UNCERTAINTIES AND RESEARCH NEEDS IN QUANTIFYING VOC REACTIVITY FOR STATIONARY SOURCE EMISSION CONTROLS

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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.

SOUTHERN CALIFORNIA HAS THE WORST OZONE PROBLEM IN THE UNITED STATES. BUT MANY OTHER URBAN AREAS ALSO 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 POLLUTANT OF CONCERN IN PHOTOCHEMICAL 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.

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 NECESSARY TO DETERMINE THE MOST COST EFFECTIVE OZONE CONTROL STRATEGY.

CHEMISTRY OF O_3 IN PHOTOCHEMICAL SMOG

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

$$NO_2 + h\nu \xrightarrow{k_1} NO + O \qquad O + O_2 \xrightarrow{M} O_3$$

OR OVERALL: $NO_2 + h\nu \rightarrow NO + O_3$

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

$$NO + O_3 \xrightarrow{k_2} NO_2 + O_2$$

THESE PROCESSES RESULT IN A "PHOTOSTATIONARY STATE" BEING ESTABLISHED, WHERE O_3 IS PROPORTIONAL TO THE NO_2 TO NO RATIO

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

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 (VOCs) REACT THEY FORM RADICALS WHICH CONVERT NO TO NO_2

FOR EXAMPLE, **ETHANE**:

$$CH_3CH_3 + OH \longrightarrow CH_3CH_2\cdot + H_2O$$

$$CH_3CH_2\cdot + O_2 \longrightarrow CH_3CH_2OO\cdot \qquad \text{(FAST)}$$

$$CH_3CH_2OO\cdot + NO \longrightarrow CH_3CH_2O\cdot + NO_2$$

$$CH_3CH_2O\cdot + O_2 \longrightarrow CH_3CHO + HO_2\cdot$$

$$HO_2\cdot + NO \longrightarrow OH + NO_2$$

OVERALL PROCESS:

$$CH_3CH_3 + 2\ O_2 + 2\ NO \xrightarrow{OH} CH_3CHO + 2\ NO_2 + H_2O$$

COMBINED WITH:

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

YIELDS:

$$CH_3CH_3 + 2\ O_2 + h\nu \xrightarrow{NO_x\ OH} CH_3CHO + H_2O + 2\ O_3$$

OZONE FORMATION CONTINUES UNTIL NO_x IS REMOVED

MAJOR NO_x SINKS:

- $OH + NO_2 \longrightarrow HNO_3$

- $NO_2 + O_3 \xrightarrow{NO_2} NO_3 \xrightleftharpoons{H_2O} N_2O_5 \longrightarrow 2\ HNO_3$ (NIGHTTIME SINK)

- ALDEHYDES $\xrightarrow{OH}\ \xrightarrow{O_2}$ RCO-OO. $\xrightarrow{NO_2}$ $RCO\text{-}OONO_2$ (PANs)

- AROMATICS $\xrightarrow{OH}\ \xrightarrow{O_2}$ PHENOLS $\xrightarrow{NO_3,\ NO_2}$ NITROPHENOLS

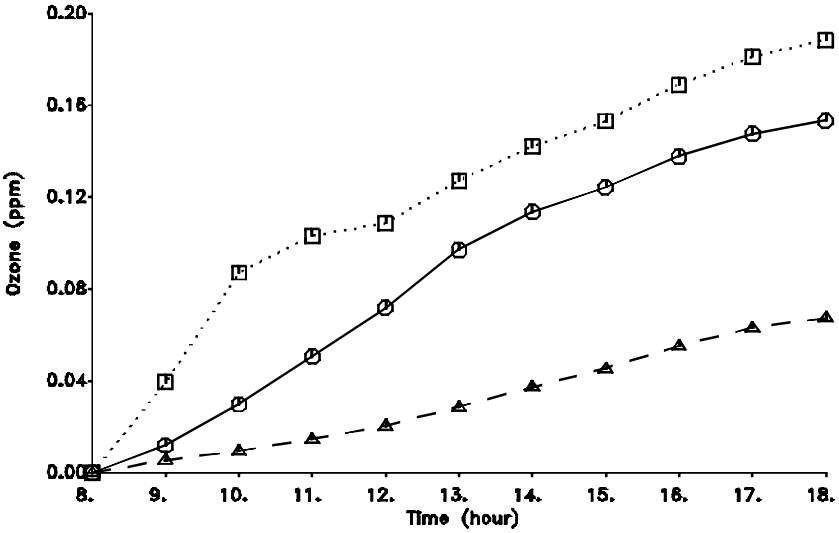
- ALKANES $\xrightarrow{OH}\ \xrightarrow{O_2}$ $RO_2 \xrightarrow{NO} RONO_3$

NO_x IS REMOVED IN THE ATMOSPHERE MORE RAPIDLY THAN VOCs.

THEREFORE, NO_x AVAILABILITY ULTIMATELY LIMITS THE AMOUNT OF O_3 WHICH CAN BE FORMED.

EFFECT OF VOCs AND NO_x ON O_3 FORMATION

VARY VOC EMISSIONS

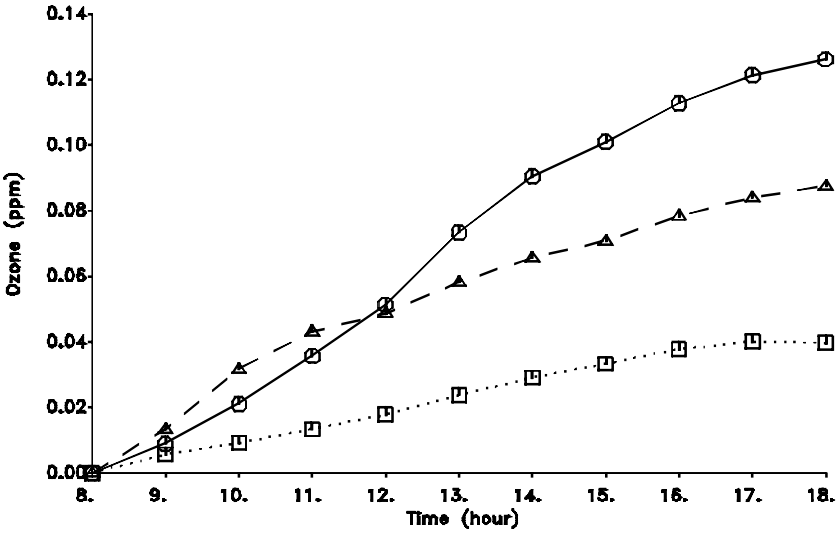


HIGH (x 3)

MEDIUM

LOW (x 1/3)

VARY NO_x EMISSIONS



MEDIUM

LOW (x 1/3)

HIGH (x 3)

IMPLICATIONS OF ATMOSPHERIC CHEMISTRY FOR OZONE CONTROL STRATEGIES

NO_x CONTROL:

- NO_x IS REQUIRED FOR OZONE FORMATION. IF NO_x WERE ABSENT, NO O_3 WOULD BE FORMED. WHEN NO_x IS CONSUMED, OZONE FORMATION ENDS.

