

CURRENT STATUS OF REACTIVITY RESEARCH

BACKGROUND

- DEFINITION OF REACTIVITY
- FACTORS AFFECTING REACTIVITY
- MEASUREMENT OR CALCULATION OF REACTIVITY

RESEARCH AREAS AND UNCERTAINTIES

- CHEMICAL MECHANISM
 - STATUS OF MECHANISM DEVELOPMENT
 - DATA NEEDS FOR MECHANISM AND REACTIVITY EVALUATION
 - UNCERTAINTY ANALYSIS
- AIRSHED MODEL UNCERTAINTY
- DEPENDENCE OF REACTIVITY ON ENVIRONMENTAL CONDITIONS AND OZONE QUANTIFICATION METHOD

INCREMENTAL REACTIVITY

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

NOT AN INTRINSIC PROPERTY OF THE MOLECULE.
DEPENDS ON THE EPISODE AS WELL AS THE VOC.

THIS IS THE MOST DIRECTLY RELEVANT REACTIVITY
MEASURE FOR APPLICATION TO CONTROL STRATEGIES:

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

NOT SAME AS OZONE PRODUCTIVITY, THE AMOUNT OF O₃
ATTRIBUTABLE TO NO TO NO₂ CONVERSIONS CAUSED BY
PEROXY RADICALS FORMED FROM THE VOC.

FACTORS AFFECTING INCREMENTAL REACTIVITY

$$\text{INCREMENTAL REACTIVITY} = \text{KINETIC REACTIVITY} \times \text{MECHANISTIC REACTIVITY}$$

$$\text{MECHANISTIC REACTIVITY} = \text{DIRECT MECHANISTIC REACTIVITY} + \text{INDIRECT MECHANISTIC REACTIVITY}$$

KINETIC REACTIVITY: FRACTION OF EMITTED MOLECULE WHICH REACTS.

- PROPORTIONAL TO REACTION RATE FOR SLOWLY REACTING COMPOUNDS
- INDEPENDENT OF REACTION RATE (APPROACHES 1.0) FOR RAPIDLY REACTING COMPOUNDS

MECHANISTIC REACTIVITY: AMOUNT OF OZONE FORMED PER MOLECULE REACTING

DIRECT REACTIVITY ("PRODUCTIVITY"): O₃ FORMED FROM THE PEROXY RADICALS FROM THE VOC.

INDIRECT REACTIVITY: CHANGE IN O₃ FORMED FROM PEROXY RADICALS FROM THE OTHER VOCs PRESENT.

- EFFECTS ON RADICAL LEVELS AFFECTS HOW MUCH THE OTHER VOCs REACT.
- EFFECTS ON NO_x CONSUMPTION AFFECTS HOW MUCH O₃ IS FORMED FROM A PEROXY RADICAL.

ENVIRONMENTAL FACTORS WHICH AFFECT INCREMENTAL REACTIVITY

NO_x AVAILABILITY IS MOST IMPORTANT SINGLE FACTOR AFFECTING MECHANISTIC REACTIVITIES.

- O₃ MOST SENSITIVE TO VOCs WHEN NO_x IS HIGH, NOT SENSITIVITY TO VOCs WHEN NO_x LOW.
- REACTIVITIES AT HIGH NO_x ARE SENSITIVE TO MECHANISTIC FACTORS WHICH AFFECT RATES OF O₃ FORMATION (E.G. RADICAL INITIATION/TERMINATION).
- REACTIVITIES AT LOW NO_x ARE SENSITIVE TO FACTORS WHICH AFFECT RATES OF NO_x REMOVAL.

DURATION OF SCENARIO AND RADICAL LEVELS AFFECTS REACTIVITIES OF SLOWLY REACTING COMPOUNDS.

SENSITIVITY TO RADICAL INITIATION/TERMINATION IS AFFECTED BY LEVELS OF OTHER RADICAL INITIATORS.

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

MEASUREMENT OR CALCULATION OF ATMOSPHERIC INCREMENTAL 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 NECESSARY TO TEST THE RELIABILITY OF A MECHANISM TO PREDICT ATMOSPHERIC REACTIVITY.

MECHANISMS FOR REACTIVITY ASSESSMENT

SAPRC-90 MECHANISM

REFLECTS KNOWLEDGE AS OF 1989.

