

VOC Reactivity Policy White Paper

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Prepared for
Reactivity Research Work Group

by
RRWG Policy Team

DISCLAIMER

The members of the RRWG Policy Team have developed this White Paper to highlight scientific issues and to identify future research needs concerning VOC emissions. It should be noted, however, that this White Paper does not necessarily represent the opinion of each individual member of the RRWG Policy Team, the organizations with which these individuals are affiliated, or the RRWG Policy Team as a whole. The RRWG Policy Team does not intend this White Paper to constitute consensus advice or recommendations to EPA or any other regulatory body regarding future regulation of VOC.

EPA has been a participant in the work of the RRWG Policy Team and in the preparation of this White Paper in order to promote an open dialog regarding scientific issues and necessary research. Nevertheless, EPA notes that it must comply with current statutory mandates to regulate VOC emissions, and that any reconsideration of EPA's policies regarding regulation of VOC emissions does not delay or suspend the Agency's obligations to comply with such mandates. If additional studies that arise as a result of this White Paper justify the Agency's reconsideration of any regulatory program in the future, EPA will take such action as the Agency deems appropriate at that time. The Agency does not consider this White Paper or any other materials created by the RRWG to be consensus advice or recommendations for the Agency.

TABLE OF CONTENTS

1. INTRODUCTION	1-1
1.1 Background	1-1
1.2 Reactivity Research Work Group	1-2
1.3 Scope of This Document	1-2
2. HISTORY OF VOC REACTIVITY POLICY	2-1
2.1 U. S. Environmental Protection Agency Policy	2-1
2.1.1 VOC as a Focus of Ozone Policy	2-1
2.1.1.1 1970 to 1990 VOC Policy	2-1
2.1.1.2 History of Volatility in VOC Definition	2-4
2.1.2 VOC Definition and Exemption Policy	2-6
2.1.3 Implications of VOC Policy Implementation	2-8
2.1.3.1 Impacts of Volatility Thresholds and Test Methods	2-8
2.2 California Air Resources Board's Use of Reactivity	2-9
2.2.1 Activities Undertaken to Support Reactivity Policy Development	2-10
2.2.1.1 Selection of a Reactivity Scale for Use in the California Regulations	2-10
2.2.1.2 Research Performed to Address Issues of Concern	2-10
2.2.1.3 Effect of the Air Quality Model on Reactivity	2-11
2.2.1.4 Effect of the Chemical Mechanism on Reactivity	2-12
2.2.1.5 Effect of Uncertainties on Reactivity	2-12
2.2.2 California's Regulatory Programs Using Reactivity	2-14
2.2.2.1 Low Emission Vehicles and Clean Fuels Regulation	2-14
2.2.2.2 VOC Reactivity Control Program for Consumer Products	2-15
2.2.2.2.1 Using the MIR Scale as a Voluntary Compliance Option for Aerosol Coatings	2-15
2.2.2.2.2 Assigning MIR Values to VOCs	2-16
2.2.2.2.3 Uncertainty Bins	2-16
2.2.2.2.4 Upper Limit MIR Calculations	2-18
2.2.2.2.5 Hydrocarbon Solvent Bins	2-18
2.2.2.2.6 Proposed Methodologies to Calculate Limits	2-19
3. PURPOSE AND SCOPE OF REACTIVITY POLICY	3-1
3.1 Control VOCs That Impact Nonattainment Areas	3-1
3.2 Use VOC Substitution to Reduce Ozone, PM and Haze Formation	3-2
3.3 Provide Progress Toward Other Air Quality Goals	3-3
3.4 Consistency with Existing Authority and Programs	3-3

TABLE OF CONTENTS

4. OPTIONS FOR A VOC REACTIVITY POLICY	4-1
4.1 General Issues	4-1
4.1.1 Impacts of Concern	4-1
4.1.2 Geographic Applicability	4-2
4.1.3 Variation by Source Type	4-4
4.1.4 Atmosphere Availability	4-5
4.2 Regulatory Approaches	4-6
4.2.1 Classification Schemes	4-6
4.2.2 Treatment Schemes	4-9
4.2.2.1 Exemption Schemes	4-9
4.2.2.2 Weighting Schemes	4-10
4.2.3 Implementation Opportunities and Challenges	4-11
4.2.3.1 Planning and Assessments	4-11
4.2.3.2 Control Measure Design and Implementation	4-12
4.2.3.3 Compliance and Enforcement	4-14
4.3 Summary of Design Issues	4-15
5. ORIGINS OF VOC REACTIVITY FOR OZONE & PM FORMATION	5-1
5.1 Ozone and Particulate Matter Formation	5-1
5.2 Reactivity of VOCs	5-4
5.2.1 Explaining Reactivity	5-4
5.2.2 Explaining Sensitivity to VOC Change	5-5
5.2.2 Demonstration of Effects of Environmental Conditions on Reactivity ..	5-8
5.3 Computing Reactivities of VOCs	5-9
6. TOPICS FOR VOC REACTIVITY RESEARCH	6-1
6.1 Implementation Issues	6-1
6.2 Scientific Issues	6-2
6.2.1 Concept Scoping Questions	6-2
6.2.2 Important Broad-scope Questions	6-3
6.3 Some Short-term Research Projects	6-3
7. Appendix	7-1
7.1 RRWG Policy Team Participants	7-1

1. INTRODUCTION

1.1 BACKGROUND

The Environmental Protection Agency (EPA) has promulgated regulations and developed implementation control strategies over three decades to reduce the photochemical smog afflicting many urban areas across the nation. The photochemical oxidants ozone (O₃) and oxides of nitrogen (NO_x), which are the major constituents of photochemical smog, pose risks to human health and the environment. To protect human health and the environment, EPA sets a national ambient air quality standard (NAAQS) for ozone.

The EPA provides guidance for each State with areas not attaining the applicable ozone standard to develop its State Implementation Plan (SIP) to attain the standard by the designated attainment date. The Clean Air Act directs EPA to regulate both VOC and NO_x emissions. Since 1970, EPA's underlying strategy to reduce tropospheric levels of ozone in nonattainment areas has focused mainly on reducing the total mass of volatile organic compound (VOC) emissions because they are a precursor of ozone pollution. In the 1990's EPA began developing policies and guidance for reducing NO_x emissions as a strategy, in addition to VOC emission reductions, to achieve the ozone standard, especially in those situations where upwind transport significantly contributes to nonattainment.

Although EPA has focused its VOC control strategy on the reduction of all VOC emissions without regard to the reactivity of the individual species of VOC, EPA has made some attempts over the years to consider variations in VOC reactivity in its SIP policy and guidance. These efforts eventually led to the development of EPA's exemption policy for negligibly reactive VOCs. The paucity of chemical reactivity data and the lack of a viable reactivity scale or index that is invariant to location, however, are major issues which have limited the development of a VOC control policy based on the differences in reactivity between different compounds. Advances in the understanding of atmospheric photochemistry and in the improvement of the models simulating atmospheric processes and ozone formation made over recent years, however, may afford EPA an opportunity to develop a VOC control policy which reflects differences in VOC reactivity, provided further research can resolve a number of technical issues.

After several decades of total VOC emission reductions in nonattainment areas, the least expensive and most cost-effective control measures have generally been implemented. But, to attain the 1-hour ozone standard in nonattainment areas further reductions in ozone formation from VOCs may be needed in some of the areas. The development of a broader-based VOC regulatory policy recognizing the relative reactivity of individual species of VOC may have potential benefits to both the environment and industry by lowering the ozone forming potential of pollutants released to the atmosphere while extending the cost-effectiveness of a VOC control strategy and affording greater flexibility to the regulated community. Also a VOC control policy based on relative reactivity could provide a viable way of dealing with interrelated

and competing environmental issues such as fine particle formation, toxicity, stratospheric ozone depletion, and global warming through VOC substitution and exemption strategies to the extent permitted by the Clean Air Act. However, while there are potential benefits that may be realized by such a VOC control policy, there are significant hurdles associated with developing a practical, cost-effective, enforceable VOC policy based on relative reactivity of VOCs. Additional research may help to solve these problems.

1.2 REACTIVITY RESEARCH WORK GROUP

If EPA were to develop VOC control policy based on relative reactivity, a number of technical issues would need to be addressed by additional research. In May 1998, EPA invited interested parties to participate in a public-private partnership to sponsor research that would help to address technical issues relevant to the formulation of a VOC control policy. As a result of this invitation, representatives of Federal and State agencies, the academic community and industrial companies and associations formed the Reactivity Research Work Group (RRWG). The stated mission of the RRWG is ...

To provide an improved scientific basis for reactivity-related regulatory policies. That [mission] will be accomplished by bringing together all parties actively interested in sponsoring, planning, performing or assessing policy-relevant scientific research on the reactivities of organic compounds emitted to ambient air, as related to the formation of ozone, PM_{2.5}, and regional haze. This [work group] is for the purposes of coordinating such research and defining potential applications, while continuously involving key policy makers.¹

The activities of RRWG are not intended to formulate or develop policy nor to develop consensus advice on policy options; but, rather, to identify areas of research that may assist policy makers in making decisions about VOC control policy and to sponsor this research.

As a first step in its mission, the RRWG formed two teams to prepare white papers on the state of knowledge and the status of current research in the field of VOC reactivity (research team) and on possible policy options and the relevant technical issues related to reactivity (policy team).

1.3 SCOPE OF THIS DOCUMENT

The purpose of this white paper is to provide a starting point to identify possible areas of research which could assist Federal, State or local policy makers in developing VOC emission control strategies and related guidance and policy based on the reactivity of individual species of VOC. This paper gives (chapter

¹ RRWG adopted this mission statement at its December 2-3, 1998 meeting in Research Triangle Park, NC.

2) an overview of past and current EPA and State guidance and policies associated with VOC reactivity issues. Chapters 3 and 4 outline potential opportunities and goals for a VOC control policy based upon reactivity and identify possible concept options or approaches which could be considered in such a policy. Our intent here is not to devise or recommend policy *per se* nor to provide an exhaustive list of options, but to create a framework for identifying and examining possible technical issues and related research areas that would help to inform future policy decisions. A brief overview of the significance of VOC reactivity and fine particulate matter formation is given in chapter 5. Chapter 6 attempts to identify the technical issues and research topics associated with the options presented in chapter 4.

2. HISTORY OF VOC REACTIVITY POLICY

2.1 U. S. ENVIRONMENTAL PROTECTION AGENCY POLICY

2.1.1 VOC as a Focus of Ozone Policy

2.1.1.1 1970 to 1990 VOC Policy

Volatile organic compounds (VOCs) are defined in 40 CFR 51.100 as “any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.” The initial version of the current control regulation was issued in 1971 as part of the U.S. Environmental Protection Agency’s (EPA) guidance to States for the preparation of State Implementation Plans (SIPs) for demonstrating ozone attainment. In this initial guidance, EPA emphasized the reduction of the total mass of organic emissions, but also offered that “substitution of one compound for another might be useful where it would result in a clearly evident decrease in reactivity and thus tend to reduce photochemical oxidant formation.” This latter statement encouraged States to promulgate SIPs with organic emission control provisions similar to those outlined in Los Angeles District’s Rule 66, which allowed many VOC species with minimal adverse effects to be exempted from control.

The Rule 66 exempt status for many of these organic emission species was questioned a few years later when research results from field studies conducted between 1971-1974 revealed that pollutant transport conditions were capable of enhancing ozone formation such that these “exempt” compounds were now considered significant ozone producers. Thus, in 1977 the EPA issued the “Recommended Policy on Control of Volatile Organic Compounds,” offering its own, much more limited list of exempt compounds. Specifically, in the “Recommended Policy” there were only 12 listed organic compounds that EPA judged at the time to be “negligibly reactive” and of those compounds, only 4 qualified for an exemption. However, in recent years, as research data have become available, additional compounds (primarily from the halocarbon family of compounds) have been found to be “negligibly reactive” and further exemptions have been granted for specific compounds (see Table 2-1).

Table 2-1. Organic Compounds That EPA Has Exempted from the Definition of Volatile Organic Compounds (VOCs) in 40 CFR 51.100.

	Compound	Exemption Date^a	FR Citation
1	methane	July 8, 1977	42 FR 35314
2	ethane	July 8, 1977	42 FR 35314
3	1,1,1 trichloroethane (methyl chloroform)	July 8, 1977	42 FR 35314
4	1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)	July 8, 1977	42 FR 35314
5	dichloromethane (methylene chloride)	June 4, 1979 May 16, 1980	44 FR 32042 45 FR 32424
6	trichlorofluoromethane (CFC-11)	July 22, 1980	45 FR 48941
7	dichlorodifluoromethane (CFC-12)	July 22, 1980	45 FR 48941
8	chlorodifluoromethane (HCFC-22)	July 22, 1980	45 FR 48941
9	trifluoromethane (HFC-23)	July 22, 1980	45 FR 48941
10	1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114)	July 22, 1980	45 FR 48941
11	chloropentafluoroethane (CFC-115)	July 22, 1980	45 FR 48941
12	1,1,1-trifluoro-2,2-dichloroethane (HCFC-123)	January 18, 1989	54 FR 1988
13	1,1,1,2-tetrafluoroethane (HFC-134a)	January 18, 1989	54 FR 1988
14	1,1-dichloro-1-fluoroethane (HCFC-141b)	January 18, 1989	54 FR 1988
15	1-chloro-1,1-difluoroethane (HCFC-142b)	January 18, 1989	54 FR 1988
16	2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124)	March 18, 1991	56 FR 11418
17	pentafluoroethane (HFC-125)	March 18, 1991	56 FR 11418
18	1,1,2,2-tetrafluoroethane (HFC-134)	March 18, 1991	56 FR 11418
19	1,1,1-trifluoroethane (HFC-143a)	March 18, 1991	56 FR 11418
20	1,1-difluoroethane (HFC-152a)	March 18, 1991	56 FR 11418
	<i>Perfluorocarbon compounds which fall into these classes:</i>		
21	cyclic, branched, or linear, completely fluorinated alkanes;	March 18, 1991	56 FR 11418
22	cyclic, branched, or linear, completely fluorinated ethers with no unsaturations;	March 18, 1991	56 FR 11418
23	cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations; and,	March 18, 1991	56 FR 11418
24	sulfur containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine	March 18, 1991	56 FR 11418
	<i>EPA adopted a definition of VOC in 40 CFR 51.100(s)</i>	February 3, 1992	57 FR 3941
25	parachlorobenzotrifluoride (PCPTF)	October 5, 1994	59 FR 50693

	Compound	Exemption Date^a	FR Citation
26	cyclic, branched, or linear completely methylated siloxanes	October 5, 1994	59 FR 50693
27	acetone	June 16, 1995	60 FR 31633
28	tetrachloroethane (perchloroethylene)	February 7, 1996	61 FR 4588
29	3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca)	October 8, 1996	61 FR 52848
30	1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb)	October 8, 1996	61 FR 52848
31	1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-43-10mee)	October 8, 1996	61 FR 52848
32	difluoromethane (HFC-32)	August 25, 1997	62 FR 44900
33	ethylfluoride (HFC-161)	August 25, 1997	62 FR 44900
34	1,1,1,3,3,3-hexafluoropropane (HFC-236fa)	August 25, 1997	62 FR 44900
35	1,1,2,2,3-pentafluoropropane (HFC-245ca)	August 25, 1997	62 FR 44900
36	1,1,2,3,3-pentafluoropropane (HFC-245ea)	August 25, 1997	62 FR 44900
37	1,1,1,2,3-pentafluoropropane (HFC-245eb)	August 25, 1997	62 FR 44900
38	1,1,1,3,3-pentafluoropropane (HFC-245fa)	August 25, 1997	62 FR 44900
39	1,1,2,3,3-hexafluoropropane (HFC-236ea)	August 25, 1997	62 FR 44900
40	1,1,1,3,3-pentafluorobutane (HFC-365mfc)	August 25, 1997	62 FR 44900
41	chlorofluoromethane (HCFC-31)	August 25, 1997	62 FR 44900
42	1-chloro-1-fluoroethane (HCFC-151a)	August 25, 1997	62 FR 44900
43	1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a)	August 25, 1997	62 FR 44900
44	1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane (C ₄ F ₉ OCH ₃)	August 25, 1997	62 FR 44900
45	2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane ((CF ₃) ₂ CF ₂ OC ₂ H ₅)	August 25, 1997	62 FR 44900
46	1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane (C ₄ F ₉ OCH ₂ H ₃)	August 25, 1997	62 FR 44900
47	2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane ((CF ₃) ₂ CF ₂ OC ₂ H ₅)	August 25, 1997	62 FR 44900
48	methyl acetate	April 9, 1998	63 FR 17331

^a
Date shown is publication date of the Notice in the Federal Register. Actual exemption date is generally 30 to 60 days after this publication date.

