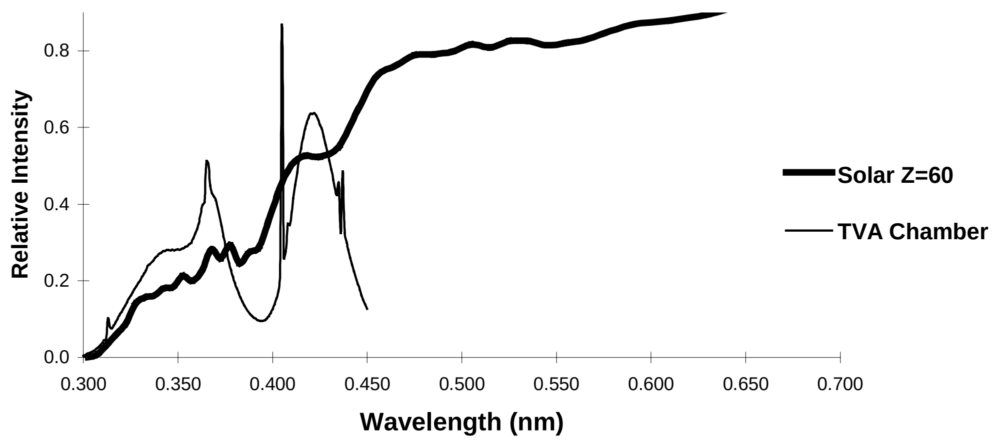


ACTION SPECTRA

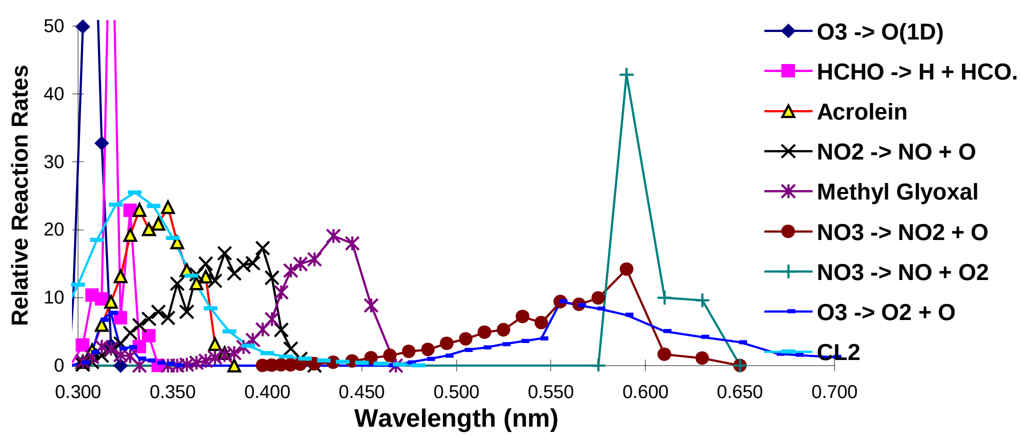


RELATIVE INTENSITY
(Normalized to give same k(NO_2))





ACTION SPECTRA



AIR PURIFICATION SYSTEM

SPECIFICATIONS

- REMOVE NO_x TO BELOW 50 PPT
- REMOVE VOCs TO TOTAL kOH REACTIVITY LESS THAN 0.2 PPM CO EQUIVALENTS, E.G.,
  - CO $\leq$ 0.1 ppm
  - METHANE $\leq$ ~1 PPM
  - ETHANE $\leq$ 2 PPB
  - PROPANE $\leq$ 1 PPB
  - C_{4+} VOCs LESS THAN 1 PPBC TOTAL
- DEW POINT < -40^{o}C (200 PPM H_2O)
- NO MEASURABLE PARTICLES OR CONDENSATION NUCLEII
- OUTPUT CAPACITY: $\geq$1500 LITERS MIN^{-1}

PROPOSED SYSTEMS:

- <u>OPTION 1</u>: PRESSURE SWING ABSORPTION USING CHARCOAL, PURAFIL, HOPCOLITE, HEPA FILTERS
- <u>OPTION 2</u>: MIX EVAPORATED O_2 AND N_2

TEMPERATURE CONTROL SYSTEM

SPECIFICATIONS

- CONTROL TEMPERATURE WITHIN A 6M x 6M x 12M AREA THAT CONTAINS THE LIGHT SOURCE
- TEMPERATURE CONTROL AND UNIFORMITY WITHIN $\pm 1^{o}C$
- COOL TO $10^{o}C$
- HEAT TO $50^{o}C$ (OR HIGHER IF USEFUL FOR CHAMBER CLEANING)

