#### QUANTIFICATION OF OZONE IMPACTS OF VOLATILE ORGANIC COMPOUNDS

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Ozone in photochemical smog is formed from the gas-phase reactions of oxides of nitrogen  $(NO_x)$  and volatile organic compounds (VOCs). VOCs differ in their effects on ozone formation, and methods for quantifying these differences would aid in the development of cost-effective ozone control strategies. In this presentation, the role of VOCs and  $NO_x$  in ozone formation and the process of developing and evaluating chemical mechanisms for simulating these processes in the atmosphere will be summarized. Following that, the problems and recent progress in developing quantitative reactivity scales measuring ozone impacts of VOCs will be discussed.

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### QUANTIFICATION OF OZONE REACTIVITIES OF VOLATILE ORGANIC COMPOUNDS

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### THE PHOTOCHEMICAL OZONE PROBLEM

OZONE IN PHOTOCHEMICAL SMOG IS FORMED FROM REACTIONS OF VOLATILE ORGANICS COMPOUNDS (VOCs) AND OXIDES OF NITROGEN (NO<sub>x</sub>) IN SUNLIGHT.

LOS ANGELES HAS THE WORST OZONE PROBLEM IN THE UNITED STATES. BUT MANY OTHER URBAN AREAS ALSO EXCEED OZONE AIR QUALITY STANDARDS.

CONTROL OF BOTH VOC AND NO $_{\rm x}$  IS NEEDED TO REDUCE OZONE. BUT ALL THE "EASY" CONTROLS HAVE BEEN IMPLEMENTED. ADDITIONAL CONTROLS WILL BE COSTLY.

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).

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

### FORMATION OF O<sub>3</sub> IN PHOTOCHEMICAL SMOG

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

$$NO_2 + hv \stackrel{k_1}{\rightarrow} NO + O \qquad O + O_2 \stackrel{M}{\rightarrow} O_3$$

BUT THIS IS REVERSED BY THE RAPID REACTION OF  $\mathrm{O}_{3}$  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<sub>2</sub> 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<sub>2</sub>, 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 $\mathrm{NO}_2$

FOR EXAMPLE, ETHANE:

$$\begin{array}{rcl} & \operatorname{CH}_{3}\operatorname{CH}_{3} & + & \operatorname{OH} & - & \to & \operatorname{CH}_{3}\operatorname{CH}_{2}^{\circ} & + & \operatorname{H}_{2}\operatorname{O} \\ & & \operatorname{CH}_{3}\operatorname{CH}_{2}^{\circ} & + & \operatorname{O}_{2}^{\circ} & - & \to & \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{OO}^{\circ} & & (\mathsf{FAST}) \\ & & \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{OO}^{\circ} & + & \operatorname{NO}_{2}^{\circ} & \stackrel{\leftarrow}{=} & \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{OONO}_{2} & & (\mathsf{NO} \mbox{ EFFECT}) \\ & & & \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{OO}^{\circ} & + & \operatorname{NO}^{\circ} & - & \to & \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{O}^{\circ} & + & \operatorname{NO}_{2} \\ & & & \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{O}^{\circ} & + & \operatorname{O}_{2}^{\circ} & - & \to & \operatorname{CH}_{3}\operatorname{CHO}^{\circ} & + & \operatorname{NO}_{2} \\ & & & & \operatorname{HO}_{2}^{\circ} & + & \operatorname{O}_{2}^{\circ} & - & \to & \operatorname{CH}_{3}\operatorname{CHO}^{\circ} & + & \operatorname{HO}_{2}^{\circ} \\ & & & & & \operatorname{HO}_{2}^{\circ} & + & \operatorname{NO}_{-}^{\circ} & & \operatorname{OH}^{\circ} & + & \operatorname{NO}_{2} \end{array}$$

### **OVERALL PROCESS:**

 $CH_{3}CH_{3} + 2 O_{2} + 2 NO \rightarrow CH_{3}CHO + 2 NO_{2} + H_{2}O$ 

**COMBINED WITH:** 

$$NO_2 + O_2 \stackrel{hv}{=} NO + O_3$$

YIELDS:

