

EVALUATION OF ATMOSPHERIC OZONE IMPACTS OF COATINGS VOC EMISSIONS

BY

WILLIAM P. L. CARTER

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

September 25, 2003

OUTLINE

CHEMISTRY OF OZONE FORMATION

QUANTIFICATION OF REACTIVITY AND EXAMPLES

UNCERTAINTIES IN REACTIVITY SCALES

**ONGOING REACTIVITY RESEARCH FOR
ARCHITECTURAL COATINGS VOCs**

ADDITIONAL INFORMATION AVAILABLE

THE PHOTOCHEMICAL OZONE PROBLEM

GROUND LEVEL OZONE IS FORMED WHEN SUNLIGHT REACTS WITH EMITTED OXIDES OF NITROGEN (NO_x) AND VOLATILE ORGANICS COMPOUNDS (VOCs).

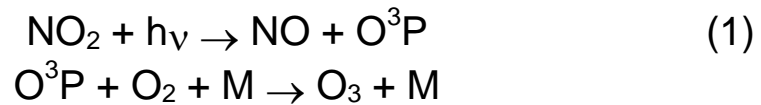
THE PROCESS OF OZONE FORMATION FROM VOCs AND NO_x IS COMPLEX

- VOC AND NO_x CONTROL ARE NOT EQUALLY EFFECTIVE IN REDUCING OZONE.
- DIFFERENT TYPES OF VOCs HAVE DIFFERENT OZONE IMPACTS (REACTIVITIES).

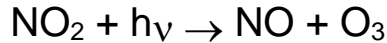
AN UNDERSTANDING OF THE PROCESS OF OZONE FORMATION IS NECESSARY TO DETERMINE THE MOST COST EFFECTIVE CONTROL STRATEGY.

CHEMISTRY OF O₃ FORMATION IN PHOTOCHEMICAL SMOG

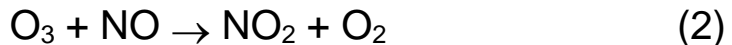
THE ONLY SIGNIFICANT CHEMICAL REACTION WHICH FORMS OZONE IN THE TROPOSPHERE IS THE PHOTOLYSIS OF NO₂



OR OVERALL



BUT THIS IS REVERSED BY THE RAPID REACTION OF O₃ WITH NO:



THIS RESULTS IN A "PHOTOSTATIONARY STATE" BEING ESTABLISHED, WHERE O₃ IS PROPORTIONAL TO THE NO₂ TO NO RATIO

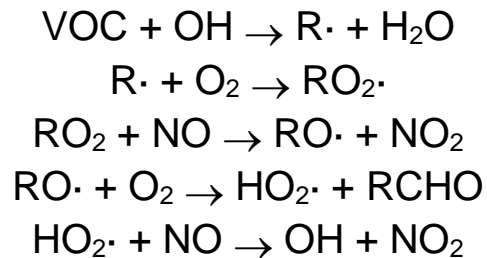
$$[\text{O}_3] = \frac{k_1[\text{NO}_2]}{k_2[\text{NO}]}$$

IF OTHER REACTANTS ARE NOT PRESENT TO CONVERT NO TO NO₂, ONLY VERY LOW LEVELS OF OZONE ARE FORMED.

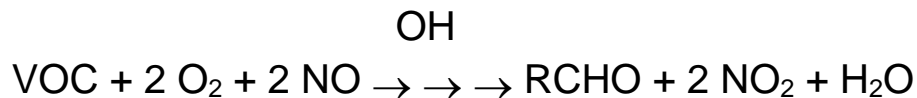
ROLE OF VOCs IN OZONE FORMATION

WHEN VOLATILE ORGANIC COMPOUNDS REACT
THEY FORM RADICALS THAT CONVERT NO TO NO₂

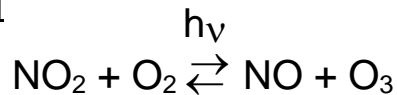
SIMPLIFIED EXAMPLE:



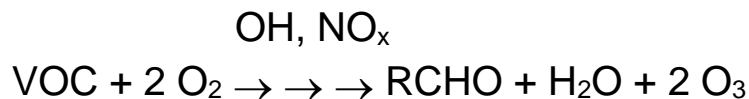
OVERALL



COMBINED WITH



YIELDS



**OZONE FORMATION CONTINUES UNTIL NO_x IS
REMOVED**

IMPLICATIONS OF ATMOSPHERIC CHEMISTRY FOR OZONE CONTROL STRATEGIES

NO_x CONTROL:

- NO_x IS REQUIRED FOR OZONE FORMATION AND LIMITS HOW MUCH O₃ CAN BE FORMED.
- BUT NO_x REDUCES THE RATE OF O₃ FORMATION BECAUSE IT REACTS WITH O₃ AND RADICALS
- NO_x CONTROL HAS GREATEST BENEFIT DOWNWIND, BUT CAN MAKE O₃ WORSE NEAR EMISSIONS SOURCE AREAS.

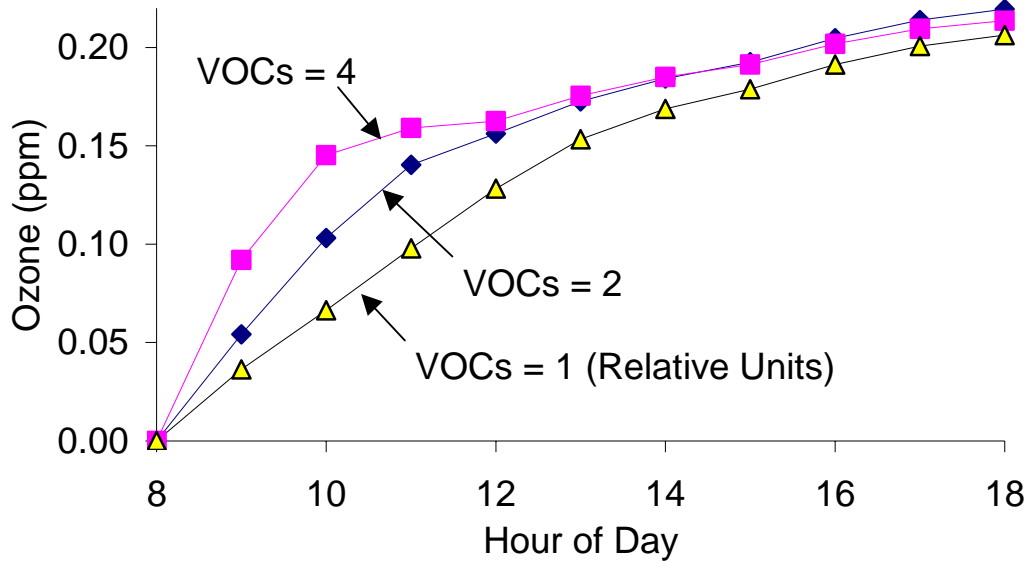
VOC CONTROL

- VOCs ENHANCE THE RATE OF O₃ FORMATION FROM NO_x
- VOC CONTROL IS MOST EFFECTIVE NEAR THE SOURCE AREAS WHERE NO_x IS HIGH.
- LESS EFFECTIVE IN NO_x-LIMITED AREAS, SUCH AS DOWNWIND AND MOST RURAL AREAS.
- NATURAL EMISSIONS OF VOCs LIMITS THE MAXIMUM EXTENT OF VOC CONTROLS.

