

EVALUATION OF ATMOSPHERIC OZONE IMPACTS OF COATINGS VOC EMISSIONS

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OUTLINE

CHEMISTRY OF OZONE FORMATION

QUANTIFICATION OF REACTIVITY AND EXAMPLES

UNCERTAINTIES IN REACTIVITY SCALES

**REACTIVITY RESEARCH NEEDS FOR
ARCHITECTURAL COATINGS VOCs**

**COMPONENTS OF ONGOING AND PROPOSED
RELATED PROJECTS AT U. C. RIVERSIDE**

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).

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.

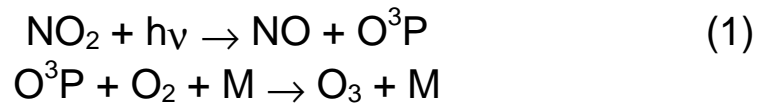
THE PROCESS OF OZONE FORMATION FROM VOCs AND NO_x IS COMPLEX

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

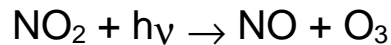
AN UNDERSTANDING OF THE PROCESS OF OZONE FORMATION IS NECESSARY TO DETERMINE THE MOST COST EFFECTIVE CONTROL STRATEGY.

CHEMISTRY OF O₃ FORMATION IN PHOTOCHEMICAL SMOG

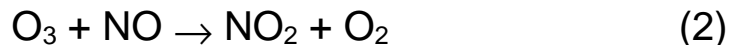
THE ONLY SIGNIFICANT CHEMICAL REACTION WHICH FORMS OZONE IN THE TROPOSPHERE IS THE PHOTOLYSIS OF NO₂



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

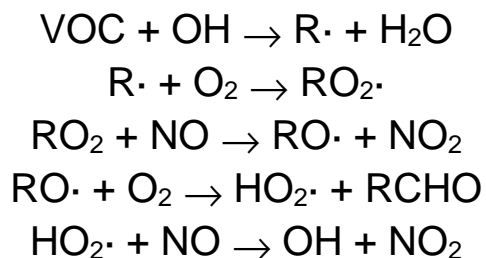
$$[\text{O}_3] = \frac{k_1[\text{NO}_2]}{k_2[\text{NO}]}$$

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

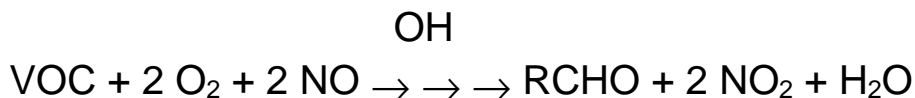
ROLE OF VOCs IN OZONE FORMATION

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

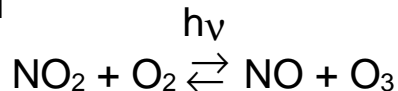
SIMPLIFIED EXAMPLE:



