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

MARCH 26, 2001

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 EMMITED OXIDES OF NITROGEN (NOₓ) 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\textsubscript{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\textsubscript{x} IS COMPLEX

• VOC AND NO\textsubscript{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

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + O^3\text{P} \quad \text{(1)} \]
\[ O^3\text{P} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]

OR OVERALL

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}_3 \]

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

\[ \text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(2)} \]

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:

\[ \text{VOC} + \text{OH} \rightarrow R\cdot + \text{H}_2\text{O} \]
\[ R\cdot + \text{O}_2 \rightarrow \text{RO}_2\cdot \]
\[ \text{RO}_2 + \text{NO} \rightarrow \text{RO}\. + \text{NO}_2 \]
\[ \text{RO}\. + \text{O}_2 \rightarrow \text{HO}_2\. + \text{RCHO} \]
\[ \text{HO}_2\. + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]

OVERALL

\[ \text{OH} \]
\[ \text{VOC} + 2\text{O}_2 + 2\text{NO} \rightarrow \rightarrow \rightarrow \text{RCHO} + 2\text{NO}_2 + \text{H}_2\text{O} \]

COMBINED WITH

\[ h\nu \]
\[ \text{NO}_2 + \text{O}_2 \leftrightarrow \text{NO} + \text{O}_3 \]

YIELDS

\[ \text{OH}, \text{NO}_x \]
\[ \text{VOC} + 2\text{O}_2 \rightarrow \rightarrow \rightarrow \text{RCHO} + \text{H}_2\text{O} + 2\text{O}_3 \]

OZONE FORMATION CONTINUES UNTIL NO\textsubscript{x} IS REMOVED
IMPLICATIONS OF ATMOSPHERIC CHEMISTRY FOR OZONE CONTROL STRATEGIES

NOx CONTROL:

- NOx is required for ozone formation and ultimately limits how much ozone can be formed.
- But NOx also reduces the rate of ozone formation because it reacts with O3 and radicals.
- Therefore, NOx 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 NOx.
- VOC control is most effective near the source areas where NOx is high.
- VOC control is less effective in areas where ozone is NOx-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 NOx into account.
EFFECT OF VOCs AND NO\textsubscript{x} ON O\textsubscript{3} FORMATION

VARY NO\textsubscript{x} EMISSIONS

- MEDIUM
- LOW (x 1/3)
- HIGH (x 3)

VARY VOC EMISSIONS

- HIGH (x 3)
- MEDIUM
- LOW (x 1/3)
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 NOx REMOVAL. THIS AFFECTS ULTIMATE O3 YIELDS BECAUSE NOx 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**:

\[
\text{INCREMENTAL REACTIVITY OF A VOC IN AN EPISODE} = \lim_{[\text{VOC}] \to 0} \frac{\text{OZONE FORMED WHEN VOC ADDED TO EPISODE}}{\text{AMOUNT OF VOC ADDED TO EMISSIONS IN THE EPISODE}} - \frac{\text{OZONE FORMED IN AN EPISODE}}{}
\]

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 NOx 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$_x$

- Toluene
- Ethene /4
- Ethanol
- n-Butane

Mol O$_3$/Mol C_Voc vs. ROG/NO$_x$

High NO$_x$: 4.0 - 6.0
Low NO$_x$: 8.0 - 10.0

Max React: 6.5
Max O$_3$: 7.5

MAXIMUM O$_3$

0.08 0.11 0.13 0.14 0.16 0.18

High NO$_x$: 4.0 - 6.0
Low NO$_x$: 8.0 - 10.0
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 URBAN CONDITIONS WHERE OZONE IS MOST SENSITIVE TO VOC EMISSIONS
- GIVES GOOD CORRELATIONS TO EFFECTS OF VOCs ON INTEGRATED OZONE EXPOSURE.
- BUT DOES NOT REPRESENT CONDITIONS WHERE HIGHEST OZONE CONCENTRATIONS ARE FORMED.
## Examples of Incremental Reactivities in Scales Representing Different NO\textsubscript{x} Levels