The foundation of this policy uses the “ k_{OH} ” method for determining a specific compound’s reactivity relative to the reactivity of ethane under set conditions. The k_{OH} -value represents the molar rate constant for reactions between the subject compound (e.g., ethane) and the hydroxyl radical (i.e., $\cdot OH$). This reaction is very important since it is the primary pathway by which organic compounds initially participate in atmospheric photochemical reaction processes. Under the current policy, compounds with reactivity equal to or less than that of ethane would be considered “negligibly reactive” and exempt from

the current VOC regulations. The comparison of reactivities for specific compounds is based on the chemical premise that chemical reactions occur on a mole (i.e. number of molecules) basis, not on a mass (i. e. mass of the molecule) basis. The latter concept is extremely important because the use of ethane as the benchmark compound is only valid given that reactivity comparisons with ethane are performed on an equimolar concentration basis. The policy emphasizes positive controls on all organic compounds since the available transport studies suggest that all VOCs eventually would react in the photochemical process.

With the adoption of the Clean Air Act Amendments of 1990 (1990 CAA), Congress shifted the focus of ozone attainment strategies away from solely VOCs and began to recognize and acknowledge the benefits associated with co-control of VOCs and oxides of nitrogen (NO_x). In essence, the 1990 CAA continued controls for VOCs and added NO_x control requirements in areas that had more persistent problems with attaining the National Ambient Air Quality Standard (NAAQS) for ozone. The EPA has highlighted the need for an integrated pollutant assessment when developing attainment strategies for photochemically-derived pollution. Thus, in light of the 1990 CAA and the numerous advances in science and technology over the past two decades, it may be appropriate to revisit the VOC policy originally defined in the early- to mid-1970s.

2.1.1.2 History of Volatility in VOC Definition

In the late 1970s, EPA began publishing a series of control techniques guidelines (CTGs) at the request of several States for assistance in determining what control technologies are reasonably available to control volatile organic compound (VOC) emissions. Volume II of the CTG series (Control of Volatile Organic Emissions from Existing Stationary Sources - Volume II: Surface Coating of Cans, Coils, Paper, Fabrics, Automobiles, and Light-Duty Trucks," May 1977, EPA-450/2-77-008) contained an appendix which gave guidance to aid in writing rules containing the emission limitations recommended in the document. In this appendix, a series of definitions were given including a definition for "volatile organic compounds." This definition said:

Volatile organic compound is any compound of carbon (excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate) that has a vapor pressure greater than 0.1 mm of Hg at standard conditions.

Based on the vapor pressure limits, EPA's VOC definition above (0.1 mm Hg) appeared to be more stringent (i. e. classifying more organic compounds as VOCs) than the older Rule 66 definition (0.5 mm Hg) which Los Angeles AQMD had provided. A closer analysis of these two definitions, however, revealed that the above VOC definition was actually less stringent because of the different temperatures at which the vapor pressures are specified and different carbon number cutoffs for VOCs. The VOC definition above defined VOCs as organic compounds having vapor pressures at standard conditions (20E F) greater than 0.1 mm Hg; whereas, Rule 66 defined VOCs as having vapor pressures at 220E F (104E

C) greater than 0.5 mm Hg. The VOC definition included in the surface coating CTGs further considered compounds with carbon numbers less than 12 as VOCs compared to Rule 66 which considered compounds with carbon numbers below 18 as VOCs.

Several States adopted the 0.1 mm Hg vapor pressure cutoff. It soon became apparent to EPA that this cutoff exempted from controls organic compounds which do in fact evaporate into the air where the compounds are available to participate in photochemical reactions. In addition, EPA and States learned that Method 24 (the test method used to measure VOC in paints and coatings) measured as VOC some organic compounds which have vapor pressures below 0.1 mm Hg at standard conditions (20E F). Scientific literature published after EPA's surface coating CTGs showed that organic compounds with much higher carbon number than 12 are found in the vapor state. Compounds with carbon numbers up to 18 are routinely found in the vapor state. Compounds with carbon numbers over 24 are found partially in the vapor state and partly condensed. Some alkane compounds with carbon numbers up to 31 have been found in the vapor state.

For these reasons, EPA decided to revise its guidance regarding the vapor pressure cutoff in the definition of VOC. The EPA decided that if a compound could be vaporized, especially at elevated temperatures, it could be available in the vapor state to participate in photochemical reactions. Whether or not a compound is vaporized depends to a large extent on how it is heated during use. This can not be determined in advance by EPA. The EPA decided that it would be appropriate to remove the vapor pressure cutoff altogether from the definition of VOC.

On November 24, 1987, EPA proposed a new ozone and carbon monoxide policy statement. In that proposal, the Agency described a process to make State Implementation Plan (SIP) deficiency "calls" pursuant to Section 110 (a)(2)(H) of the 1977 CAA. Appendix D of the proposed policy statement contained a listing of SIP deficiencies and inconsistencies that States should address and correct when responding to such SIP calls. In this Federal Register notice (52 FR 45108), EPA said "Many rules incorrectly contain a vapor pressure cutoff (e.g., 0.1 mm Hg) that effectively exempts some photochemically reactive compounds (such as diethylene glycol monobutyl ether, a solvent, and certain mineral oils) from control." The notice then provided a model definition of "volatile organic compound" for use which did not contain a vapor pressure cutoff.

Later, in May 1988, EPA issued additional guidance to States to clarify the SIP call policy in a document titled: "Issues Relating to VOC Regulation Cut points, Deficiencies, and Deviations - Clarification to Appendix D of November 24, 1987 Federal Register." This document provided that States "Cannot use 0.1 mm Hg vapor pressure cutoff to define VOC -- inconsistent with EPA reactivity policy. Such a definition would exempt compounds of low volatility, which, under certain processes, would volatilize and,

therefore, would participate in photochemical reactions. A State must eliminate this loophole from the SIP."²

The 1990 CAA in effect codified EPA's SIP call process by requiring areas to correct existing deficiencies in their reasonably available control technology (RACT) rules.³ States responded by correcting the deficiencies, including removing the 0.1 mm Hg vapor pressure cutoff from the definition of VOC.

On February 3, 1992, EPA published (57 FR 3941) a definition of VOC that was subsequently codified in the Code of Federal Regulations [40 CFR 51.100(s)] for use in evaluating SIPs to control ozone ambient air non-attainment. This definition does not contain the vapor pressure cutoff. Most States have now adopted this definition of VOC or something very similar for use in their own VOC regulations.

The absence of a vapor pressure cutoff has caused a certain amount of confusion within the regulated community. People ask if there is any organic material of such low vapor pressure that it cannot be considered volatile. Suppliers are often asked by their customers to specify what percent of a product is VOC. If part of the product is a very low vapor pressure material, perhaps a solid at room temperature, should this material be counted as VOC in the product? If the material is a paint or ink, the answer can be found by running a Method 24 test. The solid film forming part of the coating is not counted as VOC even though it may be partly organic. However, for many products there is no test method analogous to Method 24 which can be used to calculate VOC mass content. This raises the question of whether a compound with a vapor pressure that is so low that compounds of like vapor pressure are never found in the air in a vapor state should really be considered a volatile organic compound. Such a question suggests that some vapor pressure cutoff may be appropriate, but one much lower than 0.1 mm Hg at 20E F.

2.1.2 VOC Definition and Exemption Policy

At various times in the past, EPA has recommended example VOC definitions which States might use for regulatory purposes. For example, EPA published a model VOC definition in the May 1977 control technique guideline document "Control of Volatile Organic Emissions from Existing Stationary Source - Volume II: Surface Coating of Cans, Coils, Paper, Fabrics, Automobiles, and Light-Duty Trucks." This model definition did not recognize any exempted compounds, except those that had a vapor pressure below a certain cutpoint.

² U. S. Environmental Protection Agency, "Issues Relating to VOC Regulation Cut points, Deficiencies, and Deviations - Clarification to Appendix D of November 24, 1987 Federal Register," Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, May 25, 1988, p. 1-2a. (Note: This document is often called the "Blue Book".)

³ Clean Air Act section 182(a)(2)(A)

On July 8, 1977, the "Recommended Policy on Control of Volatile Organic Compounds" was published that established the basic policy which EPA has used regarding photochemical reactivity since that time. That statement listed the following four compounds as being of negligible photochemical reactivity and said these should be exempt from regulation under State Implementation Plans: methane; ethane; 1,1,1-trichloroethane (methyl chloroform); 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113). That policy statement said that as new information becomes available the list of compounds may be revised periodically to add compounds to or delete them from the list of negligibly reactive compounds. Organic compounds listed as entries 1 to 24 in Table 2-1 above were added to the list by revisions to policy statements which were published in the Federal Register.

The EPA's decision to exempt certain compounds in its 1977 policy was heavily influenced by experimental smog chamber work done earlier in the 1970's. In this experimental work, smog chamber runs were made with various compounds at a molar concentration that is typical of the total molar concentration of volatile organic compounds in Los Angeles ambient air. If the compound in the smog chamber did not result in ozone formation of 0.08 ppm of ozone, which was the oxidant standard at that time, it was assumed that emissions of the compound would not cause the ozone standard to be exceeded. The compound could then be considered to be negligibly reactive. Ethane was the most reactive compound tested that did not cause the 0.08 ozone level in the smog chamber to be exceeded.

These experiments were somewhat of a simplification in that only one organic compound was in the chamber during the tests. Researchers have since learned that if a variety of organic species are present, their reactivities can sometimes have a synergistic effect, and a new increment of a given species added to such a mixture may cause more ozone to form than if the aliquot is added to air containing only that compound (plus NO_x). Also the smog chamber experiments were one day experiments, and the effects of multi day sunlight exposure was not evaluated. Both of these factors might tend to produce more ozone in the real world than under the laboratory conditions.

The July 8, 1977 policy referred to above provided a basis for a definition of VOC, but did not contain a specific VOC definition. The most recent model definition appeared in the May 25, 1988 document of guidance to States for use in revising State implementation plans "Issues Relating to VOC Regulation Cutpoints, Deficiencies, and Deviations" which contained a model VOC definition for States to use in State implementation plans. This model definition excluded all the compounds for which EPA had excluded from the definition of VOC in previously issued policy statements, saying that the compounds were negligibly reactive.

Therefore, EPA decided that there should be an official VOC definition in the Code of Federal Regulations to which EPA could refer as a reference in various other places. On February 3, 1992 (57 FR 3941), EPA adopted a definition of VOC in 40 CFR 51.100(s). The new definition of VOC had a list of negligibly reactive compounds which States did not need to control in ozone nonattainment areas. (There was no vapor pressure cut-off in this definition.) The negligibly reactive list consisted of the original

four compounds from the 1977 policy statement plus all other compounds which EPA had recognized as negligibly reactive in Federal Register policy revisions since then. Prior to this time EPA had classified compounds negligibly reactive through policy revisions. After this date, EPA has added compounds to the negligibly reactive list by revising the definition of VOC at 40 CFR 51.100(s). Compounds which EPA has added since 1992 to the negligibly reactive list in the definition of VOC are given in Table 2-1 above as entries 25 to 48 along with the date the action was announced in the Federal Register.

2.1.3 Implications of VOC Policy Implementation

2.1.3.1 Impacts of Volatility Thresholds and Test Methods

While the definition of VOC in 40 CFR 51.100 (s) does not consider volatility of the organic compound, EPA does consider the volatility of organic compounds in the development of new source performance standards and in recommendations of control technology guidelines (CTG's) for use by States. Thus, the definition of VOC in 40 CFR 51.100(s) is but one part of the overall regulatory approach that EPA has used to reduce the formation of photochemical oxidants. For rules established under section 111 of the Clean Air Act, EPA has defined VOC as

Volatile Organic Compound means any organic compound which participates in atmospheric photochemical reactions; or which is measured by a reference method, an equivalent method, an alternative method, or which is determined by procedures specified under any subpart. [40 CFR 60.2]

In part 60 and in CTGs, the EPA has used both approaches allowed by this definition. Specifically, the EPA has used volatility of the material (or the emission rate) as an explicit applicability criterion or has implicitly factored it in through the method used to determine compliance or applicability. For example, the new source performance standard (NSPS) for storage of volatile organic liquids, 40 CFR Part 60, subpart Kb, only applies to storage vessels greater than a specified size which are used to store organic liquids with vapor pressures greater than 0.75 psig. The vapor pressure (and other factors) determine the emission rate from the storage vessel. In other cases, the standard does not explicitly include a vapor pressure cutoff because it only applies to specific solvent blends or products. In such cases, the volatility and the emission rate were explicit considerations in the rule development process. An example of such a standard is the NSPS for Petroleum Refinery Wastewater Systems (40 CFR Part 60, subpart QQQ). In other NSPS, the requirements apply to gas streams that are discharged to the atmosphere and control or monitoring requirements are based on a number of factors including the emission rate of the gas stream. Examples of NSPS using this approach are the process vent standards for specific unit operations in the synthetic organic chemical manufacturing industry (SOCMI), 40 CFR Part 60, subparts III, NNN, and RRR. The CTGs for SOCMI process vents use the same approach with slightly different cutoff criteria.

VOCs are determined in a large number of standards and CTGs by using a prescribed method or procedure as allowed for in the previous definition. Where this approach is used, a volatility cutoff is implicitly included in the standard. In these cases, the specified method for determining concentration of organic materials in a material reflects the emission potential under specified conditions. For example, Method 25D was developed to reflect emission potential from improperly managed waste management units. Method 25D does not determine the composition of the waste in that it does not measure compounds which are not volatilized under the conditions of the procedure. Method 25D gets different results than methods that determine the composition of the waste such as some of the methods developed by EPA's Office of Solid Waste. Regulations that use Method 25D include air emission standards for tanks, surface impoundments, and containers under RCRA⁴ and a proposed NSPS for wastewater from SOCM processes. The Alternative Control Techniques document for wastewater also references use of Method 25D for determining VOC concentration in wastewater. Like Method 25D, Method 24 measures VOC emitted from the coating under specified conditions and does not necessarily yield the same mass content as the actual composition of the coating. New source performance standards that apply to coating operations typically determine compliance using Method 24, although the rules may allow use of formulation data, or other reasonable means to determine the content of the coating.

2.2 CALIFORNIA AIR RESOURCES BOARD'S USE OF REACTIVITY

One of the main goals of the RRWG is to examine current volatile organic compound (VOC) reactivity policies and identify the research needed to fill data gaps, to ensure that regulatory strategies have a firm basis. However, in this process, it is important not to overlook the VOC photochemical reactivity research that has been conducted over the past several decades. It is certainly desirable to gain additional data in the field of hydrocarbon reactivity. However, the State of California's Air Resources Board (CARB) believes that sufficient research has been done in assessing the State's atmospheric conditions to warrant the use of reactivity as a part of their regulatory control strategy in certain situations.

Moreover, to ensure that hydrocarbon reactivity is used appropriately in its proposals, CARB created the Reactivity Scientific Advisory Committee (RSAC), a group of leading researchers in the field of atmospheric science, to provide recommendations on the use of reactivity in regulations. The members of the RSAC are Professor John H. Seinfeld of the California Institute of Technology, Professor Roger Atkinson of the University of California, Riverside, Professor Jack G. Calvert of the National Center for Atmospheric Research, Professor Harvey E. Jeffries of the University of North Carolina, Chapel Hill, Professor Jana B. Milford of the University of Colorado, and Professor Armistead G. Russell of the Georgia Institute of Technology.

⁴ Resource Conservation and Recovery Act

CARB was the first regulatory agency to incorporate hydrocarbon reactivity into a regulation. In 1991, it adopted the Low-Emission Vehicles and Clean Fuels (LEV/CF) regulations that were designed to reduce mass emissions of ozone precursors from motor vehicles, and also account for reactivity differences in organic gas emissions from alternatively fueled vehicles (AFVs). CARB is currently developing a new regulatory approach that utilizes reactivity for control of VOCs in aerosol coatings.

2.2.1 Activities Undertaken to Support Reactivity Policy Development

2.2.1.1 Selection of a Reactivity Scale for Use in the California Regulations

The first step in designing a regulation based on reactivity is to select the most appropriate reactivity scale. For ozone control strategies, the scale selected should be designed for the best overall air quality benefit. Carter investigated 18 different methods of ranking the reactivity of individual VOCs in the atmosphere using a single-cell trajectory model with the SAPRC90 chemical mechanism⁵. Considering those 18 scales, Carter concluded that, if only one scale is to be used for regulatory purposes, the maximum incremental reactivity (MIR) scale is the most appropriate. The MIR scale is defined in terms of environmental conditions where ozone production is most sensitive to changes in hydrocarbon emissions and, therefore, represents conditions where hydrocarbon controls would be the most effective.