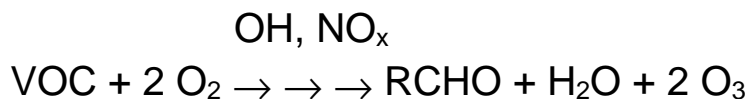
OVERALL



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

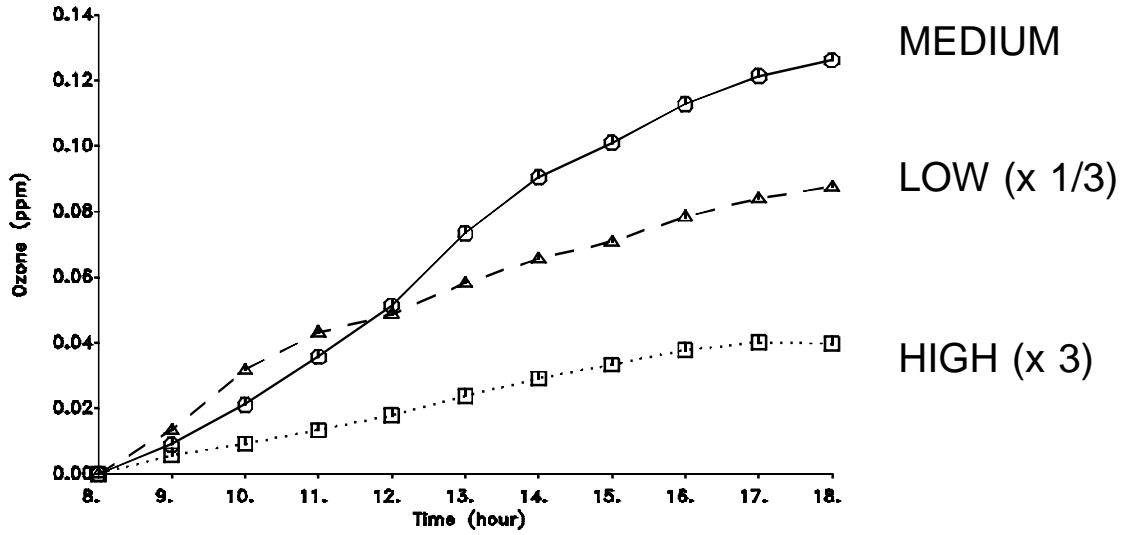
VOC CONTROL

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

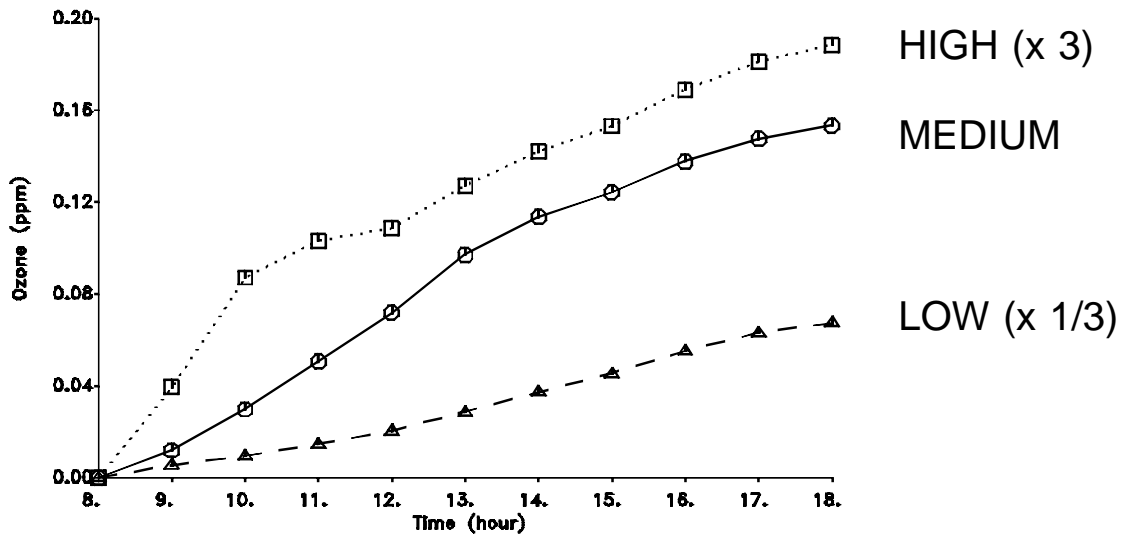
ANY COMPREHENSIVE OZONE CONTROL STRATEGY SHOULD TAKE BOTH VOC AND NO_x INTO ACCOUNT.

EFFECT OF VOCs AND NO_x ON O₃ FORMATION

VARY NO_x EMISSIONS



VARY VOC EMISSIONS



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.

- NOT PRACTICAL TO EXPERIMENTALLY DUPLICATE ALL ATMOSPHERIC CONDITIONS AFFECTING 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

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.

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.