- NO_x IS REMOVED MORE RAPIDLY THAN VOCs. THEREFORE, AVAILABILITY OF NO_x LIMITS HOW MUCH OZONE CAN ULTIMATELY BE FORMED.

- BUT NO_x ALSO REDUCES THE RATE OF OZONE FORMATION. THIS IS BECAUSE:
    - NO REACTS WITH O_3
    - NO_2 REACTS WITH RADICALS. LOWER RADICALS CAUSE LOWER VOC CONSUMPTION RATES

THEREFORE, NO_x CONTROL HAS THE GREATEST BENEFIT ON OZONE DOWNWIND, BUT CAN MAKE O_3 WORSE NEAR THE EMISSIONS SOURCE AREAS.

IMPLICATIONS OF ATMOSPHERIC CHEMISTRY FOR OZONE CONTROL STRATEGIES

VOC CONTROL:

- REACTIVE ORGANICS ENHANCE THE RATES OF OZONE FORMATION FROM NO_x. IF VOCs WERE ABSENT, OZONE WOULD BE LOW.

- VOC CONTROL HAS THE GREATEST EFFECT ON OZONE NEAR THE SOURCE AREAS.

- VOC CONTROL IS LESS EFFECTIVE IN AREAS WHERE OZONE IS NO_x-LIMITED. THIS INCLUDES DOWNWIND AND RURAL AREAS.

- NATURAL EMISSIONS OF VOCs ARE IMPORTANT IN MANY AREAS. THIS LIMITS MAXIMUM EXTENT OF VOC CONTROLS.

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

AIRSHED MODELS ARE REQUIRED FOR QUANTITATIVE PREDICTIONS OF EFFECTS OF VOC AND NO_x CONTROL ON OZONE.

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 O_3 IS FORMED DIRECTLY FROM ITS REACTIONS AND THOSE OF ITS PRODUCTS.
- WHETHER IT ENHANCES OR INHIBITS RADICAL. THIS AFFECTS HOW FAST O_3 IS FORMED FROM ALL VOCs.
- WHETHER IT ENHANCES RATES NO_x REMOVAL. THIS AFFECTS ULTIMATE O_3 YIELDS BECAUSE NO_x IS REQUIRED FOR O_3 TO BE FORMED.

A VOC's EFFECT ON O_3 ALSO DEPENDS ON THE NATURE OF THE ENVIRONMENT WHERE THE VOC IS REACTING.

QUANTIFICATION OF REACTIVITY

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

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

THIS CAN BE MEASURED EXPERIMENTALLY IN SMOG CHAMBERS OR CALCULATED FOR POLLUTION EPISODES USING AIRSHED MODELS.

THIS DEPENDS ON THE CONDITIONS OF THE EPISODE (OR THE EXPERIMENT) AS WELL AS ON THE VOC.