The California regulations specify use of the MIR scale because it has been determined to be the most appropriate reactivity scale to complement California's nitrogen oxides (NOx) control program. NOx controls are being implemented in California to reduce ozone under conditions that are sensitive to NOx reductions. Such conditions are typically downwind of emission source areas. In a complementary manner, the organic gas controls are designed to reduce ozone under conditions most sensitive to reductions in organic gases. These conditions are generally found near emission source areas. Concerns have been raised and addressed about the use of the MIR scale in a regulation. A brief summary of some of the issues and research performed to address them is provided in the next section.

2.2.1.2 Research Performed to Address Issues of Concern

Several general concerns have been raised about the regulatory use of reactivity, especially if scales based on less complex models, such as the MIR scale, are used. Reactivities are based on chemical kinetics and the calculation of reactivities is extremely complex. The calculations require both a chemical mechanism to represent hydrocarbon chemistry of the troposphere and an air quality model to represent physical processes of the atmosphere. Both components have been investigated in two ways: using a more complex algorithm and using a simplified algorithm. While the complex algorithms may better represent the

⁵ Carter, W. P. L. "Development of Ozone Reactivity Scales for Organic Gases," *J. Air Waste Manage. Assoc.*, **44**:881-899, (1994).

actual processes, they are computationally demanding. Simplification allows multiple calculations, with the advantage that numerous scenarios can be examined in a reasonable time frame.

The complexity of the calculations naturally raises questions about the uncertainty associated with reactivities. For example, concern has been expressed about the effect of the simple, zero-dimensional, Langrangian air quality model used in calculating MIR values. Other issues include the effect of uncertainties in the chemical mechanism, kinetic parameters, and precursor ratios. All of these concerns were addressed in a paper by Russell *et al.*⁶ Their findings and additional work are summarized below.

2.2.1.3 Effect of the Air Quality Model on Reactivity

To allow examination of multiple scenarios, MIRs are calculated with a single cell box model. This type of model lacks physical details, such as wind shear, as well as spatial and temporal details of emissions. As such, the model does not address processes such as pollutant transport and mixing that may affect reactivity. In addition, the MIR values are based on a 10-hour episode; however, it is not unusual for a severe episode in California to last for two or three days. The effect of using a three-dimensional model instead of the simpler zero-dimensional model has been examined by Russell in two papers.^{6,7} Russell used the same SAPRC90 chemical mechanism as Carter in calculating MIR values with a three-dimensional Eulerian airshed model. The airshed model incorporates pollutant transport and mixing, and models an episode (August 27-29, 1987) using input data from the South Coast Air Quality Study.

The comparison showed that MIR values correlate well with the model metric of population exposure to ozone concentrations greater than the federal and California ambient ozone standards. Thus, the simpler model's lack of physical detail and shorter episode time does not limit the use of the MIR values. Differences between MIR and exposure were observed for species in which photolysis plays a major role in the mechanism. This difference was attributed to the difference between the clear sky condition used in calculating the MIR values and the cloud cover used in the airshed model.

⁶ Russell, A. G., Milford, J., Bergin, M.S., McBride, S., McNair, L., Yang, Y., Stockwell, W., Croes, B., "Urban Ozone Control and Atmospheric Reactivity of Organic Gases", *Science*, **269**:491-495 (July 28, 1995).

⁷ Bergin, M. S., Russell, A. .G., Milford, J. B., "Quantification of Individual VOC Reactivity Using a Chemically Detailed, Three-Dimensional Photochemical Model", *Environ Sci Tech* **29**: 3029-3037, (1995)

2.2.1.4 Effect of the Chemical Mechanism on Reactivity

The effect of different chemical mechanisms on reactivity has been examined by a number of people. A comparison of significantly different types of mechanisms was done by Derwent *et al.*,⁸ in which ozone concentrations calculated with the Master Chemical Mechanism (MCM) were compared to concentrations from two mechanisms derived from smog chamber data, CBM-IV⁹ and CAL¹⁰. To make a more compact mechanism, the CBM-IV and CAL mechanisms treat many compounds by using a lumped molecule approach that combines compounds into classes that are assumed to have similar chemical reactivity. For example, the CBM-IV mechanism includes approximately 100 reactions. The MCM was developed using a more theoretical approach and explicitly includes over 2400 chemical species and over 7100 reactions. Despite these differences, ozone concentrations calculated with all three mechanisms agreed within 16% over a five-day scenario.

In a comparison directly related to reactivities, Derwent also compared two reactivity scales; Photochemical Ozone Creation Potential (POCP), calculated using the MCM and a multi-day trajectory air quality model, and MIR values calculated using the SAPRC mechanism. Even using different chemical mechanisms and different air quality models, the majority of organic compounds showed excellent agreement between the two reactivity scales. A small number of compounds, such as formaldehyde and 1,3-butadiene, did exhibit anomalous behavior in the comparison. Recently, a second version of MCM was developed in which formaldehyde's POCP and its MIR are better correlated¹¹.

2.2.1.5 Effect of Uncertainties on Reactivity

The calculations needed to estimate reactivities require numerous kinetic parameters. Some rate constants and product yields have been determined experimentally and, as such, have experimental uncertainties associated with them. However, the kinetic parameters for many of the reactions have never been directly measured and are estimated by analogy with known reactions. The effect of these

⁸ Derwent, R. G., Jenkin, M. E., Saunders, S. M., Pilling, M. J., "Photochemical Ozone Creation Potentials For Organic Compounds in Northwest Europe Calculated with a Master Chemical Mechanism" *Atmos Env* **32**:2429-2441, (1998)

⁹ Gery, M. W., Whitten, G. Z., Killus, J.P., Dodge, M. C., "A Photochemical Kinetics Mechanism for Urban and Regional Scale Computer Modeling" *J Geophys Res* **94**:12925-12956, (1989)

¹⁰ Lurman, F. W., Carter, W. P. L., Coyner, R. A., "A Surrogate Species Chemical Reaction Mechanism for Urban-Scale Air Quality Simulation Models. Volume I Adaptation of the Mechanism", US EPA Report EPA-600/3-87-014a (1987)

¹¹ Derwent, R. G. Personal communication to CARB January 1999.

uncertainties in the rate parameters on calculated incremental reactivities was examined by Yang *et al*¹². They found that uncertainties of 1F (1 standard deviation) in the MIRs of 26 organic compounds ranged from 27% to 68% and a significant portion of the uncertainty was controlled by a small subset of rate parameters. Thus, reducing the uncertainty of a relatively small number of parameters will significantly improve the overall uncertainties. Also, the rate parameter uncertainties had directionally similar effects on the reactivities of most of the compounds investigated and, thus, the use of normalized reactivities is recommended to lessen the effect of rate parameter uncertainty. California's LEV/CF regulations use normalized reactivity in the reactivity adjustment factors (RAFs). In the proposed consumer products regulation CARB intends to quantify the uncertainty associated with each MIR value. A more detailed description of this approach is given in the section on uncertainty bins.

Another paper by Yang *et al*¹³ combined estimates of the variability in the composition of motor vehicle exhaust with the uncertainties of the rate constants to estimate the overall uncertainty of the reactivity of the exhaust. The results showed that, for gasoline vehicles, variabilities in emission composition were a more significant contributor to uncertainty in the RAF than uncertainties associated with kinetic parameters in the MIR calculations.

Criticism of the regulatory use of reactivity has also been based on the variability caused by different initial conditions. Carter's MIR values are the average results from 39 scenarios, in which the initial nonmethane organic gases (NMOG) and NO_x concentrations, aloft ozone concentration and mixing height were varied. The use of average reactivities can lessen the effect of the variability caused by environmental conditions. In the paper by Bergen *et al*,⁷ a three-dimensional air quality model for the Los Angeles basin was compared with MIR values based on only the Los Angeles inputs, as well as the MIR results based on the average of all 39 scenarios. While it might be expected that the Los Angeles MIR scale would more closely agree with the 3D model, the MIR scale based on the average of the 39 scenarios showed better correlation with the 3D model.

In summary, ARB staff concluded that the simple box-model calculations used to calculate the MIR scale yield sufficiently certain reactivity rankings to allow incorporation into regulation. They concluded that the effect of the uncertainties associated with the chemistry, variable environmental conditions, and the composition of a source's hydrocarbon emissions on the calculated MIR values were acceptably small, and that their use in the regulation was appropriate and technically sound.

¹² Yang, Y. J., Stockwell, W. R., Milford, J. B., "Uncertainties in Incremental Reactivities of Volatile Organic Compounds", *Environ Sci Tech*, **29**: 1336-1345, (1995)

¹³ Yang, Y. J., Milford, J. B., "Quantification of Uncertainty in Reactivity Adjustment Factors from Reformulated Gasoline and Methanol Fuels", *Environ Sci Tech* **30**: 196-203, (1996)

2.2.2 California's Regulatory Programs Using Reactivity

2.2.2.1 Low Emission Vehicles and Clean Fuels Regulation

In many California cities NO_x and organic gases emitted from motor vehicles are the primary cause of excessive levels of ozone.¹⁴ The earliest studies of photochemical air pollution showed that individual hydrocarbons make different amounts of ozone, or, stated another way, some hydrocarbons are more reactive than others.¹⁵ CARB was the first regulatory agency to incorporate hydrocarbon reactivity into a regulation when it adopted the LEV/CF regulations to reduce mass emissions of ozone precursors from motor vehicles, and also account for reactivity differences in organic gas emissions from alternatively fueled vehicles (AFVs).^{16,17} The regulations established increasingly stringent vehicle certification standards for emissions of NMOG, NO_x, carbon monoxide, and formaldehyde.

The California regulations are "fuel neutral" in that all AFVs can compete in the marketplace, so long as they meet exhaust emission standards that are equivalent in ozone-forming potential as those established for vehicles fueled with conventional gasoline. Manufacturers who chose to build automobiles powered by alternative fuels, including reformulated gasoline, can take advantage of the lower ozone-forming potential of these vehicles through the use of reactivity adjustment factors (RAFTs). A RAFT is defined as the ratio of the exhaust reactivity (per gram) of an AFV to the exhaust reactivity of a comparable conventionally fueled vehicle (CFV). The mass emission rates of NMOG exhaust for each AFV is adjusted by the RAFT before comparison with the emission standards. For example, if an AFV's exhaust is determined to be half as reactive as the exhaust of a CFV, the AFV mass emissions are multiplied by 0.5 before comparison to the emission standard. In this way, AFVs are allowed to have a higher mass of NMOG emissions than CFVs, as long as the ozone-forming potential of the AFV is no greater than a CFV that just meets the standards.

The procedure for determining the RAFT for each type of AFV is set forth in the California regulations.¹⁷ Manufacturers may determine RAFTs for their specific engine families in accordance with this

¹⁴ National Research Council *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, National Academy Press, Washington, D. C. (1991).

¹⁵ Haagen-Smit, A. J., Bradely, C.E., and Fox, M.M., "Ozone Formation in Photochemical Oxidation of Organic Substances", *Ind. Eng. Chem.*, **45**:2086 (1953)

¹⁶ California Air Resources Board "Proposed Regulations for Low-Emission Vehicles and Clean Fuels--Staff Report and Technical Support Document," State of California, Air Resources Board, P.O. Box 2815, Sacramento, CA 95812, August 13, 1990.

¹⁷ California Air Resources Board "Proposed Regulations for Low-Emission Vehicles and Clean Fuels--Final Statement of Reasons," State of California, Air Resources Board, July 1991.

procedure, or they may use default RAFs established by the ARB. To calculate RAFs, the full range of organic gases that contribute to ozone formation must be identified and quantified. The emission rates of all NMOG species are converted to an appropriate mass of ozone using the MIR scale and summed to estimate the reactivity of the entire exhaust sample.

The use of reactivity in the form of RAF in the LEV/CF regulation allows California to develop regulations that, while decreasing the emissions standards for motor vehicles, are fuel neutral, thus encouraging the development of alternatively fueled vehicles.

2.2.2.2 VOC Reactivity Control Program for Consumer Products

To help meet the consumer products commitment in the State Implementation Plan for Ozone, CARB staff committed to investigate the feasibility of incorporating photochemical reactivity into their regulatory strategy. As a first step, CARB is developing a new regulatory approach for the control of VOC emissions from aerosol coating products, based on the photochemical reactivity of the VOCs used in them. At present, California's consumer products regulations limit the total VOC content of products, with no consideration of the differing reactivity of the VOC ingredients. The regulations include the U.S. EPA exemptions. Based on the experience in California's reactivity-based LEV/CF Program, CARB staff determined that reactivity could be a feasible control strategy for the control of VOC emissions from consumer products.

To develop a successful reactivity program, the following elements are needed: 1) an inventory of speciated VOC data for the source category; 2) a scale that allows a comparison of VOC reactivities based on the atmospheric conditions; 3) a speciated inventory that consists largely of VOCs that have well-characterized reactivities; 4) product sales data that allow weighting of VOC reactivities; and 5) a method to establish limits.

2.2.2.2.1 Using the MIR Scale as a Voluntary Compliance Option for Aerosol Coatings

The MIR scale was selected for the consumer product regulation for the same reasons stated earlier in this section. Once a scale is selected, source categories can be evaluated to determine if reactivity can be a more effective ozone control strategy. As part of this analysis, it is essential to analyze the type of VOCs used, or potentially used, in the source category to determine if adequate reactivity data exist for the majority of VOCs. In California, based on recently conducted manufacturer surveys, data on the types and amounts of VOCs used in aerosol coatings are available. Analyzing these data show that, on a weight basis, over 80 percent of the VOCs used have well-characterized reactivities. The reactivity regulation for aerosol coatings is being designed as a voluntary compliance alternative that will provide equivalent ozone reductions as will be achieved through the existing mass-based regulation. However, in the future, CARB may be investigating the use of reactivity as a more effective ozone control strategy for aerosol coatings,

consumer products, and architectural coatings by targeting reductions from VOCs that have a high potential to form ozone.

Another aspect to consider in determining the feasibility of a reactivity-based VOC control strategy is the efficacy and performance of the lower-reactive reformulated product. To investigate this, several consumer product manufacturers participated in a pilot project for CARB in June 1996. The results of that project indicated that the performance and efficacy of products could be maintained while formulating products with less reactive VOCs.

2.2.2.2.2 *Assigning MIR Values to VOCs*

Industry has suggested that the current VOC exemption policy is “unfair” because a variety of VOCs with reactivities near that of ethane, the current U.S. EPA standard for determining exemption status, continue to be regulated just like the higher-reactive VOCs. Therefore, there is no incentive to use lower-reactive VOCs. This same strategy is used in California’s existing consumer products regulations. Essentially these regulations use a reactivity scale of zero and one for non-reactive and reactive VOCs, respectively. This is simple for the implementation of mass-based regulations. However, in contrast to this type of reactivity scale, the MIR scale allows CARB to distinguish each VOC by its characteristic reactivity value. Thus, another advantage to using reactivity in regulation is that the “bright-line” approach to determine if a VOC is reactive or non-reactive is eliminated. This leads to a more efficient ozone control strategy, while also recognizing that low reactive VOCs do contribute to ozone formation once they are emitted; they are just less efficient in forming ozone. Given their low reactivity values, the use of low reactive VOCs is encouraged in a reactivity regulation.

2.2.2.2.3 *Uncertainty Bins*

The most recent table of MIR values¹⁸ represents years of scientific research which has allowed better understanding of VOC photochemistry. However, as with any reactivity scale derived from predictive models (including the MIR scale) there are uncertainties associated with them. The majority of the concerns arise from the uncertainties in the experimental data and the uncertainty of the chemical mechanistic reactivity. However, the MIR scale is robust for the inclusion of the data accounting for the VOCs’ impacts on ozone levels.¹² Depending on the source category to be regulated, these uncertainties need not preclude regulatory development. To account for uncertainties, within the regulation, adjustment factors may be used to modify the estimated MIR values for VOCs to account for the degree of uncertainty associated with the value.

¹⁸ Carter, W. P. L. “Updated Maximum Incremental Reactivity Scale for Regulatory Applications.” Preliminary Report to California Air Resources Board. Contract No. 95-308. August 6, 1998.

In proposing adjustment factors for VOCs, CARB's goal is to have an uncertainty protocol that is straight-forward and easy to apply. The protocol must also be flexible enough to allow compounds to be recategorized as new information becomes available. In establishing a method to treat uncertainty, caution should also be used if, on a mass basis, a high percentage of VOCs in the source category fall into categories with limited data.