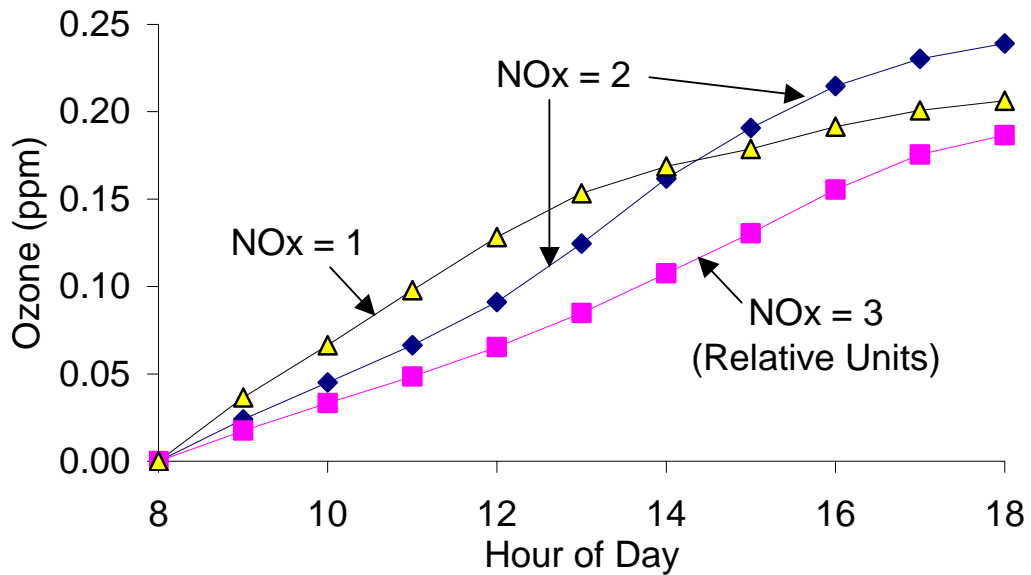
ANY COMPREHENSIVE OZONE CONTROL STRATEGY SHOULD TAKE ALL THESE FACTORS INTO ACCOUNT.

EFFECTS OF VOCs AND NO_x ON OZONE

VARY VOCs



VARY NO_x



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 NO_x IS REQUIRED FOR O₃ TO BE FORMED.

A VOC's EFFECT ON O₃ ALSO DEPENDS ON THE NATURE OF THE ENVIRONMENT WHERE IT REACTS

QUANTIFICATION OF REACTIVITY

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

$$\left[\begin{array}{l} \text{INCREMENTAL} \\ \text{REACTIVITY} \\ \text{OF A VOC IN} \\ \text{AN EPISODE} \end{array} \right] = \lim_{[\text{voc}] \rightarrow 0} \frac{\left[\begin{array}{l} \text{OZONE} \\ \text{FORMED} \\ \text{WHEN VOC} \\ \text{ADDED TO} \\ \text{EPISODE} \end{array} \right] - \left[\begin{array}{l} \text{OZONE} \\ \text{FORMED} \\ \text{IN AN} \\ \text{EPISODE} \end{array} \right]}{\left[\begin{array}{l} \text{AMOUNT OF VOC} \\ \text{ADDED TO EMISSIONS} \\ \text{IN THE EPISODE} \end{array} \right]}$$

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.

- IMPRACTICAL TO EXPERIMENTALLY DUPLICATE ALL CONDITIONS THAT AFFECT REACTIVITY
- CHAMBER EXPERIMENTS HAVE WALL EFFECTS, USUALLY HIGHER LEVELS OF NO_x 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

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

- CHAMBER EXPERIMENTS ARE USED TO TEST THE RELIABILITY OF CHEMICAL MECHANISMS TO PREDICT ATMOSPHERIC REACTIVITY.

REACTIVITY CALCULATIONS ALSO REQUIRE APPROPRIATE MODELS FOR AIRSHED CONDITIONS

MODELS FOR AIRSHED CONDITIONS

BOX OR TRAJECTORY (“EKMA”) MODELS

REPRESENTS AIR PARCELS AS WELL-MIXED BOXES WHERE EMISSIONS AND REACTIONS OCCUR

CAN REPRESENT VARIATION OF CONDITIONS WITH TIME AND POLLUTION FORMATION AT ONE LOCATION

ADVANTAGES

- PERMITS USE OF DETAILED MECHANISMS TO CALCULATE IMPACTS OF >500 TYPES OF VOCs
- USE OF MANY SCENARIOS CAN REPRESENT WIDE RANGE OF CONDITIONS THAT AFFECT REACTIVITY
- **USED TO DERIVE THE "MIR" REACTIVITY SCALE USED IN CALIFORNIA REGULATIONS**

DISADVANTAGES

- HIGHLY SIMPLIFIED REPRESENTATION OF ACTUAL AIRSHEDS.
- DOES NOT REPRESENT TRANSPORT OR HOW VOC IMPACTS VARY WITH LOCATION
- UNCERTAIN HOW COMPLEXITIES OF TRANSPORT AFFECT REACTIVITY
- BOX MODELS NOT CONSIDERED TO BE APPROPRIATE FOR SIP MODELING

MODELS FOR AIRSHED CONDITIONS

3-D URBAN OR REGIONAL MODELS

REPRESENTS AIRSHEDS AS 3-DIMENSIONAL GRIDS WITH THOUSANDS OF WELL-MIXED BOXES (CELLS) WITH EXCHANGE BETWEEN ADJACENT CELLS