O₃ PREDICTION EVALUATED AGAINST CHAMBER DATA FOR REPRESENTATIVES OF MAJOR VOC CLASSES

HIGHLY SIMPLIFIED REPRESENTATION OF LOW-NO_x CHEMISTRY.

HIGHLY SIMPLIFIED REPRESENTATION OF HIGHER OXYGENATED PRODUCTS.

OVER >100 TYPES OF VOCs REPRESENTED

- A FEW SIMPLE COMPOUNDS (FORMALDEHYDE, ACETALDEHYDE, ETC.) REPRESENTED EXPLICITLY.
- AROMATICS REACTIONS BASED ON PARAMETERIZED MECHANISMS ADJUSTED TO FIT CHAMBER DATA.
- ALKANE MECHANISMS GENERATED BY A COMPUTER PROGRAM USING PUBLISHED ESTIMATION METHODS
- MECHANISMS FOR MANY TYPES OF COMPOUNDS HIGHLY APPROXIMATE AND UNTESTED.

USED TO DERIVE VARIOUS REACTIVITY SCALES FOR >100 VOCs, INCLUDING THE WIDELY-USED MIR SCALE.

SAPRC MECHANISM UPDATES

SAPRC-93 MECHANISM

CHANGES TO PAN KINETICS CAUSED HIGHER ABSOLUTE REACTIVITIES FOR ALMOST ALL VOCs.

ALKENE MECHANISMS CHANGED TO REFLECT NEW DATA ON O₃ + ALKENE REACTIONS

MECHANISMS FOR MTBE AND A FEW OTHER VOCs MODIFIED BASED ON AVAILABLE DATA.

UPDATED ISOPRENE CHEMISTRY ADDED

NOW BEING USED IN SEVERAL RESEARCH-GRADE AIRSHED MODELS

SAPRC-97 MECHANISM

AROMATICS MECHANISMS MODIFIED TO FIT NEW CHAMBER DATA AND TO ACCOUNT FOR ISOMERIC DIFFERENCES. MOST MORE REACTIVE.

MECHANISMS FOR A NUMBER OF VOCs UPDATED BASED ON ONGOING REACTIVITY STUDIES

USED TO DERIVE REACTIVITY DATA AND UNCERTAINTY SUMMARY RECENTLY PREPARED FOR THE CARB.

CURRENT WORKING MECHANISM AVAILABLE ON THE INTERNET.

SAPRC MECHANISM UPDATES

SAPRC-98 MECHANISM (UNDER DEVELOPMENT)

BASE MECHANISM HAS BEEN COMPLETELY UPDATED.
MANY SMALL CHANGES.

THE IMPORTANT OH + NO₂ RATE CONSTANT FOUND TO
BE HIGHLY UNCERTAIN BUT WAS NOT CHANGED.

MORE DETAILED REPRESENTATION OF LOW NO_x ORGANIC
REACTIONS. CHANGES IN PRODUCT DISTRIBUTION AT
LOW NO_x CAN NOW BE PREDICTED.

ESTIMATED MECHANISMS FOR ALKANES, ALKENES, AND
MANY OXYGENATES ARE GENERATED AS FOLLOWS:

COMPUTERIZED ESTIMATION PROCEDURE
GENERATES EXPLICIT MECHANISMS WHICH ARE
USED TO DERIVE PRODUCT YIELD PARAMETERS FOR
THE MODEL.

PROCEDURE USES ESTIMATED OR ASSIGNED RATE
CONSTANTS FOR THE COMPETING REACTIONS.

REPRESENTATION OF ORGANIC PRODUCTS BEING
UPDATED USING PREDICTED PRODUCT DISTRIBUTIONS.

STILL NECESSARY TO USE PARAMETERIZED MECHANISMS
FOR AROMATICS ADJUSTED TO FIT CHAMBER DATA.

MECHANISM IS INCORPORATING RESULTS OF RECENT
STUDIES OF CONSUMER PRODUCT AND OTHER VOCs.

STATUS OF MECHANISM DEVELOPMENT AND UNCERTAINTIES BY VOC CLASS

ALKANES

MECHANISMS FOR LOWER ALKANES WELL ESTABLISHED,
ESTIMATION METHODS USED FOR HIGHER ALKANES.

