EVALUATION OF OZONE IMPACTS OF VOLATILE ORGANIC COMPOUNDS AND CHLORINE

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BACKGROUND

- O_3 PROBLEM, CHEMISTRY OF O_3 FORMATION, AND IMPLICATIONS TO CONTROL STRATEGIES
- QUANTIFICATION OF VOC AND CL_2 REACTIVITY

VOC REACTIVITY AND OZONE CONTROL STRATEGIES

- EXAMPLES OF REACTIVITY DIFFERENCES
- EXAMPLES OF REGULATORY POLICIES

UNCERTAINTIES IN REACTIVITY SCALES

ENVIRONMENTAL CHAMBER STUDIES

- NEED FOR REDUCING REACTIVITY UNCERTAINTY
- PROBLEMS WITH CURRENT CHAMBERS
- NEW UCR CHAMBER FACILITY AND PROGRESS TO DATE

ADDITIONAL INFORMATION AVAILABLE

THE PHOTOCHEMICAL OZONE PROBLEM

PHOTOCHEMICAL SMOG IS CHARACTERIZED BY THE FORMATION OF OZONE AND OTHER “OXIDANTS" IN SUNLIGHT

EXCESSIVE GROUND LEVEL OZONE IS AN AIR QUALITY PROBLEM BECAUSE IT CAUSES ADVERSE HEALTH EFFECTS AND DAMAGE TO MATERIALS.

MANY URBAN AREAS EXCEED OZONE AIR QUALITY STANDARDS.

OZONE IS NOT EMITTED DIRECTLY. IT IS FORMED WHEN SUNLIGHT REACTS WITH EMITTED OXIDES OF NITROGEN (NO_x) AND VOLATILE ORGANICS COMPOUNDS (VOCs).

MOLECULAR CHLORINE IS BELIEVED TO CAUSE THE OZONE “SPIKES” IN OBSERVED IN HOUSTON. ITS ROLE OTHER AREAS IS UNCERTAIN.

OZONE IS NOT THE ONLY CONCERN IN SMOG. BUT IT IS THE FOCUS OF MOST CONTROL REGULATIONS FOR VOCs (OTHER THAN TOXICS).

OZONE CONTROL

THE ONLY WAY TO REDUCE OZONE FORMATION IS TO REDUCE EMISSIONS OF ITS VOC AND NO_x PRECURSORS.

BUT ALL THE "EASY" CONTROLS HAVE BEEN IMPLEMENTED. ADDITIONAL CONTROLS WILL BE COSTLY AND DISRUPTIVE.

THE PROCESS OF OZONE FORMATION FROM VOCs AND NO_x IS COMPLEX

- VOC AND NO_x CONTROL ARE NOT EQUALLY EFFECTIVE IN REDUCING OZONE.
- DIFFERENT TYPES OF VOCs HAVE DIFFERENT OZONE IMPACTS (REACTIVITIES).
- CHLORINE CAUSE ADDITIONAL VOC AND NO_x REACTIONS THAT FORM OZONE

AN UNDERSTANDING OF THE PROCESS OF OZONE FORMATION IS NECESSARY TO DETERMINE THE MOST COST EFFECTIVE CONTROL STRATEGY.

CHEMISTRY OF O_3 FORMATION IN PHOTOCHEMICAL SMOG

THE ONLY SIGNIFICANT CHEMICAL REACTION WHICH FORMS OZONE IN THE TROPOSPHERE IS THE PHOTOLYSIS OF NO_2

$$NO_2 + h\nu \rightarrow NO + O^3P \qquad (1)$$
$$O^3P + O_2 + M \rightarrow O_3 + M$$

OR OVERALL

$$NO_2 + h\nu \rightarrow NO + O_3$$

BUT THIS IS REVERSED BY THE RAPID REACTION OF O_3 WITH NO:

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (2)$$

THIS RESULTS IN A "PHOTOSTATIONARY STATE" BEING ESTABLISHED, WHERE O_3 IS PROPORTIONAL TO THE NO_2 TO NO RATIO

$$[O_3] = \frac{k_1[NO_2]}{k_2[NO]}$$

IF OTHER REACTANTS ARE NOT PRESENT TO CONVERT NO TO NO_2, ONLY VERY LOW LEVELS OF OZONE ARE FORMED.

ROLE OF VOCs IN OZONE FORMATION

WHEN VOLATILE ORGANIC COMPOUNDS REACT THEY FORM RADICALS THAT CONVERT NO TO NO_2

SIMPLIFIED EXAMPLE:

$$VOC + OH \rightarrow R\cdot + H_2O$$
$$R\cdot + O_2 \rightarrow RO_2\cdot$$
$$RO_2 + NO \rightarrow RO\cdot + NO_2$$
$$RO\cdot + O_2 \rightarrow HO_2\cdot + RCHO$$
$$HO_2\cdot + NO \rightarrow OH + NO_2$$

OVERALL

$$VOC + 2\ O_2 + 2\ NO \xrightarrow{OH} RCHO + 2\ NO_2 + H_2O$$

COMBINED WITH

$$NO_2 + O_2 \overset{h\nu}{\rightleftarrows} NO + O_3$$

YIELDS

$$VOC + 2\ O_2 \xrightarrow{OH,\ NO_x} RCHO + H_2O + 2\ O_3$$

OZONE FORMATION CONTINUES UNTIL NO_x IS REMOVED

ROLE OF Cl_2 IN OZONE FORMATION

Cl_2 PROMOTES OZONE FORMATION IN TWO WAYS:

- DIRECTLY REACTS WITH VOCs FORMING RADICALS THAT CONVERT NO TO NO_2
- FORMING "NEW" OH RADICALS THAT CAUSES MORE VOCs TO REACT TO FORM O_3

SIMPLIFIED EXAMPLE:

$$Cl_2 + h\nu \rightarrow 2\ Cl\cdot \qquad (t_{1/2} \approx 5\ min)$$
$$Cl\cdot + VOC \rightarrow R\cdot + HCl$$
$$R\cdot + O_2 \rightarrow RO_2\cdot$$
$$RO_2 + NO \rightarrow RO\cdot + NO_2$$
$$RO\cdot + O_2 \rightarrow HO_2\cdot + RCHO$$
$$HO_2\cdot + NO \rightarrow OH + NO_2$$

<u>OVERALL</u>

$$Cl_2 + 2\ VOC + 4\ NO \xrightarrow{O_2} 2\ RCHO + 4\ NO_2 + 2\ HCl + 2\ OH$$

<u>COMBINED WITH</u>

$$NO_2 + O_2 \overset{h\nu}{\rightleftarrows} NO + O_3$$

<u>YIELDS</u>

$$Cl_2 + 2\ VOC \xrightarrow{O_2,\ NO_x} 2\ RCHO + 2\ HCl + 4\ O_3 + 2\ OH$$

$$OH + VOC \xrightarrow{NO_x} MORE\ O_3$$

IMPLICATIONS OF ATMOSPHERIC CHEMISTRY FOR OZONE CONTROL STRATEGIES

NOx CONTROL:

- NO_x IS REQUIRED FOR OZONE FORMATION AND LIMITS HOW MUCH O_3 CAN BE FORMED.
- BUT NOx REDUCES THE RATE OF O_3 FORMATION BECAUSE IT REACTS WITH O_3 AND RADICALS
- NOx CONTROL HAS GREATEST BENEFIT DOWNWIND, BUT CAN MAKE O_3 WORSE NEAR EMISSIONS SOURCE AREAS.