REPRESENTS TRANSPORT AND SPATIAL VARIATIONS OF POLLUTANTS AS WELL AS EVOLUTION OVER TIME

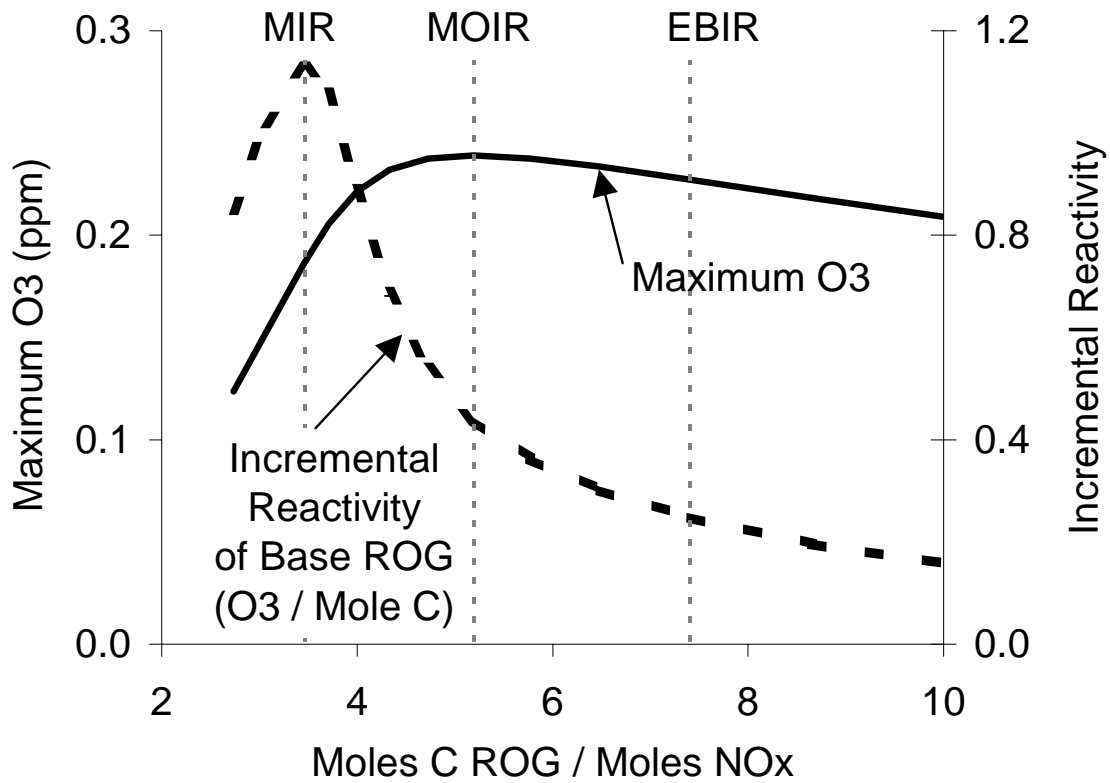
ADVANTAGES

- MOST REALISTIC PHYSICAL REPRESENTATION OF ACTUAL EPISODES
- CAN BE USED TO PREDICT HOW POLLUTION VARIES OVER LARGE REGIONS
- CAN REPRESENT HOW COMPLEXITIES OF TRANSPORT AFFECT CHEMICAL PROCESSES

DISADVANTAGES

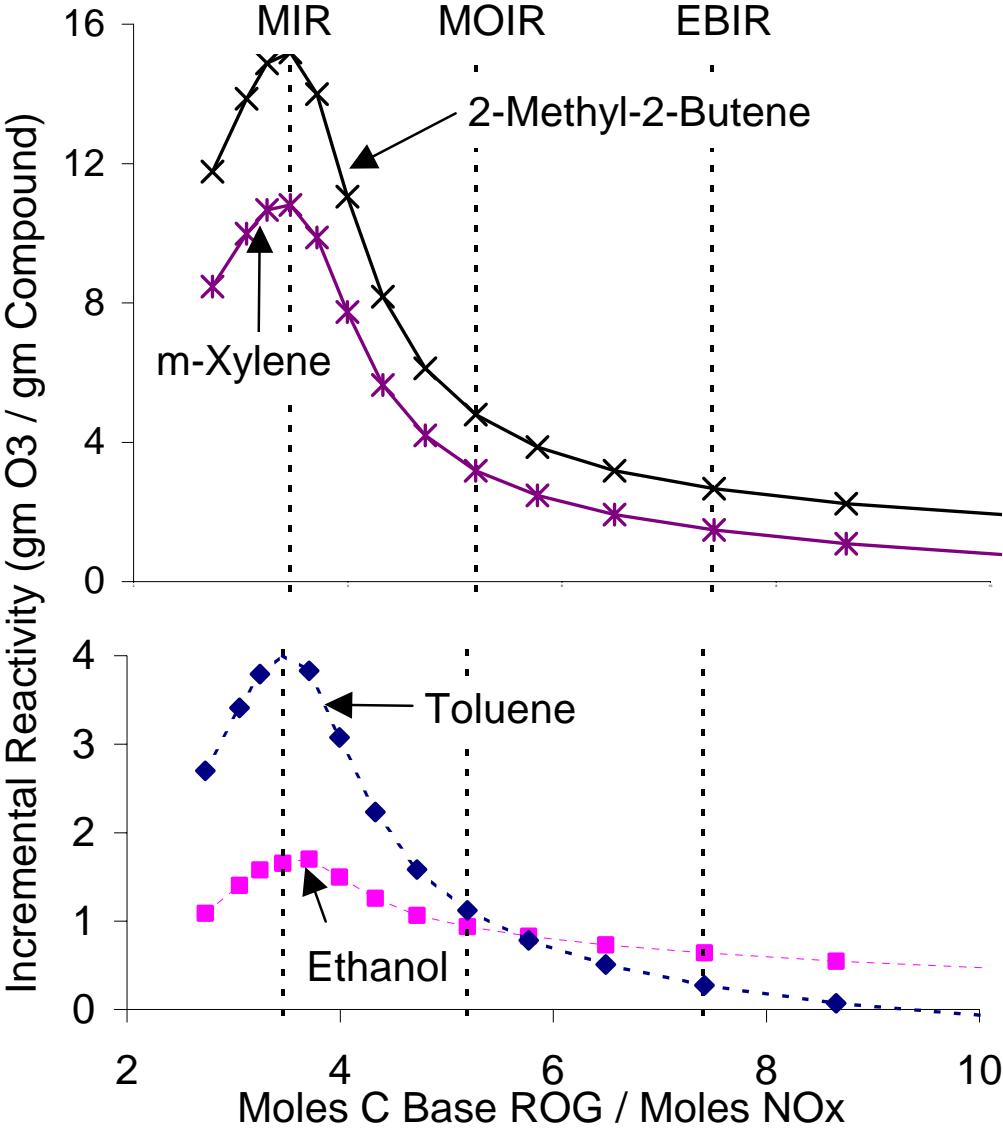
- EXPENSIVE TO RUN AND VERY EXPENSIVE TO PREPARE INPUTS FOR NEW SCENARIOS
- MUST USE CONDENSED MECHANISMS THAT LUMP MANY VOCs INTO A FEW GROUPS
- NOT OBVIOUS HOW BEST TO QUANTIFY O₃ IMPACTS FOR REACTIVITY ASSESSMENT.
- **NO COMPREHENSIVE VOC REACTIVITY SCALE HAS YET BEEN DEVELOPED USING SUCH MODELS**

