

PHOTOCHEMICAL REACTIVITY WORKSHOP

U.S. Environmental Protection Agency

May 12-14, 1998

PROCEEDINGS

**Regal University Hotel
2800 Campus Walk Avenue
Durham, North Carolina 27705**

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PRESENTATIONS

Reactivity Workshop

Meeting Objectives

1. Obtain participant input on important reactivity-related issues.
(Incorporate finalized list in Proceedings Report)
2. Obtain participant input on reactivity-related research needs.
(Incorporate finalized list in Proceedings Report)
3. Establish a volunteer Reactivity Research Planning Group to develop a responsive research program plan.
4. Identify follow-up action items and an associated time table.
5. Determine type of partnership forum to be used in planning and implementing the reactivity research program

J. M. Hales, May 1998



Some Design Features of this Meeting

- Focus on scientific aspects of reactivity concepts. "Policy-relevant, but not policy-driven science;" (the NARSTO paradigm).
- Structured around "science questions" and related "policy questions." (Initial sets to be modified by group process).
- Define science issues associated with policy issues; don't attempt to resolve policy issues.
- No pre-conceptions; no loaded agendas; a level playing field. This is an information-gathering and distillation process.
- "Everybody wins" environment. *(Including the citizen and the taxpayer).*

J. M. Hales, May 1998



Having Said This . . .

. . . There are some "complicating realities:"

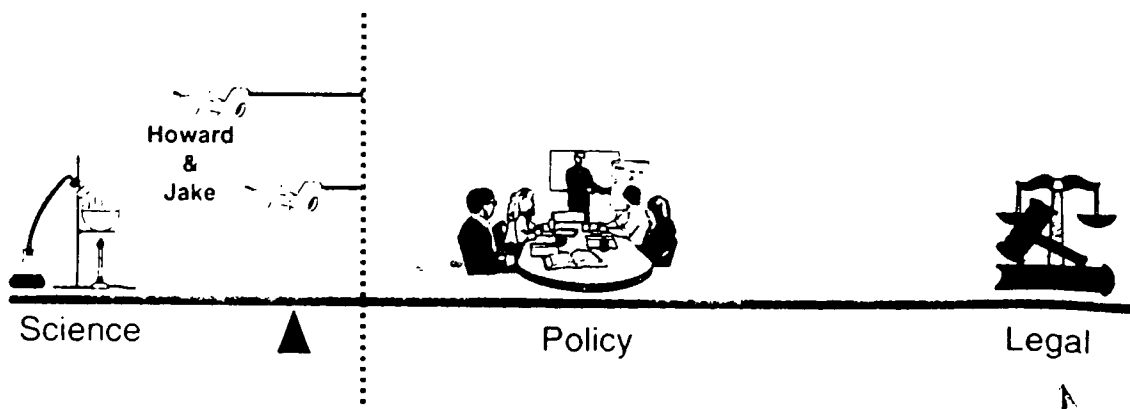
- The term "reactivity" is used, *but not defined explicitly* in the 1990 CAAA.
- Any attempt to define this term explicitly, including adoption of any particular reactivity scale, has immediate policy implications.
- Associated legal action is contemplated and/or in progress.

J. M. Hales, May 1998



Therefore . . .

. . . It's critically important that we maintain an objective and scientifically oriented atmosphere at this workshop.



J. M. Hales, May 1998



Welcoming Remarks

Dr. Gary Foley, Director
National Exposure Research Laboratory
US Environmental Protection Agency
Office of Research and Development

Welcoming remarks were offered on behalf of EPA by Dr. Gary Foley, Director, National Exposure Research Laboratory, EPA Office of Research and Development, and Ms. Sally Shaver, Director, Air Quality Strategies and Standards Division, EPA Office of Air Quality Planning and Standards. Dr. Foley welcomed the idea of incorporating reactivity research into the North America Research Strategy for Tropospheric Ozone (NARSTO) program. He stressed that the NARSTO partnership between government and the private sector has been very effective in investigating the photochemical ozone problem and that he is confident that the reactivity research effort will be equally successful.

Sally Shaver, Director
Air Quality Strategies and Standards Division
Office of Air Quality Planning and Standards
US Environmental Protection Agency

Sally Shaver made welcoming remarks on behalf of EPA's Office of Air Quality Planning and Standards. She stated that it is important that EPA's policies reflect the best science, and she said EPA looked forward to hearing the information which participants would provide.

A Public-Private Partnership
for
Photochemical Reactivity Research

Ronald K. Patterson
Associate Management Coordinator
NARSTO International

U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory

ABSTRACT

The decision of the U.S. Environmental Protection Agency to re-evaluate its policy on photochemical reactivity in an open forum, where regulated industries, the science community, and other stakeholders can participate, sets the stage for forming a public-private partnership to resolve the science and policy issues identified by the process. The partnership approach to complex environmental issues normally provides an opportunity for joint research planning, and a platform that the stakeholder community can use to coordinate research activities, limit research gaps and duplication, leverage resources, and share results.

NARSTO is a model for this type of partnership. NARSTO was established, under a non-binding Charter in 1995, as a science-driven, tri-national, public-private partnership. To date, membership consists of science agencies, regulatory agencies, regulated industries, academic institutions and public interest groups in Canada, Mexico, and the United States. NARSTO facilitates, plans, and coordinates policy-relevant research on atmospheric processes in the troposphere over North America. Ozone and particulate matter are the current focus of the NARSTO program. However, the research emphasis is placed on atmospheric chemistry, modeling, emissions, monitoring, meteorology, methods development, and integrated analysis and assessment. NARSTO provides quality assurance, data management, data archival, and data accessibility guidelines and services to its members. Peer review of major NARSTO outputs is provided by the National Research Council.

Photochemical reactivity is an integral part of the NARSTO research agenda, and this area of research could be expanded under the NARSTO Modeling and Chemistry Team. If this workshop selects the NARSTO partnership as its forum for conducting future reactivity research, then a NARSTO subcommittee could be formed from volunteers identified in this audience. The subcommittee would develop a strategic research plan for implementation by the member organizations. Each member organization would accomplish its portion of the work using their individual institutional planning and funding mechanisms. Under the NARSTO scenario, each organization involved must sign the NARSTO Charter as a sponsoring or participating partner. Participating partners are usually academic and contractor institutions. Many of the organizations attending this workshop are already NARSTO partners.

This workshop will be declared a success, if those in attendance can (1) identify the major policy and science issues, (2) agree upon a partnership arrangement for planning and implementing future reactivity research, (3) commit to participation in the planning process, and (4) commit to funding the research agenda.