THE C₈₊ N-ALKANE MECHANISMS WHICH FIT CHAMBER
DATA HAVE UNREASONABLE ASSUMPTIONS.

MINERAL SPIRITS DATA SUGGEST REACTIVITIES FOR C₁₀₊
BRANCHED AND CYCLIC ALKANES ARE OVERESTIMATED.

ALKENES

SAPRC-98 EVALUATION SHOW MORE PROBLEMS WITH
ALKENE MECHANISMS THAN PREVIOUS SUSPECTED.

MODELS USING ACCEPTED OH YIELDS FOR O₃
REACTIONS GREATLY OVERPREDICT REACTIVITIES OF C₄₊
1-ALKENES.

UNCERTAIN O(³P) REACTIONS AFFECT MECHANISM
ADJUSTMENTS FOR PROPENE, BUTENES, AND ISOPRENE.

EXTENT TO WHICH MECHANISMS MODIFICATIONS WILL
AFFECT ALKENE REACTIVITY IS UNCERTAIN.

STATUS OF MECHANISM DEVELOPMENT AND UNCERTAINTIES BY VOC CLASS

AROMATICS HYDROCARBONS

STILL NECESSARY TO USE PARAMETERIZED MECHANISMS.

YIELDS AND PHOTOLYSIS RATES OF UNCHARACTERIZED PRODUCTS CANNOT BE UNAMBIGUOUSLY DETERMINED.

NO MECHANISM CAN SATISFACTORILY FIT ALL CHAMBER DATA FOR BENZENE.

NO OBVIOUS EXPLANATION FOR LOWER MECHANISTIC REACTIVITY FOR ETHYLBENZENE COMPARED TO TOLUENE.

CURRENT MECHANISMS PROBABLY ARE INCONSISTENT WITH PRODUCT DATA FOR REACTIONS OF PHENOLS

UNCERTAIN WHETHER PARAMETERIZED MECHANISMS EXTRAPOLATE CORRECTLY TO LOW NO_x CONDITIONS.

HIGHER OXYGENATES (HIGHER KETONES, ETHERS, ESTERS, GLYCOLS, ETC.)

EXPERIMENTAL REACTIVITY DATA ARE BECOMING AVAILABLE, SIGNIFICANTLY REDUCING UNCERTAINTIES.

CURRENT ESTIMATION METHODS OFTEN PERFORM POORLY IN SIMULATING CHAMBER DATA PRIOR TO ADJUSTMENTS.

ATTEMPTS TO IMPROVE PERFORMANCE OF ESTIMATION METHODS ARE UNDERWAY.

STATUS OF MECHANISM DEVELOPMENT AND UNCERTAINTIES BY VOC CLASS

HALOGENATED COMPOUNDS

REACTIVITY DATA ONLY AVAILABLE FOR CHLOROPICRIN (CCl_3NO_2), TRICHLOROETHYLENE, AND ALKYL BROMIDES.

NO REASONABLE MECHANISM SATISFACTORILY FITS ALL CHAMBER DATA FOR TCE AND ALKYL BROMIDES.

STUDIES ARE NEEDED ON SIMPLER SYSTEMS.

NITROGEN-CONTAINING COMPOUNDS

REACTIVITY DATA LIMITED TO N-METHYL PYRROLIDINONE (NMP) AND SEVERAL AROMATIC ISOCYANATES.

NMP IS UNUSUAL IN THAT NO_3 REACTIONS CONTRIBUTE TO ITS REACTIVITY.

THE AROMATIC ISOCYANATES STUDIED DO NOT PROMOTE OZONE FORMATION. MECHANISM UNKNOWN.

SILOXANES

CHAMBER DATA SHOW THAT THESE ARE O_3 INHIBITORS, BUT MECHANISMS WHICH FIT CHAMBER DATA ARE NOT CONSISTENT WITH RESULTS OF PRODUCT STUDIES.

MECHANISM UNCERTAINTY ANALYSIS

REACTIVITY-BASED CONTROL STRATEGIES WILL PROBABLY NEED TO TAKE INTO ACCOUNT VARYING LEVELS OF UNCERTAINTIES FOR DIFFERENT VOCs.

PROPOSALS TO USE ADJUSTMENT FACTORS OR UPPER LIMITS FOR UNCERTAIN VOCs IN REACTIVITY-BASED VOC CONTENT REGULATIONS.