ENVIRONMENTAL FACTORS WHICH AFFECT REACTIVITY

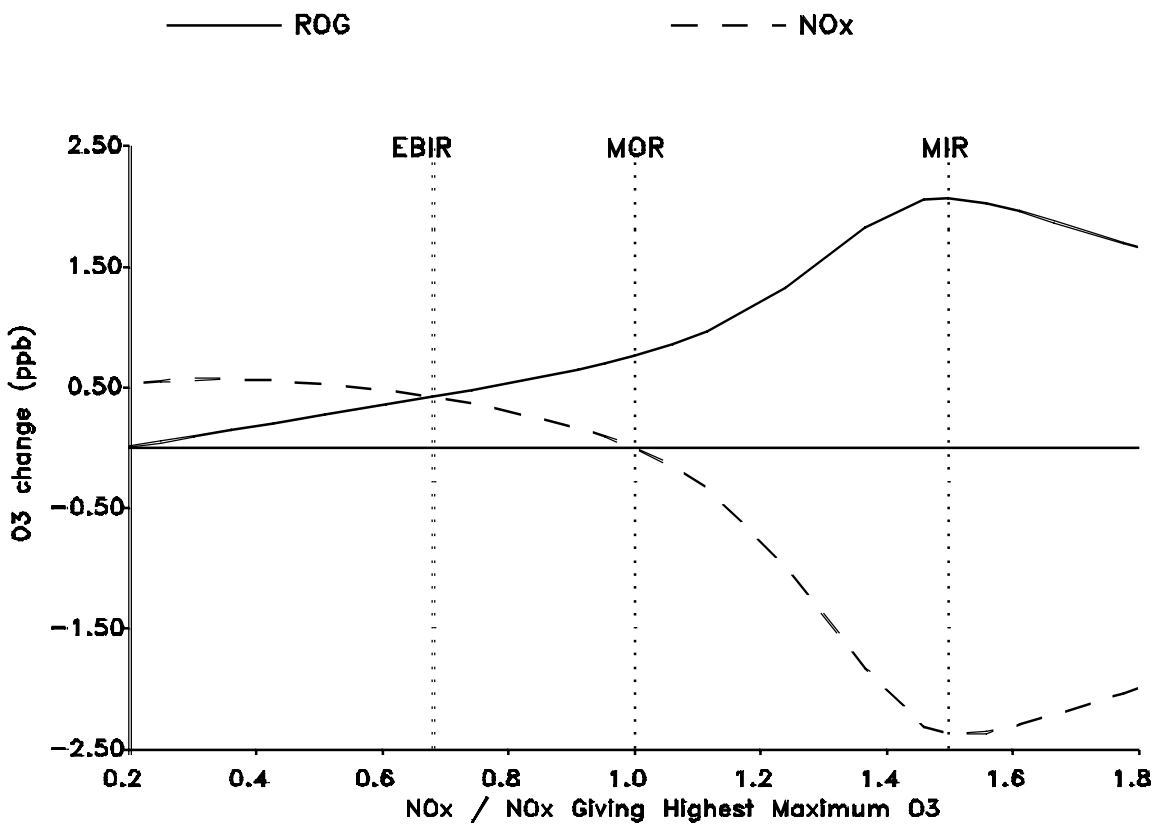
AVAILABILITY OF NO_x (ROG/NO_x RATIO) IS MOST IMPORTANT SINGLE FACTOR

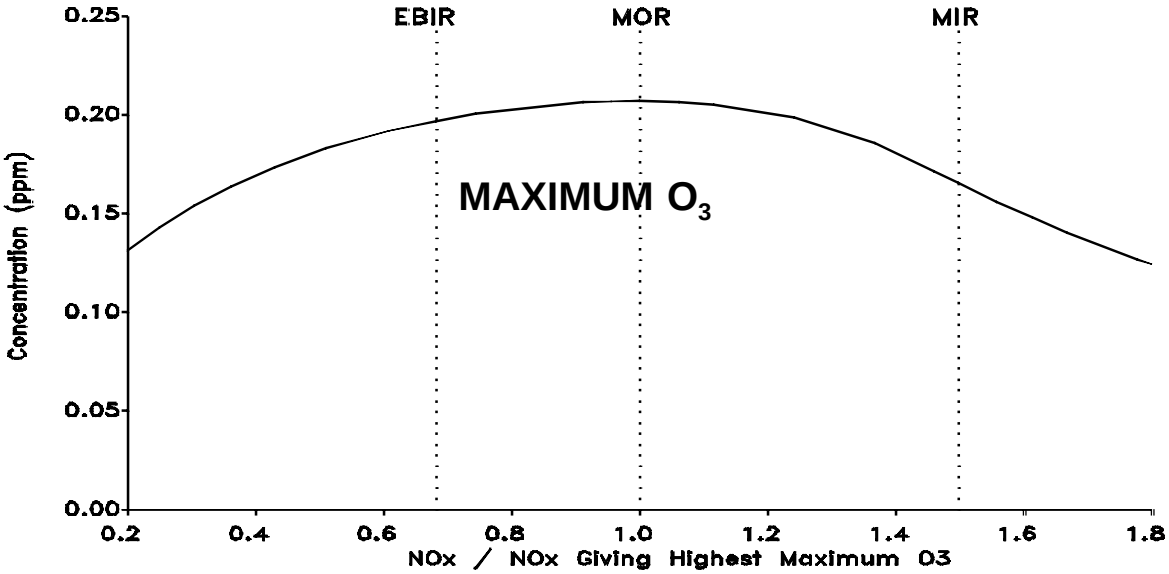
- VOCs FORM THE MOST OZONE (REACTIVITIES ARE THE HIGHEST) WHEN NO_x IS ABUNDANT
- VOCs HAVE THE SMALLEST EFFECTS ON OZONE (REACTIVITIES LOWEST) WHEN NO_x IS LOW.

NATURE OF OTHER VOCs PRESENT AFFECT REACTIVITIES OF VOCs WITH STRONG RADICAL SOURCES OR SINKS.

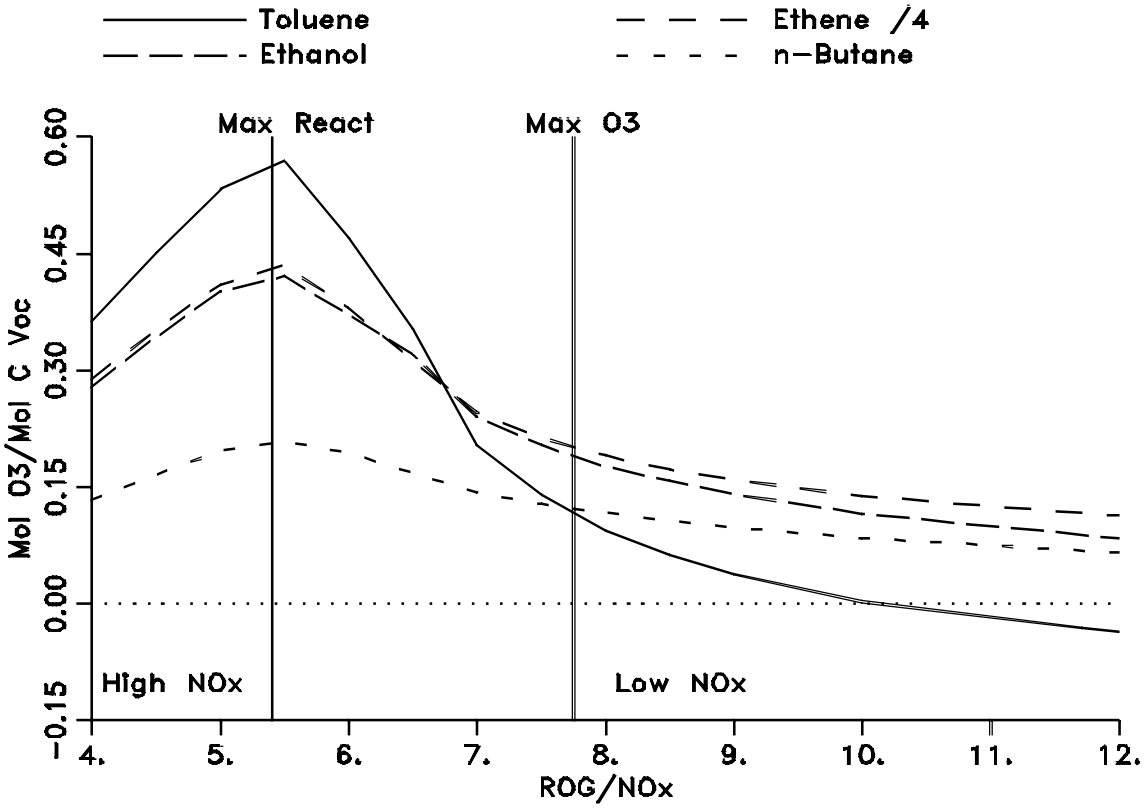
OTHER FACTORS (E.G., AMOUNT OF SUNLIGHT AND TEMPERATURE) AFFECT DEPENDENCE OF REACTIVITY ON ROG/NO_x RATIO.)