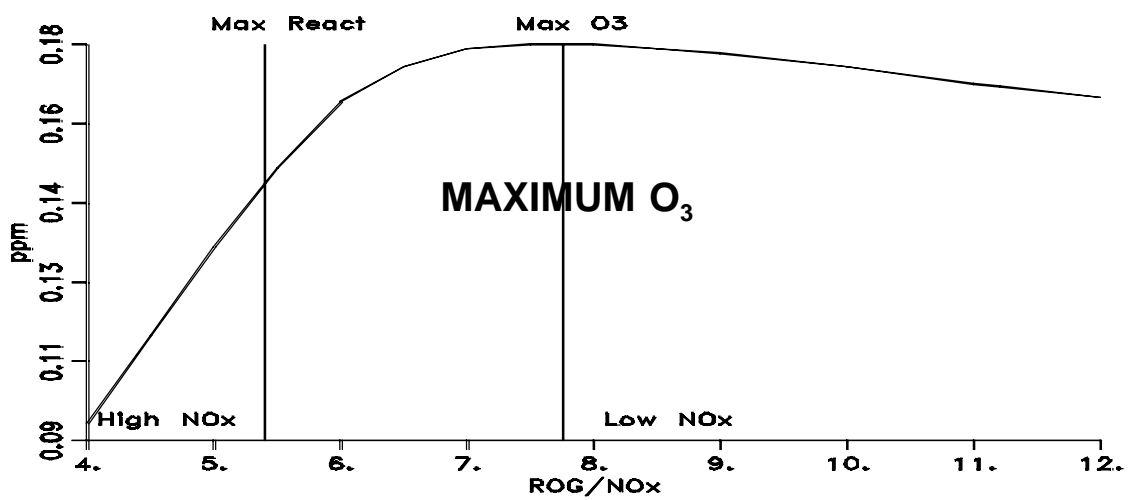
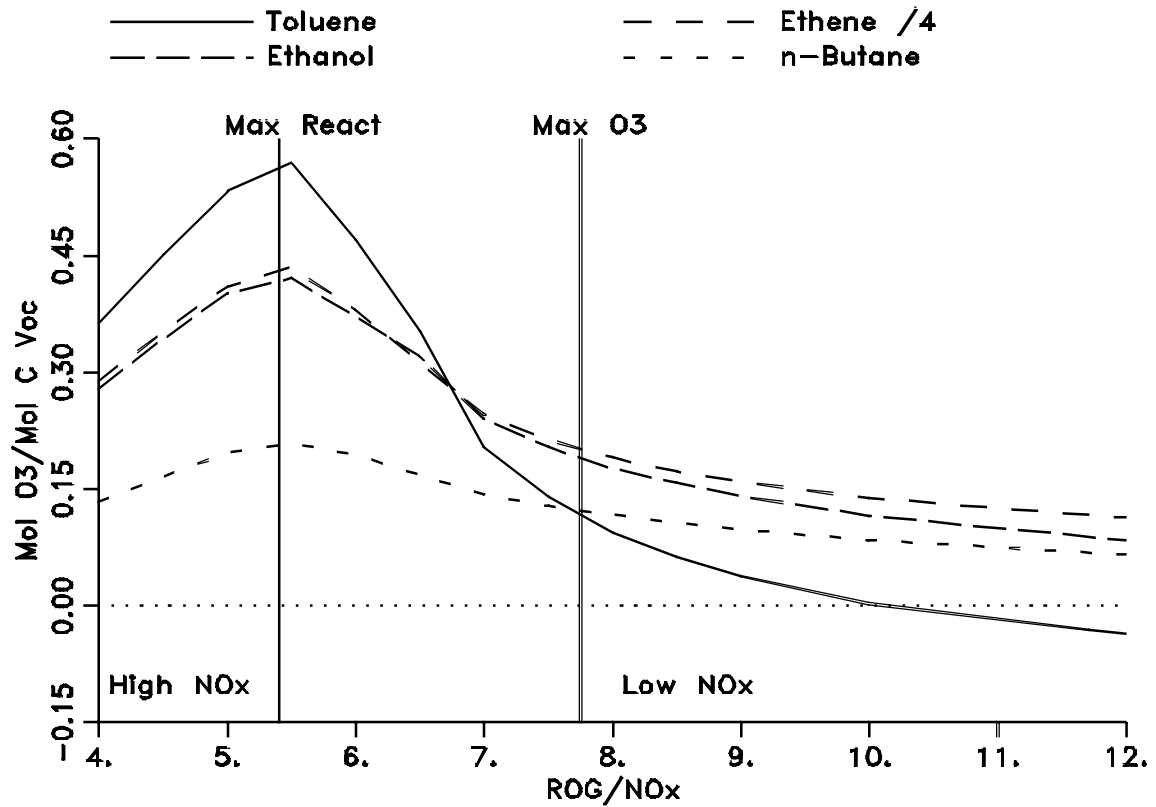
EXAMPLES INCLUDE:

- 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



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

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

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

**EXAMPLES OF INCREMENTAL REACTIVITIES
IN SCALES REPRESENTING
DIFFERENT NO_x LEVELS**

COMPOUND OR MIXTURE	MAXIMUM VOC IMPACT (HIGH NO _x) (MIR)	NO _x GIVING MAXIMUM OZONE (MOIR)	NO _x & VOC IMPACTS EQUAL (LOW NO _x) (EBIR)
ETHANE	0.31	0.20	0.15
ALL-ALKANE MINERAL SPIRITS	0.78	0.48	0.25
TEXANOL®	0.89	0.47	0.28
ETHYL BENZENE	2.79	1.00	0.42
M-XYLENE	10.6	3.2	1.5
AMBIENT VOC MIXTURE	3.7	1.5	0.85

NOTE

- UNITS ARE GRAMS OF OZONE PER GRAM OF VOC
- REACTIVITIES CALCULATED FOR **OVER 400 TYPES OF VOCs** IN MIR, MOIR, EBIR AND OTHER SCALES
- DATA AT <http://cert.ucr.edu/~carter/reactdat.htm>

EXAMPLES OF RELATIVE REACTIVITIES 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	0.08	0.14	0.17
ALL-ALKANE MINERAL SPIRITS	0.21	0.33	0.30
TEXANOL®	0.24	0.32	0.33
ETHYL BENZENE	0.75	0.69	0.50
M-XYLENE	2.9	2.2	1.8
AMBIENT VOC MIXTURE	1	1	1

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 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.