VOC CONTROL

- VOCs ENHANCE THE RATE OF O_3 FORMATION FROM NO_x
- VOC CONTROL IS MOST EFFECTIVE NEAR THE SOURCE AREAS WHERE NO_x IS HIGH.
- LESS EFFECTIVE IN NOx-LIMITED AREAS, SUCH AS DOWNWIND AND MOST RURAL AREAS.
- NATURAL EMISSIONS OF VOCs LIMITS THE MAXIMUM EXTENT OF VOC CONTROLS.

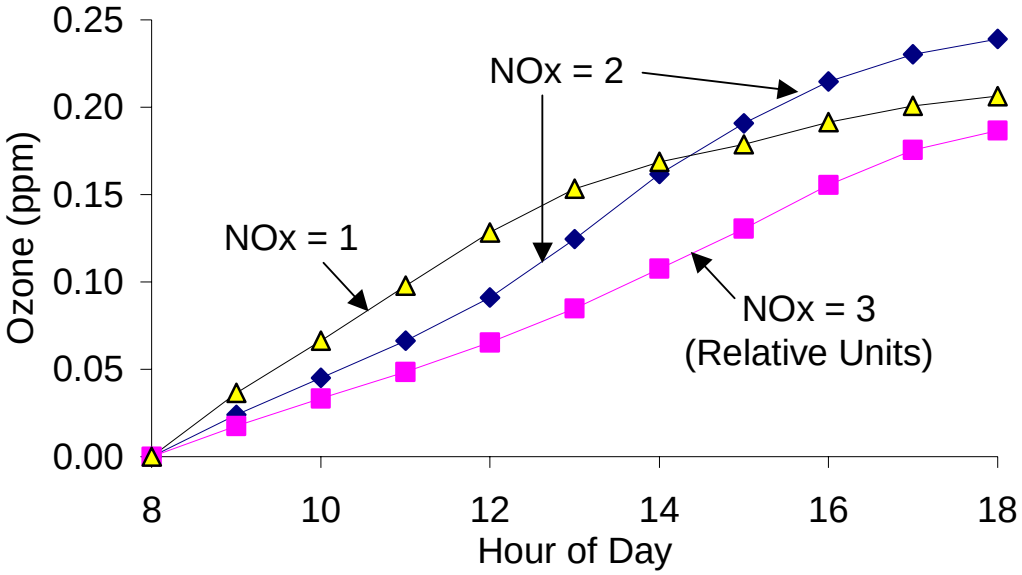
CHLORINE CONTROL

- Cl_2 HAS SIMILAR EFFECTS ON O_3 AS VOCs, BUT IMPACTS ARE MUCH MORE LOCALIZED

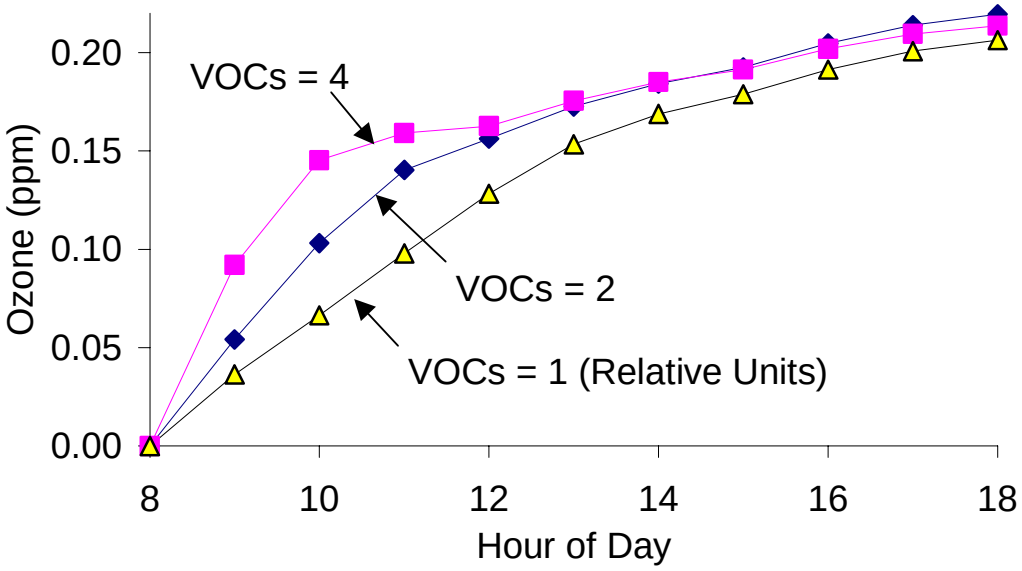
ANY COMPREHENSIVE OZONE CONTROL STRATEGY SHOULD TAKE ALL THESE FACTORS INTO ACCOUNT.