### OZONE FORMATION CONTINUES UNTIL $\mathrm{NO}_{\mathrm{x}}$ is removed

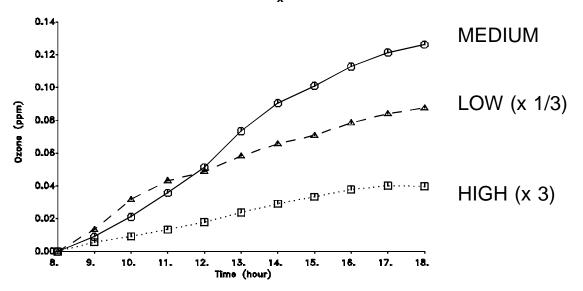
MAJOR NO<sub>x</sub> SINKS:

• OH + NO<sub>2</sub> 
$$\rightarrow$$
 HNO<sub>3</sub>  
NO<sub>2</sub>  $H_2O$  (NIGHTTIME SINK)  
• NO<sub>2</sub> + O<sub>3</sub>  $\rightarrow$  NO<sub>3</sub>  $\stackrel{\leftarrow}{\longleftrightarrow}$  N<sub>2</sub>O<sub>5</sub>  $\rightarrow$  2 HNO<sub>3</sub>  
• ALDEHYDES  $\stackrel{OH O_2}{\rightarrow}$   $\stackrel{NO_2}{\rightarrow}$  RCO-OO.  $\rightarrow$  RCO-OONO<sub>2</sub> (PANS)  
• AROMATICS  $\stackrel{OH O_2}{\rightarrow}$   $\stackrel{NO_3, NO_2}{\rightarrow}$   
• AROMATICS  $\stackrel{OH O_2}{\rightarrow}$   $\stackrel{NO_3, NO_2}{\rightarrow}$   
• AROMATICS  $\stackrel{OH O_2}{\rightarrow}$   $\stackrel{NO}{\rightarrow}$  HENOLS  $\rightarrow$   $\rightarrow$  NITROPHENOLS  
• ALKANES  $\stackrel{OH O_2}{\rightarrow}$   $\stackrel{NO}{\rightarrow}$  RONO<sub>3</sub>

 $\mathrm{NO}_{\mathrm{x}}$  is removed in the atmosphere more rapidly than vocs.

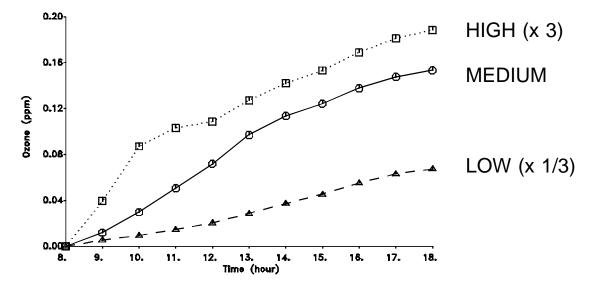
THEREFORE, NO, AVAILABILITY ULTIMATELY LIMITS THE AMOUNT OF O3 WHICH CAN BE FORMED.

EFFECT OF VOCs AND NO<sub>x</sub> ON O<sub>3</sub> FORMATION



VARY NO<sub>x</sub> EMISSIONS

VARY VOC EMISSIONS



### IMPLICATIONS OF ATMOSPHERIC CHEMISTRY FOR OZONE CONTROL STRATEGIES

### NO<sub>x</sub> CONTROL:

- NO<sub>x</sub> IS REQUIRED FOR OZONE FORMATION. IF NO<sub>x</sub> WERE ABSENT, NO O<sub>3</sub> WOULD BE FORMED. WHEN NO<sub>x</sub> IS CONSUMED, OZONE FORMATION ENDS.
- NO<sub>x</sub> IS REMOVED MORE RAPIDLY THAN VOCS. THEREFORE, AVAILABILITY OF NO<sub>x</sub> LIMITS HOW MUCH OZONE CAN ULTIMATELY BE FORMED.
- BUT NO<sub>x</sub> ALSO REDUCES THE RATE OF OZONE FORMATION. THIS IS BECAUSE:
  - NO REACTS WITH O<sub>3</sub>
  - NO<sub>2</sub> REACTS WITH RADICALS. LOWER RADICALS CAUSE LOWER VOC CONSUMPTION RATES

THEREFORE, NO<sub>x</sub> 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<sub>x</sub>. 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<sub>x</sub>-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<sub>x</sub> INTO ACCOUNT.