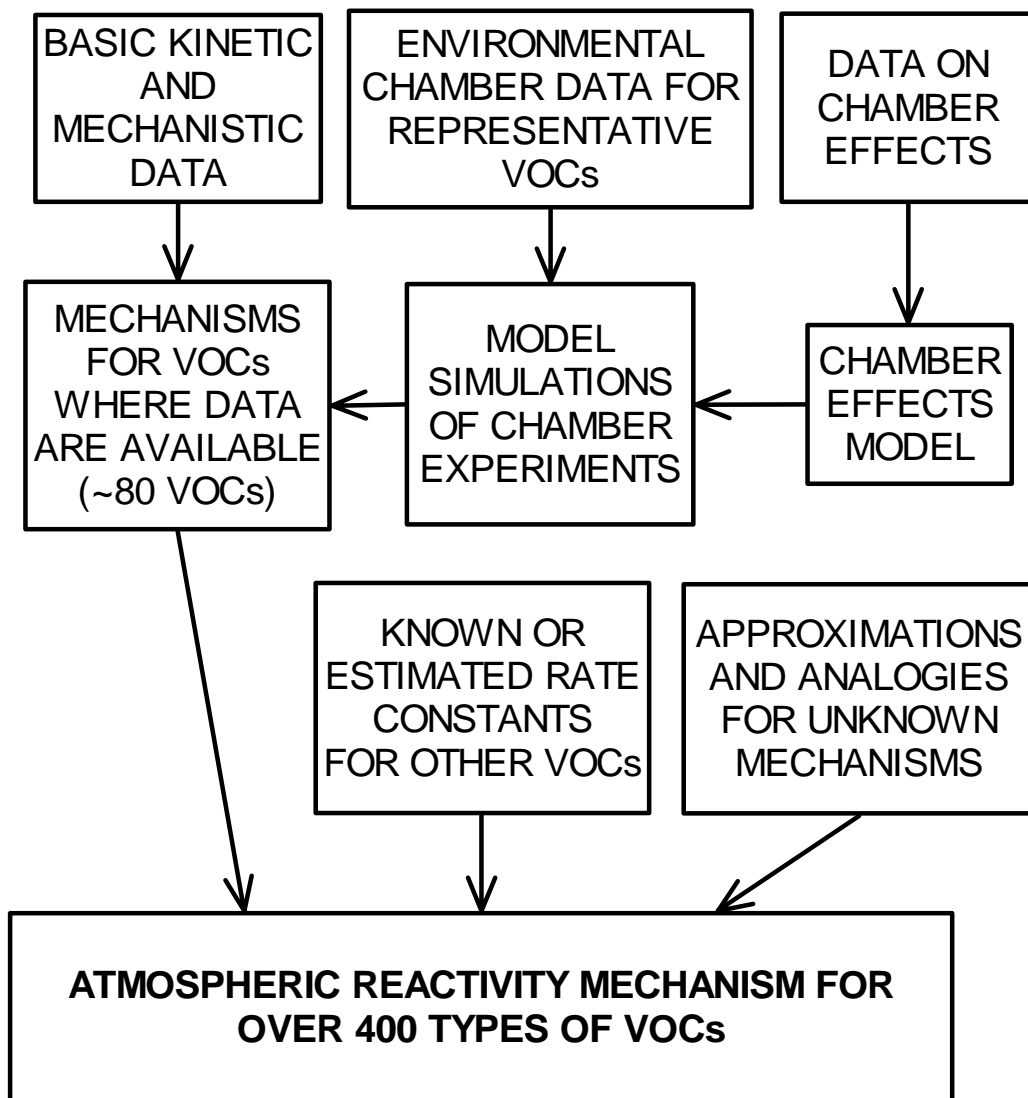
CHEMICAL MECHANISM UNCERTAINTY

- 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 PETROLEUM DISTILLATES

DEVELOPMENT OF AN ATMOSPHERIC CHEMICAL MECHANISM TO CALCULATE VOC REACTIVITIES



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
- 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**

COMPONENTS OF CE-CERT COATINGS PROJECT FOR THE CALIFORNIA ARB

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

CONDUCT ENVIRONMENTAL CHAMBER STUDIES OF
SELECTED COATINGS VOCs USING A NEW CHAMBER
BEING DEVELOPED FOR THE EPA

APPLY A DIRECT REACTIVITY SCREENING METHOD
TO LOW VOLATILITY VOCs, PETROLEUM
DISTILLATES, OTHER COATINGS CONSTITUENTS

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

**HOWEVER, AVAILABLE FUNDING NOT SUFFICIENT TO
DO ALL THE WORK NEEDED IN THESE AREAS.**

**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	

MAJOR TYPES OF PETROLEUM DISTILLATES

PRELIMINARY DATA FROM CALIFORNIA ARB
1998 ARCHITECTURAL COATINGS SURVEY

DESCRIPTION	EMIT	MIR [a]	MIR x EMIT
Stoddard Solvent	19%	~3	25%
Aromatic 100	5%	~8	20%
Protected Data [b]	15%	~2 [c]	16%
Medium Aliphatic Solvent Naphtha	33%	~1	15%
Vm & Painters Naphtha	7%	~2	8%
Petroleum Naphtha, Heavy Alkylate	7%	~1.5	6%
Distillate (Petroleum), Hydrotreated Light	5%	~1.5	4%
Kerosene	2%	~2	2%
Petroleum Ether	2%	~1.5	1%

[a] Estimated by the ARB using the California ARB Hydrocarbon "Binning" Protocol (CA code of regulations, title 17, CCR 94701)

[b] Distillates that were used by fewer than 3 companies.