To make the uncertainty of VOC MIR values more understandable, Carter provided CARB with a numerical ranking to categorize the uncertainty associated with each MIR value. The uncertainty designations are ranked from 1 to 11¹⁸. The rankings are not intended to be a measure of the magnitude of the uncertainty, but rather to provide useful guidance on the type of uncertainty associated with the MIR value. The rankings, however, can serve as a basis for establishing adjustment factors. For example, a number of VOCs listed were studied extensively in smog chamber experiments to serve as the basis for CARB's LEV/CF Program.^{5,19,20,21,22} For these VOCs, the reaction mechanisms and reaction rates have been well-characterized; their photochemical reactivity can be reliably predicted for purposes of regulatory applications. MIR values for these VOCs are expected to remain stable and the adjustment of MIR values for uncertainty may not be warranted. These compounds fall into uncertainty bins 1 through 4.

However, experimental smog chamber data for all VOCs are not available to calculate MIR values. Although techniques for estimating the MIRs are available, scientific understanding of certain VOCs is limited with differing degrees of uncertainty. Hence, some MIR values are based on limited understanding. These compounds are designated as uncertainty bins 5 through 11. MIR value uncertainties for these compounds must be addressed for the implementation of a reactivity program, so that ozone reductions are not compromised. One possible method is to establish numerical adjustment factors that can be applied to these MIR values based on the available data. For example, compounds that have some data available could be adjusted slightly, while MIR values for compounds with very little data available can be assigned higher adjustment factors.

¹⁹ Carter, W. P. L. "Computer Modeling of Environmental Chamber Measurements of Maximum Incremental Reactivities of Volatile Organic Compounds", *Atmos Env* **29**:2513-2527, (1995)

²⁰ Carter, W. P. L., Pierce, J. A., Luo, D., Malkina, I. L., "Environmental Chamber Study of Maximum Incremental Reactivities of Volatile Organic Compounds", *Atmos Env* **29**:2499-2511, (1995)

²¹ Kwok, E. S. C., Atkinson, R., "Estimation of Hydroxyl Radical Reaction Rate Constants for Gas-Phase Organic Compounds Using a Structure-Reactivity Relationship: An Update", *Atmos Env* **29**:1685-1695, (1995)

²² Carter, W. P. L., Lurman, F. W., "Evaluation of a Detailed Gas-Phase Atmospheric reaction Mechanism Using Environmental Chamber Data", *Atmos Env* **25A**: 2771-2806, (1991)

2.2.2.2.4 Upper Limit MIR Calculations

For VOCs with no published MIR values, the use of Upper-Limit MIR (ULMIR) values has been proposed. To calculate the ULMIR values a methodology, developed by Carter, can be used. This methodology is a simplified model based on the MIR scale. The basic framework, except for the latest August 6, 1998, update¹⁸, has undergone peer review by the RSAC. The ULMIR methodology is based on empirical results of tested VOCs and reflects the best of knowledge on the accuracy of the science of incremental reactivity.

For the calculation of the ULMIRs, the upper-limit kinetic reactivity is multiplied by its mechanistic reactivity.^{18,23} The kinetic reactivity is the fraction of emitted VOC which reacts during the episode. The mechanistic reactivity is the amount of ozone formed per molecule of VOC reacted.

To calculate the ULMIR values a methodology, developed by Carter, can be used. The ULMIR value calculated is based on the fraction of the compound that has reacted (kinetic reactivity) and the literature information on the reaction mechanism (mechanistic reactivity).²³

Because an ULMIR infers the highest reactivity for a given VOC, no additional uncertainty adjustment factor need be applied to any calculated ULMIR. It is important to note that for aerosol coatings, this methodology would only need to be applied to VOCs representing less than one percent of the aerosol coatings emissions inventory.

2.2.2.2.5 Hydrocarbon Solvent Bins

Hydrocarbon solvents are a diverse product group that are used in a variety of consumer product categories. Typical hydrocarbon solvents are mineral spirits and naphtha. These solvents are not composed of a single chemical component, but rather many hydrocarbon constituents. Because of this, a methodology to assign MIR values is necessary. Hydrocarbon solvents are produced from the fractionation of a broader distillation range petroleum stream. Distillation range, or boiling range, is a primary parameter for characterizing hydrocarbon solvents. They often contain hydrocarbons that differ in structure (e.g., paraffin, aromatic, etc.), activity, and number of carbon atoms. Hydrocarbons of similar volatility and general composition can be “binned” and an MIR value can be assigned to each bin. Characteristics that are considered in proposing these bins include boiling range, aromatic content, and paraffin content (for products greater than 70 percent alkane). For example, one bin could include hydrocarbon solvents with constituents of five, six, and seven carbon atoms with similar functional groups.

²³ Carter, W. P. L. “Estimation of Upper Limit Maximum Incremental Reactivities of VOCs.” Statewide Air Pollution Research Center and College of Engineering. Center for Environmental Research and Technology. University of California, Riverside.

2.2.2.2.6 Proposed Methodologies to Calculate Limits

The methodologies to calculate limits can be designed to be equivalent to already existing mass-based VOC limits, or can be designed as the sole regulatory strategy for a source category. Depending on the source categories, the limits set will help reduce ozone in the most efficient manner.

To establish reactivity limits, one approach is to calculate the sales-weighted-average reactivity of all products in the particular category that are complying with a mass-based limit and use that average as the limit. This method would be appropriate for establishing an alternative for currently regulated categories. If a manufacturer chooses to comply with the reactivity limits, the ozone formation potential, or weighted-reactivity, of the product must be no more than the reactivity limit for that product category.

3. PURPOSE AND SCOPE OF REACTIVITY POLICY

Before considering the various issues involved in designing a possible reactivity-based VOC control policy and the research questions generated by these issues, it is important to consider what the purpose of a reactivity-based policy might be. In other words, what goals are a reactivity-based policy designed to achieve? Historically, a variety of justifications have been offered for the reactivity policies described in the previous chapter. These justifications suggest several goals for a reactivity-based policy:

- C Improve efficiency of NAAQS attainment and regional haze policy by focusing resources on controlling compounds that have a larger impact on nonattainment (and excluding from regulation those compounds that have a minimal impact on nonattainment), where efficiency refers to minimizing both the public and private costs of implementing, administering, maintaining, and enforcing controls necessary to achieve our air quality goals.
- C Improve efficiency of NAAQS attainment and regional haze policy by encouraging substitution of VOCs to reduce O₃ and PM forming potential.
- C To the extent permitted by statute, assure continued progress towards other air quality goals, including prevention of significant deterioration and decreasing hazardous air pollutants exposure, acidifying deposition, eutrophication, stratospheric O₃ depletion, and climate change.
- C Develop a practical, cost-effective, and enforceable means to implement policies based upon relative reactivity of VOCs that would not impose huge burdens on industry, States and EPA to achieve.

In addition to these goals, any reactivity-based VOC control policy must be consistent with the existing legislative authority and regulatory policies of Federal and State agencies. Each of these goals and considerations is discussed further below.

3.1 CONTROL VOCs THAT IMPACT NONATTAINMENT AREAS

Controlling photochemical precursors (e.g., VOCs) is a challenge because such a strategy requires a detailed understanding of their chemical structure and composition and a thorough knowledge of the atmosphere's ability to transport these substances to non-source regions (i.e., downwind). The ozone research conducted in the 1980's and early-1990's has clearly defined the role of atmospheric transport in determining the ability of a given source region to influence another downwind receptor region's attainment status. Thus, the question becomes what is a specific VOC's "area of influence," with respect to contributing to a specific region's nonattainment status. Inherent in such a statement is the assumption

that one can adequately assess the ability or likelihood of a given compound or species to participate in photochemical reactions and thus contribute to a region's ambient ozone or fine particulate conditions. Additionally, similar analyses could also corroborate the environmental fate of such compounds or species, relative to global warming potential (GWP) and stratospheric ozone depletion.

Given today's limited financial resources, a future VOC control policy based on reactivity could focus on initially controlling VOCs which provide the greatest net environmental benefit. In other words, maximize the return on the investment in VOC control strategies and/or VOC substitution policies. Initially, a policy could focus on those compounds and species which are widely used and are known precursors for ozone, fine particles and toxics or have quantifiable GWP or stratospheric disbenefits. In essence, one would define a "living" policy that would identify compounds which are currently identified to be detrimental to net environmental health, while reserving the option to expand/contract this list in the future as the science and knowledge base evolves to support such changes. Such a focused approach would provide incentive for researchers to quantify the effects of their compounds, while also providing incentives for industry to select and formulate products containing lower reactive compounds/species.

3.2 USE VOC SUBSTITUTION TO REDUCE OZONE, PM AND HAZE FORMATION

A good deal of attention in recent months has been focused on the concept of substituting newly formulated, less reactive compounds for currently used more highly reactive compounds. At face value, this concept appears to have merit; however, the overall implications and logistics of such a program could be cost prohibitive if not structured properly. The foundational element of any viable substitution program is an accurate accounting of the compound's usage (i.e., emission inventory). Inventorying and reporting requirements for a VOC substitution program would have to be stringent in order to model and analyze adequately the net environmental benefits across the nation (and the globe) resulting from any proposed/approved VOC substitutions. Additionally, the proper market-based incentives would have to be present to motivate industry and consumers to select the often higher-cost, lower reactive compounds as substitutes for the cheaper, higher reactive compounds currently in use.

One key element in any VOC substitution policy would be the assessment of what is really gained by substituting a ton of VOC-x for a ton of VOC-y. A good deal of discussion has been entertained lately regarding the replacement of highly-reactive toluene and xylene with other, less-reactive compounds; however, without proper inventorying and reporting the possible net environmental benefits of such a substitution are not quantifiable. Thus, the first step in establishing a policy which would allow VOC substitutions as a control strategy would be to establish accurate, comprehensive emission inventories for all VOCs currently in use. The initial focus could be on higher-reactive compounds and those compounds which are widely used (regardless of their respective reactivities). These inventories would have to be collected nationwide so that the substitutions could be modeled effectively, including the effects of atmospheric transport and the inherent differences in rural and urban ambient environments. However,

substantial improvements would be required to our current understanding of the chemistry of fine particle formation and air toxics generation before these scenarios could be effectively simulated in numerical models.

3.3 PROVIDE PROGRESS TOWARD OTHER AIR QUALITY GOALS

One approach to developing a workable VOC exemption/substitution policy rests in a regulatory body's ability to craft a policy that would provide for a net environmental benefit for all areas of interest: ozone and particulate formation, generation of air toxics, stratospheric ozone depletion and global warming. As outlined earlier, a VOC control policy based upon reactivity should be "living" in nature, since the state-of-the-science is currently incomplete. Just as the focus of ozone attainment demonstrations has shifted from a VOC-based strategy in the early 1990s to the current NO_x-based approaches, as our understanding of fine particle and toxics chemistry improves so should our reactivity policy incorporate and embrace the best, policy-relevant science. Additionally, since reactivity issues span Titles I (NAAQS), III (Air Toxics) and VI (Stratospheric Ozone) of the 1990 Clean Air Act, the future reactivity policy could attempt to integrate these three different initiatives into a common, cost-effective national program.

3.4 CONSISTENCY WITH EXISTING AUTHORITY AND PROGRAMS

Any future reactivity-based VOC control policy alternatives must be evaluated in the context of the existing regulatory programs and legislative authority of federal and state agencies. The consistency of policy alternatives with existing programs must be considered along with the scientific and economic justifications for the policy alternatives. Thus, it is important to recognize that while the RRWG is concerned with helping to improve the scientific basis for designing a reactivity-based VOC control policy, that the actual design of such a future policy may include other considerations outside the scope of the RRWG's efforts. For example, there are significant hurdles associated with development of a practical, cost-effective, enforceable policy based upon relative reactivity; and unless such problems can be resolved, Federal, State, and local regulatory bodies may be unable to implement such policies.

4. OPTIONS FOR A VOC REACTIVITY POLICY

The purpose of this section is to identify the possible ways that differences in the reactivity of VOCs may be addressed in future air quality management policies and to identify the research questions that must be resolved before such policies can be evaluated or implemented. The advantages and disadvantages of different regulatory approaches for addressing VOC reactivity are discussed, not to advocate for particular policy alternatives, but to help focus future research on those questions related to the possible policy responses. This section begins with a discussion of four general, or overarching, issues that should be addressed in defining the scope and content of any reactivity-based policy. The discussion of these general issues is followed by a discussion of alternative regulatory approaches and the opportunities and challenges associated with their use.

4.1 GENERAL ISSUES

In developing a VOC reactivity policy, there are several issues that should be addressed regardless of the regulatory options under consideration. Some of these issues deal with the scope of the policy, including the impacts of concern, the geographic area of applicability, and the applicability to different source types. Other issues include accounting for the actual atmospheric availability of VOCs. Each of these general issues is discussed in this section and is referred to in the discussion of the specific regulatory options below.

4.1.1 Impacts of Concern

Historically, VOCs have been regulated as a class because of their potential to contribute to ground-level ozone. Individual VOCs, however, may also cause or contribute to a variety of other environmental concerns. Certain compounds raise toxicity concerns and may cause other adverse health or environmental effects. Some VOCs may also deplete stratospheric ozone; others may contribute, either directly or indirectly, to global warming. VOCs above a certain molecular weight can also react photochemically to form secondary organic aerosols (SOA), contributing to fine particulate matter concentrations. EPA has recently determined that fine particulate matter (often referred to as “PM fine” or PM_{2.5}) can pose a significant risk to human health and the environment. Thus, in developing a reactivity-based policy, it is important to consider which VOC-related impacts to address and which impacts to address in other ways.

While EPA's current VOC control policy is generally focused on the impact of VOCs on tropospheric ozone, the scope of future policies could be expanded to address any combination of the various impacts associated with VOC emissions, if the statute permits. The current feasibility of addressing different combinations of impacts depends on the regulatory approaches chosen. At the opposite end of the spectrum from EPA's current policy is a “one atmosphere” approach, under which all the environmental

impacts of a VOC would be taken into account in determining how it would be regulated. In between an ozone-focused policy and a "one atmosphere" policy, there is a range of options that could be considered.

One consideration in deciding which combination of impacts to address is the existence of other regulatory programs to address specific impacts. For example, the toxicity impacts associated with VOCs are generally addressed under Title III of the 1990 Clean Air Act Amendments and the impacts of VOCs on stratospheric ozone are addressed under Title VI. If these existing programs are sufficient to address those impacts of concern and a reactivity policy does not conflict with these programs, it may not be necessary to integrate the management of those impacts into a reactivity-based policy. Given EPA's current efforts to integrate ozone, particulate matter, and regional haze management strategies, all of which are addressed under Title I of the Clean Air Act, a VOC reactivity policy that addresses these impacts in an integrated fashion may be more desirable than one that does not.

As the number of impacts that are addressed by a reactivity policy increase, the information needed to formulate and implement such a policy also increases. Given that the relationship between VOC emissions and some impacts, such as ozone formation, are currently better characterized than the relationships with other impacts, including fine particle formation, it is possible that a reactivity policy could be designed to evolve. Initially, the policy could address those impacts that are well characterized. Later, as more information is developed through research, the policy could be adapted to integrate other impacts of concern.

Thus, policy decisions about the scope of a reactivity-based VOC control policy could be informed by further research on the relative contribution of different VOCs to all of the impacts of concern. Of particular interest are situations in which substituting one VOC for another decreases one type of impact but increases another impact. Furthermore, in developing a reactivity research program, the RRWG should attempt to project the amount of time and effort that will be necessary to develop better characterizations of the relationship between VOC emissions and each of the impacts of concern. The RRWG will then have to consider how to prioritize research efforts so as to provide policy makers with the most useful information in a timely fashion.

4.1.2 Geographic Applicability

In designing a reactivity-based VOC control policy, another overarching consideration is determining the geographic area, and thus the pool of sources, to which it will apply. In selecting the area of application, there are at least two issues that should be considered: 1) Over what geographic area will changes in VOC composition have an effect on the impacts of concern? 2) Over what geographic area is it most effective to implement control requirements? Each of these issues is discussed below.

The first issue is related to the characteristics of the environment in which the policy is applied. If the purpose of the reactivity policy is to control ozone, the characteristic that is most important is the relative

effectiveness of VOC and NO_x controls in decreasing ozone concentrations. In some areas of the country, which are characterized as "NO_x-limited," reducing VOC emissions may have little or no impact on reducing ozone formation. In such areas from a scientific perspective, reducing NO_x emissions is expected to be the more effective strategy for controlling ozone and reactivity-based VOC control strategies are of less value. However, large areas can be very heterogeneous with respect to NO_x or VOC limitation. In some areas, VOC control may be effective in small pockets (such as in the city center core or within plumes of large emission sources), while the surrounding area is NO_x-limited. Any viable VOC control policy must also recognize that there are factors other than scientific ones which regulatory bodies must consider in reducing ozone and fine particulate pollution, such as enforceability and cost-effectiveness of controls both for industry and the regulatory body.