PROPOSED SYSTEM

- COMMERCIAL REFRIGERATION SYSTEM USED FOR SUPERMARKETS AND RESTAURANTS
- WITH APPROPRIATE ENHANCEMENTS TO TEMPERATURE CONTROL AS NEEDED

SUMMARY OF DESIRED ANALYTICAL CAPABILITY FOR INITIAL PHASE

EMPHASIS WILL BE ON DATA NEEDED FOR CHAMBER EFFECTS CHARACTERIZATION

COMPOUND	METHOD	SENS'Y. (ppb)
O_3	Photometric	1
NO	Chemiluminescent	0.05
NO_2	GC / Luminol	0.02
HNO_3	TDLAS	0.1
HONO	TDLAS	0.1
H_2O_2	TDLAS	0.1
CO	Gas Filter Correl.	100
HCHO	TDLAS or Dasgupta	0.1
VOCs (ppbC)	GC/FID	0.1
NMHC (ppbC)	Trap/Backflush/FID	0.5
PAN	GC / ECD	1
$NO \rightarrow NO_2$ Reactivity	HONO Flow Photolysis System	1 ppm CH_4 equivalent
TEMP.	Shielded Thermister	1°C
H_2O	GC / TC ?	10 ppm

CONSTRUCTION AND EVALUATION PHASES

CONSTRUCTION PHASE

- ACQUIRE OR CONSTRUCT CHAMBER ENCLOSURE, SAMPLING, LIGHTING, AIR PURIFICATION SYSTEMS

EVALUATION PHASE

- EVALUATE PERFORMANCE OF SYSTEMS
- CONDUCT CHARACTERIZATION EXPERIMENTS
- CONDUCT EXPERIMENTS FOR COMPARISON WITH PREVIOUS DATA
- EVALUATE INSTRUMENTATION FOR EXPERIMENTAL PHASE
- ACQUIRE INSTRUMENTATION FOR EXPERIMENTAL PHASE

CURRENT LIST OF DESIRED ANALYTICAL INSTRUMENTATION FOR THE EXPERIMENTAL PHASE

DESIRED GAS-PHASE CAPABILITIES

ORGANIC PRODUCTS	GC/MS AND GC/IR
ORGANIC NITRATES, PANs	GC/ECD, GC/LUMINOL?
ALDEHYDES	DNPH/HPLC
GLYOXAL	DOAS
OTHER DICARBONYLS	(Not Determined)
HYDROPEROXIDES	(Not Determined)
NO_3	DOAS

AEROSOL INSTRUMENTATION

TSI AERODYNAMIC PARTICLE SIZER
TSI SCANNING MOBILITY PARTICLE SIZER
CONSTANT OUTPUT ATOMIZER WITH DRYER AND CHARGE NEUTRALIZER

INITIAL EVALUATION EXPERIMENTS

CHAMBER CHARACTERIZATION RUNS

MEASURE LIGHT INTENSITY, UNIFORMITY

MEASURE TEMPERATURE UNIFORMITY

SINGLE ORGANIC - NO_x RUNS FOR COMPARISON WITH PREVIOUS DATA

- REPRESENTATIVE ALKENES, AROMATICS, ALDEHYDES

AMBIENT SURROGATE VOC - NO_x RUNS TO COMPARE WITH PREVIOUS DATA

- SURROGATES OF VARYING COMPLEXITY
- SURROGATES USED IN REACTIVITY STUDIES

AEROSOL-FORMING EXPERIMENTS FOR COMPARISON WITH CALTECH DATA

REPRODUCIBILITY TESTS FOR ALL TYPES OF EXPERIMENTS

EQUIVALENCY TESTS IF DUAL OR MULTIPLE REACTORS USED

EXPERIMENTAL PHASE: MECHANISM EVALUATION EXPERIMENTS

SINGLE ORGANIC - NO_x EXPERIMENTS

GIVES STRAIGHTFORWARD TESTS OF MECHANISMS OF VOCs WITH INTERNAL RADICAL SOURCES.

BUT **NOT** USEFUL FOR VOCs WITH INHIBITING CHARACTERISTICS

REPRESENTATIVE COMPOUNDS WITH UNCERTAIN MECHANISMS IMPORTANT IN EMISSIONS OR ALTERNATIVE SOLVENTS

REPRESENTATIVE OF REACTIVE ORGANIC PRODUCTS

VARY NO_x LEVELS, INCLUDING VERY LOW OR NO ADDED NO_x RUNS

VARY TEMPERATURE AND HUMIDITY

IDENTIFY, MONITOR MAJOR ORGANIC PRODUCTS AND DETERMINE CHANGES AS NO_x IS REDUCED

DETERMINE SECONDARY AEROSOL FORMATION, WHERE APPLICABLE

SIMPLE MIXTURE - NO_x EXPERIMENTS

SIMPLE CHEMICAL SYSTEMS TO EVALUATE MECHANISMS FOR RADICAL INHIBITORS

TESTS HOW LOW NO_x VOC OXIDATION PRODUCTS AFFECTED BY VOCs

EVALUATE VOC INTERACTIONS THAT AFFECT SOA FORMATION

MOST USEFUL EXPERIMENTS NOT YET DETERMINED

AMBIENT SURROGATE EXPERIMENTS

USED TO EVALUATE MECHANISMS UNDER SIMULATED ATMOSPHERIC CONDITIONS.