[c] No MIR estimate given by the ARB. Estimated based on assuming primarily alkane compositions.

ENVIRONMENTAL CHAMBER STUDIES OF SELECTED COATINGS VOCs

VOCs WILL BE CHOSEN BASED ON RESULTS OF SURVEY

- ONLY SUFFICIENT FUNDS FOR A SINGLE VOC
- TEXANOL® APPEARS TO BE THE PRIORITY

NEW LARGE ENVIRONMENTAL CHAMBER BEING DEVELOPED FOR THE EPA WILL BE EMPLOYED

- CONSTRUCTED AND EVALUATED USING ~\$3 MILLION FUNDING FROM CONGRESS
- CAN OBTAIN DATA AT LOWER CONCENTRATIONS THAN PREVIOUSLY POSSIBLE
 - MORE REPRESENTATIVE OF CURRENT AMBIENT ATMOSPHERES
 - EASIER TO STUDY LOW VOLATILITY VOCs
- INSTRUMENTATION FOR MORE COMPREHENSIVE CHEMICAL ANALYSIS
- INSTRUMENTATION FOR INFORMATION ON AEROSOL (PM) IMPACTS

METHODS FOR STUDIES OF LOW VOLATILITY VOCs WILL BE INVESTIGATED IF NEEDED

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

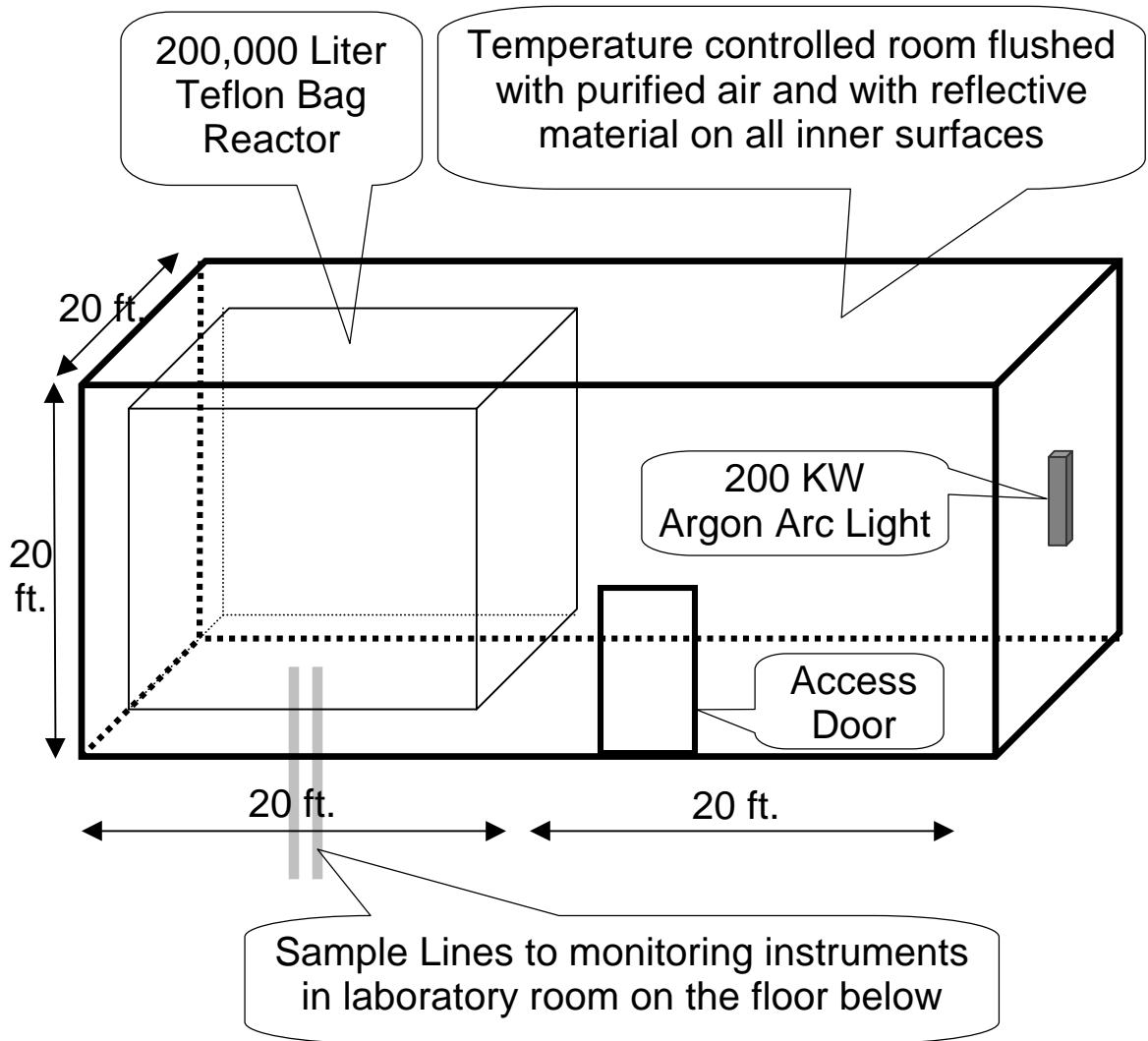
- VARIOUS TYPES OF WALL MATERIAL TESTED
- BACKGROUND NO_x OFFGASING ~1 PPB/DAY

OBTAINING INSTRUMENTATION MOST NEEDED FOR
ASSESSING LOW NO_x EFFECTS

DESIGN AND CONSTRUCTION OF CHAMBER AND
LIGHT SOURCE FACILITY

- DESIGN WORK COMPLETED
- NEW BUILDING BEING CONSTRUCTED.