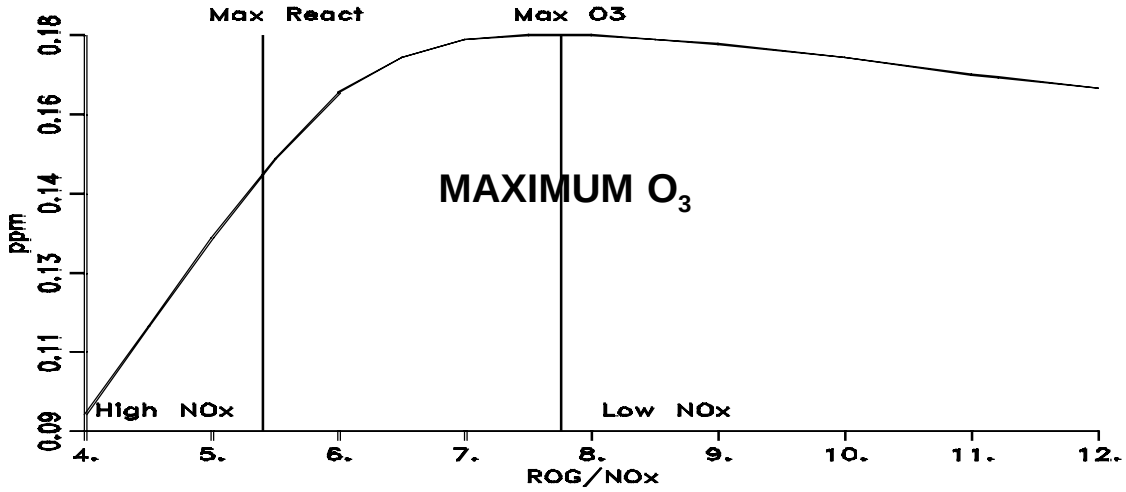
O_3 CHANGES CAUSED BY 1% CHANGES IN ROG OR NO_x





DEPENDENCE OF INCREMENTAL REACTIVITIES ON ROG/NO_x





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

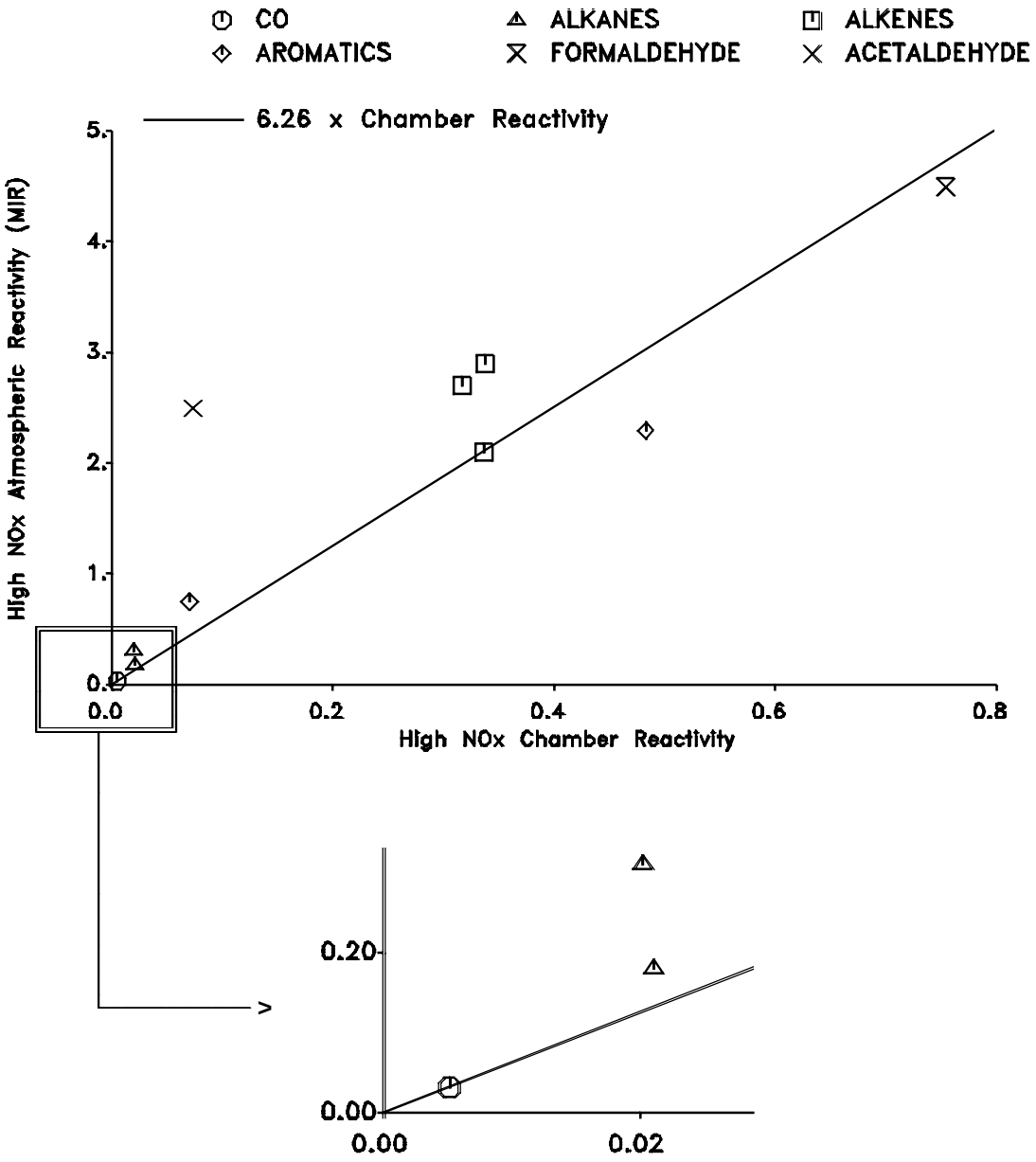
- CHEMICAL MECHANISMS FOR THE VOC's ATMOSPHERIC REACTIONS

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

REACTIVITY MEASUREMENTS IN ENVIRONMENTAL CHAMBERS ARE NECESSARY TO TEST THE RELIABILITY OF A MECHANISM TO PREDICT ATMOSPHERIC REACTIVITY.