- EXAMPLES OF BOX MODEL CALCULATIONS:
DEPENDENCE OF INCREMENTAL REACTIVITIES
ON ROG/NO_x



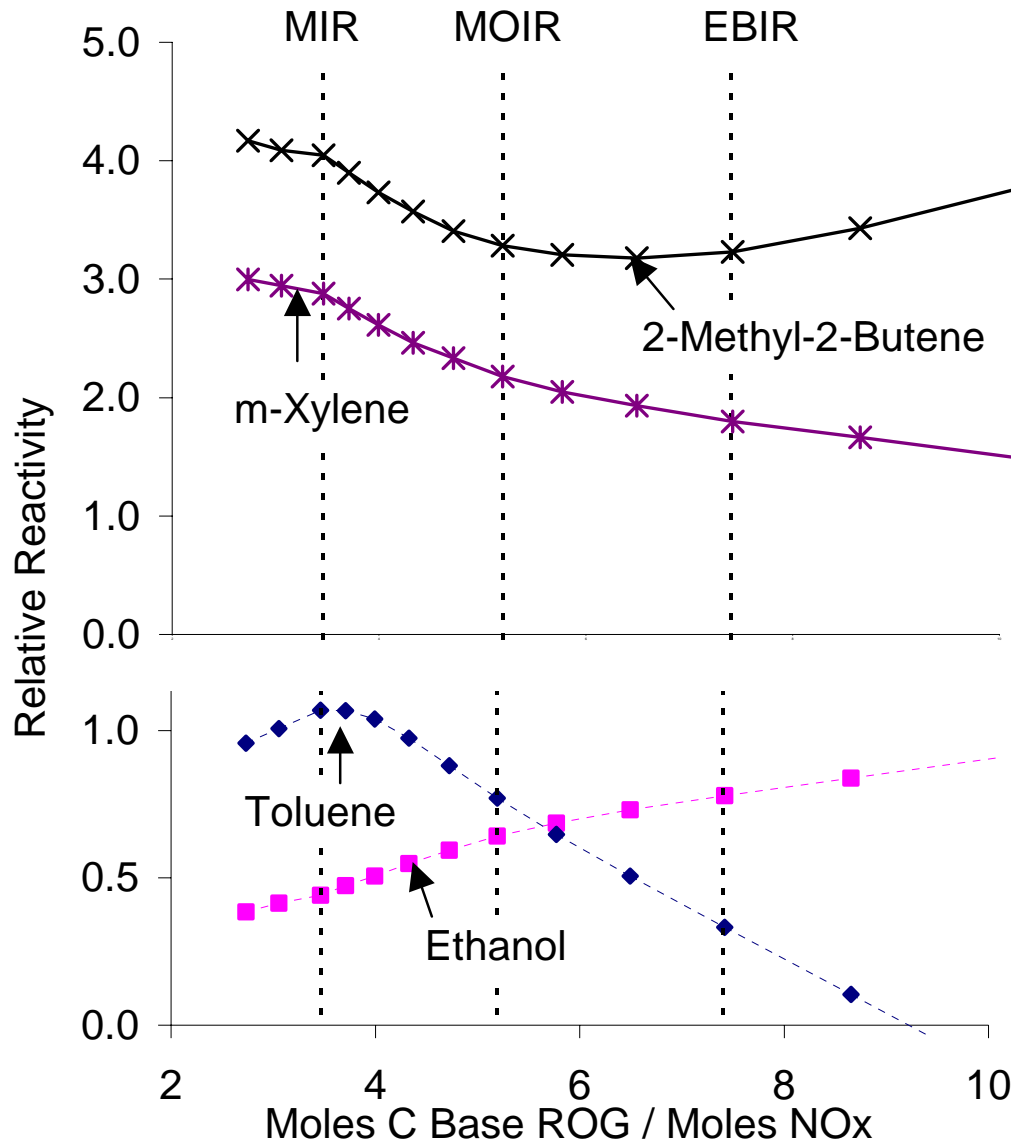
BASE ROG:	VOC MIXTURE USED TO REPRESENT VOCs FROM ALL SOURCES IN THE EPISODE
MIR:	ROG/NO _x WITH MAXIMUM INCREMENTAL REACTIVITY OF AMBIENT VOC MIXTURE
MOIR:	ROG/NO _x WITH MAXIMUM PEAK O ₃ CONCENTRATION
EBIR:	ROG/NO _x WHERE VOC AND NO _x CONTROLS ARE EQUALLY EFFECTIVE IN REDUCING O ₃

EXAMPLES OF BOX MODEL CALCULATIONS FOR INDIVIDUAL COMPOUNDS: 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)

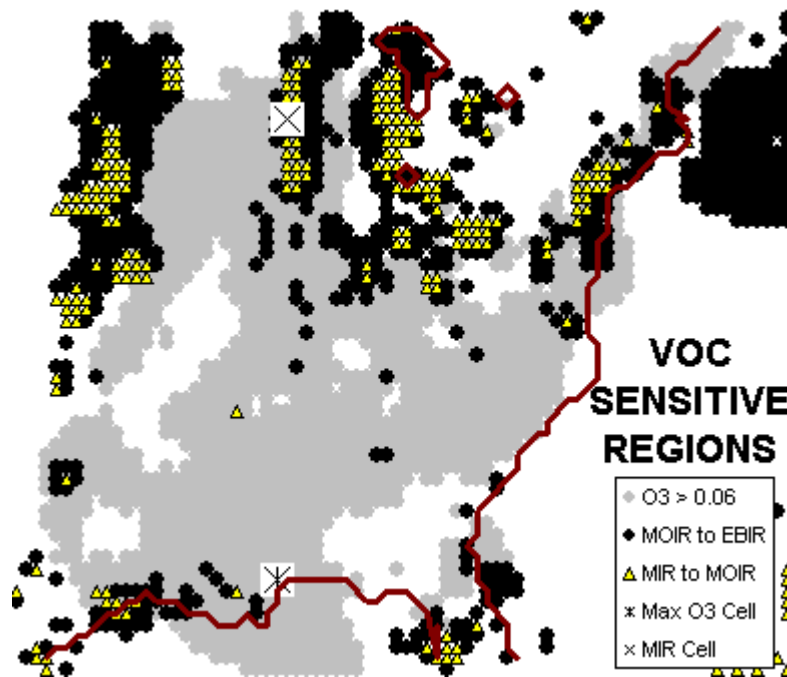
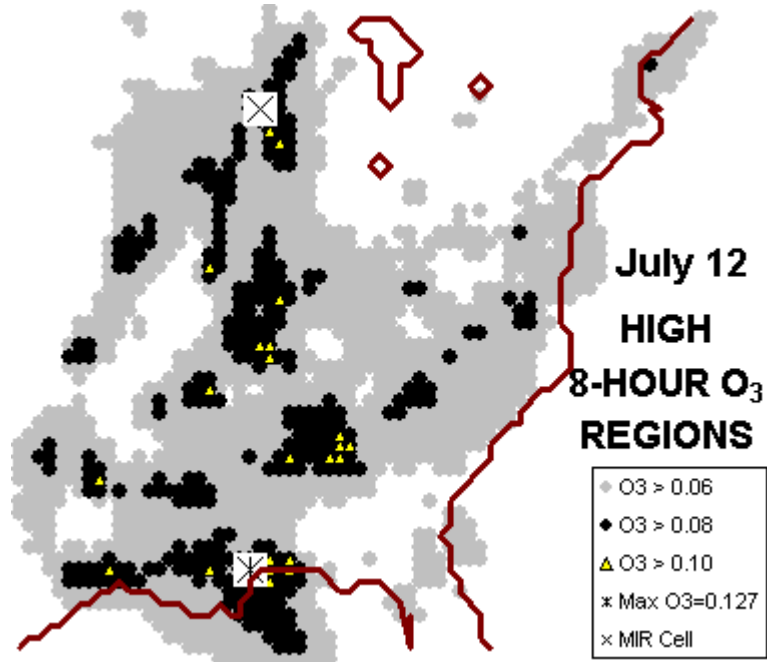