<table>
<thead>
<tr>
<th>Compound or Mixture</th>
<th>Maximum VOC Impact (High NO\textsubscript{x})</th>
<th>NO\textsubscript{x} Giving Maximum Ozone (MOIR)</th>
<th>NO\textsubscript{x} &amp; VOC Impacts Equal (Low NO\textsubscript{x}) (EBIR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETHANE</td>
<td>0.31</td>
<td>0.20</td>
<td>0.15</td>
</tr>
<tr>
<td>ALL-ALKANE MINERAL SPIRITS</td>
<td>0.78</td>
<td>0.48</td>
<td>0.25</td>
</tr>
<tr>
<td>TEXANOL®</td>
<td>0.89</td>
<td>0.47</td>
<td>0.28</td>
</tr>
<tr>
<td>ETHYL BENZENE</td>
<td>2.79</td>
<td>1.00</td>
<td>0.42</td>
</tr>
<tr>
<td>M-XYLENE</td>
<td>10.6</td>
<td>3.2</td>
<td>1.5</td>
</tr>
<tr>
<td>AMBIENT VOC MIXTURE</td>
<td>3.7</td>
<td>1.5</td>
<td>0.85</td>
</tr>
</tbody>
</table>

**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](http://cert.ucr.edu/~carter/reactdat.htm)
## EXAMPLES OF RELATIVE REACTIVITIES AT DIFFERENT NO\textsubscript{x} LEVELS

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

<table>
<thead>
<tr>
<th>COMPOUND OR MIXTURE</th>
<th>MAX. VOC IMPACT (MIR) (HIGH NO\textsubscript{x})</th>
<th>NO\textsubscript{x} GIVING MAXIMUM OZONE</th>
<th>NO\textsubscript{x} &amp; VOC IMPACTS EQUAL (LOW NO\textsubscript{x})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETHANE</td>
<td>0.08</td>
<td>0.14</td>
<td>0.17</td>
</tr>
<tr>
<td>ALL-ALKANE MINERAL SPIRITS</td>
<td>0.21</td>
<td>0.33</td>
<td>0.30</td>
</tr>
<tr>
<td>TEXANOL®</td>
<td>0.24</td>
<td>0.32</td>
<td>0.33</td>
</tr>
<tr>
<td>ETHYL BENZENE</td>
<td>0.75</td>
<td>0.69</td>
<td>0.50</td>
</tr>
<tr>
<td>M-XYLENE</td>
<td>2.9</td>
<td>2.2</td>
<td>1.8</td>
</tr>
<tr>
<td>AMBIENT VOC MIXTURE</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
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

- Basic kinetic and mechanistic data
- Environmental chamber data for representative VOCs
- Data on chamber effects
- Model simulations of chamber experiments
- Chamber effects model
- Known or estimated rate constants for other VOCs
- Approximations and analogies for unknown mechanisms

Atmospheric reactivity mechanism for over 400 types of VOCs
## MECHANISM UNCERTAINTY CLASSIFICATION AND MINIMUM UNCERTAINTY ESTIMATES FOR RELATIVE MIR SCALE

<table>
<thead>
<tr>
<th>NO.</th>
<th>DESCRIPTION</th>
<th>MIN. UNC’Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MECHANISM NOT EXPECTED TO CHANGE SIGNIFICANTLY</td>
<td>15%</td>
</tr>
<tr>
<td>2</td>
<td>SOME UNCERTAINTIES BUT MECHANISM ADEQUATELY TESTED</td>
<td>15%</td>
</tr>
<tr>
<td>3</td>
<td>ESTIMATED MECHANISM BASED ON DATA FOR SIMILAR COMPOUNDS</td>
<td>30%</td>
</tr>
<tr>
<td>4</td>
<td>ESTIMATED MECHANISM BASED ON UNCERTAIN ASSUMPTIONS</td>
<td>75%</td>
</tr>
<tr>
<td>5,6</td>
<td>MECHANISM OR ESTIMATE IS HIGHLY SIMPLIFIED OR MAY BE INCORRECT</td>
<td>100%</td>
</tr>
</tbody>
</table>

**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

<table>
<thead>
<tr>
<th>NO.</th>
<th>EXAMPLES</th>
<th>MIN. UNC’Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>METHANOL, ACETALDEHYDE^[A]], 1-METHOXY-2-PROPANOL^[B]]</td>
<td>15%</td>
</tr>
<tr>
<td>2</td>
<td>ETHYLENE GLYCOL, ETHYLBENZENE, 1-METHOXY-2-PROPYL ACETATE^[C]]</td>
<td>15%</td>
</tr>
<tr>
<td>3</td>
<td>C\textsubscript{8+} ALKANES^[D]], MOST GLYCOLS, GLYCOL ETHERS, ESTERS, ETC.^[E]]</td>
<td>30%</td>
</tr>
<tr>
<td>4</td>
<td>C\textsubscript{13} NAPHTHALENES, FURAN, C\textsubscript{3+} ACETYLENES^[D]]</td>
<td>75%</td>
</tr>
<tr>
<td>5</td>
<td>AMINES, OXIMES, HALOGENATED COMPOUNDS, OXIMES, ETC.^[E]]</td>
<td>100%</td>
</tr>
</tbody>
</table>