AIRSHED MODELS ARE REQUIRED FOR QUANTITATIVE PREDICTIONS OF EFFECTS OF VOC AND NO<sub>x</sub> CONTROL ON OZONE.

### CONCEPT OF VOC REACTIVITY

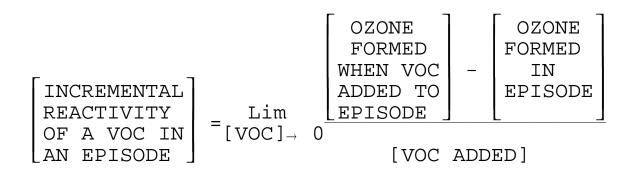
VOCs DIFFER IN THEIR EFFECTS ON OZONE FORMATION. THE TERM **REACTIVITY** IS USED TO REFER TO THIS.

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

- HOW FAST THE VOC REACTS.
- HOW MANY MOLECULES OF NO ARE OXIDIZED WHEN THE VOC REACTS.
- EFFECTS OF THE VOC'S REACTIONS ON RADICAL LEVELS. THIS AFFECTS HOW MUCH  $O_3$  IS FORMED FROM REACTIONS OF THE OTHER VOCS.
- EFFECTS ON RATES OF NO<sub>x</sub> REMOVAL. O<sub>3</sub> FORMATION ENDS ONCE NO<sub>x</sub> IS REMOVED. (IMPORTANT ONLY WHEN O<sub>3</sub> IS NO<sub>x</sub>-LIMITED.)
- REACTIVITIES OF THE VOC'S MAJOR OXIDATION PRODUCTS.

### **QUANTIFICATION OF REACTIVITY**

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



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

IMPORTANT TO NOTE THAT 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<sub>x</sub>

- THIS IS THE MOST IMPORTANT SINGLE FACTOR
- VOCs FORM THE MOST OZONE (REACTIVITIES ARE THE HIGHEST) WHEN NO<sub>x</sub> IS ABUNDANT
- VOCs HAVE THE SMALLEST EFFECTS ON OZONE (REACTIVITIES LOWEST) WHEN NO<sub>x</sub> IS LOW.
- THE ROG/NO, RATIO IS COMMONLY USED TO MEASURE NO, AVAILABILITY.

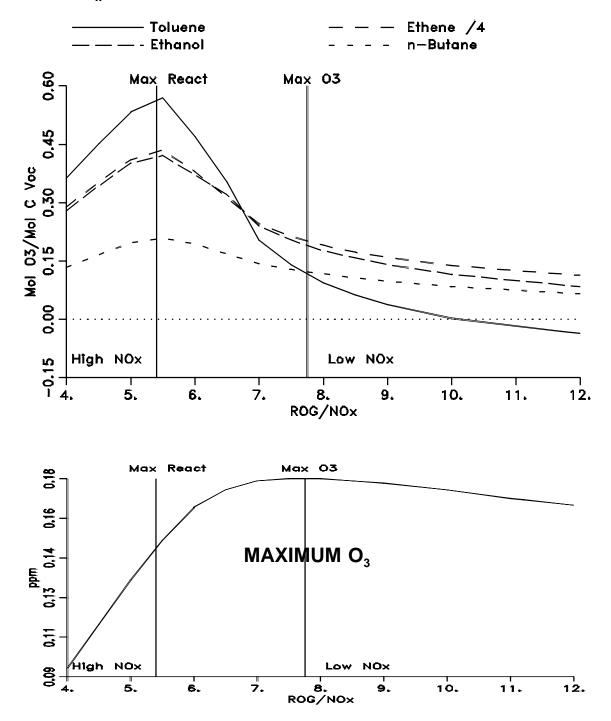
NATURE OF OTHER VOCs PRESENT.

• VOCs WITH STRONG RADICAL SOURCES DECREASE THE IMPORTANCE OF RADICAL SOURCES OR SINKS IN AFFECTING A VOC'S REACTIVITY.