EXAMPLES OF RELATIVE REACTIVITIES OF COATINGS-RELATED AND OTHER SELECTED VOCs AT DIFFERENT NO_x LEVELS

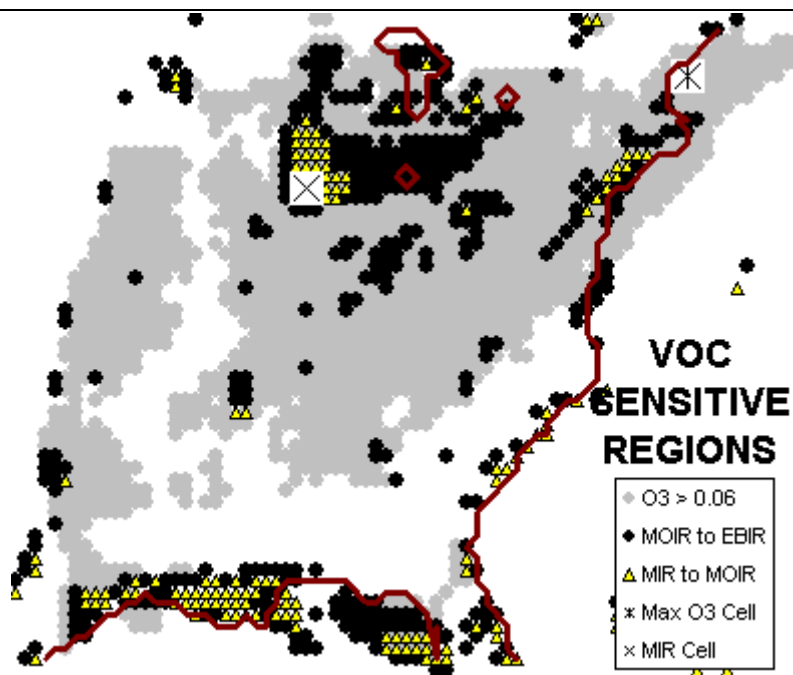
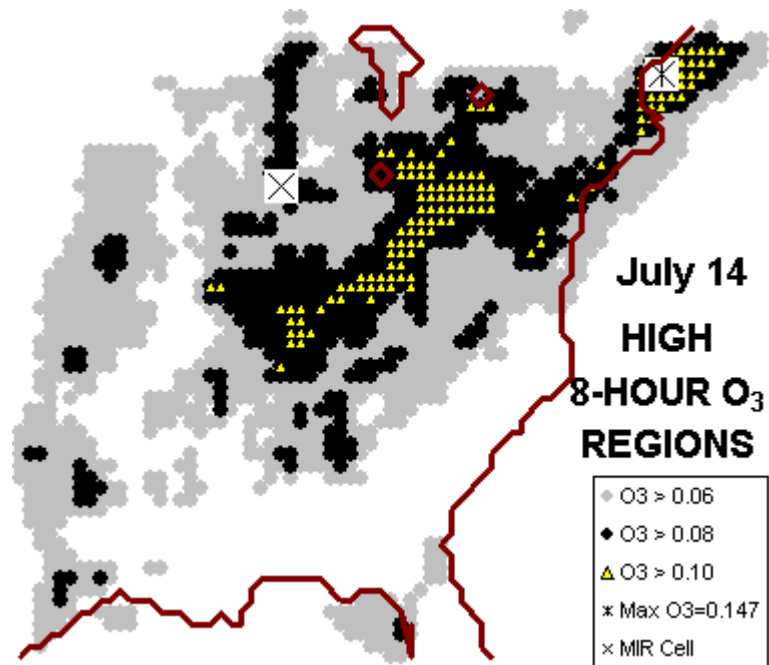
OZONE IMPACTS PER GRAM OF EXAMPLE VOC
/ IMPACT PER GRAM OF AMBIENT VOC MIXTURE.

COMPOUND OR MIXTURE	MAX. VOC IMPACT (MIR) (HIGH NO _x)	NO _x GIVING MAXIMUM OZONE	NO _x & VOC IMPACTS EQUAL (LOW NO _x)
ETHANE (EPA'S "BORDERLINE EXEMPT" STANDARD)	0.08	0.14	0.17
ALL-ALKANE MINERAL SPIRITS	0.21	0.33	0.30
TEXANOL®	0.24	0.32	0.33
VMP-NAPHTHA	0.37	0.55	0.54
AROMATICS-100	2.0	1.6	1.3
AMBIENT VOC MIXTURE	1	1	1