A PUBLIC-PRIVATE PARTNERSHIP FOR PHOTOCHEMICAL REACTIVITY RESEARCH

Ronald K. Patterson
Associate Management Coordinator
NARSTO International

U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory

Purpose of this Reactivity Workshop

- Examine the policy issues
- Evaluate the state-of-the-science
- Commit to forming a partnership to resolve the science and policy issues
- Commit to funding research under the partnership

Public-Private Partnership

- Involves all stakeholders
- Provides a forum for joint research planning
- Leverages resources
- Coordinates research agenda
- Limits research gaps and duplication
- Shares data and information

The NARSTO Forum

- Science driven, tri-national, public-private partnership
- Established by a non-binding Charter in 1995
- Facilitates, plans, and coordinates policy relevant research on atmospheric processes in the troposphere over North America
- Provides quality assurance, data management, data archival, and data accessibility guidelines and services
- Provides NRC peer review of major products

The NARSTO Organization

- **Members**
 - Science Agencies
 - Regulatory Agencies
 - Regulated Industries
 - Academic Institutions
 - United States, Canada, Mexico, (Europe)
- **Membership Types**
 - Sponsoring Partners (54)
 - Participating Partners (20)
 - Affiliated Partners (2)
 - ◆ EUROTRAC
 - ◆ IGAC

(See Poster: "A New Approach to Complex Environmental Problems in the Continental Troposphere")

The NARSTO Program

- Programmatic focus on Ozone and PM
- Research emphasis on:
 - atmospheric chemistry
 - modeling
 - emissions
 - monitoring
 - meteorology
 - methods development
 - Integrated analysis and assessment

The NARSTO Process (if selected as your partnership forum)

- Organized as a Subcommittee under the Modeling and Chemistry Science Team
- Planned and Coordinated by the Subcommittee
- Implemented through the normal planning and funding mechanisms of the sponsoring Institutions
- Quality assured, peer reviewed, archived, and assimilated using existing NARSTO systems

Success for this Workshop

- Identify the major Policy and Science Issues
- Agree Upon a Research Partnership Arrangement
- Commit to Participation in the Strategic Planning Process
- Commit to Funding the Research Plan

COMMITMENT QUESTIONNAIRE

My organization _____
is in favor of a public-private partnership for developing a Reactivity
Research Strategy

My organization prefers to use _____ NARSTO / _____ another partnership as the
forum for developing the Reactivity Research Strategy, understanding that the
NARSTO Partnership requires signing the NARSTO Charter as a Sponsoring
Partner *

My organization will appoint Mr / Ms / Dr _____
as our representative on the Reactivity Research Planning Group

My organization will support the approved Reactivity Research Strategy and
will sponsor portions of the research described therein on an annual basis
subject to the availability of funds

My organization's estimated annual support is \$ _____

Signed by _____ Date _____

* Note Academic institutions and contractor organizations sign the Charter as Participating Partners
to avoid Conflict of Interest issues

EPA Current Regulatory Viewpoint on Reactivity

Bill Johnson
Photochemical Reactivity Workshop
May 12-14, 1998



What is the History of ... EPA's VOC Reactivity Policy?

- ▶ EPA announced its reactivity policy on July 8, 1977. This policy classified VOC's into categories ...
 - *Reactive*
 - *Negligibly Reactive*
- ▶ Four compounds were originally classified *Negligibly Reactive* ...
 - Methane
 - Ethane
 - Methyl chloroform
 - Freon 113
- ▶ Today EPA still uses this 1977 Reactivity Policy.

What VOC's have been ... Classified as Negligibly Reactive ?

- ▶ Early additions to the *Negligibly Reactive* list tended to be chlorofluorocarbons which possessed *low reactivity* and which could serve as *replacements for stratospheric ozone depleters*.
- ▶ Later Ethane was used as the standard cut-off comparing the reactivity of compounds. Those compounds with reactivities *below* ethane might be considered for Exemption
- ▶ Since 1977 more than 42 additional compounds or classes of compounds have been classified *Negligibly Reactive* and added to the Exempt list.

How is the Reactivity of ... a Compound Determined?

- ▶ Most Exemptions were determined using the kOH value (the reaction rate constant for the reaction of a compound with the OH hydroxyl radical), expressed in units of *cm³/molecule-sec*, and compared to the kOH value of Ethane.
- ▶ In 1993, EPA began receiving VOC Exemption Petitions based on the Maximum Incremental Reactivity (MIR) scale developed by Dr. William Carter at the University of California at Riverside. MIR values are expressed in units of *grams ozone produced per gram of compound reacted*.
- ▶ Acetone was the first compound evaluated for Exemption using MIR values. This evaluation was made on a per gram basis as stated in the Federal Register.

Questions Raised in using ... MIR Values to Compare Reactivity

The MIR values raised a number of questions.

- ▶ Are MIR values better to use than KOH values for comparing reactivity?
- ▶ Should a *per gram* or *per mole* be used for comparing compounds to ethane?
- ▶ Could the ranking of compounds in order of reactivity by MIR value be used in some kind of *substitution* scheme of control? How would such a scheme work?

A review of the original 1977 experimental work used to select ethane as the Exempt cut-off showed that the experiments were done on a *mole basis*. Comparisons to ethane on a per gram basis may not be valid.

Questions Petitions Raised about ... Consideration of Collateral Effects

Recent Petitions have raised questions about considering collateral effects in granting exemptions to compounds.

- ▶ Should special consideration be given to exempting a compound slightly more reactive than ethane, but may displace more reactive and/or toxic compounds such as xylene? Would this be a positive environmental move, even if unlimited amounts of the exempt compound could then be used?
- ▶ Should very toxic compounds or stratospheric ozone depleters be exempted if they are of low reactivity?

The 1977 policy indicates EPA should consider such environmental impacts in making exemption decisions (e.g. we have never exempted benzene even though of low reactivity.)

What is the Current Status of ... Petitions Submitted to EPA?

EPA has received 14 petitions on which action is pending. Most of these compounds are:

- ▶ **Not less reactive than ethane on a per mole basis or**
- ▶ **Hazardous air pollutants (under section 112) or are stratospheric ozone depleters.**

Text for vapor pressure figure

EPA's definition of VOC does not include a vapor pressure cut off. At one time in the late 1970's, EPA recommended a 0.1 mm Hg vapor pressure cut off. In 1987, EPA asked States to remove this from the VOC definition in their regulations. The reason for removing the 0.1 mm Hg cut off can be seen from Figure 1.