DETERMINE EFFECTS OF VARYING

- SURROGATE COMPOSITION
- VOC AND NO_x LEVELS
- TEMPERATURE, HUMIDITY, AND LIGHT INTENSITY

DETERMINE MOST USEFUL “BASE CASE” SYSTEMS FOR REACTIVITY ASSESSMENT

- DIFFERENT SURROGATES WILL BE USEFUL FOR DIFFERENT PURPOSES

EVALUATE WHETHER USEFUL DATA CAN BE OBTAINED IN LONG TERM (MULTI-DAY) EXPERIMENTS. SUCH DATA USEFUL FOR

- EVALUATING MODELS FOR NIGHTTIME CHEMISTRY
- EVALUATING EFFECTS OF SECONDARY PRODUCTS ON REACTIVITY.

INCREMENTAL REACTIVITY EXPERIMENTS

DETERMINE EFFECTS OF ADDING VOCs TO "BASE CASE" SURROGATE EXPERIMENTS

DETERMINE EFFECTS OF VOCs ON ON O_3, PM, NO_x SINKS, OXIDATION PRODUCTS, ETC.

CONDITIONS VARIED WILL INCLUDE:

ROG AND NO_x LEVELS	ROG SURROGATE COMPOSITION
TEMPERATURE	HUMIDITY
AEROSOL IN SURROGATE	DURATION OF EXPERIMENT

COMPOUNDS TO BE STUDIED

- EMITTED VOC CLASSES WITH UNCERTAIN MECHANISMS
- VOCs WHERE DATA WILL BE USEFUL GENERAL MECHANISM DEVELOPMENT
- VOCs OF SPECIAL RELEVANCE TO CONTROL STRATEGY ASSESSMENT

PRIORITIES WILL BE DEVELOPED WORKING THROUGH THE REACTIVITY RESEARCH WORKING GROUP (RRWG).

EXPERIMENTAL PHASE: EXPERIMENTS TO ADDRESS OTHER OBJECTIVES

CHARACTERIZATION OF NO_Y AND RADICAL BUDGETS

- RELEVANT DATA WILL BE OBTAINED FROM SURROGATE RUNS CARRIED OUT UNDER VARYING CONDITIONS.
- PRIORITIES FOR INSTRUMENTATION TO ADDRESS THIS NOT YET DETERMINED.

EVALUATION OF FACTORS AFFECTING SECONDARY PM FORMATION

- RELEVANT DATA OBTAINED FROM SOA-FORMING EXPERIMENTS CONDUCTED UNDER VARIOUS CONDITIONS

EXPERIMENTAL PHASE: EXPERIMENTS TO ADDRESS OTHER OBJECTIVES (CONTINUED)

EVALUATION OF INDICATORS OF OZONE SENSITIVITY TO PRECURSOR EMISSIONS

- RELEVANT DATA WILL BE OBTAINED FROM SURROGATE RUNS CARRIED OUT WITH VARYING VOC AND NO_x LEVELS
- CANDIDATE INDICATORS WILL BE MONITORED AS NEEDED

EVALUATION OF AMBIENT MONITORING METHODS

- PROVIDES A MEANS TO TEST METHODS WITH SIMULATED ATMOSPHERES WITH **KNOWN** REACTANTS AND HISTORY
- LARGE CHAMBER VOLUME ALLOWS EVALUATION OF METHODS WITH LARGE SAMPLING RATES
- COLLABORATION WITH INSTRUMENT DEVELOPERS WILL BE SOUGHT

TARGET SCHEDULE

START OF PROGRAM	Summer 1999
DESIGN PHASE AND INITIAL EVALUATION	Summer 1999 - Summer 2000
CONSTRUCTION OF BUILDING	Spring 2000 - Summer, 2000
COMPLETION OF FACILITY	Fall, 2000
COMPLETE EVALUATION PHASE	Winter, 2000-01
EXPERIMENTAL PHASE	Winter, 2000-01 - Summer, 2003
FACILITY AVAILABLE FOR OTHER PROJECTS	Spring, 2001