EFFECTS OF VOCs AND NO_x ON OZONE

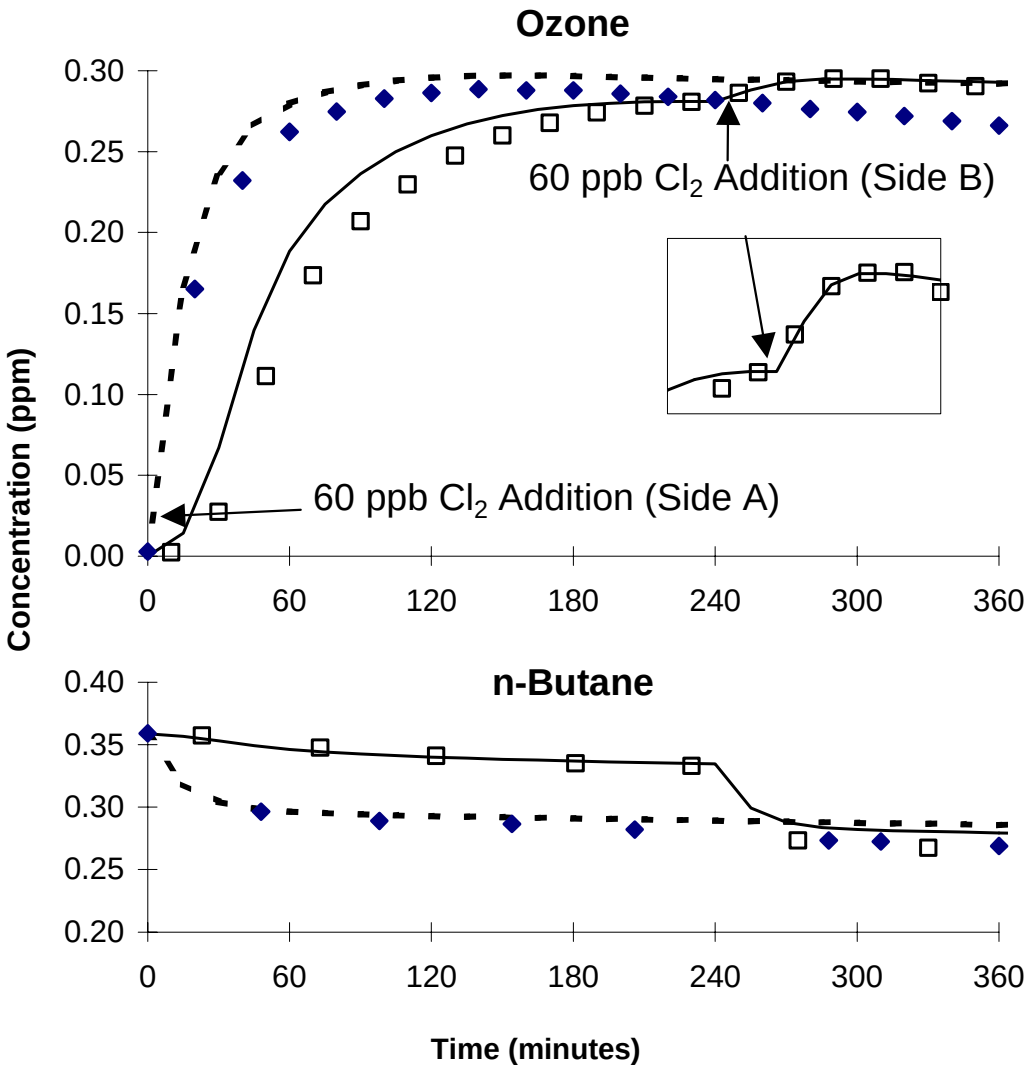
VARY NO_x EMISSIONS



VARY VOC EMISSIONS



EXPERIMENTAL AND CALCULATED EFFECTS OF CL2 ADDITION ON OZONE



Run DTC-323 NOx: 0.11 ppm "Full Surrogate": 4.4 ppmC Blacklight Irradiation	Model Used SAPRC-99 Mechanism with Preliminary Cl_2 Chemistry added

VOC REACTIVITY

VOCs DIFFER IN THEIR EFFECTS ON OZONE FORMATION. THE TERM **REACTIVITY** IS USED TO REFER TO THIS.

SEVERAL DIFFERENT ASPECTS OF A VOCs ATMOSPHERIC REACTIONS AFFECT ITS REACTIVITY:

- HOW FAST IT REACTS.
- HOW MUCH O3 IS FORMED DIRECTLY FROM ITS REACTIONS AND THOSE OF ITS PRODUCTS.
- WHETHER IT ENHANCES OR INHIBITS RADICAL LEVELS. THIS AFFECTS HOW FAST O3 IS FORMED FROM ALL VOCs.
- WHETHER IT ENHANCES RATES NO_x REMOVAL. THIS AFFECTS ULTIMATE O3 YIELDS BECAUSE NOx IS REQUIRED FOR O3 TO BE FORMED.

A VOC's EFFECT ON O_3 ALSO DEPENDS ON THE NATURE OF THE ENVIRONMENT WHERE IT REACTS

THE SAME FACTORS AFFECTING VOC REACTIVITY ALSO APPLY TO CHLORINE

QUANTIFICATION OF REACTIVITY

A USEFUL MEASURE OF THE EFFECT OF A VOC ON OZONE FORMATION IS **INCREMENTAL REACTIVITY**:

$$\begin{bmatrix}\text{INCREMENTAL}\\ \text{REACTIVITY}\\ \text{OF A VOC IN}\\ \text{AN EPISODE}\end{bmatrix} = \lim_{[\text{VOC}]\to 0} \frac{\begin{bmatrix}\text{OZONE}\\ \text{FORMED}\\ \text{WHEN VOC}\\ \text{ADDED TO}\\ \text{EPISODE}\end{bmatrix} - \begin{bmatrix}\text{OZONE}\\ \text{FORMED}\\ \text{IN AN}\\ \text{EPISODE}\end{bmatrix}}{\begin{bmatrix}\text{AMOUNT OF VOC}\\ \text{ADDED TO EMISSIONS}\\ \text{IN THE EPISODE}\end{bmatrix}}$$

THIS DEPENDS ON THE CONDITIONS OF THE EPISODE AS WELL AS ON THE VOC

MEASUREMENT OR CALCULATION OF ATMOSPHERIC REACTIVITY

REACTIVITY CAN BE MEASURED IN ENVIRONMENTAL CHAMBER EXPERIMENTS. BUT THE RESULTS ARE NOT THE SAME AS REACTIVITY IN THE ATMOSPHERE.

- NOT PRACTICAL TO EXPERIMENTALLY DUPLICATE ALL ATMOSPHERIC CONDITIONS AFFECTING REACTIVITY
- CHAMBER EXPERIMENTS HAVE WALL EFFECTS, USUALLY HIGHER LEVELS OF NOx AND ADDED TEST VOC, STATIC CONDITIONS, ETC.

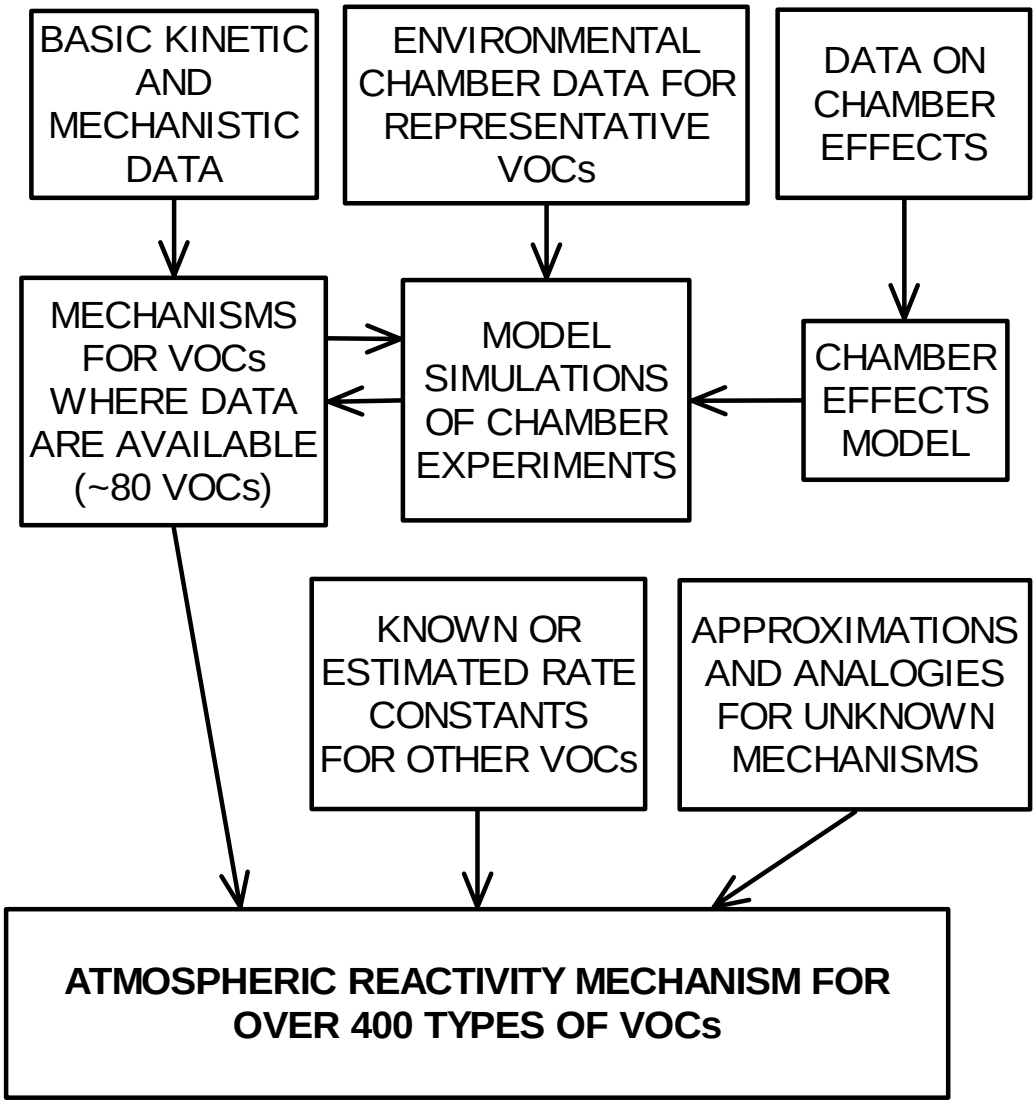
ATMOSPHERIC REACTIVITY MUST BE CALCULATED USING COMPUTER AIRSHED MODELS, GIVEN:

- MODELS FOR AIRSHED CONDITIONS
- CHEMICAL MECHANISMS FOR THE VOC's ATMOSPHERIC REACTIONS

CALCULATIONS OF ATMOSPHERIC REACTIVITY CAN BE NO MORE RELIABLE THAN THE CHEMICAL MECHANISM USED.

ENVIRONMENTAL CHAMBER EXPERIMENTS ARE USED TO TEST THE RELIABILITY OF MODELS TO PREDICT ATMOSPHERIC REACTIVITY.

DEVELOPMENT OF AN ATMOSPHERIC CHEMICAL MECHANISM TO CALCULATE VOC REACTIVITIES



VOC REACTIVITY AND OZONE CONTROL STRATEGIES

VOC CONTROLS AND CONTENT STANDARDS THAT CONSIDER REACTIVITY CAN BE MORE EFFECTIVE THAN THOSE THAT TREAT ALL VOC'S EQUALLY.

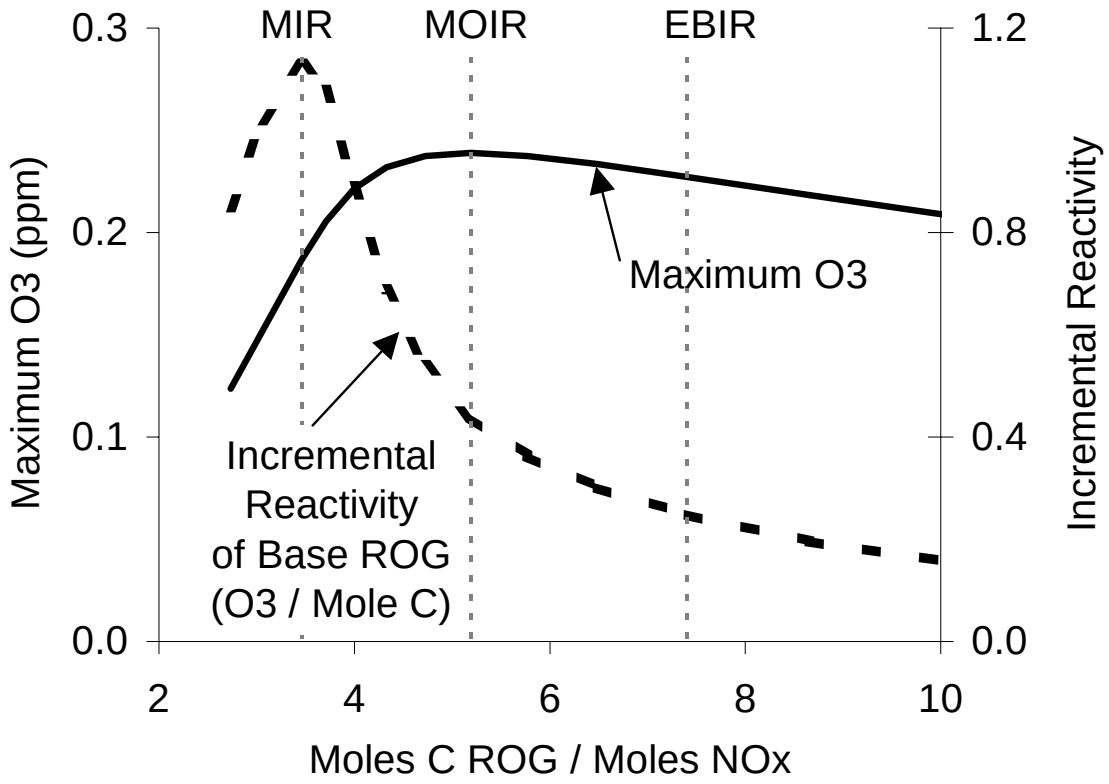
EXAMPLES INCLUDE:

- ENCOURAGING USE OF ALTERNATIVE FUELS
- ENCOURAGING USE OF LESS REACTIVE SOLVENTS

HOWEVER REACTIVITY-BASED CONTROLS AND STANDARDS REQUIRE USE OF A SINGLE SCALE TO QUANTIFY OZONE IMPACTS

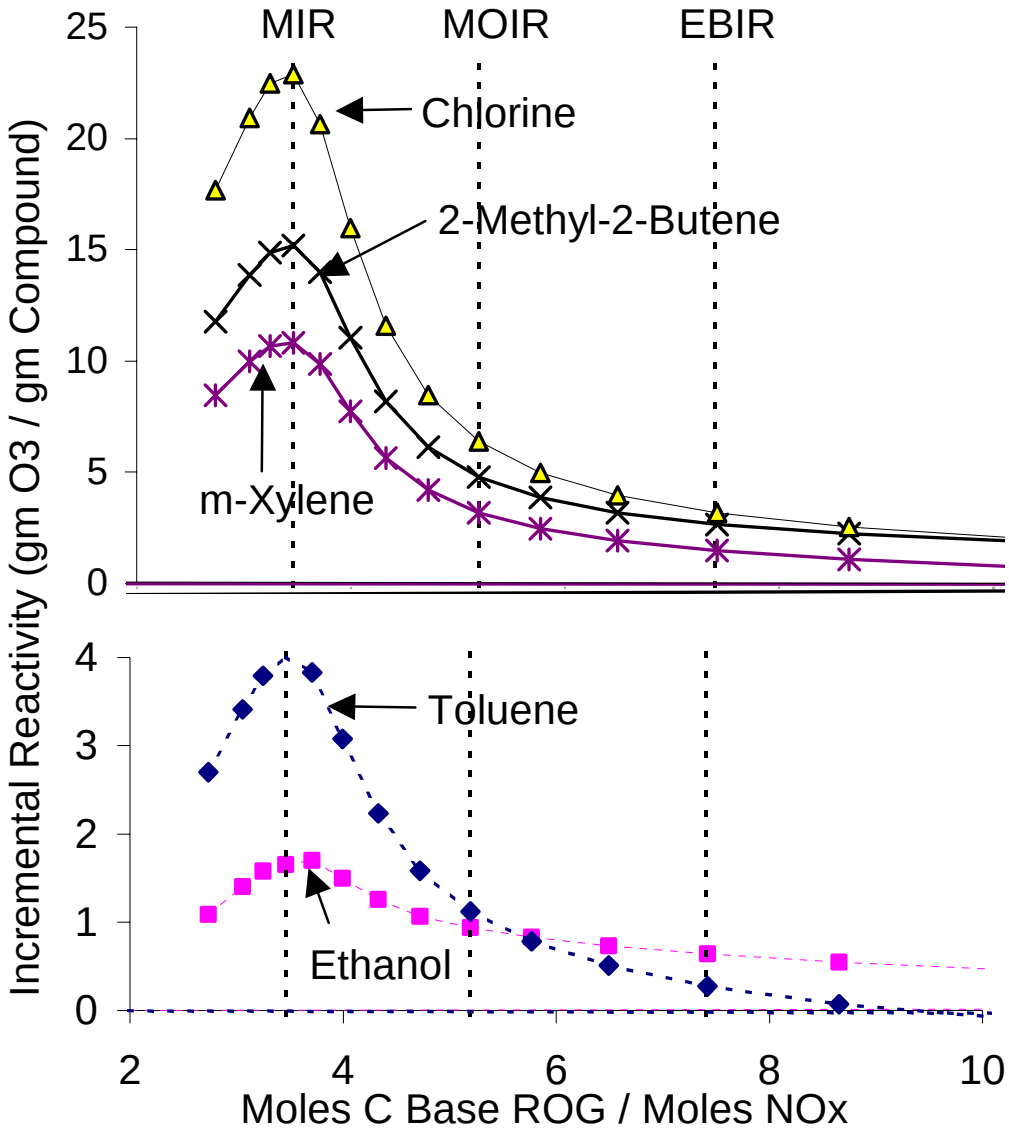
BUT REACTIVITIES DEPEND ON ENVIRONMENTAL CONDITIONS. THIS COMPLICATES DEVELOPMENT OF A SINGLE GENERAL REACTIVITY SCALE.