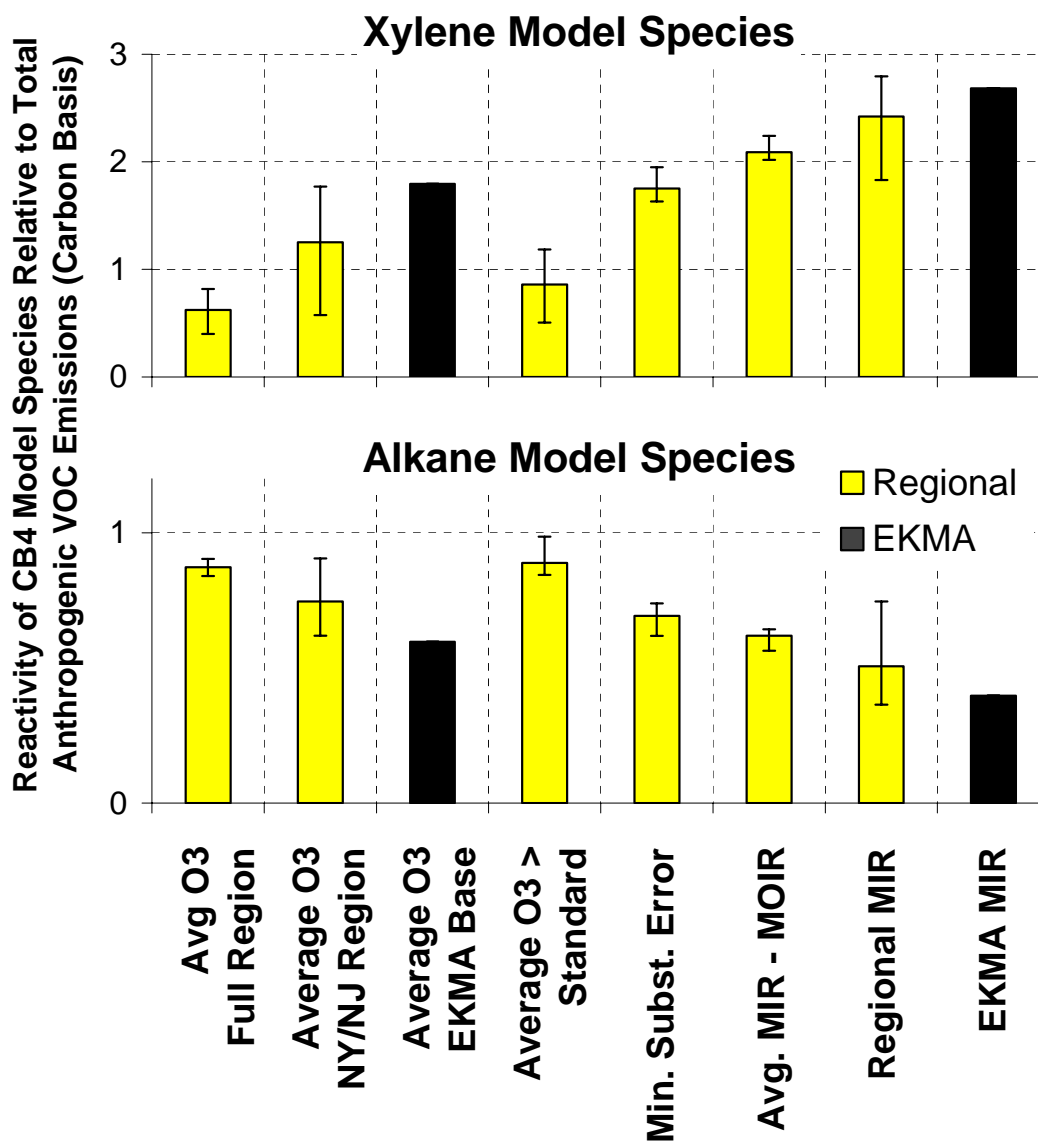
EXAMPLES OF 3-D MODEL CALCULATIONS: HIGH O₃ AND VOC SENSITIVE REGIONS



EXAMPLES OF 3-D MODEL CALCULATIONS: HIGH O₃ AND VOC SENSITIVE REGIONS



COMPARISON OF REGIONAL AND BOX MODEL RELATIVE REACTIVITIES FOR AROMATIC AND ALKANE MODEL SPECIES



CAMx MODEL WITH CB4 MECHANISM USED. ERROR BARS SHOW RANGE FOR DIFFERENT EPISODE DAYS.

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 CONDITIONS AND HOW O₃ IMPACTS ARE QUANTIFIED. THIS COMPLICATES DEVELOPMENT OF A GENERAL SCALE

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.

USE MULTIPLE SCALES REPRESENTING THE RANGE OF APPLICABLE CONDITIONS.

- ALLOWS ASSESSMENTS OF VARIABILITY.
- BUT NOT USEFUL WHEN SINGLE SCALE NEEDED

BASE THE SCALE ON CONDITIONS WHERE HIGHEST O₃ FORMED (**MOIR SCALE**).

- DOES NOT REFLECT CONDITIONS WHERE O₃ IS MOST SENSITIVE TO VOCs
- NOT WELL CORRELATED TO O₃ EXPOSURE IMPACTS

BASE SCALE ON CONDITIONS WHERE O₃ FORMATION IS MOST SENSITIVE TO VOCs (**MIR SCALE**).

- REFLECTS URBAN CONDITIONS WITH HIGHEST POPULATION EXPOSURE.
- **USED IN REACTIVITY-BASED REGULATIONS IN CALIFORNIA**
- BUT DOES NOT REPRESENT CONDITIONS WHERE HIGHEST OZONE LEVELS 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 WORKING WITH **THE REACTIVITY RESEARCH WORKING 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 ON THE MOST APPROPRIATE SCALE FOR REGULATIONS.
- CALIFORNIA HAS ADOPTED THE MIR SCALE. THE EPA WANTS MORE RESEARCH BEFORE ADOPTING A SCALE FOR REGULATIONS.

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 EXHAUSTS AND PETROLEUM DISTILLATES

**MECHANISM UNCERTAINTY
CLASSIFICATION AND MINIMUM
UNCERTAINTY ESTIMATES FOR RELATIVE
MIR SCALE**

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

NOTES:

^[A] SIMPLE, WELL-ESTABLISHED MECHANISMS

^[B] RELEVANT REACTION ROUTES WELL-ESTABLISHED BY LABORATORY STUDIES

^[C] ENVIRONMENTAL CHAMBER DATA USED TO VERIFY OR DERIVE MECHANISMS

^[D] MIRs SENSITIVE TO GENERAL MECHANISM UNCERTAINTIES

^[E] MECHANISM UNKNOWN OR VERY UNCERTAIN

EXAMPLES OF COMPOSITIONAL UNCERTAINTY FOR COMPLEX MIXTURES

COMPONENT	MIR UNC'Y
ALL-ALKENE PETROEUM 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%

EXAMPLE WORKSHEET TO ESTIMATE OZONE IMPACTS OF A FORMULATION

COMPONENT	GM /LITER	MIR (GM O ₃ / GM)	MIR UNC'Y COMP	MECH	O ₃ FORM. (GM O ₃ / LITER)
ALKANE MIX	100	0.85	15%	30%	85 ± 29
AROMATIC MIX	10	6.4	50%	30%	64 ± 37
TEXANOL®	20	0.89	0	30%	18 ± 5
AMINE	5	~7	0	100%	35 ± 35
UNIDENTIFIED VOCs	2	~4	200%		8 ± 16
WHOLE FORMULATION					210 ± 61

REACTIVITY RESEARCH NEEDS FOR VOCs FOR ARCHITECTURAL COATINGS

REACTIVITY DATA ARE ALREADY AVAILABLE FOR
MANY TYPES OF VOCs USED IN COATINGS

- DATA AVAILABLE FOR REPRESENTATIVE ALKANES, AROMATICS, ALCOHOLS, GLYCOLS, ESTERS, ESTERS AND A FEW OTHERS.
- BUT NOT ALL ASPECTS OF MECHANISMS ARE ADEQUATELY EVALUATED.