UNCERTAINTY ANALYSIS APPROACHES

FORMAL UNCERTAINTY ANALYSIS

- ULTIMATELY THE BEST APPROACH, BUT HAS ITS OWN UNCERTAINTIES.
- RELIES ON SUBJECTIVE UNCERTAINTIES FOR INPUT DATA. INCONSISTENCES AMONG EVALUATORS.
- DIFFICULT TO TREAT POSSIBILITIES OF FOR "MISSING" REACTIONS OR INCORRECT PARAMETERIZATIONS.
- NOT PRACTICAL TO DO FOR ALL TYPES OF VOCs IN USEFUL TIME FRAME.
- NEAR-TERM UTILITY IS TO AID EVALUATION OF SUBJECTIVE OR CATEGORIZATION APPROACHES.
- PROJECT UNDERWAY TO ANALYZE UNCERTAINTIES IN MECHANISMS ADJUSTED TO FIT CHAMBER DATA.

UNCERTAINTY ANALYSIS APPROACHES (CONTINUED)

CATEGORIZATION BASED ON EXPERT ASSESSMENT OF QUALITY OF MECHANISM AND EXTENT TO WHICH MECHANISM EVALUATED.

- PRELIMINARY CATEGORIZATION HAS BEEN DONE FOR ALL VOCs IN THE SAPRC-97 MECHANISM.
- NEED TO BE UPDATED AND PEER-REVIEWED BEFORE INCORPORATED IN ANY REGULATIONS.
- DOES NOT GIVE NUMERICAL UNCERTAINTIES.

UPPER AND LOWER LIMIT REACTIVITY ANALYSIS

- CAN BE USED FOR QUANTIFYING UNCERTAINTIES FOR ALL VOCs.
- RELATIVELY STRAIGHTFORWARD TO ESTIMATE UPPER LIMIT REACTIVITIES FOR A GIVEN SCALE. PROPOSED APPROACH HAS BEEN DEVELOPED.
- LOWER LIMIT REACTIVITIES FOR VOCs OF UNKNOWN MECHANISM IS ZERO, SINCE THEY MAY INHIBIT O₃.
- THIS METHOD GIVES HIGH UNCERTAINTY RANGES. MAY NOT BE ACCEPTABLE FOR REGULATORY USE.
- UNCERTAINTY RANGES FOR SOME VOC CLASSES CAN BE NARROWED BY MECHANISTIC CONSIDERATIONS.

CHEMICAL MECHANISM UNCERTAINTIES

BASE MECHANISM (INORGANIC, COMMON PRODUCT REACTIONS) HAS NON-NEGLIGIBLE UNCERTAINTIES.

- REACTIVITIES VOCs WITH LARGE INDIRECT REACTIVITIES (E.G., INITIATORS/INHIBITORS) SENSITIVE TO BASE MECHANISM CHANGES.
- REACTIVITY UNCERTAINTIES FOR WELL-STUDIED VOCs ESTIMATED TO BE ~30%

UNCERTAINTIES IN MECHANISMS FOR INDIVIDUAL VOCs CAN BE MUCH GREATER IF VOC INADEQUATELY STUDIED.

- ONGOING RESEARCH IS REDUCING NUMBER OF VOC CLASSES WITH INADEQUATE DATA.
- UNSTUDIED VOCs MORE OF A CONCERN FOR STATIONARY SOURCES THAN MOBILE SOURCES.

REACTIVITY CHANGES DUE TO UPDATING MECHANISM GIVE AN INDICATION OF UNCERTAINTIES

- REFLECTS RESULTS OF ONGOING RESEARCH.
- CHANGES FOR WELL-STUDIED CONSISTENT WITH ~30% MINIMUM UNCERTAINTY ESTIMATE.

TYPES OF ENVIRONMENTAL CHAMBER EXPERIMENTS CURRENTLY USED TO TEST CHEMICAL MECHANISMS

SINGLE VOC-NO_x-AIR RUNS:

- MOST STRAIGHTFORWARD TEST OF A VOC'S MECHANISM, THOUGH ONLY USEFUL FOR VOCs WITH RADICAL SOURCES.
- NOT A "REALISTIC" ENVIRONMENT. CORRELATES POORLY WITH REACTIVITY.