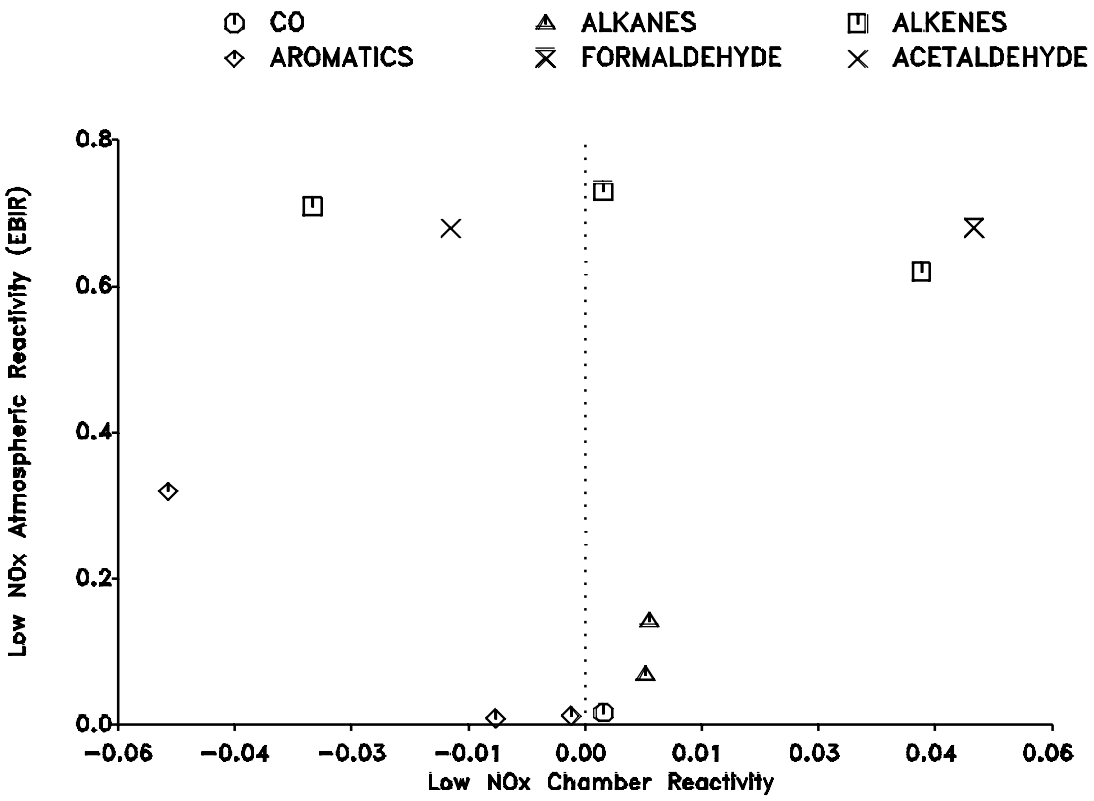
CORRESPONDENCE BETWEEN ENVIRONMENTAL CHAMBER AND CALCULATED ATMOSPHERIC REACTIVITIES.

HIGH NO_x CONDITIONS

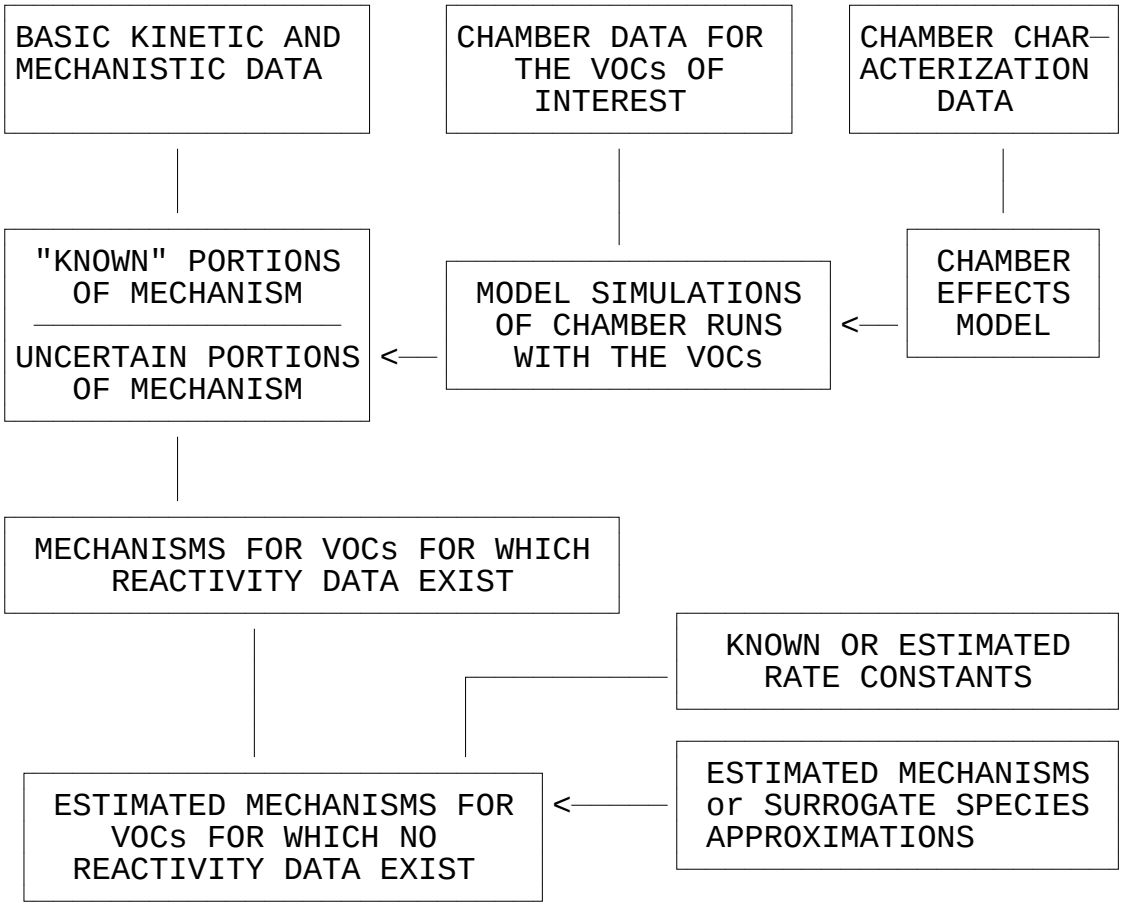


CORRESPONDENCE BETWEEN ENVIRONMENTAL CHAMBER AND CALCULATED ATMOSPHERIC REACTIVITIES.