REACTIVITY ESTIMATES ARE UNCERTAIN FOR SOME
IMPORTANT TYPES OF COATINGS VOCs

- NO DATA FOR LOW VOLATILITY COMPOUNDS SUCH AS TEXANOL®
- PETROLEUM DISTILLATES HAVE LARGE COMPOSITIONAL UNCERTAINTY AND COMPONENTS INCLUDE UNSTUDIED VOCs
- AMINES AND ALCOHOL AMINES HAVE VERY LARGE MECHANISM UNCERTAINTY

NEED TO DEVELOP LOWER COST REACTIVITY
SCREENING AND ENFORCEMENT METHODS

UNCERTAIN HOW MUCH DEPOSITION ON SURFACES
AND OTHER NON-ATMOSPHERIC LOSS PROCESSES
ARE AFFECTING ATMOSPHERIC AVAILABILITY

**PRELIMINARY RESULTS OF SURVEY OF
COATINGS EMISSIONS REACTIVITY**

**VOCs IN DRAFT COATINGS INVENTORY FOR
WHICH REACTIVITY DATA ARE UNAVAILABLE**

MIR x EMIT	TYPE OF VOC	MECH UNC'Y
<u>WATER BASED COATINGS</u>		
~10%	Texanol®	3
~5%	Butyl Carbitol	3
~3%	Various Petroleum Distillates	-
~1%	Methyl Carbitol®	3
~0.5%	Diethylene Glycol	3
~0.5%	Di (propylene glycol) Methyl Ether	3
~0.5%	2-Amino-2-Methyl-1-Propanol	6
~25%	UNCERTAIN VOC TOTAL	
<u>SOLVENT BASED COATINGS</u>		
~50%	Various Petroleum Distillates	-
~1%	n-Butyl Alcohol	3
~0.5%	Ethyl 3-Ethoxypropionate	3
~50%	UNCERTAIN VOC TOTAL	

DATA FROM CALIFORNIA ARB
1998 ARCHITECTURAL COATINGS SURVEY

COMPONENTS OF CE-CERT COATINGS PROJECT FOR THE CALIFORNIA ARB

CONDUCT EMISSIONS, REACTIVITY AND
UNCERTAINTY SURVEY OF COATINGS VOCs TO
PRIORITIZE RESEARCH

DEVELOP AND EVALUATE IMPROVED PROCEDURES
TO QUANTIFY REACTIVITIES AND COMPOSITIONAL
UNCERTAINTIES FOR PETROLEUM DISTILLATES

CONDUCT ENVIRONMENTAL CHAMBER STUDIES OF
SELECTED COATINGS VOCs

- VOCs CHOSEN BY CARB'S REACTIVITY RESEARCH
ADVISORY COMMITTEE BASED ON USAGE AND
UNCERTAINTY
- TEXANOL® (MAJOR WATER-BASED COMPONENT)
- 6 TYPES OF PETROLEUM DISTILLATES
 - VMP Naphtha
 - ASTM Type IA "Regular Mineral Spirits"
 - ASTM Type IB "Mineral Spirits 75 (<8% Aromatic)"
 - ASTM Type IC "Low Aromatic Mineral Spirits"
 - ASTM Type IIIC1 "Odorless Mineral Spirits"
 - Aromatic 100
- MOST EXPERIMENTS CONSIST OF INCREMENTAL
REACTIVITY MEASUREMENTS UNDER VARIOUS
CONDITIONS

CHAMBER EXPERIMENTS WITH PETROLEUM
DISTILLATES ARE NOW UNDERWAY

ADVANTAGES OF THE UCR-EPA ENVIRONMENTAL CHAMBER

INDOOR CHAMBER DESIGN FOR BEST CONTROL OF
TEMPERATURE AND LIGHTING CONDITIONS

CURRENTLY THE LARGEST INDOOR CHAMBER
AVAILABLE FOR MODEL EVALUATION

- MINIMIZES WALL EFFECTS
- MINIMIZES PM WALL LOSSES
- PROVIDES SAMPLE VOLUME NECESSARY FOR
SPECIALIZED MEASUREMENTS.

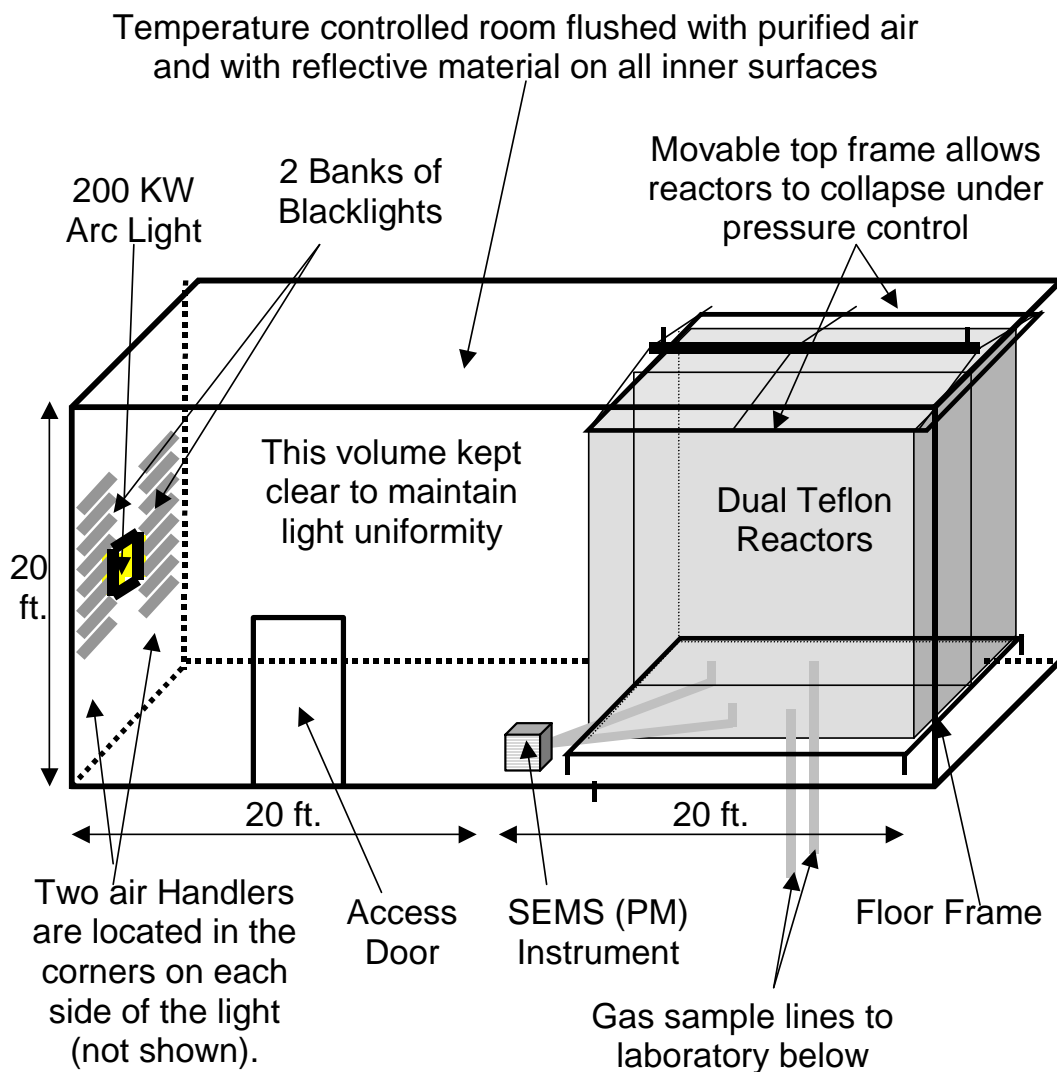
A 200 KW FILTERED ARGON ARC SIMULATES THE
INTENSITY AND SPECTRUM OF SUNLIGHT BETTER
THAN COMMONLY USED BLACKLIGHTS.