**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

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>MIR UNC’Y</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ALL-ALKENE PETROLEUM DISTILLATES</strong></td>
<td></td>
</tr>
<tr>
<td>• MINIMAL INFORMATION GIVEN</td>
<td>~33%</td>
</tr>
<tr>
<td>• CARBON NUMBER DISTRIBUTIONS KNOWN</td>
<td>~17%</td>
</tr>
<tr>
<td>• FRACTIONS OF NORMAL AND TOTAL BRANCHED AND CYCLIC ALSO KNOWN</td>
<td>0%</td>
</tr>
<tr>
<td><strong>MIXTURES OF AROMATICS</strong></td>
<td></td>
</tr>
<tr>
<td>• MINIMAL INFORMATION GIVEN</td>
<td>~60%</td>
</tr>
<tr>
<td>• CARBON NUMBER DISTRIBUTIONS KNOWN</td>
<td>~55%</td>
</tr>
<tr>
<td>• FRACTIONS OF MONO-, DI-, AND POLY-SUBSTITUTED BENzenes AND NAPHTHALENES ALSO KNOWN</td>
<td>0%</td>
</tr>
<tr>
<td><strong>OTHERS</strong></td>
<td></td>
</tr>
<tr>
<td>• UNSPECIFIED GLYCOL ETHERS</td>
<td>~30%</td>
</tr>
<tr>
<td>• PETROLEUM DISTILLATE WITH AROMATIC FRACTION NOT SPECIFIED</td>
<td>~100%</td>
</tr>
</tbody>
</table>
**EXAMPLE WORKSHEET TO ESTIMATE OZONE IMPACTS OF A FORMULATION**

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>GM /LITER</th>
<th>MIR (GM O₃ / GM)</th>
<th>MIR UNC’Y COMP</th>
<th>O₃ FORM. (GM O₃ / LITER)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALKANE MIX</td>
<td>100</td>
<td>0.85</td>
<td>15%</td>
<td>30%</td>
</tr>
<tr>
<td>AROMATIC MIX</td>
<td>10</td>
<td>6.4</td>
<td>50%</td>
<td>30%</td>
</tr>
<tr>
<td>TEXANOL®</td>
<td>20</td>
<td>0.89</td>
<td>0</td>
<td>30%</td>
</tr>
<tr>
<td>AMINE</td>
<td>5</td>
<td>~7</td>
<td>0</td>
<td>100%</td>
</tr>
<tr>
<td>UNIDENTIFIED VOCs</td>
<td>2</td>
<td>~4</td>
<td>200%</td>
<td></td>
</tr>
<tr>
<td>WHOLE FORMULATION</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>MIR x EMIT</th>
<th>TYPE OF VOC</th>
<th>MECH UNC’Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>~10%</td>
<td>Texanol®</td>
<td>3</td>
</tr>
<tr>
<td>~5%</td>
<td>Butyl Carbitol</td>
<td>3</td>
</tr>
<tr>
<td>~3%</td>
<td>Various Petroleum Distillates</td>
<td>-</td>
</tr>
<tr>
<td>~1%</td>
<td>Methyl Carbitol®</td>
<td>3</td>
</tr>
<tr>
<td>~0.5%</td>
<td>Diethylene Glycol</td>
<td>3</td>
</tr>
<tr>
<td>~0.5%</td>
<td>Di (propylene glycol) Methyl Ether</td>
<td>3</td>
</tr>
<tr>
<td>~0.5%</td>
<td>2-Amino-2-Methyl-1-Propanol</td>
<td>6</td>
</tr>
<tr>
<td>~25%</td>
<td>UNCERTAIN VOC TOTAL</td>
<td></td>
</tr>
</tbody>
</table>

WATER BASED COATINGS

<table>
<thead>
<tr>
<th>MIR x EMIT</th>
<th>TYPE OF VOC</th>
<th>MECH UNC’Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>~50%</td>
<td>Various Petroleum Distillates</td>
<td>-</td>
</tr>
<tr>
<td>~1%</td>
<td>n-Butyl Alcohol</td>
<td>3</td>
</tr>
<tr>
<td>~0.5%</td>
<td>Ethyl 3-Ethoxypropionate</td>
<td>3</td>
</tr>
<tr>
<td>~50%</td>
<td>UNCERTAIN VOC TOTAL</td>
<td></td>
</tr>
</tbody>
</table>