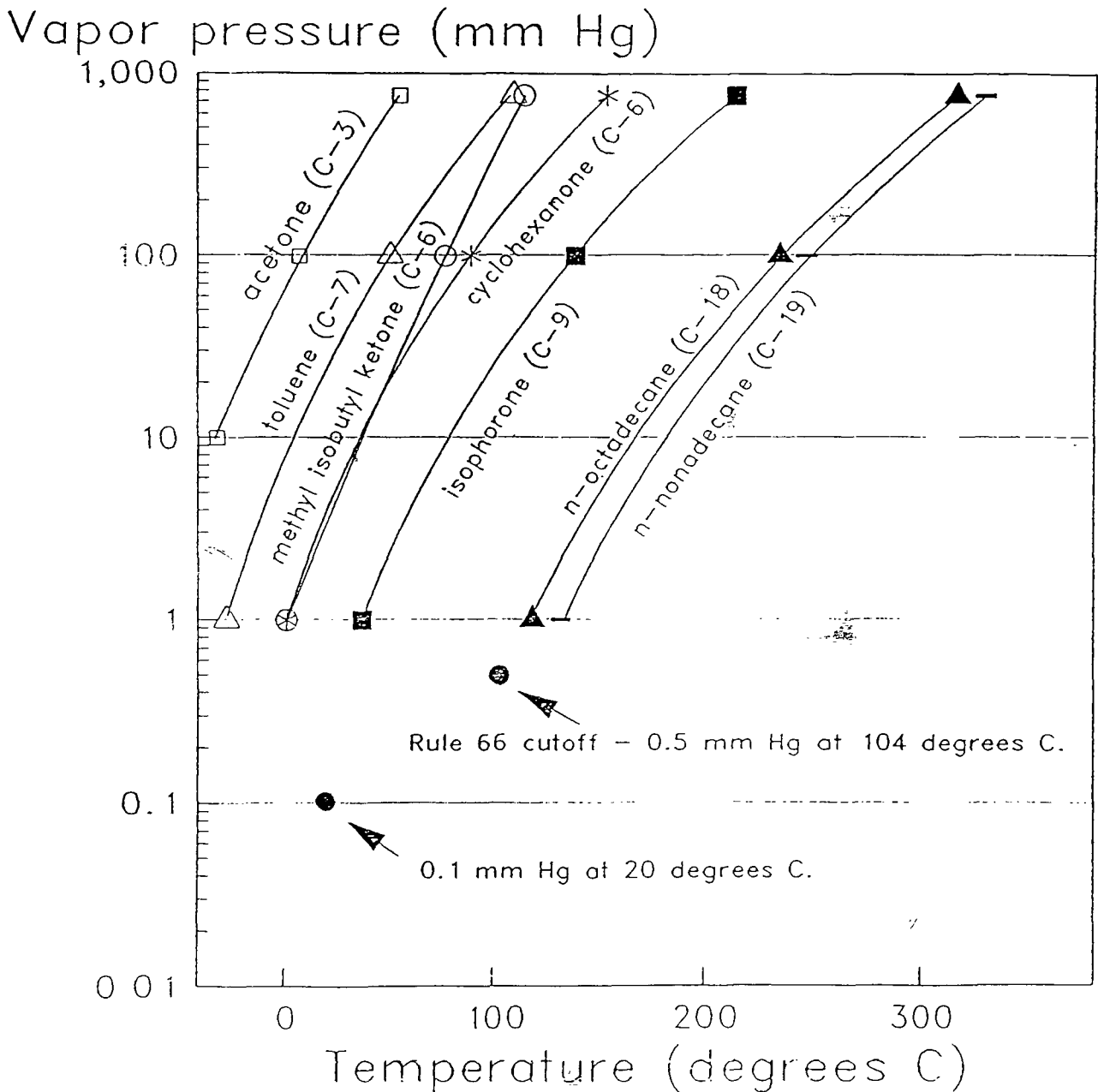
The 0.1 mm Hg at 20 °C cutoff would only control compounds with carbon number lower than about C12. The older Los Angeles Rule 66 cut point (0.5 mm Hg at 104 °C) was actually more strict and would control compounds up to about C18.

Studies have shown that compounds <C18 (around 0.001 mm Hg) are mostly in the vapor phase in the air. Above C24 (around 0.00001 mm Hg) compounds occur with the greatest percentage in the condensed phase in the air. However, some researchers have reported that aliphatic compounds as high as C31 have been found in the gas phase.

We have placed on the handout table copies of an EPA memo which addresses the issue of vapor pressure of compounds and their physical state in the air. You may pick up a copy and read more about this issue, if you are interested.

FIGURE 1

Vapor Pressure and Temperature in Relation to VOC Definition



CURRENT EPA RESEARCH VIEWPOINT ON REACTIVITY

by

Basil Dimitriadis

EPA/ORD/NERL/HEASD/ACPB

RTP, NC

EPA's main reason for wanting to update its reactivity policy, is the simple fact that the "now science", that is, the scientific understanding we now have about the reactivity property of organic compounds, is considerably different than the "then science", that is the scientific understanding we had some two and a half decades ago, during the early 1970s, when the current policy was conceived and formulated. Therefore, it would be useful to include in this workshop this and other presentations that would help convey to this audience some understanding of the changes in reactivity science that took place during the past two and a half decades.

In this presentation, I will give you some historical information on the development of the current policy, and after that, I will describe the scientific bases of the policy and point out whatever weaknesses were revealed by the recent scientific evidence. This presentation and the presentations later by the active researchers in this area, should make it possible to judge the significance of the reactivity science changes that occurred during the last two and a half decades. I should mention that nearly all of the material I will be discussing today is in a report I submitted for publication in the Journal of the Air and Waste Management Association, some 3 months ago.

The initial version of the reactivity policy now in effect was developed in 1971, as part of EPA's guidance to the States for preparation of State Implementation Plans for ozone attainment. (Appendix B in EPA's 1971 Guidance...). In that version, EPA emphasized reduction of total mass of organic emissions, but it also did take into account reactivity. Specifically, it allowed for substitution of a less reactive for a more reactive organic emission, if it could be shown that such substitution would result in a reduction of the total reactivity of the emissions mixture. This latter concession encouraged States to develop organic emission substitution regulations, such as LA's Rule 66, which allowed a large number of organic emission species and emission mixtures to be exempted from the ozone control regulations on grounds that they had if not negligible, at least tolerably high reactivities.