DEPENDENCE OF INCREMENTAL REACTIVITIES ON ROG/NO_x



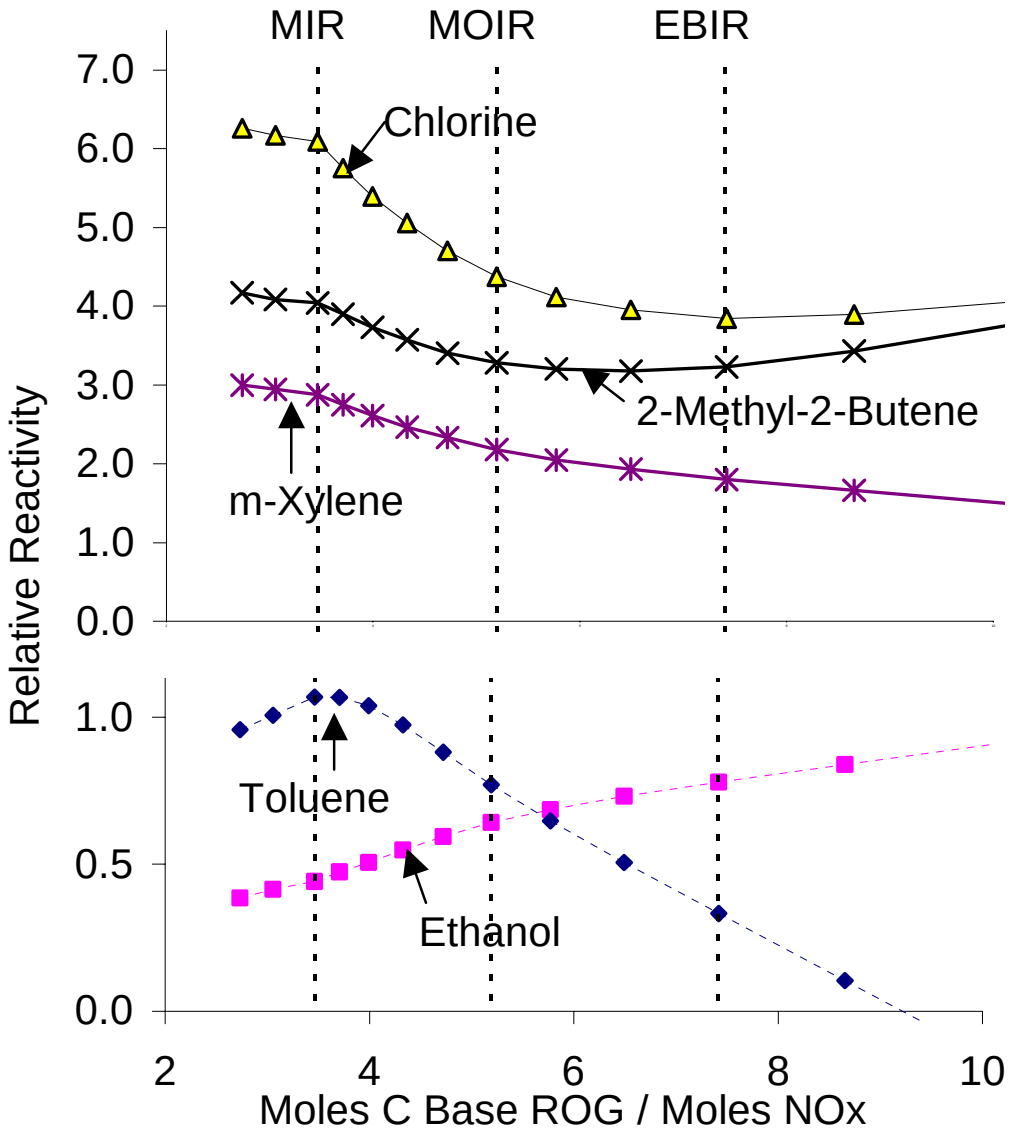
BASE ROG:	VOC MIXTURE USED TO REPRESENT VOCs FROM ALL SOURCES IN THE EPISODE
MIR:	ROG/NO_x WITH MAXIMUM INCREMENTAL REACTIVITY OF AMBIENT VOC MIXTURE
MOIR:	ROG/NO_x WITH MAXIMUM PEAK O_3 CONCENTRATION
EBIR:	ROG/NO_x WHERE VOC AND NO_x CONTROLS ARE EQUALLY EFFECTIVE IN REDUCING O_3

DEPENDENCES OF INCREMENTAL REACTIVITIES ON ROG/NO_x



DEPENDENCES OF RELATIVE INCREMENTAL REACTIVITIES ON ROG/NO_x

INCREMENTAL REACTIVITIES RELATIVE TO THE BASE ROG MIXTURE (MASS BASIS)



EXAMPLES OF REACTIVITIES AT DIFFERENT NO_x LEVELS

COMPOUND OR MIXTURE	MIR (HIGH NO_x)	MOIR (MAX O_3)	EBIR (LOW NO_x)
INCREMENTAL REACTIVITIES (GM O_3 / GM VOC)			
BASE ROG MIXTURE	3.7	1.5	0.85
REACTIVITIES RELATIVE TO BASE ROG			
ETHANE	0.08	0.14	0.17
ODORLESS MINERAL SPIRITS	0.21	0.33	0.30
AGGREGATED PET. DISTILLATES	0.54	0.63	0.59
ETHYL BENZENE	0.75	0.69	0.50
EXHAUST (RF-A)	1.10	1.08	1.05
ETHENE	2.4	2.5	2.8
M-XYLENE	2.9	2.2	1.8
CHLORINE	5.9	4.3	3.7

REACTIVITIES FOR OVER 400 TYPES OF VOCs AVAILABLE AT http://cert.ucr.edu/~carter/reactdat.htm

EXAMPLES OF WAYS TO DEAL WITH THE DEPENDENCE OF REACTIVITY ON ENVIRONMENTAL CONDITIONS

BASE THE SCALE ON A "REPRESENTATIVE" OR "WORST CASE" EPISODE.