LOW NO_x CONDITIONS



DEVELOPMENT OF A CHEMICAL MECHANISM TO CALCULATE VOC REACTIVITIES



TYPES OF CHAMBER EXPERIMENTS USED TO TEST MECHANISMS

SINGLE VOC-NO_x-AIR RUNS:

- MOST STRAIGHTFORWARD TEST OF A VOC's MECHANISM
- USED FOR MECHANISM DEVELOPMENT
- NOT USEFUL FOR SOME VOCs (E.G. ALKANES).
- NOT A "REALISTIC" ENVIRONMENT

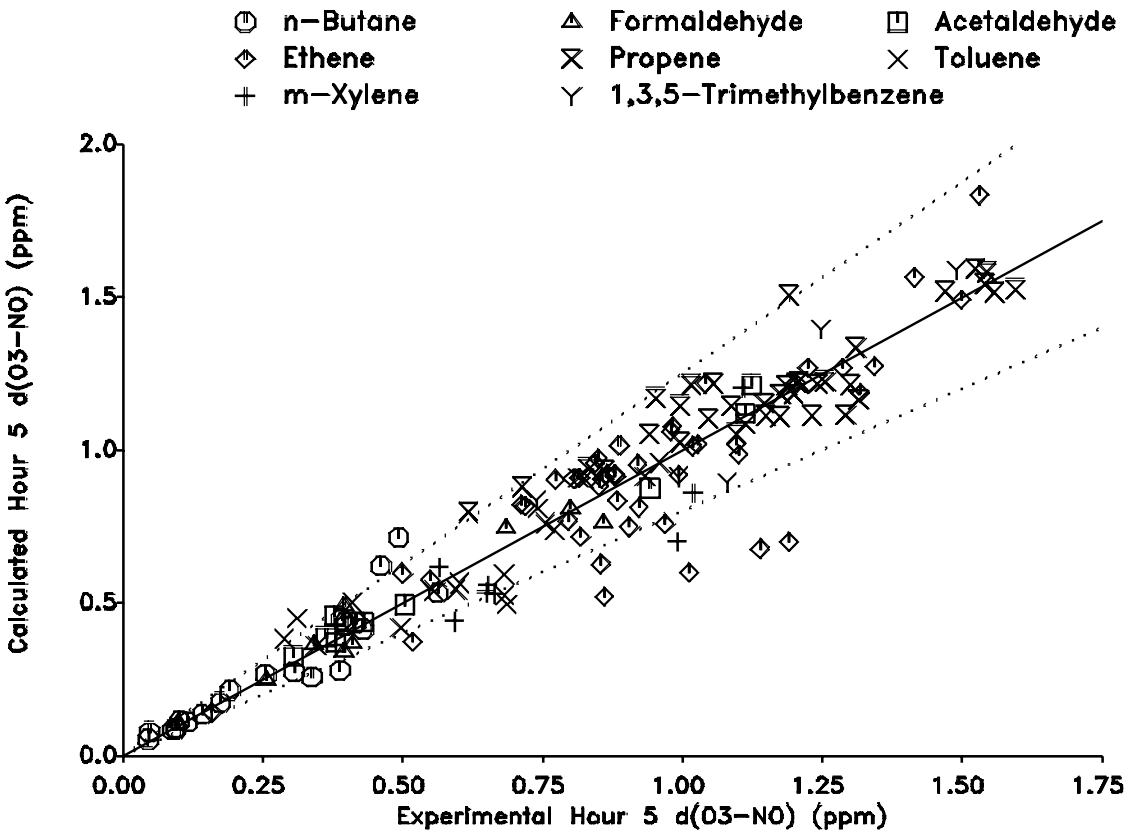
COMPLEX MIXTURE-NO_x-AIR RUNS:

- TESTS A MECHANISM'S ABILITY TO SIMULATE O_3 FORMATION UNDER REALISTIC CONDITIONS
- NOT USEFUL FOR MECHANISM DEVELOPMENT

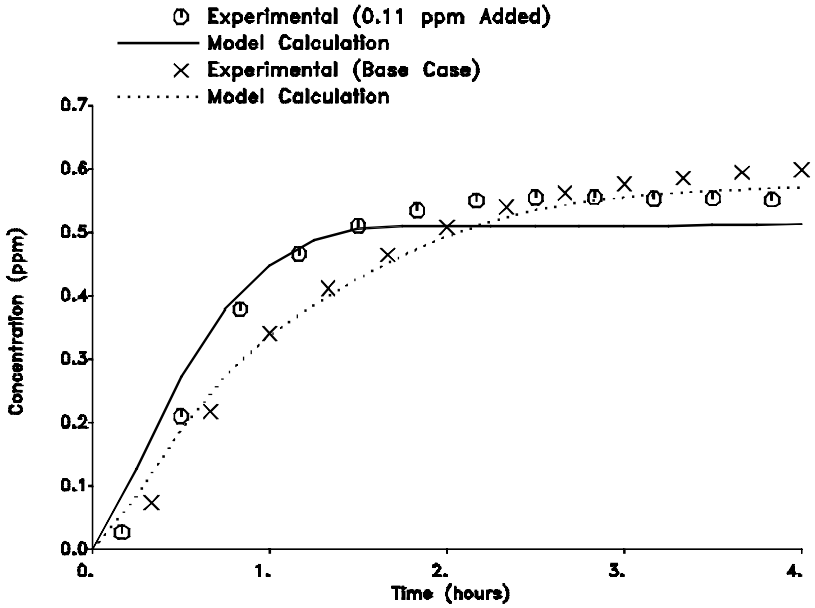
REACTIVITY EXPERIMENTS (MIXTURE-NO_x-AIR COMBINED WITH MIXTURE-NO_x-AIR RUNS WITH TEST VOC ADDED):

- BEST TEST OF MECHANISM'S ABILITY TO PREDICT INCREMENTAL REACTIVITY
- CAN TEST MECHANISMS OF SINGLE VOCs UNDER REALISTIC CONDITIONS
- NOT SAME AS ATMOSPHERIC REACTIVITY.