REPLACEABLE TEFLON® FILM REACTORS INSIDE A
"CLEAN ROOM" PERMIT EXPERIMENTS AT LOWER
CONCENTRATIONS THAN PREVIOUSLY POSSIBLE.

TEMPERATURE CONTROL TO $\pm 1^{\circ}\text{C}$ IN THE RANGE 5-
45°C ALLOWS SYSTEMATIC STUDIES OF
TEMPERATURE AND HUMIDITY EFFECTS

A VARIETY OF ADVANCED GAS-PHASE AND PM
INSTRUMENTATION AVAILABLE

DIAGRAM OF UCR-EPA ENVIRONMENTAL CHAMBER



- CONSTRUCTION COMPLETED EARLY 2002 AND EVALUATION COMPLETED LATE 2002
- MECHANISM EVALUATION AND VOC REACTIVITY ASSESSMENT EXPERIMENTS NOW UNDERWAY

CURRENT STATUS OF CARB COATINGS REACTIVITY STUDY

AN EVALUATION OF EMISSIONS, REACTIVITY, AND UNCERTAINTY WAS USED AS A BASIS FOR CHOICE OF COMPOUNDS TO STUDY IN THE CHAMBER

CARB'S "BINNING" METHOD FOR ESTIMATING REACTIVITIES OF PETROLEUM DISTILLATES WAS EVALUATED USING NEW COMPOSITIONAL DATA

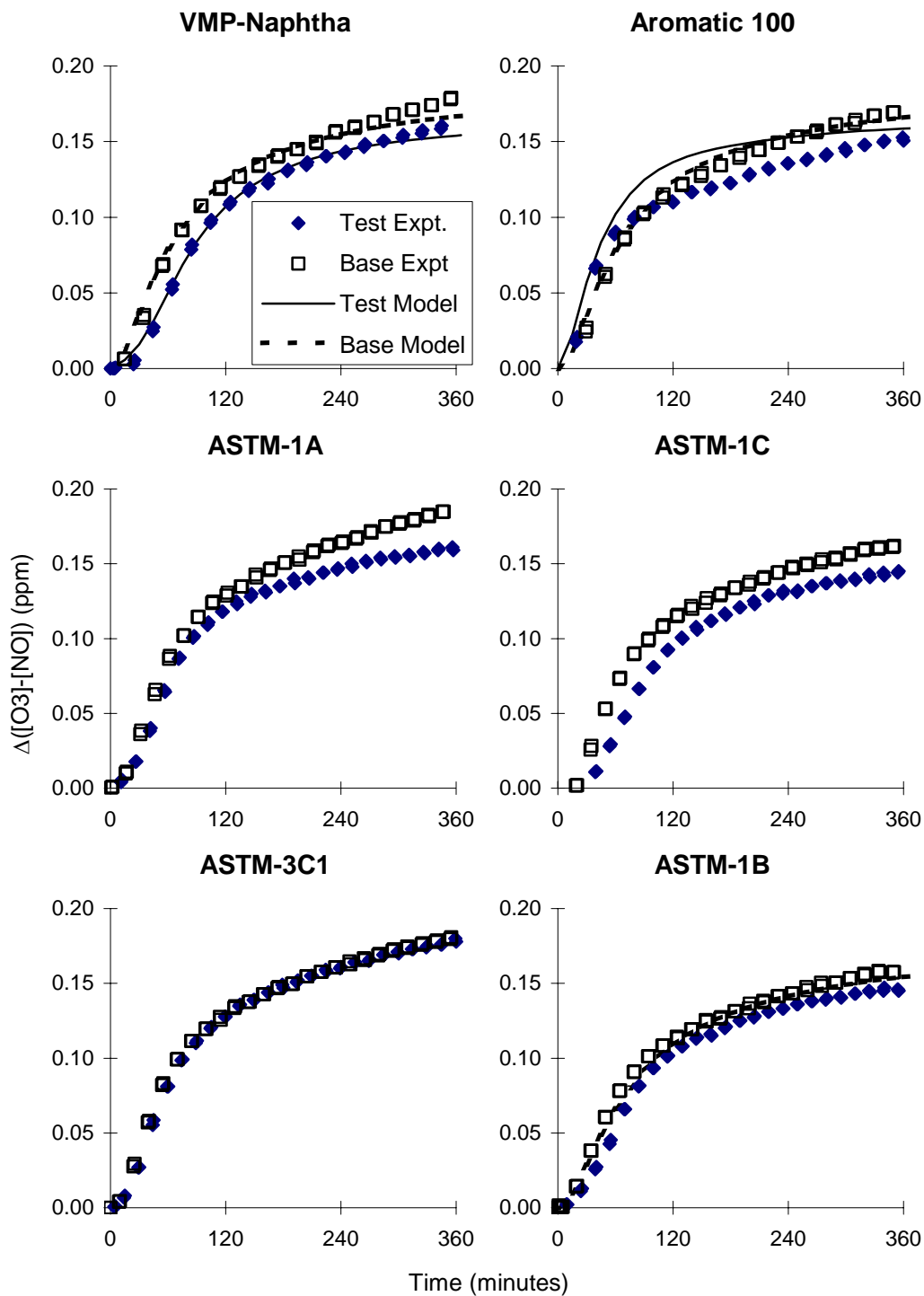
VARIOUS AMBIENT SURROGATE - NO_x EXPERIMENTS WERE CONDUCTED TO DETERMINE APPROPRIATE BASE CASES FOR REACTIVITY EXPERIMENTS

CHAMBER EXPERIMENTS WITH THE 6 PETROLEUM DISTILLATES WERE CONDUCTED AT 2 DIFFERENT ROG AND NO_x RATIOS. (ANALYSIS STILL UNDERWAY)

METHODS FOR INJECTING AND ANALYZING TEXANOL® FOR CHAMBER EXPERIMENTS ARE BEING EVALUATED.

NEW FUNDING OBTAINED FROM THE CALIFORNIA SCAQMD TO STUDY ADDITIONAL COATINGS VOCs AND TO OBTAIN PM DATA DURING EXPERIMENTS

EXAMPLE CHAMBER REACTIVITY RESULTS



ADDITIONAL INFORMATION AVAILABLE

REACTIVITY DATA AND DOCUMENTATION

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

- TABULATIONS OF REACTIVITY SCALES
- REPORT DOCUMENTING CHEMICAL MECHANISM AND METHODS USED TO CALCULATE SCALES

CE-CERT ARCHITECTURAL COATINGS PROJECT

<http://www.cert.ucr.edu/~carter/coatings>

- PROJECT SUMMARY AND PROPOSAL
- PROGRESS REPORTS AND PRESENTATIONS

UCR-EPA CHAMBER

<http://www.cert.ucr.edu/~carter/epacham>

- SUMMARY CURRENT STATUS
- PROGRESS REPORTS AND PRESENTATIONS
- DRAFT QUALITY ASSURANCE PLAN