COMPLEX MIXTURE-NO_x-AIR RUNS:

- TESTS MECHANISMS' ABILITY TO SIMULATE O₃ 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):

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

DATA NEEDS FOR MECHANISM EVALUATION (NEAR TERM)

MECHANISM EVALUATION DATA NEEDED FOR CLASSES OF COMPOUNDS NOT PREVIOUSLY STUDIED.

- **GOOD PROGRESS** BEING MADE FOR SOLVENT SPECIES SUCH AS ESTERS, GLYCOLS, ETC.
- BUT EPA EXEMPTION POLICY HAS CAUSED FOCUS OF RESEARCH TO BE ON LOW-REACTIVITY COMPOUNDS.
- REACTIVITY-BASED CONTROLS WILL ENCOURAGE RESEARCH ON COMPOUNDS OF ALL REACTIVITIES.

BETTER METHODS NEEDED TO EVALUATE REACTIVITY

- HIGH COST OF OBTAINING REACTIVITY DATA LIMITS ACCEPTABILITY OF REACTIVITY-BASED CONTROLS.
- CURRENTLY NO WAY TO ASSESS REACTIVITIES OF VERY LOW VOLATILITY COMPOUNDS.
- ONLY A FEW LABORATORIES ARE PRESENTLY CAPABLE OF GENERATING REACTIVITY DATA.

DATA NEEDS FOR MECHANISM EVALUATION (LONGER TERM)

MAJOR INVESTMENT IN CHAMBER FACILITIES NEEDED TO IMPROVE EVALUATION OF EXISTING MECHANISMS

- MECHANISMS INADEQUATELY EVALUATED FOR LOW NO_x (REGIONAL OR NEAR-ATTAINMENT) CONDITIONS.
- CHAMBERS CURRENTLY USED FOR MECHANISM EVALUATION UNSUITABLE FOR LOW NO_x STUDIES.
- ANALYTICAL CAPABILITIES AT OPERATING CHAMBER FACILITIES NOT ADEQUATE FOR FULL MECHANISM EVALUATION OR DETERMINING ALL VOC IMPACTS.
- TEMPERATURE EFFECTS UNCERTAIN. CURRENT CHAMBERS INADEQUATE TO STUDY THIS.
- LARGE TEMPERATURE-CONTROLLED INDOOR CHAMBER NEEDED TO STUDY PARTICULATE FORMATION UNDER CONTROLLED CONDITIONS.

STUDIES FOCUSED ON SPECIFIC COMPOUNDS CANNOT BE USED TO FUND THE NEEDED FACILITY IMPROVEMENTS.

DEVELOPMENT OF NEW REACTIVITY MEASUREMENT METHODS

PROJECT UNDERWAY TO DEVELOP NEW REACTIVITY MEASUREMENT METHODS.

INITIAL FOCUS IS ON USE OF HONO/VOC STIRRED FLOW SYSTEM. CALCULATIONS INDICATE THIS CAN GIVE USEFUL DATA ON FACTORS AFFECTING REACTIVITY.

- LOW TO MODERATE VOC TO HONO RATIOS: DATA SENSITIVE TO KOH AND NO TO NO₂ CONVERSIONS.
- HIGH VOC TO HONO: ALSO SENSITIVE TO RADICAL TERMINATION EFFECTS.

POTENTIALLY LOWER COST WAY TO OBTAIN DATA FOR MECHANISM EVALUATION, REACTIVITY SCREENING, DERIVING EMPIRICAL REACTIVITY-RELATED PARAMETERS.

FLOW SYSTEM POTENTIALLY ADAPTABLE TO VERY LOW VOLATILITY COMPOUNDS

CLEAN HONO GENERATION SYSTEM HAS BEEN CONSTRUCTED. FLOW SYSTEM BEING CONSTRUCTED FOR INITIAL TESTING WITH PROPANE.

AIRSHED MODEL UNCERTAINTIES

UNCERTAINTIES IN REPRESENTATION OF A GIVEN SCENARIO. (EMISSION UNCERTAINTIES, ETC.)