A few years after that, the researchers came out with the finding that pollutant transport conditions in the atmosphere enhance ozone formation so as to make many of those organics that were previously thought to be unreactive, to act as significant ozone producers. This led EPA to rethink its reactivity policy, and in 1977 it issued its next policy, under the title "Recommended Policy on Control of Volatile Organic Compounds", which is the policy version now in effect, and which policy, in contrast to the preceding one, it went from an extremely tolerant policy to an extremely conservative one. Specifically, by the 1977 policy only four organics were accepted as negligibly reactive: methane, ethane, 1,1,1-trichloroethane (methyl chloroform), and Trichlorotrifluoroethane (Freon 113). All other organic were assumed to be reactive, and, of course, subject to the ozone regulations. The policy, however, was flexible in that it allowed for reactive organics to be re-classified as negligibly reactive if and when new scientific evidence is

produced and shown to support the reclassification. It should be noted at this point that at that time EPA had not had standard test methods issued for determining whether an organic compound is negligibly reactive or not -- the burden for making this determination rested outside the Agency. The Agency did support, however, development of such methods, and eventually accepted them and offered them, unofficially at least, for public use. These methods, known as the kOH and MIR methods, have been used routinely in the recent years to produce reactivity evidence for many previously unstudied organics, and, as a result, several tens of organic compounds have been re-classified and placed in the list of negligibly reactive or exempt organics.

Lastly, in 1992, EPA restated its reactivity policy, except that this time it used the term "VOC" to denote organic compounds with significant potential for producing ozone, and declared all organic emission species to be VOCs except those that were determined by EPA to be non-VOCs.

So much about the history of the EPA reactivity policy development. Next, I will talk about the scientific basis of the existing policy and its weaknesses as we see them now.

There are five key components or elements that constitute the existing reactivity policy. Subjects of these components are:

- (1) Exemption of Organic Emissions on Reactivity Bases.
- (2) Use of the ethane reactivity as the "bright line" separating VOCs from non-VOCs.
- (3) Reactivity Classification Guideline Methods.
- (4) Assumed universal validity of reactivity scales
- (5) Consideration of Emission Volatility.

(1) "Exemption policy". This policy element mandates that non-VOCs must be exempted from the ozone-related control and inventory requirements. The bases for exempting the non-VOCs are two judgments made by EPA at that time:

-- While all organic compounds are capable of producing more or less ozone in the atmosphere, not exempting those that produce only negligible amounts of ozone would be impractical.

-- The other judgment was based on the perception at the time that there is a significant number of organic compounds that have negligible reactivity -- so, it would be worth the effort to classify organics into VOCs and non-VOCs.

And so, in 1975 EPA decided to develop for official use a two-class reactivity classification scale. To develop the requisite scale, EPA conducted a smog chamber study in

which several organic compounds were irradiated under a standard set of extremely favorable conditions, and resultant ozone yields were compared with the ozone air quality standard which at the time was 0.08 ppm O₃. The conditions used were 4ppm in moles of organic reactant -- a concentration representative of the most polluted urban atmospheres at the time in the US -- 0.2ppm in moles of NO_x (giving a VOC-to-NO_x ratio of 20:1, extremely favorable for ozone formation), radiation comparable to that of natural sunlight in Los Angeles during summer, and the test mixture was irradiated until the ozone concentration peaked out. Results showed that only four organics produced less than 0.08 ppm ozone: methane, ethane, trichloroethane, and the trichlorotrifluoroethane, and these were, therefore, the only entries in the table of negligibly reactive organics included in the 1977 policy.

Obviously, that reasoning behind the 1977 reactivity classification was judged by EPA to be consistent with the scientific evidence available and the best that could be thought of at the time. Today, however, we have several reasons for questioning the validity of that evidence and thinking. One specific and strong objection we now have is to exempting the non-VOCs from the emission inventory requirement. Non-VOCs exempted from control will accumulate in the atmosphere due to growth, and their ambient concentration will eventually reach the point at which they will contribute to ambient ozone significantly. At that point, of course, they should be taken into account in calculating control requirements. This would be impossible, however, because the models used to compute control requirements require emission inventory data. Thus, this "Non-VOC exemption" part of the EPA policy, clearly, must be re-considered.

(2) Ethane reactivity bright line. According to this policy element, organic emissions with reactivity at or below the ethane reactivity bright line shall be exempted from the ozone regulations as being non-VOCs. This policy element was never issued by EPA officially. It acquired the policy status when EPA began to use the comparison with ethane as the basis for judging whether an organic is a non-VOC, and the rationale of this basis was, of course, the fact that ethane is the most reactive species of those identified by EPA in 1977 as being negligibly reactive. Regarding the validity of this policy element, there are several questions at issue. I will discuss the most important ones, namely:

- (a) Is the choice of ethane as the boundary reactivity species an appropriate one?
- (b) To determine VOC or non-VOC nature of an organic, should the comparison of the organic with ethane be made on a per-unit-weight or on a per-mole basis?
- (c) Is the distinction between VOCs and non-VOCs really necessary?

To answer the first question, of whether the ethane reactivity is the appropriate boundary separating VOCs from non-VOCs, we need to go back to the reasoning EPA used in 1977 to classify organics into VOCs and non-VOCs. In that study there were some 20 low reactivity organic compounds tested, and of those, four were found to produce ozone less than 0.08 ppm. Of those four, ethane was the most reactive one and on those bases, ethane was taken, unofficially, to be the "boundary" reactivity species. Are these bases valid? Today we don't think so, for several reasons. First, we believe today that ethane, if allowed to accumulate in the

atmosphere at higher than 4 ppm levels, will produce more ozone than 0.08 ppm. Second, we also know today that testing organics using modern smog chamber methodology gives much higher ozone concentration results, the main reason being that nowadays the test organic is not irradiated in the smog chamber alone, as was done then; instead, it is irradiated in the presence of other organics, and this, of course, is much more realistic and it results in much more ozone.

The second question, whether organics should be compared with ethane on a per-unit-weight basis or a per-mole basis, is raised because it makes a difference whether we use the one or the other basis. Relative to the per-mole basis, comparison with ethane on a per-unit-weight basis tends to cause reactive, high molecular weight organics to have artificially reduced reactivity values and be classified as negligibly reactive, in conflict with the per-mole comparison. Which is correct? To answer this question, once again we need to go back to the EPA smog chamber study of the mid-1970s, that led to the selection of ethane as the boundary species. If you recall, the comparison of the organics in that smog chamber study was done for equimolar concentrations. Based on that, and for consistency sake, the comparison with ethane must be made on a per-mole basis. Needless to say, we could have compared the test organics in the EPA study for equal weight, rather than mole concentrations, but then the boundary reactivity species would have been not ethane but some other species. Comparing organics with that species on a per-unit-weight basis would alleviate but not eliminate the problem. In fact, our conclusion is that regardless of how we compare the reactivities of organics to the boundary level, it is not possible to avoid this problem completely, and this constitutes a conceptual weakness of this policy element that calls for classifying organics into VOCs and non-VOCs based on comparison with a given organic compound's reactivity.

The final question, whether the VOC-vs-nonVOC distinction is necessary is to some extent of policy nature. The need for making such a distinction depends on whether the Agency wants to stay with the existing policy of exempting only those organics which are shown to be negligibly reactive, or decides to adopt, another policy instead, for example, a policy of exempting organics that have non-negligible reactivity but are to be used as substitutes for other much more reactive organics.