ESTIMATED COMPLETION MARCH, 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°C
(40 - 120°F) TO ±1°C (±2°F)
- EXPECTED TO BE OPERATIONAL IN MAY, 2001

DIAGRAM OF ENVIRONMENTAL CHAMBER AND TEMPERATURE-CONTROLLED ENCLOSURE



DEVELOPMENT AND APPLICATION OF DIRECT REACTIVITY SCREENING METHOD

DIRECT REACTIVITY

- THIS IS THE RATE A VOC REACTS AND OXIDIZES NO, WHICH IS THE PROCESS THAT FORMS O₃
- THIS IS ONE OF SEVERAL FACTORS AFFECTING REACTIVITY. THIS MAY BE MORE IMPORTANT IN THE ATMOSPHERE THAN IN CHAMBER STUDIES.
- MEASURES OF DIRECT REACTIVITY WILL GIVE MORE COMPLETE MECHANISM EVALUATION AND CAN TEST UNCERTAIN REACTIVITY ESTIMATES.

OBJECTIVES

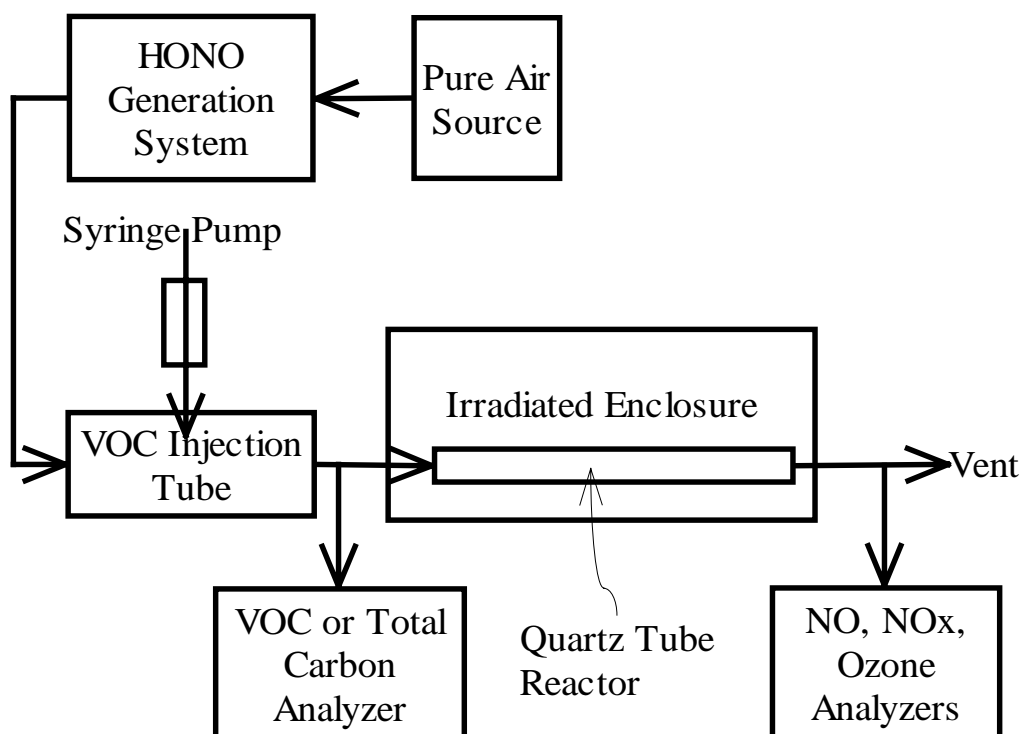
- DEVELOP A MEANS TO MEASURE DIRECT REACTIVITY THAT IS LESS EXPENSIVE AND AMBIGUOUS THAN CHAMBER STUDIES.
- ADAPT THE METHOD SO IT CAN BE USED FOR LOW VOLATILITY COMPOUNDS AND FOR COMPLEX MIXTURES.
- APPLY THE METHOD TO TEST MECHANISMS OF SELECTED VOCs
- APPLY METHOD TO TEST REACTIVITY ESTIMATION METHODS FOR PETROLEUM DISTILLATES
- APPLY METHOD TO TEST REACTIVITY ESTIMATION METHODS FOR WHOLE SOLVENTS OR COATINGS?