- MAY NOT BE OPTIMUM FOR ALL CONDITIONS.
- MAY NOT BE APPROPRIATE FOR SCALES TO BE APPLIED TO MULTIPLE REGIONS

USE MULTIPLE SCALES REPRESENTING THE RANGE OF APPLICABLE CONDITIONS.

- ALLOWS AN ASSESSMENT OF EFFECTS OF VARIABILITY.
- BUT NOT USEFUL WHEN A SINGLE SCALE IS REQUIRED.

BASE THE SCALE ON CONDITIONS WHERE VOCs HAVE MAXIMUM INCREMENTAL REACTIVITIES (**MIR SCALE**).

- REFLECTS URBAN CONDITIONS WHERE OZONE IS MOST SENSITIVE TO VOC EMISSIONS
- GIVES GOOD CORRELATIONS TO EFFECTS OF VOCs ON INTEGRATED OZONE EXPOSURE.
- BUT DOES NOT REPRESENT CONDITIONS WHERE HIGHEST OZONE CONCENTRATIONS ARE FORMED.

EXAMPLES OF REGULATORY POLICIES REGARDING VOC REACTIVITY

CALIFORNIA AIR RESOURCES BOARD

THE **MIR SCALE** IS USED IN SEVERAL REGULATORY APPLICATIONS

- "REACTIVITY ADJUSTMENT FACTORS" ARE USED FOR EXHAUST STANDARDS FOR ALTERNATIVELY FUELED VEHICLES.
- REACTIVITY-BASED STANDARDS ARE USED IN THE NEW AEROSOL COATINGS REGULATIONS.
- REACTIVITY-BASED STANDARDS ARE BEING CONSIDERED FOR ARCHITECTURAL COATINGS.

UNITED STATES EPA

PRESENT POLICY: A VOC IS EITHER **REACTIVE** OR **EXEMPT**. ETHANE IS USED TO DEFINE BORDERLINE.

- EXEMPTION CANDIDATES ARE EXAMINED ON A CASE-BY-CASE BASIS
- INCREMENTAL REACTIVITIES ARE AMONG THE FACTORS CONSIDERED.

POLICIES REGARDING REACTIVITY ARE BEING RE-EXAMINED. MORE RESEARCH IS NEEDED.

THE EPA IS WORING WITH **THE REACTIVITY RESEARCH WORING GROUP** TO IDENTIFY AND SUPPORT POLICY-RELEVANT RESEARCH.

UNCERTAINTIES IN REACTIVITY SCALES

UNCERTAINTY IN THE GENERAL APPLICABILITY OF ANY SINGLE SCALE

- NO SCALE CAN REPRESENT ALL ENVIRONMENTS.
- NOT ALL EXPERTS AGREE THAT THE MIR SCALE IS THE MOST APPROPRIATE FOR REGULATIONS.
- CALIFORNIA HAS ADOPTED THE MIR SCALE. THE EPA WANTS MORE RESEARCH BEFORE ADOPTING A SCALE FOR REGULATIONS.
- THE RRWG IS SUPPORTING RESEARCH ON ASSESSING REACTIVITY SCALES.

CHEMICAL MECHANISM UNCERTAINTY

- GENERAL MECHANISM UNCERTAINTIES CAUSE UNCERTAINTY FOR EVEN WELL-STUDIED VOCs.
- UNCERTAINTIES ARE MUCH GREATER FOR VOCs WITH NO DATA TO VERIFY THEIR MECHANISMS.

COMPOSITION UNCERTAINTY

- APPLICABLE TO COMPLEX MIXTURES SUCH AS VEHICLE EXHAUSTS AND PETROLEM DISTILLATES

MECHANISM UNCERTAINTY CLASSIFICATION AND MINIMUM UNCERTAINTY ESTIMATES FOR RELATIVE MIR SCALE

NO.	DESCRIPTION	MIR. UNC'Y
1	MECHANISM NOT EXPECTED TO CHANGE SIGNIFICANTLY	≥15%
2	SOME UNCERTAINTIES BUT MECHANISM ADEQUATELY TESTED	≥15%
3	ESTIMATED MECHANISM BASED ON DATA FOR SIMILAR COMPOUNDS	≥30%
4	ESTIMATED MECHANISM BASED ON UNCERTAIN ASSUMPTIONS	≥75%
5,6	MECHANISM OR ESTIMATE IS HIGHLY SIMPLIFIED OR MAY BE INCORRECT	≥100%

NOTE:

- MINIMUM UNCERTAINTIES SHOWN ARE **HIGHLY APPROXIMATE AND SUBJECTIVE**
- UNCERTAINTIES SHOWN ARE FOR **RATIOS** OF MIRs
- UNCERTAINTIES IN **ABSOLUTE** OZONE IMPACTS ARE MUCH HIGHER

EXAMPLE SOLVENT VOCs WITH VARIOUS MECHANISM UNCERTAINTY ASSIGNMENTS

NO.	EXAMPLES	MIR. UNC'Y
1	METHANOL[A,B], ACETALDEHYDE[A,B], 1-METHOXY-2-PROPANOL[B,C]	≥15%
2	TOLUENE[B], ETHYLENE GLYCOL[A], 1-METHOXY-2-PROPYL ACETATE[B]	≥15%
3	C_{8+} ALKANES[B,D], MOST GLYCOLS, GLYCOL ETHERS, ESTERS, ETC.[E]	≥30%
4	C_{13} NAPHTHALENES, FURAN, C_{3+} ACETYLENES[F]	≥75%
5,6	AMINES, OXIMES, HALOGENATED COMPOUNDS, OXIMES, ETC.[F]	≥100%

[A] SIMPLE, WELL-ESTABLISHED MECHANISMS

[B] ENVIRONMENTAL CHAMBER DATA USED TO VERIFY OR DERIVE MECHANISMS

[C] RELEVANT REACTION ROUTES WELL-ESTABLISHED BY LABORATORY STUDIES

[D] MIRs SENSITIVE TO OTHER MECH. UNCERTAINTIES

[E] MECH. DERIVED USING ESTIMATION METHODS

[F] MECH. UNKNOWN OR VERY UNCERTAIN

EXAMPLES OF COMPOSITIONAL UNCERTAINTY FOR COMPLEX MIXTURES

COMPONENT	MIR UNC'Y
ALL-ALKENE PETROLEUM DISTILLATES	
• MINIMAL INFORMATION GIVEN	~33%
• CARBON NUMBER DISTRIBUTIONS KNOWN	~17%
• FRACTIONS OF NORMAL AND TOTAL BRANCHED AND CYCLIC ALSO KNOWN	0%
MIXTURES OF AROMATICS	
• MINIMAL INFORMATION GIVEN	~60%
• CARBON NUMBER DISTRIBUTIONS KNOWN	~55%
• FRACTIONS OF MONO-, DI-, AND POLY-SUBSTITUTED BENZENES AND NAPHTHALENES ALSO KNOWN	0%
OTHERS	
• UNSPECIFIED GLYCOL ETHERS	~30%
• PETROLEUM DISTILLATE WITH AROMATIC FRACTION NOT SPECIFIED	~100%