AMOUNTS OF SUNLIGHT AND TEMPERATURE:

- AFFECTS OVERALL RATES OF REACTION.
- AFFECTS DEPENDENCE OF REACTIVITY ON ROG/NO<sub>x</sub> RATIO. (MORE SUNLIGHT LIKE INCREASING ROG/NO<sub>x</sub>)

TRANSPORT, ALOFT AND BACKGROUND POLLUTANTS, EMISSION SCHEDULES, AMOUNTS OF DILUTION, ALSO AFFECT REACTIVITY AND VOC/NO<sub>x</sub> DEPENDENCIES DEPENDENCE OF INCREMENTAL REACTIVITIES ON  ${\rm ROG/NO_x}$ 



### MEASUREMENT OR CALCULATION OF ATMOSPHERIC REACTIVITY

ATMOSPHERIC REACTIVITY CANNOT BE MEASURED EXPERIMENTALLY

- NOT PRACTICAL TO DUPLICATE IN AN EXPERIMENT ALL ENVIRONMENTAL CONDITIONS WHICH AFFECT REACTIVITY
- CHAMBER EXPERIMENTS HAVE WALL EFFECTS, USUALLY HIGHER NO<sub>x</sub> LEVELS, STATIC CONDITIONS, HIGH AMOUNTS OF ADDED TEST VOC, ETC.

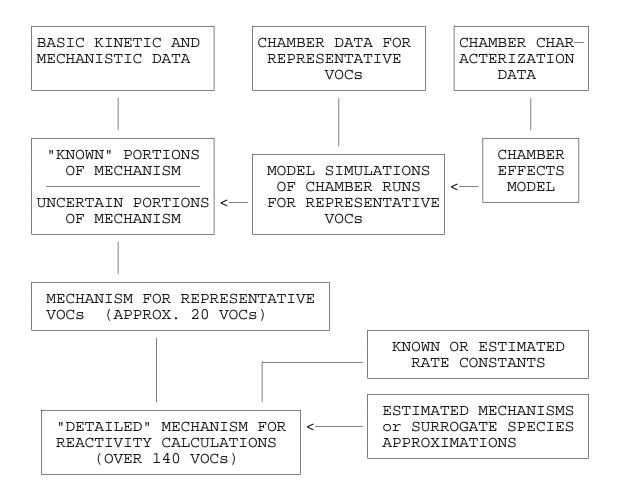
ATMOSPHERIC REACTIVITY CAN BE CALCULATED USING COMPUTER AIRSHED MODELS, GIVEN:

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

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

EXPERIMENTAL MEASUREMENTS OF REACTIVITY PROVIDE A MEANS TO TEST THE RELIABILITY OF A MECHANISM TO PREDICT ATMOSPHERIC REACTIVITY.

### DEVELOPMENT OF A CHEMICAL MECHANISM TO CALCULATE VOC REACTIVITIES



### TYPES OF ENVIRONMENTAL CHAMBER EXPERIMENTS TO TEST ATMOSPHERIC CHEMICAL MECHANISMS

### SINGLE VOC-NO<sub>x</sub>-AIR RUNS:

- MOST STRAIGHTFORWARD TEST OF A VOC's MECHANISM
- USED FOR MECHANISM DEVELOPMENT
- NOT A "REALISTIC" ENVIRONMENT
- ONLY USEFUL FOR VOCs WITH RADICAL SOURCES.

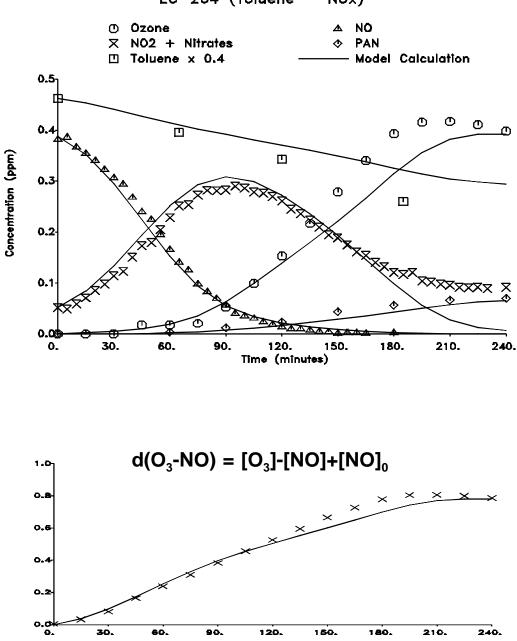
### COMPLEX MIXTURE-NO<sub>x</sub>-AIR RUNS:

- TESTS MECHANISMS' ABILITY TO SIMULATE O<sub>3</sub> FORMATION UNDER REALISTIC CONDITIONS
- NOT USEFUL FOR MECHANISM DEVELOPMENT

**REACTIVITY EXPERIMENTS** (MIXTURE-NO<sub>x</sub>-AIR COMBINED WITH MIXTURE-NO<sub>x</sub>-AIR RUNS WITH TEST VOC ADDED):

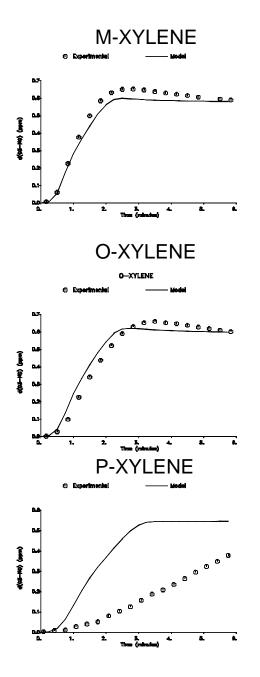
- CAN TEST MECHANISMS OF SINGLE VOCs UNDER REALISTIC CONDITIONS
- BEST TEST OF MECHANISM'S ABILITY TO PREDICT INCREMENTAL REACTIVITY
- NOT SAME AS ATMOSPHERIC REACTIVITY.

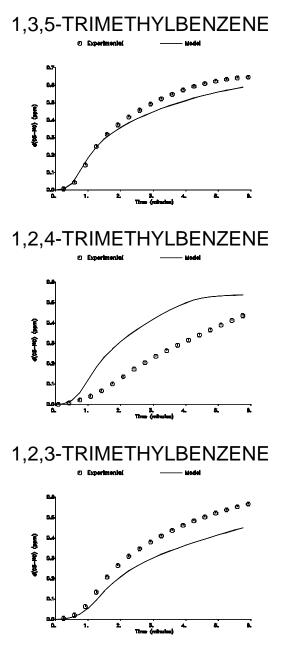
# EXAMPLE OF SINGLE VOC-NO<sub>x</sub>-AIR EXPERIMENT: FIT OF MODEL CALCULATION TO A TOLUENE - NO<sub>x</sub> - AIR EXPERIMENT



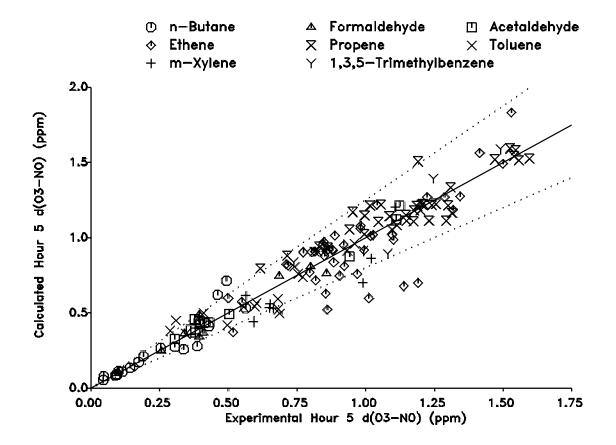
EC-264 (Toluene - NOx)