3. Reactivity Classification Guideline Methods Existing EPA guidelines for such methods are unofficial. The kOH and MIR methods acquired the status of guideline methods because data obtained with such methods have been accepted by EPA in processing petitions for exempting organic emissions from ozone regulations. What do we think today about these methods?

We now believe that the kOH method has very limited utility because it represents how fast the organic reacts with the OH radical -- the first reaction step in the ozone forming process but it tells us very little about the follow-up chemistry that results in formation of ozone. The MIR method has greater validity in that it does provide a direct measure of ozone production, but it is based on use of the EKMA model, a model now thought to be outdated. We still consider the MIR method very useful, but we believe that current science allows for development of other modeling methods which, while much more complex, can provide more accurate reactivity estimates. **[More about these methods in subsequent presentations]**

4. Universal validity of reactivity scales. The existing policy is based on the assumption that the current classification of organics into VOCs and non-VOCs is universally valid, independent of ambient conditions. We now know, however, that the ozone formation chemistry is such that reactivity varies with conditions such as organic-to-NO_x ratio, ambient organic composition, sun light intensity, and pollutant transport conditions. This, obviously, raises questions about the practicality of a reactivity scale that is not universally valid. We need to think about this and find some way of using the reactivity concept in a way that the effect of this problem is minimized. For example, consideration should be given to the fact that the uncertainty introduced by this ambient condition variability factor is much smaller for relative reactivities than for absolute reactivities. This means, of course, that policies that place the emphasis on relative reactivity data, e.g., emission substitution, may be more reliable in so far as this problem is concerned than policies that place the emphasis on absolute reactivity data, as the existing policy is.

5. Emission Volatility. The existing EPA policy distinguishes between VOCs and non-VOCs and cites reactivity as the basis for the distinction but says nothing about volatility. There are guideline methods for determining whether an organic is negligibly reactive or not, but there are no such methods for determining whether an organic is negligibly volatile or not. Thus, the reactivity and volatility properties of organic emissions have been receiving different regulatory treatments, apparently without scientific justification, and this inconsistency should perhaps be rethought.

CONCLUSIONS

In contrast to the mid-1970s thinking, our current thinking suggests that

1. exemption of non-VOCs from the inventory requirement is unjustifiable;
2. use of the ethane reactivity as the boundary level separating VOCs from non-VOCs has both validity and operational problems (basis of comparison);
3. current science allows for development of more reliable guideline methods for classifying organics into "reactive" and negligibly reactive.
4. policies that place the emphasis on relative reactivities are probably subject to less uncertainty relative to those that rely on use of absolute reactivity data; and
5. it is unjustifiable for the current policy to treat the reactivity and volatility properties of organic emissions differently with respect to the photochemical ozone pollution problem.

California's Hydrocarbon Reactivity Program

By

Randy Pasek Ph.D.

California Air Resources Board

at

U.S. EPA Reactivity

Workshop

May 12-14, 1998

California's Reactivity Beginnings

- ♦ In 1987 ARB formed advisory board on fuels.
- ♦ Needed way to compare alternatively fueled vehicle's emissions.
- ♦ Use of reactivity of vehicle exhaust for comparisons.
- ♦ Adopted LEV/CF regulations in late 1990 (RAF).
- ♦ VOC exemptions

Other Possible Reactivity Based Programs

♦ Future Possibilities

- Aerosol Coatings
- Consumer Products
- Emissions Trading
- Aerosol Forming Reactivity
- Motor Vehicles

Challenges Encountered

♦ Reactivity Scale

- MIR
 - Dual control program in CA
 - MIR scale complements NO_x controls

♦ Uncertainty

- Alternative fuels program (LEV/CF)
 - MIRs ~30 - 70%
 - RAFs ~5 - 15%
- Consumer Products
 - Most-used compounds well characterized

Challenges (continued)

- ♦ Speciation Profiles
 - Uncertainty
 - Inventory and modeling
- ♦ Unstudied Compounds
 - Alternative fuels program (LEV/CF)
 - Most compounds -- some data
 - Consumer Products
 - Some compounds -- no data
 - Upper limit MIR Estimation

Challenges (continued)

- ♦ Regulation Development
 - Good science
 - Flexibility
 - Simple
 - Equivalent ozone benefits
 - Enforceable
 - Cost effectiveness

Challenges (continued)

- ◆ How to incorporate exemptions into reactivity regulations.
 - VOC exemptions
 - CA has own review
 - Methane or ethane
 - Other policy exemptions

California's Reactivity Program

- ◆ Research
- ◆ Reactivity Team
- ◆ External Assistance

Research

- ◆ Uncertainty
 - Chamber parameters' effect on MIR values
- ◆ Reactivity Value Estimates
 - Consumer product compounds
 - Auto exhaust
 - Other important mixtures
- ◆ Improvement of Reactivity Value Estimates
 - Lower cost
 - Lower uncertainty

Research (continued)

- ◆ Atmospheric Chemistry
 - C₁₀ alkanes
- ◆ Speciation
 - Architectural & Aerosol coatings
 - “Complete picture profiles”
 - Surveys to obtain formulation data
- ◆ Model Improvement
 - Chemical mechanisms
 - Regional Scale
 - Aerosols
 - Photolysis

Features	MIR (Carter)	Previous Grid-Based Simulations (McNair et al., and Bergin et al.)	ARB's Grid-Based Simulations
Chemistry	- SAPRC-90 - SAPRC-97 (ongoing)	- Lurman, Coyner and Carter (LCC)	- SAPRC-97 - possible aqueous-phase chemistry in the near future
Physics	- Simple box model - Represents urban airshed - No transport - Simple "meteorology" - EKMA type	- Complex 3-D grid-based domain - Represents urban airshed - No long-range NO _x transport - Diagnostic meteorology - Carnegie/California Institute of Technology (CIT) with Diagnostic Wind Model	- Complex 3-D grid-based domain - Represents regional airshed - Long-range NO _x transport - Prognostic meteorology - SAQM with MM5
Emissions	- Represents 39 cities	- Detailed grid-based urban and rural emissions from most source categories - August 30 -September 1, 1982 (SC) - August 27-29, 1987 (SC)	- Detailed grid-based urban and rural emissions from most source categories
Metric	- Maximum change in O ₃ concentration	- Maximum change in peak O ₃ concentration (1-hr) - Exposure above National and State AAQS	- Maximum change in peak O ₃ concentration (1-hr, 8-hr) - Exposure above National and State AAQS - Others ?