If a reactivity policy is intended to take into account other impacts such as exposure to hazardous air pollutants, then the distribution of emission sources and ambient concentrations of pollutants may be important characteristics of the environment. Changes in VOC composition due to a reactivity policy may have little effect in areas where sources are dispersed and the ambient concentrations are low. However, in areas with a large number of sources and high ambient concentrations, some changes in VOC composition may be significant.

The geographic scale over which a VOC may contribute to an impact of interest may vary with meteorological conditions and varies with the period of time analyzed. VOCs that react slowly may not produce significant impacts near their emission source, but may be transported and dispersed over large distances and contribute to impacts over a much broader geographic area over a longer period of time. For example, methane and carbon monoxide, which are considered to be negligibly reactive on an urban scale with respect to the formation of ozone, contribute significantly to the formation of tropospheric ozone on a hemispheric or global scale.

In addition to the characteristics of the environment, the characteristics of the emission sources are also important in determining geographic applicability. For some types of emission sources, such as large stationary sources, it is possible, although administratively cumbersome, to have different types of controls across a region, or even at every individual source. For other types of sources, such as motor vehicles or consumer products, it is practical to have a set of controls that apply uniformly across a broad region. While the general issue of having different policies for different types of sources is discussed more below, it's important to understand that both the characteristics of the environment and the nature of the emission sources may play a role in determining the appropriate geographic extent for a control policy. Taking into account the ability to implement, administer, and enforce control policies, it may make sense to control VOCs, even though NO_x control would be effective in areas in a region. Alternatively, it may be that VOC control, possibly including some form of reactivity-based program, should be used to reduce ozone concentrations within certain geographic pockets, even though the overall region is largely NO_x-limited.

Therefore, research is needed to develop appropriate scientific tools to help policy makers determine the appropriate geographic extent of reactivity-based VOC control policies. In particular, tools are needed to help policy makers decide whether an area should focus its regulatory efforts on NO_x or VOCs, or whether both NO_x and VOC control are needed. Furthermore, research is needed to determine the nationwide extent of NO_x-limited conditions, in terms of geographic area, the fraction of emission sources, and their contribution to ozone nonattainment. If a policy is to address hazardous air pollutant concerns, the nationwide extent and character of "toxic hot spots" should also be characterized. Given the extent of these conditions, policy makers will be able to more effectively evaluate the potential benefits of reactivity-based policies on different geographic scales.

4.1.3 Variation by Source Type

As discussed above, it is often appropriate to regulate different types of sources using different approaches. Thus, another general question that must be addressed in designing a reactivity-based policy is to what types of sources will the policy be applied, or alternatively, how will an overall policy be applied to a variety of different sources.

To consider how a reactivity-based policy may be applied, it is helpful to consider how sources are categorized under existing regulatory policies. Under current regulatory approaches, the major sources of VOC emissions may be divided into the following categories:

- C Mobile Sources
- C Area Sources (including Consumer and Commercial Products)
- C Stationary Sources

Emissions from mobile sources are currently regulated either through (1) "tailpipe" standards that require the installation of control technology on vehicles; or (2) fuel standards that require the reformulation of motor fuels. Under current policy, fuels are required to be formulated differently for different parts of the country. On the other hand, because the same vehicle lines are sold nationwide, they are subject to uniform tailpipe standards throughout the country (with the exception of California and perhaps other states that are permitted to adopt the "California car" approach). Thus, any reactivity policy for vehicles would likely be a nationwide policy, while a reactivity program for fuels could be tailored more specifically for different parts of the country.

A similar issue arises in the case of area sources. For consumer products (such as hair sprays and cleaners), national manufacturers typically formulate one product for the entire country (with the possible exception of California). The same is true for some types of commercial products that are distributed nationwide. In such cases, product reformulation is typically the only viable approach for reducing ozone formation attributable to these products. For products in this category, any type of reactivity-based program would probably need to be a national one. There are other types of commercial products,

however, that are used in industrial settings where VOC emissions can be controlled at the source. For products in this second category, it may be feasible to have reactivity-based programs that are tailored to specific areas.

In the case of stationary sources, there may also be a need to make a distinction between national and local (or regional) approaches because new sources often consider existing rules when choosing a location. Although it may be desirable to have national guidance for states on the use of reactivity-based programs for stationary sources, such programs could be designed for local circumstances. It may be important, however, to differentiate stationary sources on the basis of the type of facility or the processes involved in the emission of VOCs. Some processes may result in well characterized emissions with stable composition that are relatively easy to control by changing the inputs to the process, e.g., a painting or degreasing operation. Other processes may involve complex mixtures of chemicals that produce poorly characterized and highly variable VOC emissions, e.g., petroleum refining operations. Each of these different types of sources presents different challenges for implementing, administering, and enforcing a reactivity-based policy.

Thus, for purposes of the RRWG, it may be helpful to think in terms of the following categories and subcategories:

- Mobile Sources
 - Tailpipe Standards
 - Fuel Standards
- Area Sources (including Consumer and Commercial Products)
 - Products subject only to reformulation
 - Products that can be regulated where used
- Stationary Sources
 - Stable, Well-Characterized Processes
 - Complex, Variable Processes

For each of these different categories, research needs to be performed to develop ways of efficiently characterizing the emission streams and their reactivity for purposes of implementing and enforcing a reactivity-based policy.

4.1.4 Atmosphere Availability

Lastly, in designing a reactivity-based VOC control policy it may be appropriate to take into account how much of the VOCs in a product, a fuel or an input stream, or in the emissions stream actually affect the impact of concern.

Depending on the process in which a VOC is used, a portion of the VOC may end up on a manufactured product, or in a solid or liquid waste stream. Current regulations attempt to take such "losses" to the emission stream into account using uniform "purge and trap" test methods that apply to specific industrial processes and uniform test methods that apply to specific types of control devices. Thus, what counts as a VOC emission for regulatory purposes may depend on the measurement method used for the specific process or control system. Further research may be able to improve the accuracy or efficiency of these test methods, providing better information about emissions and control efficiencies.

Once in the atmosphere, not all of the emitted VOC may contribute to an adverse impact. For example, VOCs can only react to form ozone if they are available in the atmosphere in the vapor phase. Some VOCs, even though they are emitted in the vapor phase, are removed from the atmosphere by a variety of processes before they can contribute appreciably to ozone formation. In some cases, they may quickly condense into the aerosol phase and be unavailable for ozone formation (although they may contribute to other environmental concerns). In addition to condensing in the aerosol phase, VOCs may be removed from the vapor phase by contact with surfaces or water droplets. The environmental fate of VOCs can be complex and can lead to a variety of adverse impacts or no impact at all.

Many of the determinants of atmospheric availability are context dependent. A reactivity-based policy could take these factors into account. More research is needed to characterize the potential environmental fate of different VOC emissions from different emission sources. Models that predict the environmental fate, or partitioning, of individual compounds may be useful to policy makers in developing a broader reactivity scheme that considers not only how much ozone a compound can form when it is available in the vapor phase, but also how much of the compound is available in the atmosphere. Section 2.1.3.1 describes how EPA takes volatility and environmental fate into account in developing regulations.

4.2 REGULATORY APPROACHES

Any regulatory approach that addresses VOC reactivity should have at least two fundamental components: 1) a classification scheme, which distinguishes or groups compounds on the basis of their characteristics; and 2) a treatment scheme, which applies different requirements to different classes. There are many combinations of classification and treatment schemes that could be used to achieve different policy goals in different contexts. These two components, however, are not completely independent; some treatment schemes suggest certain classification schemes, and vice versa. The various options for these different schemes are discussed below, followed by a more general discussion of opportunities and challenges for using combinations of the schemes in the air quality management process.

4.2.1 Classification Schemes

Under its current reactivity policy, which was developed in 1977, EPA classifies VOCs into two classes: "reactive," and therefore regulated as a VOC; and "negligibly reactive," and therefore exempt from

regulation as a VOC. This scheme can be thought of as lying near one end of a continuum of possible classification schemes. At one end of this continuum is a one class approach in which no distinction is made between different VOCs and all VOCs are treated equally. At the other end of the continuum is a continuous scale that allows every individual VOC compound to be treated differently based on the compound's particular characteristics. The MIR scale used in California's low emission vehicles and clean fuels regulations, which is described in Section 2.2, is an example of a continuous scale. In between the two extremes is the current two-class approach, followed by classification schemes using an increasing number of discrete classes, or bins. As the number of bins increase, the resolution of the classification scheme approaches that of the continuous scale.

While it is easiest to think of an actual classification scheme at one point along this continuum, it is conceivable that a complex classification scheme may be designed that combines different levels of resolution. For example, given adequate information, a multiple-bin system could be used to classify VOCs into three classes: low reactivity, medium reactivity, and high reactivity. Within the low reactivity or high reactivity classes, a continuous scale may be used to further differentiate the VOCs in these classes.

All of the classification schemes rely on some reference point or points, and incorporate some set of assumptions that provide a basis for comparing individual VOCs. For example, the MIR scale is developed on the basis of a specific set of environmental conditions where ozone formation and accumulation are believed to be most sensitive to changes in hydrocarbon emissions. In selecting the reference points on which a classification scheme is based, it is important to consider:

- 1) How generalizable are the reference points? For example, how robust is the ranking of reactivity provided by one classification scheme if the assumptions underlying that scheme are changed?
- 2) How can comparisons be made between the composition of complex emission streams and those reference points? For example, if a three-class scheme were selected, what analytical methods are available that readily distinguish between the fraction of emissions belonging to each class? Alternatively, is it necessary to fully speciate VOC mixtures before applying any classification scheme?

Such considerations are important in the implementation and enforcement of any different treatments assigned to the different VOC classes.

Further research on the generalizability of different metrics for reactivity would provide useful information for the design of a classification scheme. In particular, the identification of natural breaks in reactivity scales that are robust across a wide variety of conditions may help guide the design of reactivity policies. Ideally, such natural classes may take into account the mixtures in which VOCs are actually

emitted and the ability of existing analytical techniques to distinguish groups of VOCs, as well as the propensity to contribute to the formation of impacts of interest.

In the current two-class policy, ethane is used as the benchmark. A compound that is determined to be equal to or less than ethane in terms of photochemical reactivity, measured in terms of its molar rate of reaction with hydroxyl radicals,²⁴ is considered to be negligibly reactive. Any discrete classification scheme will involve the specification of such “bright lines” or thresholds, which conflict with the physical nature of reactivity which is more of a continuous phenomenon. Theoretically under the current reactivity policy, if a compound is 1 percent less reactive than ethane, none of it is counted as a VOC for purposes of determining compliance with VOC limits; on the other hand, if a compound is 1 percent more reactive than ethane, then 100 percent of it is counted as a VOC -- even though the two compounds have virtually the same impact on ozone formation. One possible approach to this bright line issue is to establish a “bandwidth” around the reference point that softens the distinction between classes. Within a narrow band, such as +/- 5% of the reference metric, the VOC could be classified on either side of the threshold. Further research is needed to understand the implications of choosing different reference points as the basis of a classification scheme.

As the resolution of the classification scheme increases, the amount of information needed to differentiate between individual VOCs increases, and the generalizability of the classification scheme decreases. Given our current state of knowledge, the level of uncertainty in the relative rankings of individual VOCs generally increases as the resolution of the classification scheme increases. In other words, it may possible to design a three-class scheme that is more generalizable than a continuous scale.

One advantage of using a continuous scale, however, is that it may be possible to quantify some of the uncertainty in the reactivity value for each VOC, making it possible to explicitly take uncertainty into account. Uncertainty in the reactivity value for a particular VOC may come from measurement uncertainty, incomplete knowledge of the compound’s reaction pathways, or from uncertainty about the environmental conditions in which the VOC will be found. It is possible to quantify some of these sources of uncertainty, but there is no agreed upon methodology for characterizing the uncertainty in different reactivity metrics. Furthermore, it’s not clear how this information should be used in making policy decisions. A hypothetical situation best illustrates this issue. XYZ Company needs to reformulate a product to reduce its ozone forming potential. The company determines that the new product will have a photochemical reactivity value of 1 +/- 0.5, and this will replace the old product that had a photochemical reactivity value of 1.25 +/- 0.25. With the uncertainty ranges associated with each product, it is possible that the newer reformulation may actually have a reactivity value greater than the older product it is replacing, and will adversely affect the air quality. Because there is no accepted method for estimating hydrocarbon reactivity uncertainty ranges,

²⁴ The ethane threshold has been historically applied on a molar basis except in the case of acetone, which was compared on a mass basis using a MIR values, because photolysis and not the hydroxyl reaction is the rate-controlling step for acetone.

there is no way for the user of this information to determine how likely it will be that the newer, nominally lower reactivity compound is actually more reactive.

A more qualitative approach to dealing with uncertainty in reactivity classification schemes was proposed by CARB in their consumer products regulations. While the regulation generally uses a continuous reactivity scale, CARB developed a discrete classification scheme for the uncertainty in the reactivity value based on expert judgment. Specifically, Dr. Carter, who developed the continuous scale in question, grouped compounds together on the basis of how likely it would be that their reactivity values would change if subjected to further study. Each grouping was then assigned an adjustment factor that is used to increase the measured value to ensure that the reactivity value used in the regulation is greater than the true value.

In adopting any classification scheme, it is important that policy makers understand that the state of knowledge about reactivity is constantly evolving. Thus, reactivity policies must be designed to evolve along with our changing understanding, which may involve periodically readjusting the classification scheme based on new insights from research.

Regardless of how different classes of VOCs are treated under a regulatory system, the classification system itself may have important implications for how policy makers and the public perceive the use of particular VOCs. Producers and users may be particularly concerned about the stigma attached to compounds placed in a “high” or “very high” reactivity bin. Based on past experience, there is concern among industry groups that compounds so stigmatized may be inappropriately banned under future regulatory or “voluntary” programs.

4.2.2 Treatment Schemes

The second fundamental component of any regulatory approach addressing VOC reactivity is the treatment scheme that defines how the regulatory requirements differ across the different categories in the classification scheme. In general, alternative treatment schemes can be divided into exemption schemes and weighting schemes.²⁵ The possibilities within these different types of schemes are described below.

4.2.2.1 Exemption Schemes

Given a set of regulatory requirements for VOC emissions, an exemption scheme may apply all, some, or none of the requirements to different classes within the classification scheme. Under the current reactivity policy, all VOC emission limitation and reporting requirements apply to those compounds that

²⁵ Note that an exemption scheme is actually a special case of a weighting scheme in which the weights applied to certain regulatory requirements are either 0 or 1.

are more reactive than ethane. Those compounds that are less reactive than ethane are considered “negligibly reactive” and are exempted from all of the emission limitation and reporting requirements. However, in the future it may be necessary to include emissions of even the “negligibly reactive” in the emissions inventory to improve the performance and accuracy of the airshed models and to verify that these exempt compounds produce negligible levels of ozone.

In addition to the current “all or nothing” exemption scheme, different classes within the classification scheme could be assigned partial or restricted exemptions. Restrictions could be based on:

- C **Type of Obligation.** For example, certain classes of VOCs could be exempted from emission limitation requirements, but not exempted from emission inventory and reporting requirements.
- C **Geographic Location.** Exemptions could be granted that apply only to a particular geographic area; for example, VOC emission limitations could be lifted in specific areas that are NO_x-limited.
- C **Source Category.** Exemptions from some requirements could be granted for a class of VOCs if used in a specific source category or a specific type of application or process.
- C **Facility.** Exemptions from some requirements could be granted for the use of VOCs in a particular class at a particular facility. Such an exemption could be part of a program to achieve better overall environmental performance at particular facilities, such as Project XL.
- C **Emissions Cap.** Exemptions could be granted to remove requirements as long as total emissions remain below some set cap.
- C **Time Period.** Exemptions could be granted for a limited period of time. At the end of the time period, the regulatory agency would have the opportunity to look back and reevaluate whether the exemption had had a positive or negative impact on air quality. Such a restricted exemption may be thought of as a “deferred control” approach as opposed to a pure exemption.

Further research is needed to provide information about the impacts that can be expected from such restricted exemptions. In particular, additional information is needed to determine how exemptions granted in small geographic areas may impact other areas downwind and whether or not the change in air quality due to granting VOC exemptions at the facility or process level can be detected in periodic reviews of the policy. Moreover, further research may suggest that any exemption scheme may be inappropriate because even those compounds considered “negligibly” reactive contribute to ozone formation.