PRINCIPLE OF DIRECT REACTIVITY MEASUREMENT METHOD

PHOTOLYSIS OF NITROUS ACID (HONO) IN THE PRESENCE OF ADDED VOC IN AIR

- IN ABSENCE OF ADDED VOC, HONO/AIR PHOTOLYSIS FORMS MAINLY NO AND NO₂
- ADDED VOC CAUSES NO TO DECREASE AND O₃ TO BE FORMED IF ALL THE NO IS CONSUMED
- CHANGE IN [O₃]-[NO] CAUSED BY ADDING VOC IS THE MEASURE OF DIRECT REACTIVITY

FLOW SYSTEM EMPLOYED



CURRENT STATUS OF WORK ON DIRECT REACTIVITY MEASUREMENT METHOD

METHOD BEING DEVELOPED FOR AN EXISTING CARB CONTRACT THAT ENDS IN 12/2001

METHOD TESTED SUCCESSFULLY WITH N-ALKANES THROUGH N-C16.

NEED TO TEST REPRODUCIBILITY OF THE METHOD AND APPLICABILITY TO OTHER COMPOUNDS.

SYRINGE PUMP INJECTION METHOD MAY PERMIT EVALUATION OF COMPLEX MIXTURES AND LOW VOLATILITY MATERIALS

NEED TO DEVELOP TOTAL CARBON ANALYSIS METHOD FOR COMPLEX MIXTURES AND LOW VOLATILITY MATERIALS

WORK FOR PROPOSED PROGRAM

AMOUNT OF DEVELOPMENT WORK REQUIRED ON COATINGS PROGRAM WILL DEPEND ON STATE OF PROGRESS WHEN EXISTING CONTRACT ENDS.