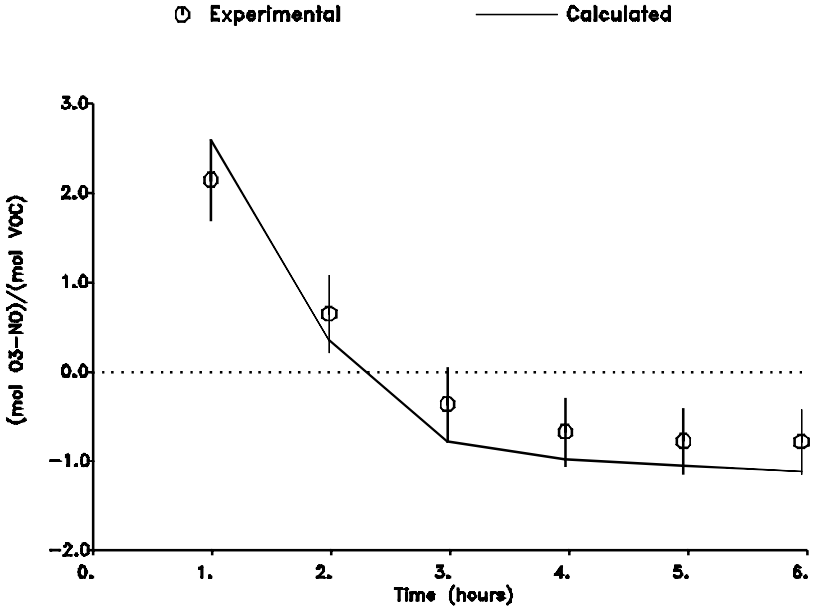
PLOT OF EXPERIMENTAL VS CALCULATED OZONE FORMED + NO OXIDIZED IN SELECTED SINGLE COMPOUND - NO_x EXPERIMENTS



EXAMPLE OF AN INCREMENTAL REACTIVITY EXPERIMENT: EFFECT OF M-XYLENE UNDER HIGH ROG/NO_x CONDITIONS



$\Delta([O_3]-[NO])$ vs TIME



{CHANGE IN $\Delta([O_3]-[NO])$} / (XYLENE REACTED) vs TIME

VOC REACTIVITY
AND OZONE CONTROL STRATEGIES

CONTROL STRATEGIES AIMED AT REDUCING EMISSIONS OF MORE REACTIVE VOC'S WILL BE MORE EFFECTIVE THAN THOSE REDUCING ALL VOC'S EQUALLY.

IF A VOC IS SUFFICIENTLY UNREACTIVE TOWARDS OZONE FORMATION, IT DOES NOT MAKE SENSE TO REGULATE IT TO REDUCE OZONE.

REPLACING REACTIVE VOC EMISSIONS WITH EMISSIONS OF VOC'S WHICH ARE LESS REACTIVE IS PROPOSED AS A VOC CONTROL STRATEGY. EXAMPLES INCLUDE:

- ALTERNATIVE FUELS
- SOLVENT SUBSTITUTION
- REFORMULATION OF VOCs IN CONSUMER PRODUCTS

A GENERAL REACTIVITY RANKING SCALE WOULD AID IN DEVELOPING SUCH CONTROL STRATEGIES.

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

REACTIVITY SCALES

DEFINITION

A REACTIVITY SCALE IS ANY SCHEME WHICH ASSIGNS NUMBERS TO VOCs WHICH ARE INTENDED TO HAVE SOME RELATIONSHIP TO THEIR LIKELY RELATIVE O_3 IMPACTS.

EXAMPLES

K^{OH} SCALE — RATE CONSTANT FOR REACTION OF THE VOC WITH OH RADICALS.

- PREDICTS HOW FAST MOST VOCs REACT.
- GOOD PREDICTOR OF UPPER LIMIT RELATIVE O_3 IMPACTS FOR SLOWLY REACTING VOCs.
- VERY POOR PREDICTOR OF RELATIVE O_3 IMPACTS FOR HIGHLY REACTIVE VOCs.

INCREMENTAL REACTIVITY SCALES — SET OF INCREMENTAL REACTIVITIES CALCULATED IN A GIVEN WAY.

- DEPENDS ON TYPE OF SCENARIO
- DEPENDS ON HOW O_3 IMPACT QUANTIFIED (PEAK, INTEGRATED, EXPOSURE)
- MIR (BASED ON PEAK O_3 IN HIGH NO_x SCENARIOS) IS ONLY ONE EXAMPLE OF SUCH A 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 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 CONDITIONS WHERE VOC CONTROL IS THE MOST EFFECTIVE OZONE CONTROL STRATEGY.
- 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

REACTIVITY ADJUSTMENT FACTORS (RAFs) ARE USED IN EXHAUST EMISSIONS STANDARDS IN THE "CLEAN FUELS/LOW EMISSIONS VEHICLE" REGULATIONS

$$\text{ADJUSTED EMISSIONS (g/mi)} = \textbf{RAF} \times \text{ACTUAL EMISSIONS (g/mi)}$$

WHERE

$$\textbf{RAF} = \frac{\text{MAXIMUM INCREMENTAL REACTIVITY (}\textbf{MIR}\text{) OF EXHAUST (g } O_3\text{/g VOC)}}{\textbf{MIR}\text{ OF STANDARD EXHAUST (g } O_3\text{/g VOC)}}$$

USE OF REACTIVITY ADJUSTMENTS IS BEING CONSIDERED FOR POSSIBLE USE IN CONSUMER PRODUCT REGULATIONS

EXAMPLES OF REGULATORY POLICIES REGARDING VOC REACTIVITY
(CONTINUED)

U.S. EPA

PRESENT POLICY: A VOC IS EITHER **REACTIVE** OR **EXEMPT**. ISSUE IS WHAT TO EXEMPT.