SOLVENT BASED COATINGS
## MAJOR TYPES OF PETROLEUM DISTILLATES

PRELIMINARY DATA FROM CALIFORNIA ARB
1998 ARCHITECTURAL COATINGS SURVEY

<table>
<thead>
<tr>
<th>DESCRIPTION</th>
<th>EMIT</th>
<th>MIR [^{[a]}]</th>
<th>MIR x EMIT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoddard Solvent</td>
<td>19%</td>
<td>~3</td>
<td>25%</td>
</tr>
<tr>
<td>Aromatic 100</td>
<td>5%</td>
<td>~8</td>
<td>20%</td>
</tr>
<tr>
<td>Protected Data [^{[b]}]</td>
<td>15%</td>
<td>~2 [^{[c]}]</td>
<td>16%</td>
</tr>
<tr>
<td>Medium Aliphatic Solvent Naphtha</td>
<td>33%</td>
<td>~1</td>
<td>15%</td>
</tr>
<tr>
<td>Vm &amp; Painters Naphtha</td>
<td>7%</td>
<td>~2</td>
<td>8%</td>
</tr>
<tr>
<td>Petroleum Naphtha, Heavy Alkylate</td>
<td>7%</td>
<td>~1.5</td>
<td>6%</td>
</tr>
<tr>
<td>Distillate (Petroleum), Hydrotreated Light</td>
<td>5%</td>
<td>~1.5</td>
<td>4%</td>
</tr>
<tr>
<td>Kerosene</td>
<td>2%</td>
<td>~2</td>
<td>2%</td>
</tr>
<tr>
<td>Petroleum Ether</td>
<td>2%</td>
<td>~1.5</td>
<td>1%</td>
</tr>
</tbody>
</table>

\[^{[a]}\] 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\textsubscript{x} OFFGASING ~1 PPB/DAY

OBTAINING INSTRUMENTATION MOST NEEDED FOR ASSESSING LOW NO\textsubscript{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 TEFILON 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

200,000 Liter Teflon Bag Reactor

Temperature controlled room flushed with purified air and with reflective material on all inner surfaces

20 ft.

20 ft.

200 KW Argon Arc Light

Access Door

Sample Lines to monitoring instruments in laboratory room on the floor below
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

[Diagram showing flow system with labels for HONO Generation System, Pure Air Source, Syringe Pump, VOC Injection Tube, Irradiated Enclosure, Quartz Tube Reactor, NO, NOx, Ozone Analyzers, and Vent.]
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

<table>
<thead>
<tr>
<th>Carbon Number</th>
<th>Direct Reactivity (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
</tr>
<tr>
<td></td>
<td>Model</td>
</tr>
</tbody>
</table>

Based on single GC sample ->

Corrected ->
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

<table>
<thead>
<tr>
<th>REACTIVITY RESEARCH WORKING GROUP</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="http://www.cgenv.com/narsto/reactinfo.html">http://www.cgenv.com/narsto/reactinfo.html</a></td>
</tr>
<tr>
<td>• MISSION STATEMENT</td>
</tr>
<tr>
<td>• REACTIVITY POLICY WHITE PAPER</td>
</tr>
<tr>
<td>• REACTIVITY SCIENCE ASSESSMENT DOCUMENTS</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>REACTIVITY DATA AND DOCUMENTATION</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="http://www.cert.ucr.edu/~carter/reactdat.htm">http://www.cert.ucr.edu/~carter/reactdat.htm</a></td>
</tr>
<tr>
<td>• TABULATION OF MIR, OTHER REACTIVITY SCALES</td>
</tr>
<tr>
<td>• REPORT DOCUMENTING CHEMICAL MECHANISM AND METHODS USED TO CALCULATE REACTIVITY</td>
</tr>
<tr>
<td>• LINKS TO OTHER REPORTS AND PRESENTATIONS CONCERNING W.P.L. CARTER’S RESEARCH</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CALIFORNIA ARB’S PROPOSED AEROSOL COATINGS REGULATION</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="http://arb.ca.gov/regact/conspro/aerocoat/aerocoat.htm">http://arb.ca.gov/regact/conspro/aerocoat/aerocoat.htm</a></td>
</tr>
<tr>
<td>• REGULATION AND RULEMAKING INFORMATION AND TECHNICAL SUPPORT DOCUMENTS</td>
</tr>
</tbody>
</table>