## EXPERIMENTAL <u>VS</u> CALCULATED $d(O_3$ -NO) IN AROMATIC ISOMER - NO<sub>x</sub> EXPERIMENTS

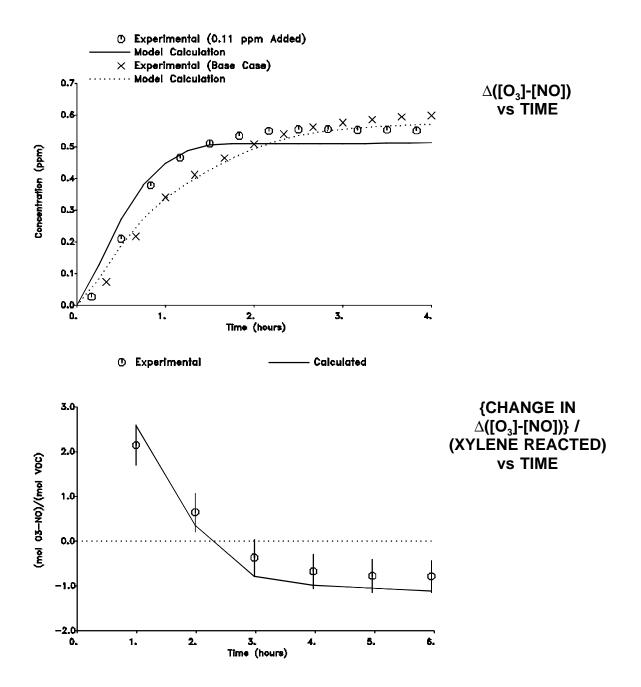




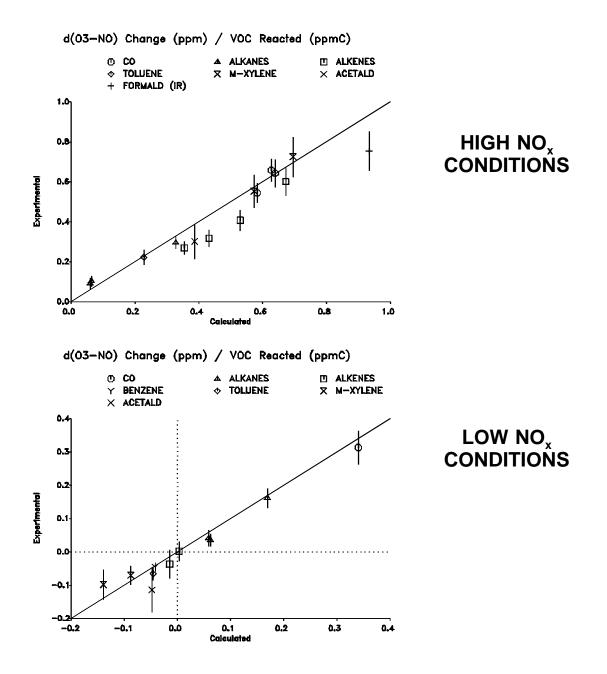
### PLOT OF EXPERIMENTAL <u>VS</u> CALCULATED OZONE FORMED + NO OXIDIZED IN SELECTED SINGLE COMPOUND - NO<sub>x</sub> EXPERIMENTS



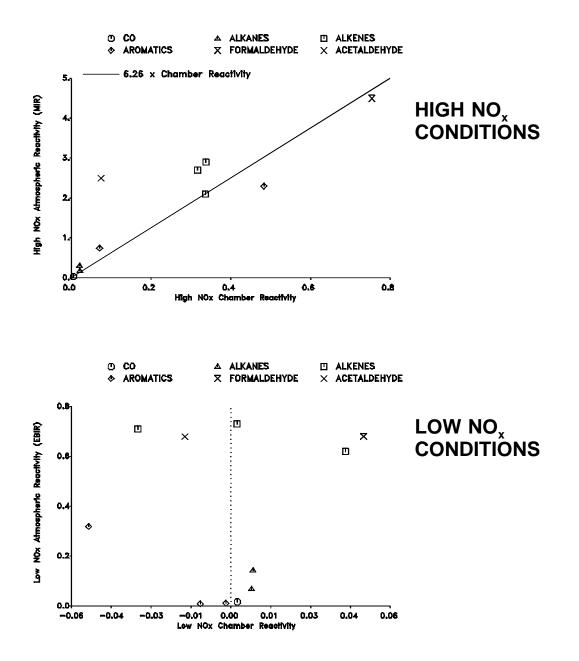
### EXMPLE OF AN INCREMENTAL REACTIVITY EXPERIMENT: EFFECT OF M-XYLENE UNDER HIGH ROG/NO<sub>x</sub> CONDITIONS



### MODEL PERFORMANCE IN SIMULATING INCREMENTAL REACTIVITY EXPERIMENTS



### CORRESPONDENCE BETWEEN ENVIRONMENTAL CHAMBER AND CALCULATED ATMOSPHERIC REACTIVITIES.



### CURRENT STATUS OF THE CHEMICAL MECHANISMS USED TO PREDICT O<sub>3</sub> IMPACTS OF VOCs AND NO<sub>x</sub>

MANY UNCERTAINTIES IN VOC REACTION MECHANISMS, ESPECIALLY FOR AROMATICS. PARAMETERIZED MODELS ADJUSTED TO FIT CHAMBER DATA.