- CANDIDATES FOR EXEMPTION EXAMINED ON A CASE BY CASE BASIS.
- ETHANE REACTIVITY IS USED AS THE INFORMAL STANDARD
- INCREMENTAL REACTIVITY IS NOW ONE OF THE FACTORS CONSIDERED
- EPA HAS EXEMPTED ACETONE IN PART BASED ON ITS CALCULATED INCREMENTAL REACTIVITY.

CLEAN AIR ACT REQUIRES THE EPA TO CONSIDER VOC REACTIVITY IN CONTROLS OF CONSUMER PRODUCTS.

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.

CHEMICAL MECHANISM UNCERTAINTY

- "BASE" MECHANISM UNCERTAINTIES CAUSE UNCERTAINTY FOR EVEN WELL-STUDIED VOCs. MILFORD ET AL. ESTIMATES UNCERTAINTIES OF:
    - ±30-50% FOR ABSOLUTE MIRs OF SINGLE VOCs
    - ±20-40% FOR RELATIVE MIRs OF SINGLE VOCs
    - ±15% FOR RELATIVE MIRs (RAFs) OF EXHAUSTS
- **UNCERTAINTIES ARE MUCH GREATER FOR VOCs WITH NO DATA TO VERIFY THEIR MECHANISMS.**

RELATIVE UNCERTAINTIES IN REACTIVITY ESTIMATES FOR VARIOUS TYPES OF COMPOUNDS
(AS OF FEBRUARY 1996)

LOWEST UNCERTAINTY (MOST REACTIVITY DATA)

C_1-C_8 ALKANES	C_1-C_2 ALDEHYDES
C_2-C_4 ALKENES *	MTBE
C_1-C_2 ALCOHOLS	ACETONE
METHYLBENZENES *	ISOPRENE *

* UNCERTAIN MECHANISM FITS CHAMBER DATA

MORE UNCERTAIN, BUT SOME DATA ARE AVAILABLE, OR CAN BE ESTIMATED FROM OTHER COMPOUNDS:

C_9-C_{15} N-ALKANES	MEK
C_{10+} ALKYLBENZENES	DIMETHYL ETHER
NAPHTHALENES	ISOPROPYL ALCOHOL
C_5-C_6 ALKENES	ETHOXYETHANOL
PROPIONALDEHYDE	CARBITOL
TERPENES	

NO DATA AVAILABLE TO VERIFY ESTIMATES:

C_7+ ALKENES	GLYCOLS
ESTERS	MOST ETHERS

C_{16+} NORMAL AND C_{8+} BRANCHED ALKANES
OTHER SATURATED O-CONTAINING COMPOUNDS

MECHANISM TOO UNCERTAIN TO ESTIMATE

COMPOUNDS WITH FUNCTIONAL GROUPS OTHER THAN THOSE IN THE COMPOUNDS LISTED ABOVE.

WHAT IS AN "ACCEPTABLE" LEVEL OF UNCERTAINTY IN QUANTITATIVE REACTIVITY RANKINGS FOR REGULATIONS?

A MINIMUM UNCERTAINTY OF ~30% MUST BE ACCEPTED.

ALL THAT IS REQUIRED FOR A EFFECTIVE REACTIVITY-BASED REGULATION IS THAT THE SCALE PREDICT THE CORRECT ORDERING MORE OFTEN THAN NOT.

BUT LOWER LEVELS OF UNCERTAINTY WOULD INCREASE REGULATORY *EFFECTIVENESS* AND *FAIRNESS*.

THE MINIMUM UNCERTAINTY SHOULD NOT BE SO LOW THAT IT CANNOT PRACTICALLY BE ACHIEVED.

EFFECTS OF UNCERTAINTIES ARE LESS WHEN RANKING COMPLEX MIXTURES (E.G, EXHAUST RAFs).

POLICY ISSUES THAT MUST BE ADDRESSED

- WHAT IS MAXIMUM ALLOWABLE UNCERTAINTY?
- HOW TO FAIRLY REGULATE COMPOUNDS WITH WIDELY DIFFERING UNCERTAINTIES.
- REGULATIONS USING HIGH REACTIVITY ESTIMATES FOR UNCERTAIN VOCs WILL GIVE INCENTIVES TO REDUCE UNCERTAINTIES.
- HOW TO DEAL WITH CHANGES IN KNOWLEDGE ABOUT A VOC’s REACTIVITY.

PROCEDURE FOR REDUCING UNCERTAINTY IN REACTIVITY ESTIMATES

REACTIVITY IS ESTIMATED USING MODELS. THEIR PREDICTIONS ARE UNRELIABLE IF THE VOC's MECHANISM HAS NOT BEEN EXPERIMENTALLY VERIFIED.

BASIC KINETIC AND MECHANISTIC DATA ARE USED FOR *DEVELOPING* MECHANISMS. THEY CANNOT *VERIFY* THEM.

MINIMUM MECHANISTIC INFORMATION NEEDED:

- STRUCTURE OF THE COMPOUND
- RATE CONSTANTS FOR INITIAL ATMOSPHERIC REACTIONS (OH, O_3, $h\nu$)

MINIMUM ENVIRONMENTAL CHAMBER DATA NEEDED TO ASSESS IF A MECHANISM CAN PREDICT REACTIVITY:

- DATA ON EFFECTS OF THE VOC ON O_3 IN MAXIMUM REACTIVITY EXPERIMENTS WITH SIMPLE MIXTURES. (MOST SENSITIVE TEST OF THE MECHANISMS.)
- DATA ON EFFECTS OF VOC IN EXPERIMENTS USING REALISTIC ATMOSPHERIC MIXTURES AND VARYING NO_x LEVELS.
- IF COMPOUND PHOTOLYZES, DATA WITH VARYING TYPES OF LIGHT SOURCES.

CHEMICAL MECHANISMS MUST BE DEVELOPED TO BE CONSISTENT WITH THE CHAMBER DATA. UNCERTAIN PORTIONS MUST BE ADJUSTED IF NEEDED.