EXAMPLES OF ENVIRONMENTAL CHAMBERS USED FOR CHEMICAL MECHANISM EVALUATION

UCR TEFLON BAG/ BLACKLIGHT CHAMBERS

- ~2-5 M^3 BAGS OF TEFLON FILM.
- BLACKLIGHT LIGHT SOURCE
- SMALL BUT VARIABLE SURFACE EFFECTS

UCR XENON ARC TEFLON CHAMBER

- SAME AS ABOVE EXCEPT XENON ARC LIGHT SOURCE FOR MORE REALISTIC SPECTRUM

UCR EVACUABLE CHAMBER

- 5.8 M^3 TEFLON COATED METAL WITH QUARTZ END WINDOWS. TEMPERATURE CAN BE VARIED
- RELATIVELY LARGE SURFACE EFFECTS

UNC OUTDOOR CHAMBER

- DUAL ~150 M^3 “A” FRAME WITH TEFLON FILM
- USES RURAL AMBIENT AIR

CALTECH CHAMBER

- DUAL ~25 M^3 BAGS OF TEFLON FILM
- STATE-OF-THE-ART AEROSOL EQUIPMENT
- OUTDOOR CHAMBER CONVERTED TO INDOOR WITH BLACKLIGHT LIGHT SOURCE

LIMITATIONS OF CURRENT ENVIRONMENTAL CHAMBERS

NOT SUITABLE FOR LOW NO_x STUDIES

- AIR PURIFICATION SYSTEM LIMITATIONS
- NO_x ABSORPTION AND OFFGASING FROM WALLS

LIMITED ANALYTICAL INSTRUMENTATION AVAILABLE

- SPECIAL INSTRUMENTATION REQUIRED MONITORING AT VERY LOW CONCENTRATIONS
- INSTRUMENTATION NEEDED FOR ASSESSING ALL TYPES OF VOC IMPACTS OF CONCERN.

LIMITED OR NO TEMPERATURE CONTROL

- TEMPERATURE EFFECTS CAN BE IMPORTANT, BUT MODELS FOR SUCH EFFECTS NOT WELL TESTED.
- EXISTING TEMPERATURE CONTROLLED CHAMBERS NOT SUITABLE FOR EVALUATION AT LOW CONCENTRATIONS.

NEED FOR IMPROVED CHAMBER FACILITY FOR REDUCING CHEMICAL MECHANISM UNCERTAINTY

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

NONLINEAR CHEMISTRY MAY NOT ALWAYS EXTRAPOLATE TO LOWER CONCENTRATIONS.

LOWER URBAN POLLUTANT LEVELS 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 NEEDED ON HOW TEMPERATURE AND HUMIDITY AFFECTS VOC IMPACTS.

NEW U.C. RIVERSIDE CHAMBER FACILITY

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 CONDITIONS.
- DETERMINE MAJOR OXIDATION PRODUCTS FORMED BY ORGANICS UNDER LOW-NO_X CONDITIONS.
- DETERMINE EFFECTS OF TEMPERATURE ON VOC REACTIVITY, AEROSOL FORMATION AND OTHER IMPACTS.
- EVALUATE USEFULNESS OF INDICATOR SPECIES FOR ASSESSING WHETHER AMBIENT ATMOSPHERES ARE NO_x LIMITED.
- PROVIDE A FACILITY TO TEST EQUIPMENT FOR AMBIENT MONITORING.

U.C. RIVERSIDE CHAMBER FACILITY PROGRESS AND CURRENT STATUS

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

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

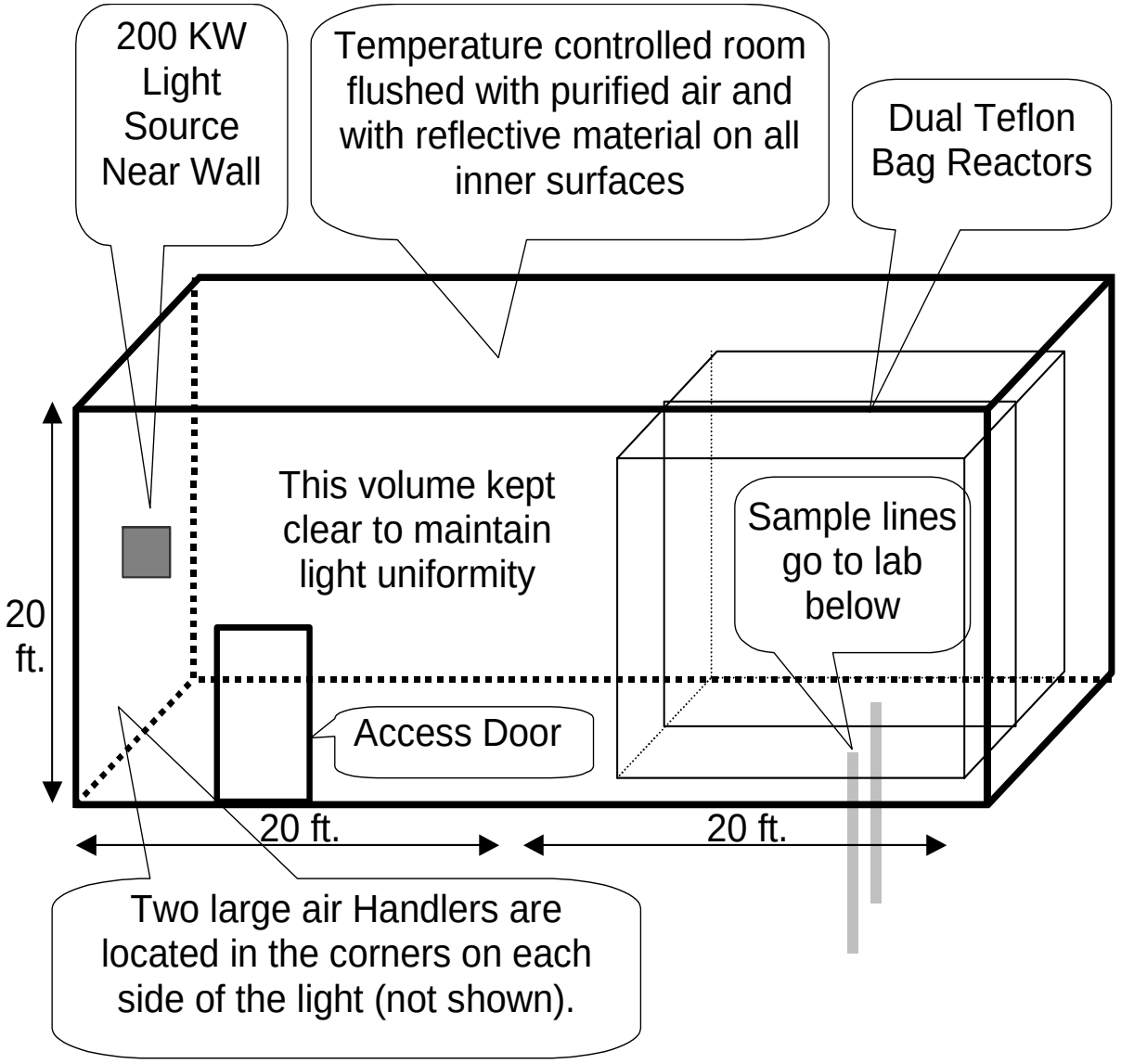
- VARIOUS TYPES OF WALL MATERIAL TESTED
- BACKGROUND NO_x OFFGASING ~1 PPB/DAY

OBTAINING INSTRUMENTATION MOST NEEDED FOR ASSESSING LOW NO_x EFFECTS

DESIGN AND CONSTRUCTION OF CHAMBER AND LIGHT SOURCE FACILITY

- NEW BUILDING CONSTRUCTED TO HOUSE FACILITY. TOOK OCCUPANCY LATE JULY 2001
- 200,000-LITER TEFLON BAG REACTOR(S) 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 SEPTEMBER, 2001