MECHANISMS CAN SIMULATE O<sub>3</sub> AND NO IN MOST WELL-CHARACTERIZED EXPERIMENTS WITHIN  $\pm$  30%. SOME EXCEPTIONS AND INCONSISTENCIES.

- POOR REPRESENTATION OF SOME AROMATIC ISOMERS.
- UNEXPLAINED VARIABILITIES IN SIMULATIONS OF ETHENE RUNS
- POSSIBLE UNDERPREDICTION BIAS IN NEW
   OUTDOOR AND XENON ARC LIGHT EXPERIMENTS.

CHAMBER DATA BASE FOR MECHANISM EVALUATION IS NOT ADEQUATE FOR MANY VOCs.

CURRENT CHAMBERS DO NOT PROVIDE GOOD TESTS FOR MECHANISMS UNDER VERY LOW NO<sub>x</sub> CONDITIONS.

EFFECTS OF CHEMICAL MECHANISM UNCERTAINTY ON AIRSHED MODEL PREDICTIONS HAVE NOT BEEN ADEQUATELY ASSESSED.

### 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.

### 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.

BASE THE SCALE ON CONDITIONS WHERE VOCs HAVE MAXIMUM REACTIVITY 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.

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.

### STEPS IN THE DEVELOPMENT OF GENERAL REACTIVITY SCALES

- 1. DEVELOP MODELS (MECHANISMS) FOR THE VOCs' ATMOSPHERIC REACTIONS. CONDUCT EXPERIMENTS WHICH TEST THEIR ABILITY TO PREDICT REACTIVITY
- 2. DEVELOP A SET OF MODEL SCENARIOS REPRESENTING THE RANGE OF AIRSHED CONDITIONS WHERE OZONE IS A PROBLEM.
- 3. DETERMINE APPROPRIATE METHOD(S) TO QUANTIFY OZONE IMPACTS IN AN AIRSHED SCENARIO.
- 4. DEVELOP APPROPRIATE METHODS TO DERIVE REACTIVITY SCALES FROM THE DISTRIBUTION OF REACTIVITIES IN THE SCENARIOS.
- 5. DETERMINE RANGES OF UNCERTAINTIES OR VARIABILITIES IN THE REACTIVITY SCALE(S).
- 6. DEVELOP APPROPRIATE CONTROL POLICIES GIVEN THE REACTIVITY SCALES AND THEIR UNCERTAINTIES.

### CRITERIA FOR MODEL SCENARIOS FOR DEVELOPMENT OF REACTIVITY SCALES

MULTIPLE SCENARIOS SHOULD BE USED TO REPRESENT THE RANGE OF CONDITIONS WHERE THE SCALE WOULD BE APPLIED

REACTIVITY IS PRIMARILY A **CHEMICAL EFFECT**. THEREFORE:

- REPRESENTATION OF AN APPROPRIATE DISTRIBUTION OF CHEMICAL CONDITIONS MOST IMPORTANT
- MODEL SHOULD USE MOST DETAILED CHEMICAL MECHANISM AVAILABLE, EVEN THOUGH THIS REQUIRES USE OF SIMPLER PHYSICAL MODELS.

ABILITY TO ACCURATELY SIMULATE ANY SPECIFIC EPISODE IS LESS IMPORTANT THAN USE OF AN APPROPRIATE DISTRIBUTION OF CONDITIONS

### ALTERNATIVES FOR QUANTIFYING OZONE IMPACTS WHEN ASSESSING VOC REACTIVITY

**OZONE YIELD REACTIVITY**: EFFECT OF VOC ON MAXIMUM OZONE CONCENTRATION OR AMOUNT OF OZONE FORMED

 $REACTIVITY = \frac{\Delta \text{ Maximum } [O_3]}{\Delta \text{ VOC}}$ 

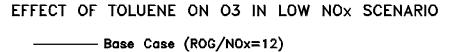
**INTEGRATED OZONE REACTIVITY**: EFFECT OF VOC ON OZONE CONCENTRATION INTEGRATED OVER TIME, OR INTEGRATED OZONE OVER A STANDARD