4.2.2.2 Weighting Schemes

While exemption schemes either apply regulatory requirements to a class of VOCs or not, a weighting scheme applies regulatory requirements to each class with a stringency that is related to the relative reactivity of the class. Such weighting schemes are usually associated with classification schemes based on continuous scales. However, it is possible to use weights with a discrete classification system. For example, given a three-bin classification scheme, a weighting scheme may apply mass adjustment factors of 0.5, 1, and 2 to the emissions of the low reactivity, medium reactivity, and high reactivity classes, respectively, for purposes of calculating emission totals and for compliance with emission caps. In this system, emissions of high reactivity VOCs could count 4 times as much as an equal mass of emissions of low reactivity VOCs.

Weighting schemes, like exemption schemes, could allow policy makers to encourage the emission of low reactivity VOCs in place of more reactive VOCs by decreasing the regulatory requirements on lower reactivity VOCs. However, weighting schemes could also allow policy makers to discourage the emission of high reactivity VOCs by increasing the stringency of requirements as reactivity increases.

As it is possible to design hybrid classification schemes that combine discrete classes and continuous scales, it is also possible to design hybrid treatment schemes that involve both exemptions and weights. For example, in the three-bin classification scheme discussed above, the low reactivity class could be exempted from all requirements except reporting for purposes of emission inventory development. For the high reactivity class, a weighting factor of 2 could be applied to all emission calculations as a penalty to encourage substitution to lower reactivity compounds.

To improve the utility of possible weighting schemes, as well as the classification schemes behind them, further research is needed to identify differences in the contribution of individual VOCs to the environmental impacts of concern. To be meaningful, weighting schemes must represent the different reactivities of classes of VOCs taking into account the uncertainty in characterizing such reactivities. By resolving differences in reactivity scales based on different metrics and assumptions, it may be possible to design a robust and generalizable weighting scheme.

4.2.3 Implementation Opportunities and Challenges

Within the air quality management process, there are a variety of opportunities to use combinations of the classification and treatment schemes discussed above to address VOC reactivity and achieve the goals discussed in Section 3. Each of these opportunities to address reactivity has associated challenges, some of which may be overcome by additional research. The opportunities and challenges associated with incorporating reactivity into the planning & assessment, control measure design & implementation, and compliance & enforcement phases of air quality management are discussed below.

4.2.3.1 Planning and Assessments

VOC reactivity can be addressed at several points in national, state, and local air quality planning processes. First, VOC reactivity classification and/or weighting schemes could be used to help prioritize future VOC control measures, so that the most reactive VOCs are addressed first. In the future, States could potentially use reactivity considerations to prioritize VOC controls needed to attain the ozone NAAQS for various source categories. As with most other efforts to address reactivity, the use of classification schemes and weighting schemes to set regulatory priorities presupposes the availability of adequate information about the chemical composition of different emission streams, the environmental conditions in which the streams are emitted, and the difference in impacts associated with the differences in composition. The amount of information that is already available and the costs to collect more information vary with the type of emission source. Considering reactivity in the planning process alone does not help generate more information from emission sources that could be fed back into the planning process, such as the information that a permitting program that requires emissions testing might generate. Gathering adequate information for incorporating reactivity in the planning process may involve a large research effort or more detailed reporting requirements for industry. Research and analysis is needed to determine the value of additional information about the reactivity of emissions. Such analysis must consider the potential costs of gathering the necessary information and the efficiency gains associated with using it in setting regulatory priorities.

The second opportunity to address reactivity in the air quality planning process is in modeling and assessment studies. Reactivity is addressed in these impact assessments through the use of computer models of atmospheric chemistry that predict the fate of different classes of compounds. However, reactivity is not usually considered in the development of economic assessments, such as the regulatory impact assessments (RIAs) that are developed by EPA for every major regulation. One of the main purposes of this type of analysis is to evaluate the cost-effectiveness of the different regulatory options that are under consideration. The cost-effectiveness of a regulation or regulatory option relating to VOC control is typically measured in terms of the cost-per-ton of the VOC emissions it would reduce. Using reactivity classification and weighting schemes, the cost-per-ton of VOC emissions may be related to a metric such as the cost-per-ppb ozone decrease. This metric would allow individual control measures to be compared on the basis of an air quality impact instead of an intermediate objective such as emission reduction. However, using such a metric presupposes that the reactivity classification and weighting scheme used are generalizable to all of the different environmental conditions of interest. Furthermore, ranking VOC control measures solely on the basis of ozone cost-effectiveness ignores all of the other potential benefits of VOC control, including decreased particle formation and exposure to toxic air pollutants.

4.2.3.2 Control Measure Design and Implementation

Exemption and weighting schemes that address VOC reactivity could potentially be incorporated into the design and implementation of control measures via permitting requirements, emission limitations, and reporting requirements. Different classification and treatment schemes may be appropriate for different emission sources.

Under the current VOC control policy, emissions that are less reactive than ethane are not counted as VOCs and are exempt from permitting and reporting requirements and emission limitations. This exemption scheme creates a strong incentive for industry to use exempted compounds in place of VOC materials wherever possible. Encouraging substitution of less reactive VOCs for more reactive VOCs could be a goal of a reactivity policy. Another goal of a reactivity policy, of course, could be to keep the higher reactive VOCs out of the air altogether or as much as is feasible.

Incentives to encourage the substitution between less and more reactive VOCs could be created with either an exemption scheme or a weighting scheme. Exemptions from requirements or limitations could provide for shifting from the use of products or processes that emit more reactive VOCs to products or processes that emit less reactive VOCs. As discussed earlier, weighting schemes could provide such rewards for low reactivity emissions as well as penalizing high reactivity emissions with more stringent requirements. Both rewards and penalties would create incentives to substitute low reactivity VOCs for high reactivity VOCs.

In designing a VOC control policy to encourage VOC substitution, it is important to consider which source types could take advantage of such rewards and penalties and which source types could not. Complex processes that cannot be easily modified to alter emissions or the production of products whose properties depend on the use of high reactivity compounds would not be able to take advantage of the benefits of substitution, but other sources that can change input streams to reduce the reactivity of emissions would respond to the system of incentives. Further research may contribute to a better understanding of where such opportunities for substitution exist. Similarly to the value of information analysis discussed with respect to the planning process, the potential costs of implementing a system to create substitution incentives should be compared to the potential environmental and economic benefits of those substitutions.

How effective the system of incentives is at encouraging substitution depends not only on the ability to change the emission source, but also on how big the changes in regulatory requirements are and how small the changes in reactivity have to be to receive credit. Under the current two-bin policy, there is little incentive to substitute between highly reactive compounds and less reactive compounds that fall within the “reactive” bin. With the threshold for exemption set at the reactivity of ethane, a relatively small number of compounds are classified as negligibly reactive (most of them halogenated compounds), and there are technical obstacles that prevent these exempt compounds from being used in most products or processes. Thus, there are few opportunities to take advantage of the exemptions through substitution, despite the fact

that the changes in requirements are significant. Additional substitution could be encouraged by raising the threshold, allowing more options, by dividing VOCs into more classes or using a continuous scale or by imposing more stringent VOC emission limits to encourage reductions in VOC emissions. With more bins or a continuous scale, there would be an incentive to substitute compounds or adjust processes so that emissions fall into a less-reactive class or are assigned a lower reactivity weight. However, the more bins used in the classification scheme, the more complex the regulatory approach becomes to design, implement, and enforce.

While the multiple environmental impacts associated with VOC emissions and the uncertainty associated with classification schemes were discussed above, it is important to consider these issues in the context of encouraging possible VOC substitution. It is important that any set of incentives designed to encourage substitutions that will decrease one environmental impact under one set of conditions will not increase other impacts under other conditions. Research on generating robust classification schemes for VOCs that address the multiple impacts will help guard against potentially harmful substitutions.

The discussion of the benefits of substitution above presupposes that higher reactive compounds have more ozone generation potential over the atmospheric lifetime of the compound than a low reactive compound over its lifetime. This hypothesis would need to be clearly demonstrated before restrictions on total mass of VOC emissions were relaxed. Any existing supporting data needs to be published so that all policy makers involved are able to take it into consideration.

Most of this discussion has focused on the systematic development and implementation of control measures that would apply to whole source categories. However, it might also be possible to incorporate reactivity exemption and weighting schemes into permitting requirements, emission limitations, and reporting requirements on a case-by-case basis. More specifically, restricted exemptions or weighting schemes could be applied to individual areas, facilities, or processes to encourage appropriate substitutions.

4.2.3.3 Compliance and Enforcement

It is not clear that VOC reactivity can be taken into account in the compliance and enforcement phase of air quality management except to the extent that reactivity has been incorporated into the design and implementation of control measures as discussed above. However, the significant challenges created by reactivity considerations for successful compliance and enforcement efforts, and thus a successful overall policy, warrant a separate discussion.

If reactivity classification or treatment schemes are incorporated into permit and reporting requirements, operators of sources and government inspectors must have the ability to monitor and verify compliance with the requirements. For some source types, monitoring and verifying compliance would require the use of emissions testing methods that could differentiate VOCs based on the classification scheme used. Ideally, these testing methods would be inexpensive and relatively simple, so that they could

be applied on a routine basis. For other sources, record keeping procedures that track process inputs and process rates might be sufficient to monitor and verify compliance. Different source types would require different approaches. Any change in a VOC control policy based upon relative reactivity and permitting substitution will potentially impose greater record keeping and testing burdens on industry. An inability to devise practical, cost-effective, enforceable means to permit such a policy will limit the ability of regulatory agencies to consider such an approach. Thus, further research regarding the development of analytical methods that can distinguish between relevant classes of VOCs would be helpful in the design, implementation, and enforcement of a reactivity policy.

4.3 SUMMARY OF DESIGN ISSUES

In summary, there are a variety of opportunities to incorporate considerations of VOC reactivity into the planning, implementation, and enforcement of control measures, permit requirements, emission limitations, and reporting requirements. Each of these opportunities has an associated set of challenges that may be overcome with additional research. In all of these possible applications, the VOC reactivity policy would have at least two fundamental components: a classification scheme and a treatment scheme. Different combinations of these schemes may be more suitable to particular source categories and contexts than others. In designing the classification and treatment schemes for any particular context, policy makers might consider:

- C The potential for multiple impacts of concern
- C The appropriate geographical scope of application
- C The suitability of the scheme to the source type
- C The atmospheric availability of the affected VOCs
- C The uncertainty in the reactivity characterization
- C The availability of analytical methods to support compliance monitoring and enforcement

Specific research questions generated from these policy design issues are discussed further in Section 6.

5. ORIGINS OF VOC REACTIVITY FOR OZONE & PM FORMATION

5.1 OZONE AND PARTICULATE MATTER FORMATION

The formation of tropospheric ozone requires the oxidation of NO to NO₂ by peroxy radicals (RO₂ and HO₂). In the symbol RO₂, the R- represents an organic chain, that is, carbon atoms bonded to other carbon atoms with the remaining bonds filled with H-atoms or with O-atoms, or with various halogen atoms. The first member of the peroxy series is HO₂, which is formed from H-atoms that were originally attached to organic compounds but are abstracted by O₂ during the VOC's oxidation. When the newly created NO₂ photolyzes, it produces an atomic oxygen atom and recreates the NO. The atomic oxygen atom combines with the atmosphere's molecular oxygen (O₂) to produce ozone (O₃). Thus, it is obvious that *both* organic compounds capable of forming RO₂/HO₂ radicals and NO are needed to form tropospheric ozone. Figure 5.1 emphasizes this dual character to VOC reactivity, i.e., that it is a function of both the VOC's chemical properties and the conditions of the environment in which it reacts.

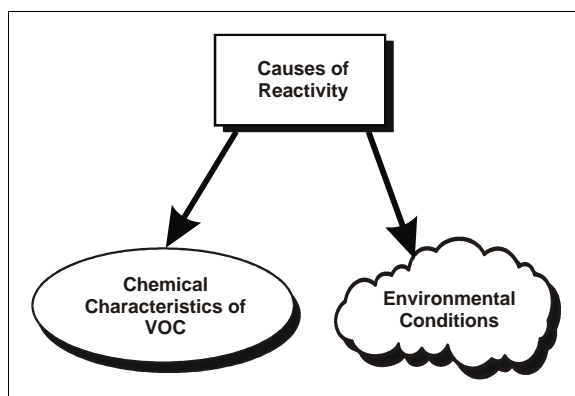


Figure 5-1

The amount of O₃ formed is a function of the supply of RO₂ and HO₂ radicals and the availability of NO to be oxidized. The former is related to the oxidization of volatile organic compounds (VOCs) via radicals or photolysis and the latter is related to the spatial and temporal emissions and atmospheric dispersion and removal of NO and NO₂. Figure 5.2 illustrates the way various VOC characteristics lead to NO to NO₂ oxidation or to some other process that may remove radicals and/or NO_x. Figure 5.3 illustrates some of the environmental factors that influence the radical supply that is oxidizing the VOCs and the factors that influence the availability of NO_x.

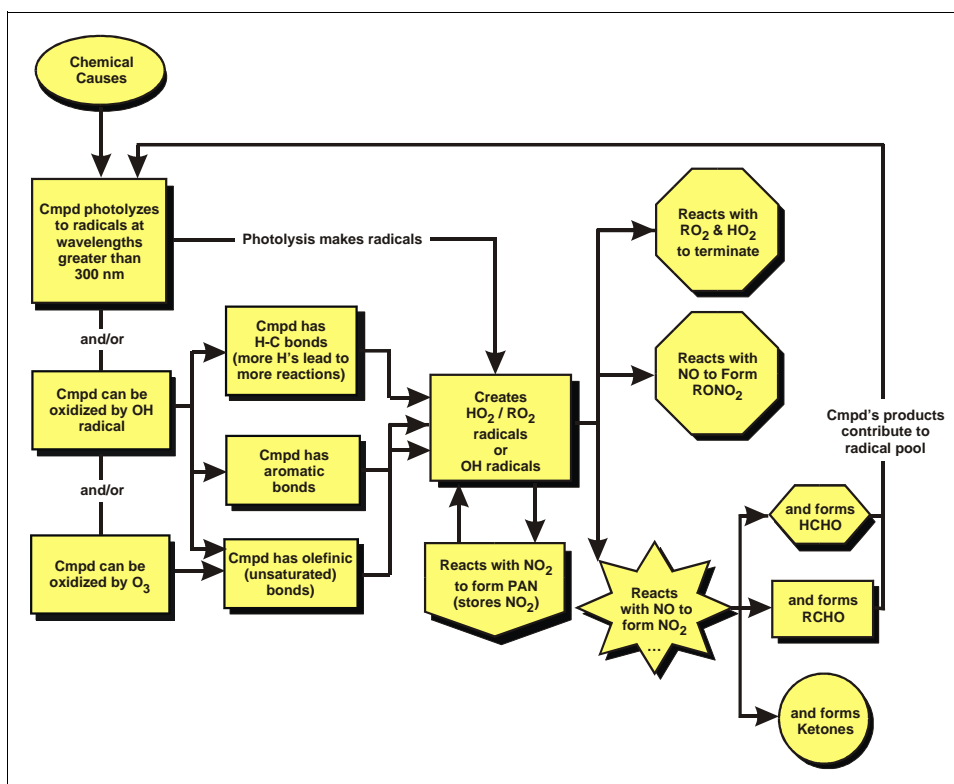


Figure 5-2

The supply of RO_2 and HO_2 radicals is determined by the photolysis of (emitted or photochemically formed) carbonyl compounds such as aldehydes (these are compounds with formulas like $\text{R}_2\text{C}=\text{O}$) or by the creation of RO_2 and HO_2 radicals subsequent to hydroxyl radical (OH) attack on virtually all organic compounds, or by O_3 or nitrate radical (NO_3) radical attack on organic compounds having double bonds between two carbon atoms. The formation of these photolyzable products creates a positive feedback loop in Figure 5.2 where the reactions of one VOC can affect the reactions of other VOCs. The largest sources of OH radicals are photolysis of O_3 and the HO_2 radical's reaction with NO to produce NO_2 and OH . As shown in Figure 5.2, VOC oxidation products---rich in aldehydes, organic nitrogen compounds like PAN, and potentially other forms of nitrogen---can be carried over or transported into a domain and add to the radical and NO_x supply.