Reactivity Team

- ◆ Airshed Modeling
- ◆ Uncertainty Analysis
 - Perform overall analysis for stationary sources
 - Includes uncertainties in speciation and reactivity estimates
- ◆ Exploring Aerosol forming potential
 - Determine implications for different control strategies

External Assistance

- ◆ Reactivity Research Advisory Committee
- ◆ Reactivity Scientific Advisory Committee

Reactivity Research Advisory Committee

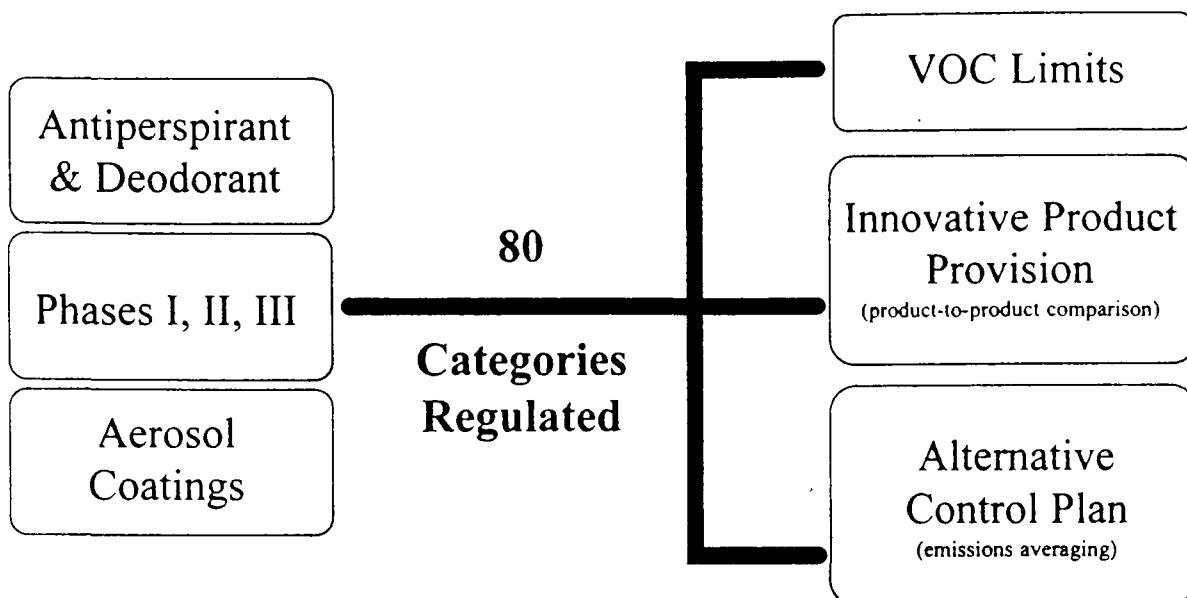
- ◆ Over 20 representatives from industry.
- ◆ Provide technical assistance on reactivity related issues -- consumer products and coatings.
- ◆ Forum to coordinate research activities between industry and government.

Reactivity Scientific Advisory Committee

- ♦ Six independent, respected scientists
 - Professors John Seinfeld, Roger Atkinson, Jack Calvert, Harvey Jeffries, Jana Milford, and Armistead Russell
- ♦ Offer recommendations on reactivity related scientific issues

Development of a Reactivity Program for Consumer Products in California

Current Ozone Control Strategy for Consumer Products (Mass Based)

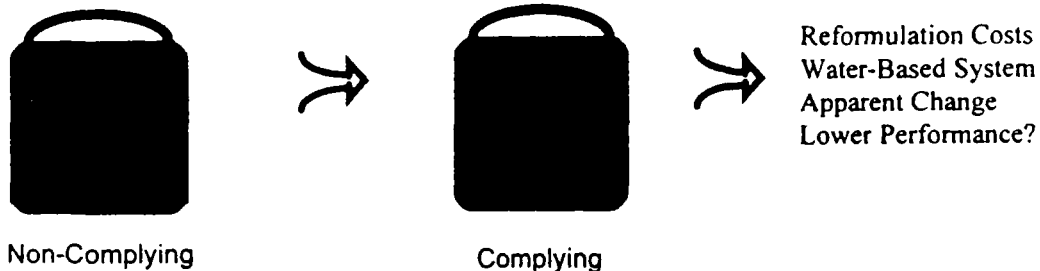


Using Photochemical Reactivity as a VOC Control Strategy

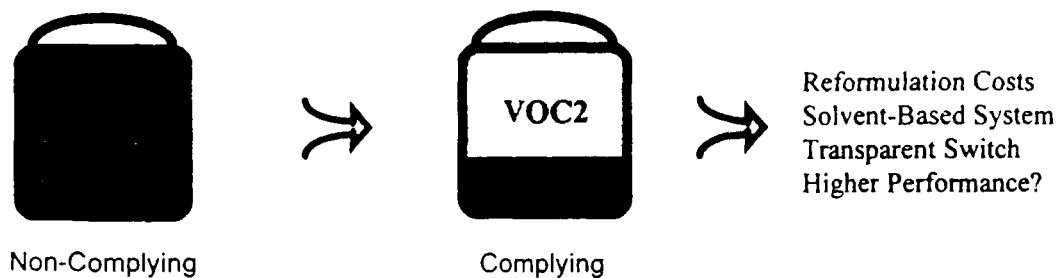
- ◆ Formed Workgroup with Industry
July 1995
- ◆ Draw on Experience from LEV Program
- ◆ MIR Scale Developed by Dr. Carter
- ◆ Voluntary Alternative
- ◆ Ensure Equivalent Ozone Reductions

Main Goal: Flexibility While Reducing Ozone Formation Potential More Efficiently

Existing Program: Decreased VOC, Decreased O₃



Reactivity Program: Decreased O₃, Little/No Change in VOC



Proposed Draft Voluntary Regulation for Aerosol Coatings

- ◆ Law Requires 60% Reduction in VOC Emissions (by end of 1999)
- ◆ Goal to Establish Equivalent Reactivity Limits to Existing Mass-based Limits
- ◆ Speciated Data are Necessary to Establish Limits

Hypothetical Paint Formula and Calculation of Weighted Reactivity

Contents	Weight Percent	MIR (Relative)	Weighted Reactivity
acetone	30%	0	0.00
toluene	20%	1.26	0.25
propane	20%	0.14	0.03
xylene	10%	2.09	0.21
butane	10%	0.29	0.03
solids	10%	0	0.00
Total	100%		0.52

Product $MIR_{abs} = 0.52 \times 4.06 = 2.11 \text{ g O}_3/\text{g product}$

Aerosol Coatings Schedule

- Workshop, 5/19/98 Draft Reactivity Reg. for
Aerosol Coatings
- Workshop, 7/98 Draft reactivity-based
VOC limits for Aerosol
Coatings
- Workshop, Late
Summer 1998 Revised draft reactivity
reg. (if necessary)
- November 1998 Board Hearing