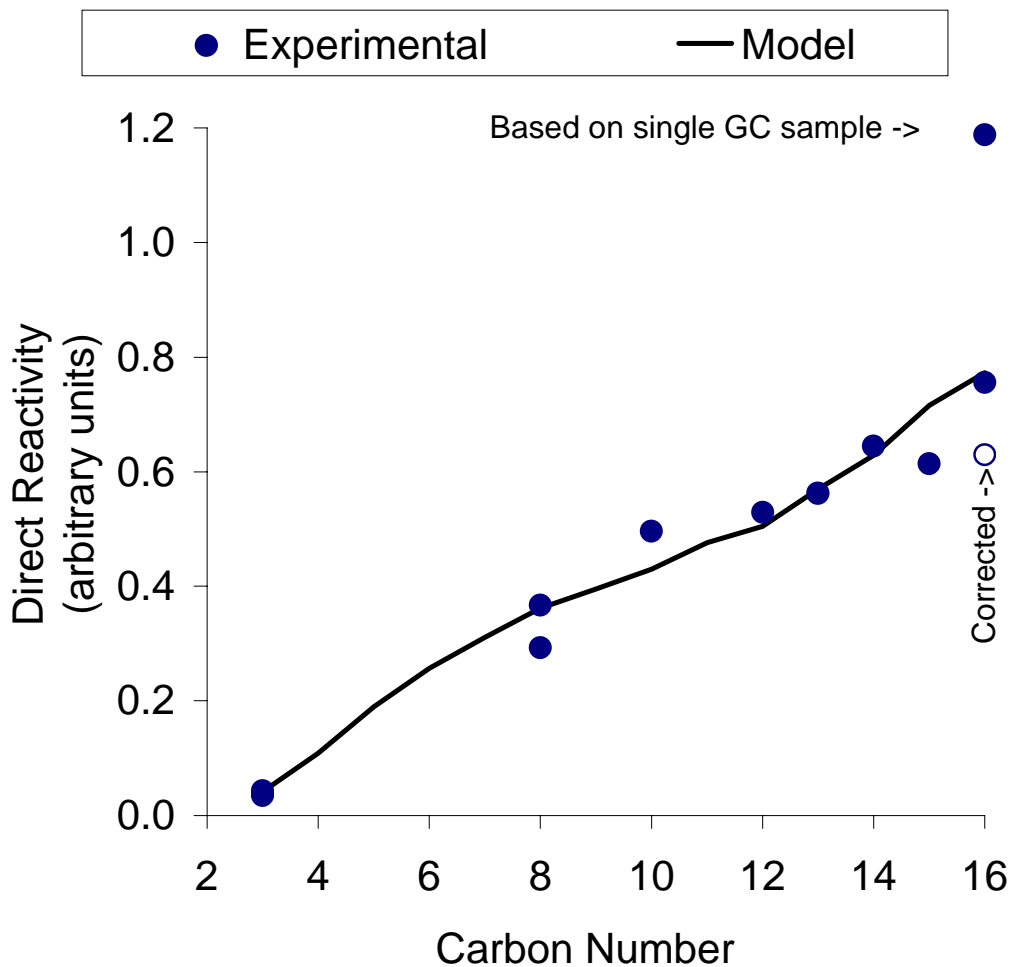
APPLICATION TO TEXANOL® AND OTHER LOW VOLATILITY COATINGS MATERIALS

APPLICATION TO PETROLEUM DISTILLATES

APPLICATION TO WHOLE COATINGS EMISSIONS MAY BE POSSIBLE BUT BEYOND SCOPE OF PROJECT

CURRENT STATUS:

DIRECT REACTIVITY MEASUREMENT RESULTS FOR NORMAL ALKANES



REACTIVITY QUANTIFICATION FOR PETROLEUM DISTILLATES

CURRENT STATUS

- PETROLEUM DISTILLATES ARE MAJOR COMPONENTS OF SOLVENT-BASED COATINGS
- FOLLOWING COMPOSITIONAL INFORMATION IS REQUIRED FOR REACTIVITY ESTIMATES:
 - ALKANE AND AROMATIC CONTENT
 - CARBON NUMBER DISTRIBUTION
 - NORMAL, BRANCHED AND CYCLIC ALKANE DISTRIBUTION
 - AROMATIC SPECIATION, IF APPLICABLE
- ESTIMATES CONSISTENT WITH CHAMBER DATA FOR THE FEW MIXTURES THAT WERE STUDIED. BUT **REPRESENTATIVENESS IS UNCERTAIN.**
- NECESSARY COMPOSITIONAL INFORMATION DIFFICULT TO OBTAIN AND OFTEN PROPRIETARY
- CARB STAFF DEVELOPED PROTOCOL FOR MAKING MIR ESTIMATES BASED ON LIMITED DATA
 - NOT EXPERIMENTALLY EVALUATED
 - BASED ON PROPRIETARY DATA
 - NO PROVISION FOR CHANGING OR UPDATING REACTIVITY SCALE.
 - NO PROVISION FOR COMPOSITIONAL UNCERTAINTY ANALYSIS.

REACTIVITY QUANTIFICATION FOR PETROLEUM DISTILLATES

PROPOSED PROJECT

- DEVELOP SPREADSHEET-BASED METHOD TO ESTIMATE REACTIVITY AND COMPOSITIONAL UNCERTAINTY FOR PETROLEUM DISTILLATES
 - ESTIMATES IN TERMS OF COMPOSITION SO ANY REACTIVITY SCALE CAN BE USED
 - ESTIMATES WHEN DATA LIMITED BASED ON AVAILABLE COMPOSITION DATA
 - UNCERTAINTY ESTIMATES WILL BE A FUNCTION OF AMOUNT OF INFORMATION
 - SPREADSHEET DOCUMENTED FOR USE BY INDUSTRY AND REGULATORS
- EVALUATE METHOD
 - COMPARING ESTIMATES WITH DETAILED COMPOSITION DATA WHERE AVAILABLE
 - COMPARING PREDICTED VS MEASURED DIRECT REACTIVITIES
 - COMPARING PREDICTIONS WITH CHAMBER DATA WHERE DATA AVAILABLE
- **INDUSTRY PARTICIPATION IS ESSENTIAL** TO OBTAIN NECESSARY INFORMATION
 - NEED TO DEVELOP PROCEDURES TO ALLOW USE OF PROPRIETARY DATA TO DEVELOP AND EVALUATE METHOD

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 MECHANISM AND METHODS USED TO CALCULATE REACTIVITY
- LINKS TO OTHER REPORTS AND PRESENTATIONS CONCERNING W.P.L. CARTER'S RESEARCH

CALIFORNIA ARB'S PROPOSED AEROSOL COATINGS REGULATION

<http://arb.ca.gov/regact/conspro/aerocoat/aerocoat.htm>

- REGULATION AND RULEMAKING INFORMATION AND TECHNICAL SUPPORT DOCUMENTS