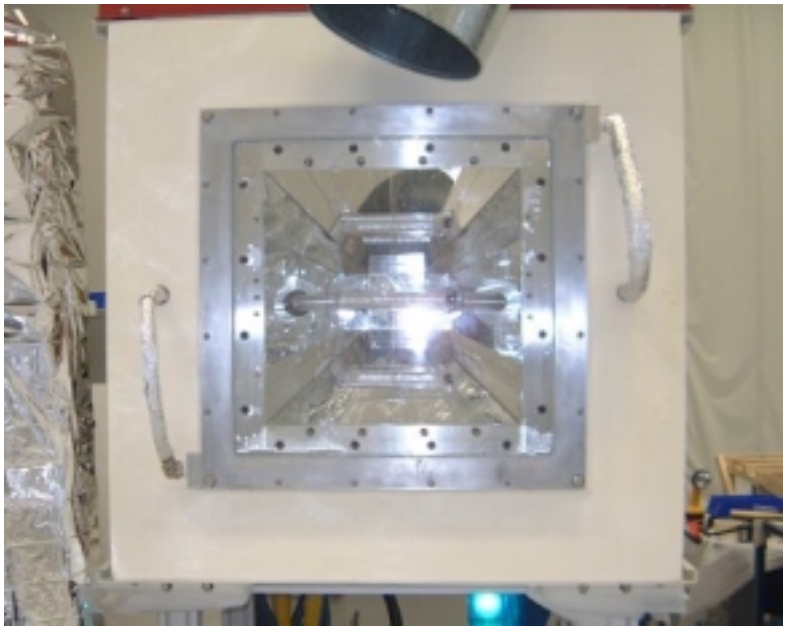
DIAGRAM OF ENVIRONMENTAL CHAMBER AND TEMPERATURE-CONTROLLED ENCLOSURE

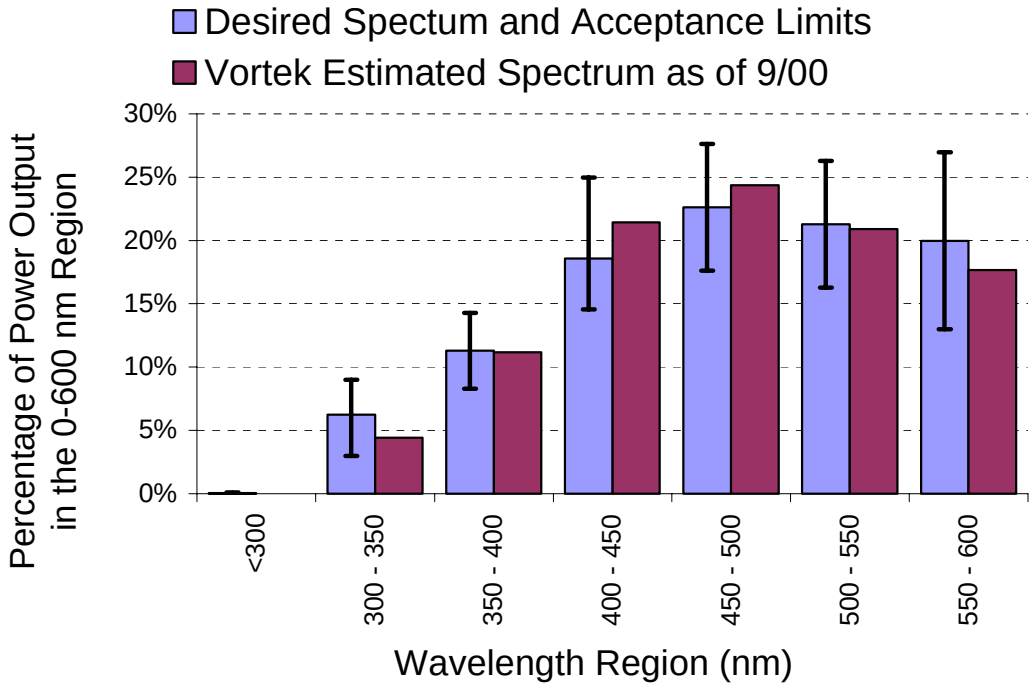


CHAMBER BUILDING AND LABORATORY

CHAMBER ENCLOSURE AS OF 8/01

LIGHT SOURCE (AT FACTORY) AND SPECTRUM SPECIFICATION





NEW UCR CHAMBER FACILITY
PLANNED PROJECTS

LOW NO_x MODEL EVALUATION EXPERIMENTS

- SIMPLE CHEMICAL SYSTEMS TO TEST PORTIONS OF MECHANISMS FOR IMPORTANT SPECIES
- COMPLEX MIXTURES FOR COMPLETE TESTING
- EVALUATE TEMPERATURE, HUMIDITY EFFECTS
- EVALUATE MODEL PREDICTIONS OF NIGHTTIME CHEMISTRY AND MULTI-DAY EFFECTS.
- EVALUATE MODEL PREDICTIONS OF RADICAL SOURCES AND SINKS

VOC REACTIVITY ASSESSMENT

- VOCs REPRESENTATIVE OF MAJOR SOURCES, INCLUDING COATINGS, SOLVENTS, VEHICLES.
- DETERMINE EFFECTS ON O_3, AEROSOL, AND OTHER PRODUCTS UNDER AMBIENT CONDITIONS
- NO_x, OTHER POLLUTANTS, TEMPERATURE, HUMIDITY VARIED

EVALUATION OF INDICATORS OF OZONE SENSITIVITY TO PRECURSOR EMISSIONS

EVALUATE AMBIENT MONITORING EQUIPMENT

- COLLABORATE WITH INSTRUMENT DEVELOPERS

ADDITIONAL INFORMATION AVAILABLE

REACTIVITY RESEARCH WORKING GROUP

http://www.cgenv.com/narsto/reactinfo.html

- MISSION STATEMENT
- REACTIVITY POLICY WHITE PAPER
- REACTIVITY SCIENCE ASSESSMENT DOCUMENTS

REACTIVITY DATA AND DOCUMENTATION

http://www.cert.ucr.edu/~carter/reactdat.htm

- TABULATION OF MIR, OTHER REACTIVITY SCALES
- REPORT DOCUMENTING CHEMICAL MECHANSM AND METHODS USED TO CALCULATE REACTIVITY
- LINKS TO OTHER REPORTS AND PRESENTATIONS CONCERNING W.P.L. CARTER'S RESEARCH

CALIFORNIA ARB'S REACTIVITY-BASED AEROSOL COATINGS REGULATION

http://www.arb.ca.gov/regact/conspro/aerocoat/aerocoat.htm

- REGULATION AND RULEMAKING INFORMATION AND TECHNICAL SUPPORT DOCUMENTS