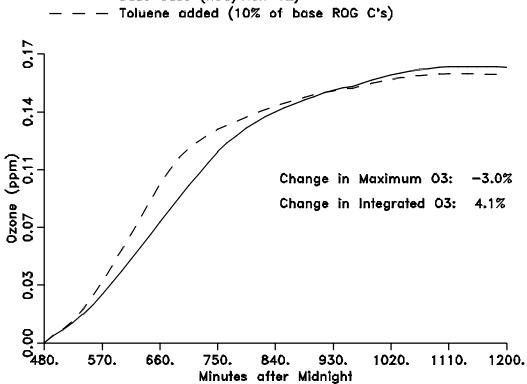
REACTIVITY =  $\frac{\Delta \int [O_3]dt}{\Delta \text{ VOC}}$ REACTIVITY -  $\frac{\Delta \int \max(0, [O_3] - [O_3]^{\text{std}}) dt}{\Delta \text{ transformation}}$ 

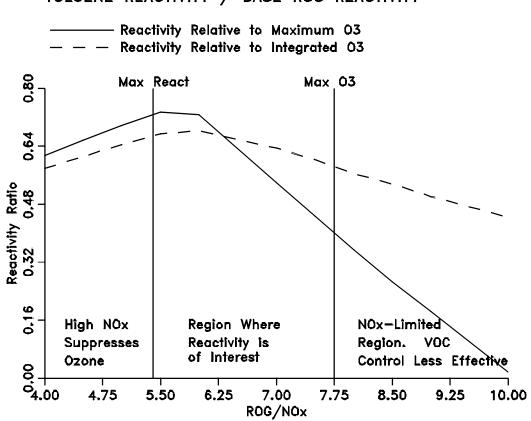
OR

 $REACTIVITY = \frac{J}{\Delta VOC}$ 

**OZONE EXPOSURE REACTIVITY**: EFFECT OF THE VOC ON EXPOSURE OF THE POPULATION TO OZONE







TOLUENE REACTIVITY / BASE ROG REACTIVITY

### EXAMPLES OF REGULATORY POLICIES REGARDING VOC REACTIVITY

### 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 PROPOSED EXEMPTING ACETONE BASED ON ITS CALCULATED INCREMENTAL REACTIVITY.
- CLEAN AIR ACT REQUIRES THE EPA TO CONSIDER VOC REACTIVITY IN CONTROLS OF CONSUMER PRODUCTS.

### 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

> ADJUSTED ACTUAL EMISSIONS = **RAF** x EMISSIONS (g/mi) (g/mi)

WHERE

MAXIMUM INCREMENTAL REACTIVITY (**MIR**) OF EXHAUST (g O<sub>3</sub>/g VOC)

RAF =

MIR OF STANDARD EXHAUST (g  $O_3/g$  VOC)

 REACTIVITY NOT NOW CONSIDERED IN STATIONARY SOURCE REGULATIONS

### SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

 PROPOSED EMISSIONS TRADING PROGRAM (RECLAIM) WILL PERMIT TRADES OF ALL NON-EXEMPT VOCS REGARDLESS OF REACTIVITY. BUT RESULTING CHANGES IN REACTIVITY WILL BE TRACKED AND ASSESSED AS PART OF ASSESSMENT OF OVERALL PROGRAM.

### SUMMARY OF RESEARCH NEEDS FOR DEVELOPING REACTIVITY SCALES

### RESEARCH AREA

MECHANISMS

SCENARIOS FOR

REACTIVITY

ASSESSMENT

FOR VOCs

### **RESEARCH NEED**

- BASIC KINETIC AND MECHANISTIC STUDIES.
- CHAMBER EXPERIMENTS TO TEST MECHANISMS.
- IMPROVE EMISSIONS DATA.
- OBTAIN DATA TO TEST AIRSHED MODELS.
- DETERMINE DISTRIBUTION OF
   OZONE EPISODE CONDITIONS.
- DEVELOP MODELS FOR MORE EPISODES.
- HEALTH EFFECTS STUDIES.
- EXPOSURE MODEL DEVELOPMENT.

METHODS TO QUANTIFY OZONE IMPACTS

- DETERMINE WHAT CONSTITUTES AN "OPTIMUM" SCALE (POLICY ISSUE).
- DEVELOP ANALYSIS METHODS TO DERIVE "OPTIMUM" SCALE FROM RESULTS OF MULTI-SCENARIO CALCULATIONS.

OZONE IMPAC DERIVE REACTIVITY

SCALE(S)