NO and NO_2 become less available in active photochemical systems due to the formation of organic and inorganic nitrogen-containing products (e.g., PAN, RONO_2 , and nitric acid, HNO_3). This occurs for some RO_2 radicals as an alternative to oxidizing NO to NO_2 . The nitric acid formation occurs via $\text{OH} + \text{NO}_2$. These reactions not only decrease NO_x they also remove radicals, thus VOC's that react this way can exhibit a "negative reactivity."

The formation of secondary organic aerosol matter occurs during the oxidations of the emitted volatile organic compounds. The organic products of the various attacks become increasingly oxygenated, become more polar, and have lower vapor pressures. These compounds can partition between the gas-phase and the surfaces provided by ambient aerosols to increase the mass of the aerosols. Subsequently, if the aerosols are transported to a different chemical environment, the organic content of the aerosol can evaporate from the aerosol and once again become gas-phase material.

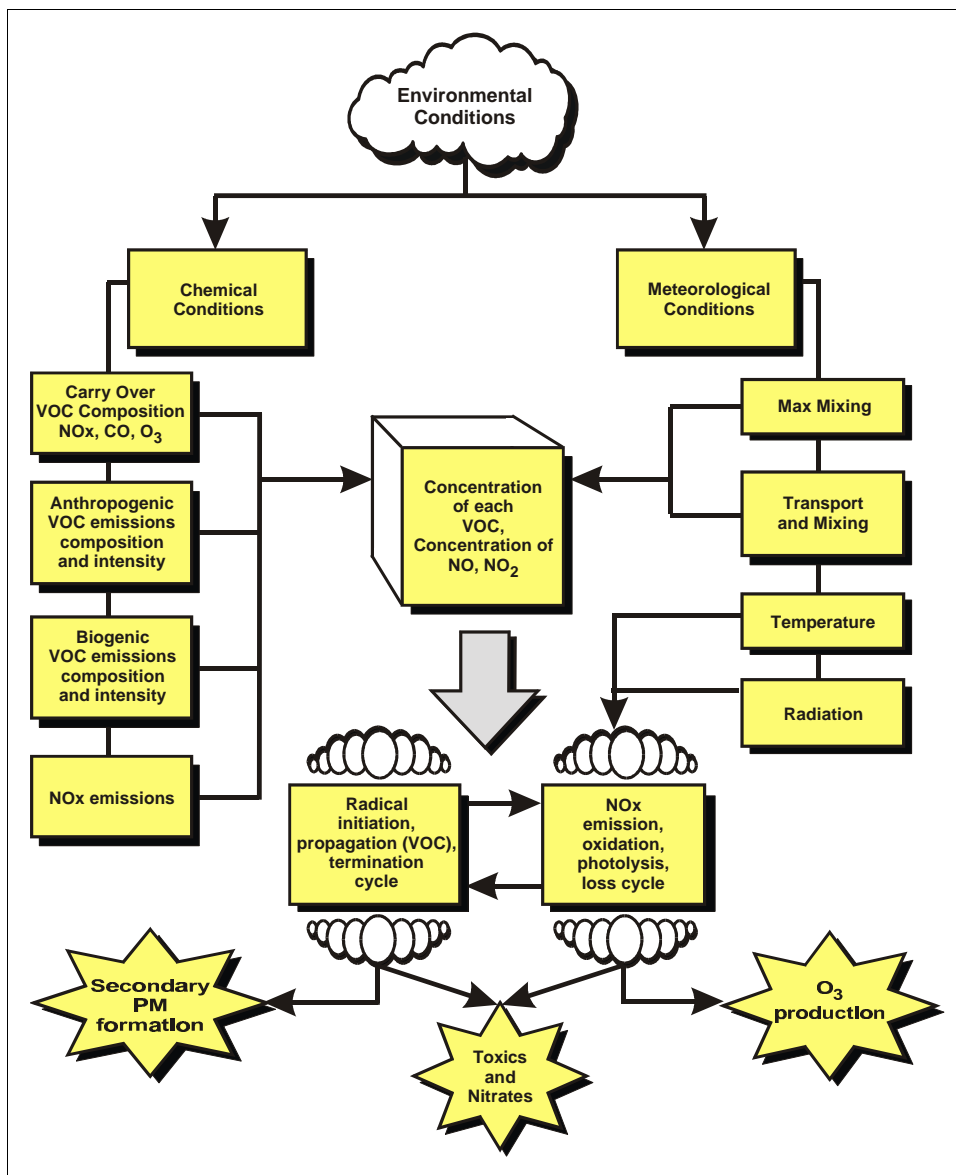


Figure 5-3

5.2 REACTIVITY OF VOCs

5.2.1 Explaining Reactivity

The term “reactivity of a VOC” can be used in two distinctly different ways:

- ! As the **amount** of O₃ that the reactions of a particular VOC (and its reaction products) have contributed to the **total** O₃ formed in a given system; or
- ! As the **sensitivity** of the **total** O₃ formed in a given system to a small change in the emissions (and ultimately, the concentration) of a particular VOC.

The first explains the origin of the O₃ in the system (i.e., the total amount of O₃ is explained by the sum of the amounts of O₃ produced by reactions of each VOC), but such explanations cannot predict how the system will respond to a change in the VOC composition. The second reactivity describes the initial tendencies of the total O₃ as the sum of the sensitivities associated with changes in the VOC composition, but can not explain the cause of the total O₃ in the system, nor even the cause of any O₃ changes in the system. That is, one can not multiply each VOC's sensitivity by the amount of VOC in the mixture and obtain the total amount of O₃ produced in the system. Furthermore, if one were to remove a given VOC from the system, multiplying the amount of VOC removed by its sensitivity may not equal the actual change in the system's O₃.

Jeffries and Crouse (1990) explained O₃ formation in model systems via a “process analysis” method (Jeffries, 1995) wherein the magnitude of the model's internal processes were recorded and subjected to subsequent analysis. Thus, in a particular simulation, the total O₃ was explained by:

$$\text{total O}_3 = \sum \text{C}_i \text{Y}_i \quad \text{over all } i \text{ VOC species}$$

where

C_i is the amount of VOC_i that reacted;

Y_i is the “ozone yield” of VOC_i

during the simulation.

The “ozone yield” of a given VOC_i is

$$Y_i = \frac{(\text{total NO}_2) - \text{VOC}_i}{(\text{O}_3) - \text{NO}_2}$$

and

$$\begin{aligned} (\text{total NO}_2) - \text{VOC}_i = & (\text{HO}_2) - \text{VOC}_i + (\text{NO}_2) - \text{HO}_2 + \\ & (\text{RO}_2) - \text{VOC}_i - (\text{NO}_2) - \text{RO}_2 \end{aligned}$$

For the CB4 Mechanism in a typical trajectory model simulation used by Carter for his scales, the total daily average values for these terms for the total “urban VOC mix” are:

(HO_2)/VOC)	= 1.06	range 0.74 -- 1.17
(NO_2)/ HO_2)	= 0.91	range 0.71 -- 1.00
(RO_2)/VOC _i)(NO_2)/ RO_2)	= 0.73	range 0.40 -- 0.79
([total NO_2]/VOC _i)	= 1.70	range 1.24 -- 1.87
(O_3)/ NO_2)	= 0.80	range 0.43 -- 0.86.

Therefore, $Y_{\text{mix}} = 1.33$, or each VOC molecule that reacted created 1.33 molecules of O_3 . The inefficiencies in the process are the low number of NO_2 's produced by the VOC's RO_2 's and the fact that not every NO_2 photolysis led to the production of O_3 . The former is due to formation of products like PAN and organic nitrates and the later is due to loss of odd oxygen in the cycling of NO, NO_2 , NO_3 , N_2O_5 , and O_3 .

Figure 5.4 shows two pie-charts from an Urban Airshed Model simulation of a Charlotte, NC episode. The chart on the left shows the amount of each VOC that reacted, and the chart on the right shows the O_3 that was formed.

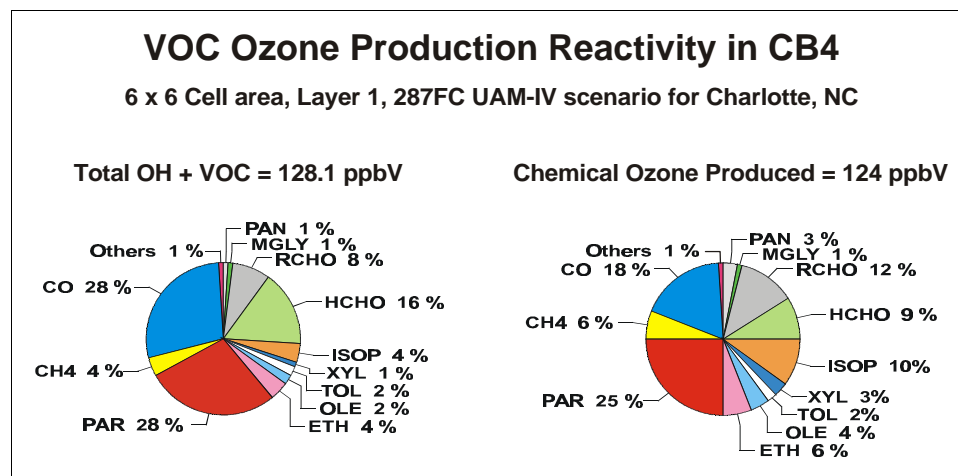


Figure 5-4

The two environmental factors that most influence a given VOC's reactivity are the origins and intensity of radical sources and the availability of NO .

5.2.2 Explaining Sensitivity to VOC Change

Figure 5.5 shows how incremental reactivity (or O_3 sensitivity) can be explained using the concepts from above. The diagram on the left of Figure 5.5 shows the amount of O_3 created by a VOC in the “base

case” simulation as a gray rectangle with sides that have lengths proportional to the amount of the VOC that reacted in the scenario and the magnitude of the O₃-yield of each reacted VOC molecule. Each VOC in the mix would have such a diagram. The sum of all the gray areas would be the total amount of O₃ produced in the simulation.

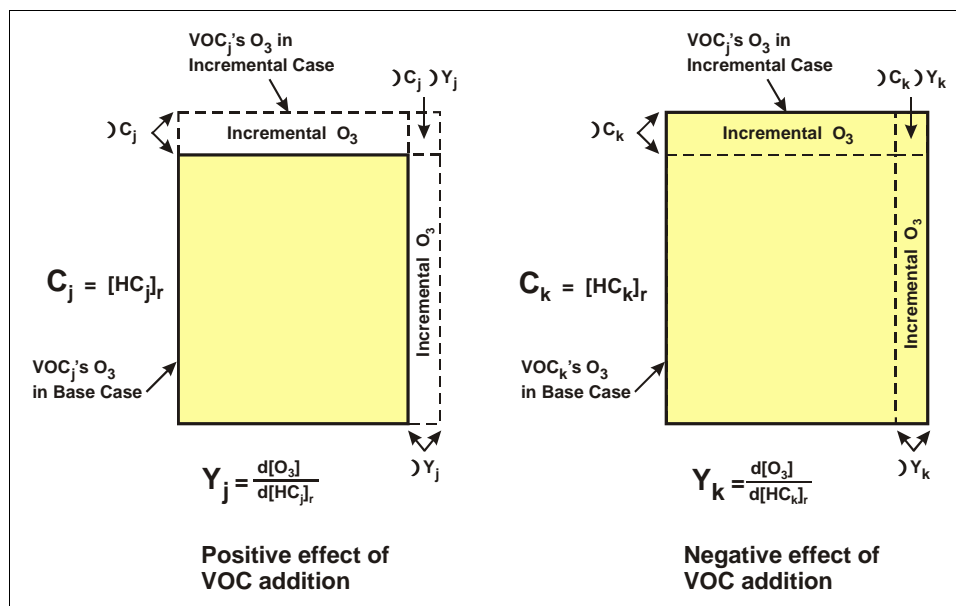


Figure 5-5

Now when a particular VOC emission or concentration is changed in the scenario, not only is the CY-diagram for the particular VOC modified, but other VOC's CY-diagrams are also likely to be changed. Say, for example, we increased the concentration of a VOC, then we would expect that more of it might react and at the same O₃-yield as in the base case, the CY-gray area for this VOC would increase vertically, but have the same width; this would increase the total O₃ in the simulation. Alternatively, this particular VOC might make faster reacting RO₂'s which compete better for the NO, compared to some other VOC whose RO₂'s make more RONO₂ than this VOC. This response, indicated by the C-Y gray area increasing horizontally, would increase the O₃-yield for the VOC, leading again to more O₃ produced. If a particular VOC, however, has a reaction process that makes substantial organic nitrates, then increasing that VOC's presence may cause other VOC's to exhibit lower O₃-yields, due to a decrease in the availability of NO to react with their RO₂ radicals. Thus, increasing a particular VOC may result in it reacting more and itself making more O₃ via an increase in its own CY-gray area, but it also make other VOC's make less O₃ due to a lower availability of NO, and the total sum of all the VOC's CY-gray areas could be significantly less.

Figure 5.6 illustrates these situations. The plots in Figure 5.6 show just the sum of the changed areas of the CY-plots (that is, just the areas labeled “incremental O₃” in the CY-plots of Figure 5.5) which were caused by a 2% increase in one of the model’s VOC species. The top plot is for addition of CB4’s OLE species, a highly reactive model species that represents olefins in urban areas. The bottom plot is for addition of CB4’s TOL species, which is used to represent toluene. Note that the OLE species is about 10 times as reactive as the TOL species. Bars are shown for two base conditions, a low HC-to-NO_x ratio of 4:1 and a more O₃ formation optimum HC-to-NO_x ratio of 6:1. In the middle of the plot are shown bars for the sum of all the VOC species changes, and to the right side of the plot are other changes in simulation ozone caused by physical processes such as dilution, which usually becomes a larger loss due to more O₃ being available to dilute, and O₃ reaction and deposition losses, which also increase because O₃ concentration increased. The last two bars are the “incremental reactivity” as would be computed by Carter for these species and these are the sum of the middle bars and the physical process bars for the two HC-to-NO_x ratio cases.

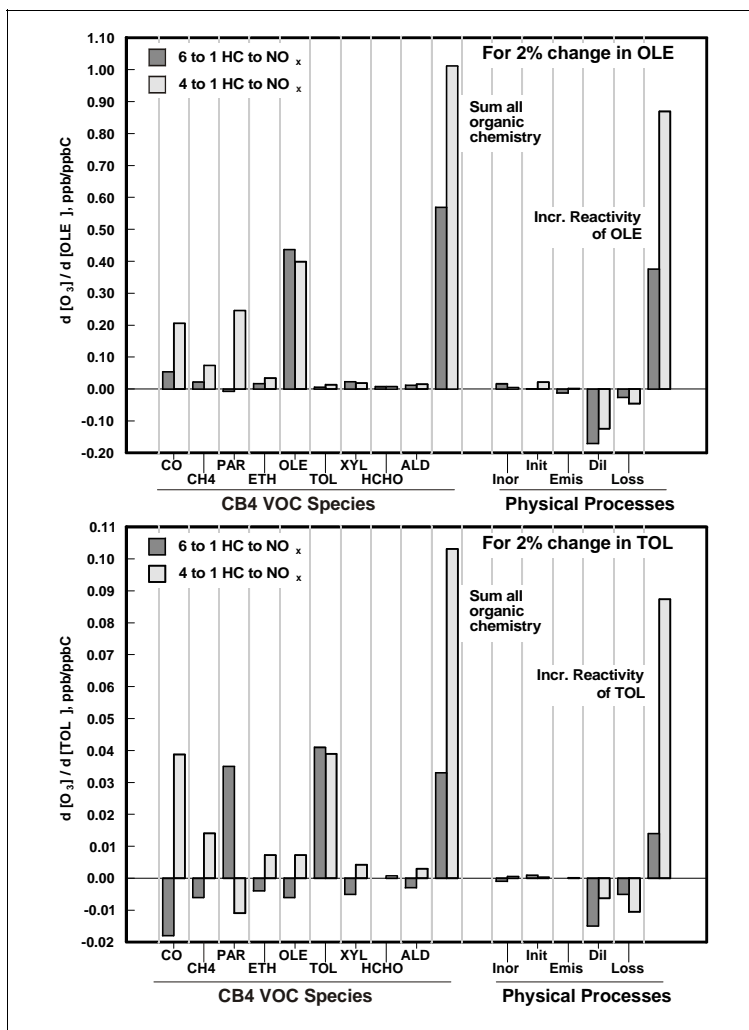


Figure 5-6

In Figure 5.6 for the top plot, the incremental reactivity for addition of OLE is about twice as high at the 4:1 ratio than at the 6:1 ratio. That is, the change in O₃ for a change in OLE is larger at 4:1, but the total O₃ produced is less at 4:1 than at 6:1. At both ratios, the change in O₃ caused *directly* by the reactions of the additional OLE are virtually the same, about 0.4 ppb O₃ per ppb of added OLE. The change in O₃ produced by *other* VOC species in the mixture, however, are quite different at the two ratios. At 4:1, the PAR-species, methane, and CO (the least reactive species) all increased their CY-gray areas over their CY-gray areas in the base case; this was mostly due to the increased amount of these long-lived species that reacted due to the increase in the radical pool caused by the photolysis of the additional OLE products. Thus, at the 4:1 ratio, about *half* of the change in O₃ that occurred when OLE was increased was due to the reactions of VOCs in the mixture other than OLE.