O₃ Equivalence to Percent Reduction

<u>Steps</u>	<u>Example</u>
(1) Determine % reduction of the VOC limit	→ Reduce emissions by 50%
(2) Calculate abs. SWA-MIR for Aerosol Paint Category	→ $MIR_{cat} = 2.0 \text{ (g O}_3\text{/ g VOC)}$
(3) Apply % reduction to MIR of category	→ Reduce MIR by 50% $= 0.5 \times 2.0 = 1.0 \text{ (g O}_3\text{/ g VOC)}$
(4) Result = abs. wtd-MIR of category equal in percent ozone reduction from VOC limit	→ Wtd-MIR Limit $= 1.0 \text{ (g O}_3\text{/ g VOC)}$

Summary

- ◆ ARB has successfully used reactivity in regulations since 1990
- ◆ ARB has an integrated program to address challenges associated with using reactivity in regulations
 - Research
 - Internal Expertise
 - External expertise

VOC Reactivity - Beyond Ozone

D. Alan Hansen
EPRI

Photochemical Reactivity Workshop
Durham, NC
12-14 May 1998

VOC Reactivity – Beyond Ozone

Outline

1. **Purpose of talk:** In keeping with the principle of integrating assessments of emissions management across air quality issues as promoted by the FACA subcommittee on ozone, PM and regional haze, I want to emphasize the point that considerations of VOC reactivity in managing tropospheric ozone should also take fine particles into account. Fine particles, of course, are largely responsible for the optical effects associated with regional haze.
2. I will briefly summarize the interplay between VOCs and NO_x in the photochemical production of ozone and fine particles.
3. I will then show some modeling results that demonstrate, assuming that the models capture the essence of the precursor chemical interactions among themselves and with meteorology, the complexity of the responses of ozone and selected fine particle constituents to reductions in precursor emissions.
4. I will finish with some issues related to VOC reactivity that should be resolved if we are to manage tropospheric ozone and fine particles (and, by extension, regional haze) effectively.

Chemistry

Referring to the chemical mechanism schematic (taken from the as yet unpublished NARSTO Critical Review paper, "Oxidant Production and Fine Particles: Issues and Needs" by Hidy, Hales, Roth and Scheffe):

1. Note precursors: NO_x, VOCs, SO₂.
2. Note route to ozone: Daytime, O₃ → O₁D → OH → RO₂ → NO₂ → O₃;
3. Note routes to fine PM:
Daytime: OH + VOC → PM ; O₃ + VOC → PM ; OH + SO₂ (NH₃) → PM ; OH + NO₂ (NH₃) → PM
Nighttime: O₃ + olefins → OH etc. ; NO₃ + VOC → PM; N₂O₅ (H₂O, NH₃) → PM
4. Note VOCs and NO_x play prominent roles in both ozone and PM formation chemistry

So what happens if we change the concentrations of VOC and NO_x through emissions changes? The picture is sufficiently complex that answering this question can rely on environmental chamber experiments. However, these cannot account for meteorological effects and usually cannot be conducted at precursor concentrations as low as those prevailing in real urban and regional atmospheres. To explore how VOC reactivity influences ozone and PM behavior under realistic conditions, we must rely on modeling.

Model Results

The modeling results shown in the four tables are taken from runs made with UAM-AERO simulating SCAQS episodes in June and December 1987. They may not be representative of results obtained with other models or from other geographical locations or episodes. They

have been selected only to demonstrate the complex interplay between changes in precursor NO_x and VOC emissions and changes in ozone and various components of PM 2.5. In the tables PM2.5 OM denotes the “organic material” component of fine particles. The values shown for PM2.5 and its components are averaged over the two days of each episode. The discussion below focuses on the Percentage Change tables:

Points to note for the June 1987 episode:

1. With 50% NO_x reduction:
 - O₃ can increase substantially (>20%) or decrease (≤15%)
 - PM2.5 NO₃ decreases substantially (20-46%)
 - PM2.5 OM increases slightly (3-6%)
 - PM2.5 SO₄ is relatively unaffected (±2%)
 - PM2.5 Mass decreases slightly (6-12%)
 - Question: What if the material of interest from a health effects perspective was in the OM component, which did not decrease with a 50% NO_x reduction?
2. With a 50% VOC reduction:
 - O₃ decreases substantially (20-42%)
 - PM2.5 NO₃ decreases slightly (6-13%)
 - PM2.5 OM decreases slightly (8-10%)
 - PM2.5 SO₄ is relatively unaffected (±2%)
 - PM2.5 Mass decreases slightly (4-9%)
3. With 50% NO_x and VOC reduction:
 - O₃ increases less than with NO_x reduction only and decreases less than with VOC reduction only.
 - PM2.5 NO₃ decreases about the same as with NO_x reduction only.
 - PM2.5 OM decreases less than with VOC reduction only and with no increases.
 - PM2.5 Mass decreases the same or slightly more than with either NO_x or VOC reduction alone.

Bottom line:

4. With 50% NO_x reduction:
 - O₃ can go up or down
 - PM2.5 NO₃ and Mass go down
 - PM2.5 OM goes up
 - PM2.5 SO₄ is relatively unaffected.
 5. With 50% VOC reduction:
 - Everything goes down.
- However, PM2.5 OM is relatively insensitive to both NO_x and VOC reductions.

Points to note for the December 1987 episode:

1. With 50% NO_x reduction:
 - O₃ increases 60-138% (even the highest value, 122 ppb, more than doubles)

- PM2.5 NO3 increases (counterintuitively) 10-42%
 - PM2.5 OM increases 4-9%
 - PM2.5 SO4 is relatively unaffected, increasing up to 3%.
 - PM2.5 Mass increases 4-17%.
2. With 50% VOC reduction:
- O3 decreases 0-37% (again a counterintuitive lack of response in some parts of the domain)
 - PM2.5 NO3 decreases 27-42% (about the same as in summer)
 - PM2.5 OM decreases 5-9% (about the same as in summer)
 - PM2.5 SO4 is relatively unaffected, decreasing 2-5%, but with no small increases as in summer.
 - PM2.5 Mass decreases 8-13%, slightly more than in summer.
3. With 50% NOx and VOC reduction:
- O3 generally increases, but less than with NOx reduction alone.
 - PM2.5 NO3 decreases about the same as with VOC reduction alone, except the domain max, which decreases half as much as with VOC reduction alone.
 - PM2.5 OM decreases slightly (3-5%).
 - PM2.5 SO4 is essentially unchanged.

Bottom line:

- NOx reduction increases everything.
- VOC reduction decreases everything.
- NOx and VOC reduction decreases PM 2.5, but not O3.