- LESS OF A PROBLEM FOR GENERAL SCALES REPRESENTING A RANGE OF CONDITIONS

USE OF SIMPLIFIED PHYSICAL SCENARIOS (EKMA MODELS) FOR COMPUTATIONAL TRACTABILITY

- LESS OF A PROBLEM FOR GENERAL SCALES REPRESENTING A RANGE OF CONDITIONS
- STUDIES SUGGEST NOT A MAJOR PROBLEM WHEN PREDICTING REACTIVITIES RELATIVE TO O₃ EXPOSURE

UNCERTAINTIES IN DISTRIBUTION OF CONDITIONS RELEVANT TO ASSESSING OZONE CONTROL

- NOT ADEQUATELY STUDIED. EPA SCENARIOS USED BY CARTER (1994) WERE NOT DEVELOPED FOR REACTIVITY ASSESSMENT.
- MAJOR PROBLEM FOR DEVELOPING GENERAL SCALES REPRESENTING A RANGE OF CONDITIONS.

LACK OF ADEQUATE STUDIES OF INCREMENTAL REACTIVITIES IN REGIONAL SCALE MODELS

- IMPORTANT WHEN ASSESSING WHAT IS "NEGLECTIBLE" REACTIVITY.

APPROACHES FOR DEALING WITH DEPENDENCE OF REACTIVITY ON AIRSHED CONDITIONS AND OZONE QUANTIFICATION METHOD

USE A "REPRESENTATIVE" OR "WORST CASE" EPISODE.

- MAY NOT BE OPTIMUM FOR ALL CONDITIONS.

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

- REFLECTS CONDITIONS MOST SENSITIVE TO VOCs AND CORRELATES WITH EFFECTS ON O₃ EXPOSURE.
- BUT DOES NOT REPRESENT CONDITIONS WHERE HIGHEST OZONE CONCENTRATIONS ARE FORMED.

USE MULTIPLE SCALES REPRESENTING THE RANGE OF APPLICABLE CONDITIONS.

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

USE A SCALE OPTIMIZED FOR A RANGE OF CONDITIONS.

- REQUIRES IMPROVED ASSESSMENT OF RANGE OF CONDITIONS RELEVANT TO OZONE FORMATION
- REQUIRES AN OBJECTIVE DEFINITION OF "OPTIMUM".
- HAS NOT RECEIVED ADEQUATE ATTENTION TO DATE.

APPROACHES FOR DEALING WITH DEPENDENCE OF REACTIVITY ON CONDITIONS

(CONTINUED)

CARB VEHICLE REGULATIONS USE THE MIR SCALE, BASED ON PEAK O₃ IN EKMA SCENARIOS WITH NO_x ADJUSTED TO GIVE MAXIMUM SENSITIVITY OF O₃ TO VOCs.

VOC EXEMPTION PROPOSALS HAVE USED DISTRIBUTIONS OF INTEGRATED AND PEAK O₃ REACTIVITIES IN THE 1-DAY EKMA SCENARIOS, AND OTHER CONSIDERATIONS.

IF THESE METHODS CHANGE, IT MAY CHANGE REACTIVITY SCALES MORE THAN UPDATES IN MECHANISM OR MODELS

POLICY ISSUES

- HOW SHOULD OZONE IMPACTS BE QUANTIFIED?
- WHAT CRITERIA SHOULD BE USED TO DETERMINE WHAT IS AN OPTIMUM REACTIVITY SCALE?
- WHAT ARE THE MOST APPROPRIATE ENVIRONMENTAL CONDITIONS TO USE WHEN ASSESSING REACTIVITY?

SCIENTIFIC CHALLENGE IS TO DERIVE SCENARIOS, MODELS AND PROTOCOLS BEST ADDRESSING POLICY PRIORITIES.

THE MIR SCALE HAS BECOME THE DEFAULT. IF NOTHING IS DONE, IT WILL CONTINUE TO BE USED.

INFORMATION AVAILABLE ON THE INTERNET

REACTIVITY TABULATIONS AND UNCERTAINTY CLASSIFICATIONS:

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

REPORTS ON RECENT REACTIVITY AND CHAMBER STUDIES AND SAPRC-97 MECHANISM DEVELOPMENT:

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

SAPRC-97 MECHANISM:

<http://cert.ucr.edu/~carter/saprc97.htm>

CHAMBER DATA BASE FOR MECHANISM EVALUATION (THROUGH 1995):

<ftp://cert.ucr.edu/pub/carter/chdata/>

SOFTWARE FOR REACTIVITY CALCULATION AND MECHANISM EVALUATION

<ftp://cert.ucr.edu/pub/carter/model/>