In Figure 5.6 for the bottom plot, the incremental reactivity for addition of TOL is also about three times as high at the 4:1 ratio than at the 6:1 ratio. Once again, at both ratios, the change in O₃ caused *directly* by the reactions of the additional TOL are virtually the same, about 0.04 ppb O₃ per ppb of added TOL. The change in O₃ produced by *other* VOC species in the mixture, however, are not only different at the two ratios, but many have changed signs! That is, addition of TOL to a 6:1 HC-to-NO_x mixture resulted in six of the other VOCs in the mix producing *less* O₃ than in the 6:1 base case. This is a result of a reaction pathway in TOL's reaction mechanism that removes NO₂ from the system. This deprives the other VOCs of NO needed to react with their RO₂ radicals and thus lowers their O₃-yields, so that even if the same amount of each VOC reacted, each VOC's products were less effective in converting NO to NO₂, resulting in an overall lessening of each VOC's contribution.

As in the OLE case, the physical conditions cause a loss in the chemical produced O₃ which differs depending upon the total amount of O₃ produced, resulting in even larger differences in the changes to O₃ between the two ratios.

5.2.2 Demonstration of Effects of Environmental Conditions on Reactivity

Figures 5.7 compares the reactivity of a complex VOC mixture that represents the exhaust from industry average gasoline (IAG) fueled automobiles with a VOC mixture that represents the exhaust from a methanol-gasoline (M85) blend fueled automobiles in the UNC Dual Outdoor Chamber. It is clear that the M85 fuel exhibits only about *half* the O₃ forming capability as the IAG fuel under these conditions. Figure 5.8 compares these same fuel emissions, but in a 50:50 mixture with a mixture of 54 VOCs that represent those found in typical urban air. Under these circumstances, there is virtually *no difference* in the O₃ forming capabilities of the two fuel emissions.

In these experiments, the HC-to-NO_x ratio is the same, only the complexity of the VOC mixture was different.

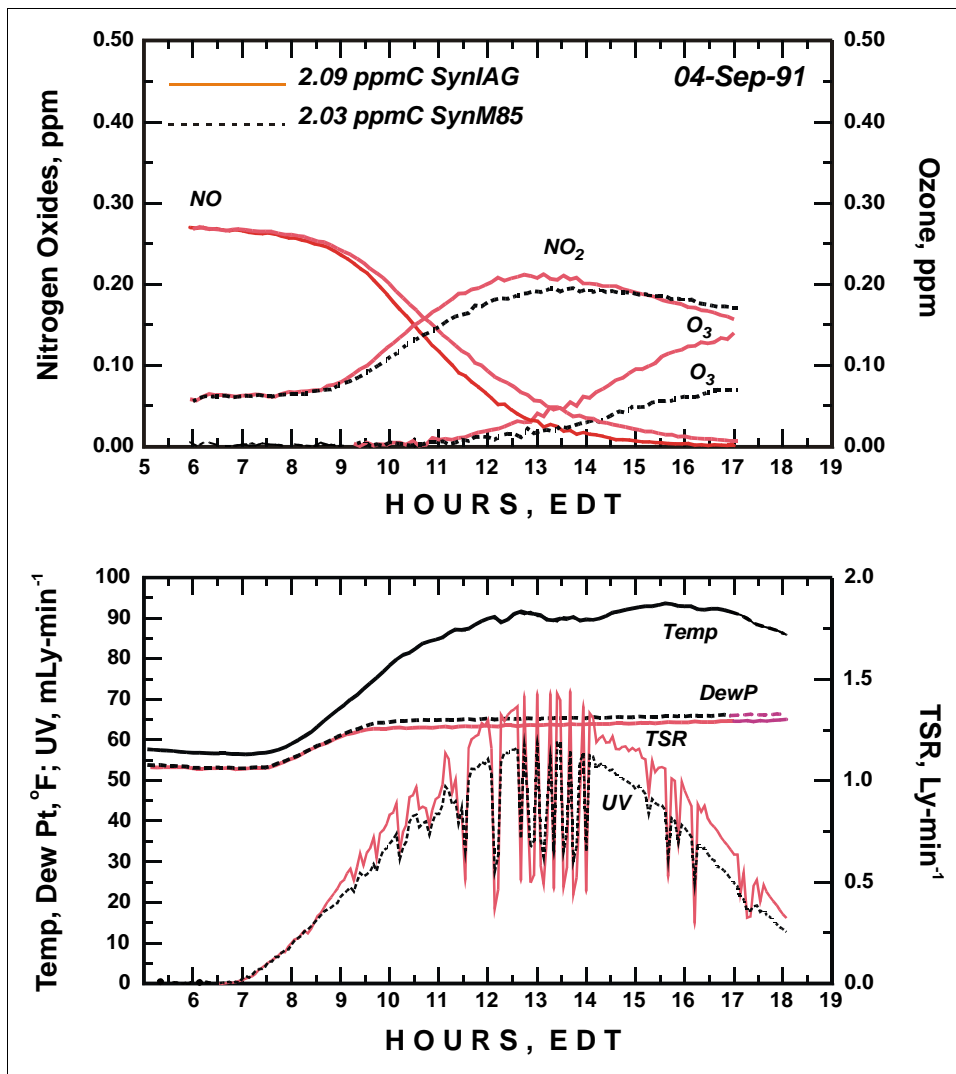


Figure 5-7

5.3 COMPUTING REACTIVITIES OF VOCs

Because of the complex interplay among the various competing reaction pathways and the major importance of availability of NO in determining O₃ formation, it is important not to investigate VOC reactivity only by experiments in environmental chambers like those shown in Figures 5.7 and 5.8. The problem is that these results may only be representative of the conditions in the chambers and may not extend to the urban and regional conditions where we wish to use the reactivity concept in a regulatory application.

The solution to this problem is that all realistic applications of VOC reactivity involve the use of photochemical reaction models to estimate the behavior of VOCs under conditions like those expected in urban areas and in regional domains. The chamber experiments are extremely useful in testing the photochemical reaction mechanism to assure that it does mimic the complex behavior of the VOC mixtures in the reasonably unambiguous conditions of an environmental chamber.

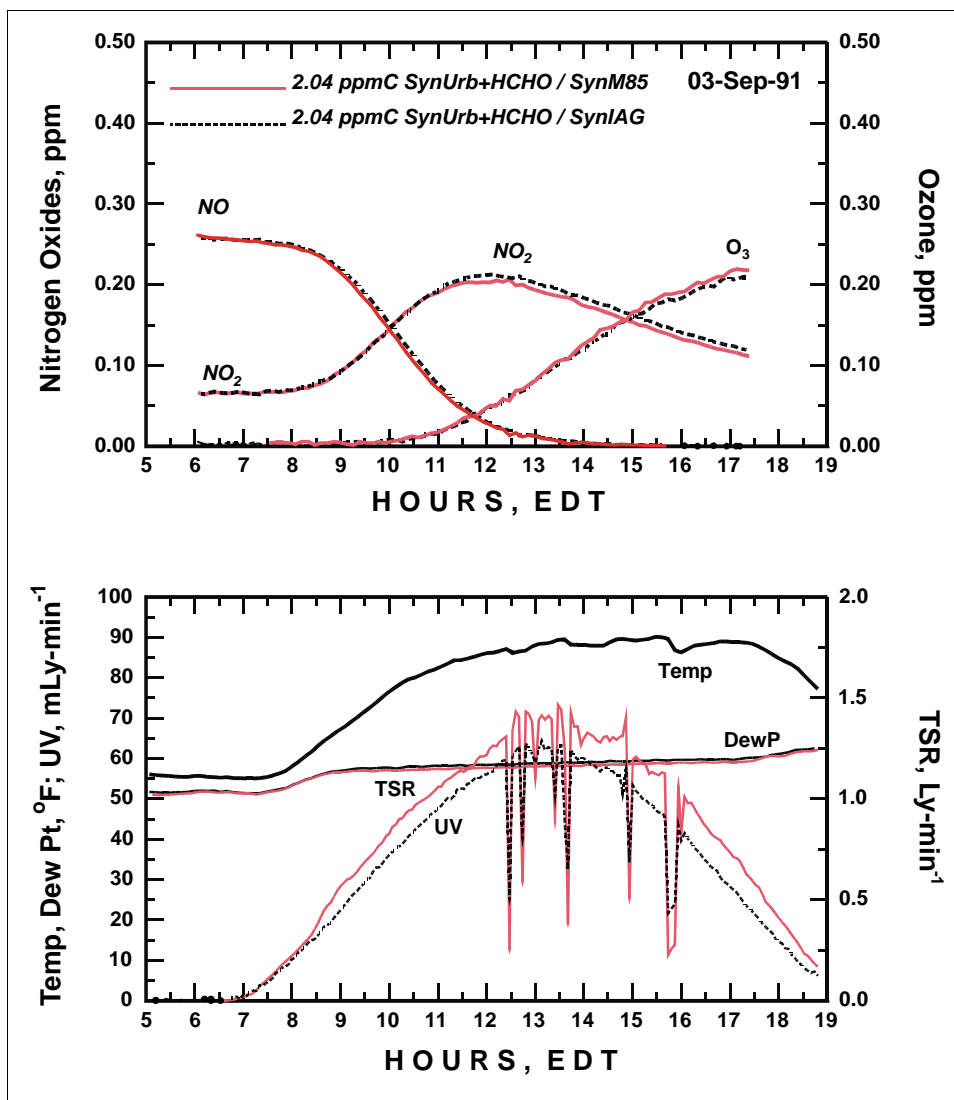


Figure 5-8

In addition to the photochemical reaction mechanism, the model must also re-create the proper availability of NO_x and the radical source strength. This most likely requires a high fidelity representation of the meteorological events and emissions strengths as a function of space and time. Even if the regulator

chooses to apply reactivity in the form of “scales”, the relative positions of VOC’s on the scales are determined by the operation of a photochemical model for a set of environmental conditions.

The subtle interactions among VOC’s and the impact that chemical and physical conditions can have on how a VOC affects the amount of O₃ it can form argue for beginning with comprehensive and relatively complex representations, and simplifying after the system’s behavior has been investigated and reasonably understood.

6. TOPICS FOR VOC REACTIVITY RESEARCH

The focus of the previous chapters has been devoted mainly to identifying potential policy-relevant VOC reactivity research issues where further research could be helpful to Federal, State and local policymakers in considering possible VOC reactivity-based control measures in regulatory policies. To this end, this chapter includes a list of related scientific questions and an associated list of possible short-term research topics that could, at the least, begin to provide some answers and further insights. These lists of questions and possible research projects, however, are not exhaustive nor intended to be complete; but they are intended to focus and initiate potential (less than 12 months) research activities.

To put these research topics in perspective and to help guide the research efforts, some of the implementation issues associated with the development of regulatory policy should be considered. For policy makers to design a viable regulatory policy incorporating VOC reactivity-based control measures, the approach must be practical, cost-effective, and enforceable. The importance of these implementation issues cannot be overemphasized because, regardless of how promising the scientific findings are in achieving an intended policy objective, a regulatory approach based on the scientific findings should translate into a course of action that is practical and cost-effective to do and can be monitored and enforced.

Section 6.1 lists some of these implementation-related questions and issues, and section 6.2 includes scientific questions and some short-term research topics that may address these science issues. Some initial short-term research projects are identified in section 6.3.

6.1 IMPLEMENTATION ISSUES

The questions below reflect some of the implementation-related issues that policy makers would need to address in VOC reactivity-based control measure regulatory policy. This list is not intended to be complete but rather to highlight some of the major implementation issues associated with a VOC reactivity-based control strategy. While these questions are not necessarily subjects of research investigations, they can serve to focus the research topics identified in section 6.2 and to help direct or prioritize investigative approaches.

1. What are the issues related to implementing, verifying, and enforcing regulatory reactivity rules?
 - a. What test methods are needed?
 - b. What record keeping is needed?
2. What are the likely costs of doing any of the activities identified in question one above?

3. What do we do with “uncertainty”?
 - a. Is the uncertainty small enough to determine if the regulation is directionally okay?
 - b. What are the ways uncertainty can be factored into a regulatory policy, and what are the associated environmental and practical implications on that policy and its implementation?

6.2 SCIENTIFIC ISSUES

6.2.1 Concept Scoping Questions

The questions listed in this section suggest, for the most part, short-term investigations aimed at identifying or scoping out some of the concepts discussed in earlier chapters for further, more detailed investigations. For example, answers to questions 2, 3, and 5 could be used to develop the analysis methodology used in subsequent studies and modeling efforts to assess the effects of various VOC control measure strategies and possible regulatory scenarios. Information derived by addressing questions 1 and 4 could provide insight about location, emission sources, and modeling scenarios to focus more detailed VOC reactivity-based control measure modeling analysis.

1. In those areas where VOC reductions may be required, does “reactivity” make a difference (relative to mass-based reductions) in O₃, PM, and RH?
 - a. How big a compositional change is needed?
 - b. How widespread is the effect?
 - c. How consistent spatially and temporally are the responses in O₃, PM, and RH?
2. What are the alternative ways of expressing the “differences” in question one above, and what are their advantages and disadvantages?
3. What are the ways of comparing the differences in VOCs found in question one above?
 - a. What are the scientific data needed to do the comparisons?
 - b. What are acceptable ways of adding new compounds to the system?
 - c. How consistent are the different approaches?
 - d. Which ones are applicable for multiple pollutants (O₃, PM, RH)?
 - e. Which are most appropriate for multi-day and multi-episode scenarios?
 - f. Do any methods have “gaps” in the response by different VOCs?
4. What are the sources of total VOCs that can be influenced (locally, regionally, nationally) by regulatory reactivity policy?
 - a. Which are the VOCs that can be influenced?
 - b. What are the forecasts for emissions under a changed policy?
 - c. If more compounds are exempted, what may be the impact on O₃, PM, and RH?
 - i. What is the impact on total mass of VOC emissions?

- ii. What are the likely forecasts of emissions under a changed policy?
5. Can we quantify “uncertainty”? What are ways to accommodate incremental improvements in science?

6.2.2 Important Broad-scope Questions

The questions below address more broad-based VOC reactivity issues than the questions listed in the preceding section. These questions focus on some of the VOC reactivity-based control measure issues to be considered in possible policy options having an “integrated” or holistic environmental regulatory perspective. Research projects aimed at answering these questions are likely long-term or multi-year efforts.

1. What are the roles of transport and multi-day stagnation?
2. What are the global implications on Global Warming Potential (GWP), stratospheric Ozone Depletion Potential (ODP), persistent organic pollutants (POP), and formation of toxic secondary products?
3. What role does “atmosphere” availability play?
 - a. Vapor pressure or evaporation rate?
 - b. Fugacity?
 - c. Water-gas phase partitioning?
 - d. Particle-gas phase partitioning?
 - e. Life cycle?
4. From the perspective of a reactivity policy with respect to multiple environmental impacts, what does “integration” mean; and how can we do this?

6.3 SOME SHORT-TERM RESEARCH PROJECTS

This section provides an initial list of potential short-term (less than 12 months) research projects that address many of the questions shown in section 6.2.2. To see a more detailed description of these research projects, refer the sections in the RRWG Science White Paper shown here in the square brackets [].

1. Survey amounts of emissions that are suitable for reactivity-based controls [3.1.1]
2. Survey existing modeling assessments [1.1]
3. Assess effects of large-scale reactivity-based substitutions on regional air quality using existing models [1.2.A]

- a. Evaluate alternative reactivity metrics [1.5.1]
- b. Uncertainty analysis
4. Improve emissions processing modules in models [6.3.2]
5. Use existing models to evaluate exemption standard [1.3.A]
6. Evaluate existing chamber data base [2.4.1]
7. Evaluate existing fugacity models/availability [4.3.1]
8. Develop model criteria for reactivity assessments [6.1]
9. Analyze available information concerning distributions of conditions, including air quality data [5.1.1]
10. Develop appropriate scenarios for 7, 10, 8; general reactivity assessment 5,6,3 ... 1,9.

7. Appendix

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