Outstanding Questions

- If higher reactivity VOCs prompt ozone formation and lower reactivity VOCs delay ozone formation, how does the relative amount of ozone formed per carbon atom compare?
- Is there a relationship between VOC reactivity and amount of PM formed?
- Does the chemical mechanism accurately reflect the SVOC produced from oxidation of HC's? From unsaturated oxygenates?
- Do current lumping schemes in chemical mechanisms accurately reflect the nuances of reactivity with respect to ozone aerosol production as well as the role of reactive intermediates in the process?
- How will the composition and rate of production of SVOC respond to changes in VOC reactivity?

- **How will rate of production and yield of nitrate and sulfate respond to changes in VOC reactivity?**
- **How will deposition of N and S respond to changes in VOC reactivity?**

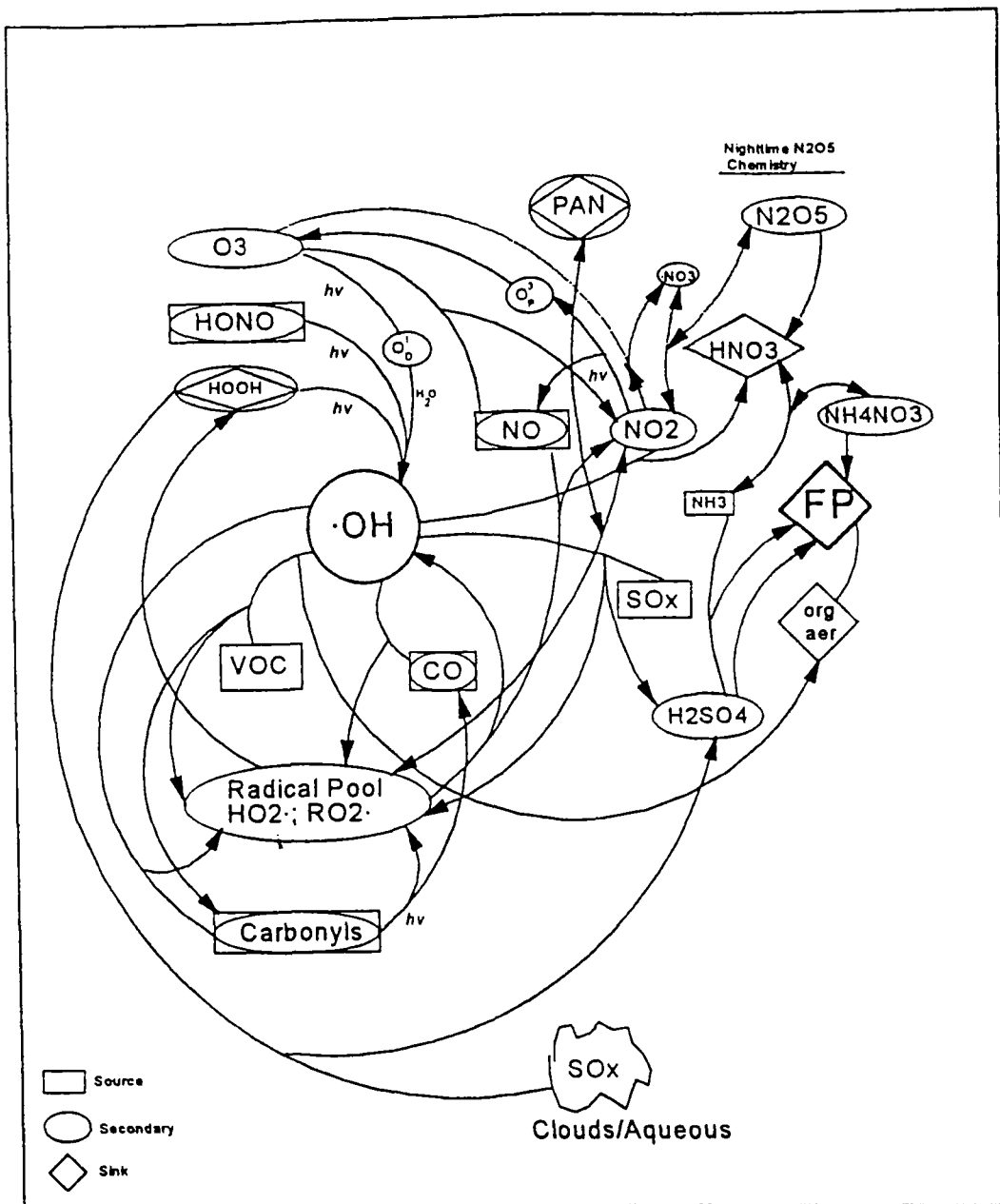


Figure 9. Process diagram illustrating tropospheric chemistry pathways linking oxidant and secondary PM_{2.5} formation. The gas phase reactions leading to atmospheric oxidant formation, including O₃, are generally to the left and the top right of the diagram. The aerosol particle formation processes are linked with the oxidant forming cycle, and are indicated in the middle and lower right of diagram.

From CR by Hidy, Roth, Hales & Scheffe
 "Oxidant Production & Fine Particles:
 Issues & needs" 1-34

ABSOLUTE CHANGE

Jun-87

		DOMAIN MAX					
		DAY 175	DAY 176	Day 175 or 176			PM
		O3	O3	PM2.5NO3	PM2.5OM	PM2.5SO4	2.5 Mass
	Baseline	404.8	353.5	48.1	19.1	32.7	100.8
	50% Red. NOx	451.2	300.5	33.5	19.6	32.2	93.8
	50% Red. VOC	272.0	230.1	42.0	17.4	32.4	91.7
	50% Red. NOX&VOC	337.8	261.2	33.7	17.8	32.2	91.7

		HIGHEST STATION					
		DAY 175	DAY 176	Day 175 or 176			PM
		O3	O3	PM2.5NO3	PM2.5OM	PM2.5SO4	2.5 Mass
	Baseline	152.2	199.1	26.8	8.7	7.4	68.0
	50% Red. NOx	183.1	185.0	14.4	9.2	7.4	60.0
	50% Red. VOC	88.9	118.2	25.1	7.8	7.4	63.9
	50% Red. NOX&VOC	146.6	164.1	15.9	8.1	7.4	58.8

		AVERAGE OF STATIONS					
		Day 175	Day 176	Day 175 or 176			PM
		O3	O3	PM2.5NO3	PM2.5OM	PM2.5SO4	2.5 Mass
	Baseline	90.6	85.5	16.8	6.4	8.1	53.1
	50% Red. NOx	103.7	103.8	13.4	6.7	8.2	50.1
	50% Red. VOC	72.2	66.3	15.5	5.9	8.0	50.8
	50% Red. NOX&VOC	89.4	86.3	13.0	6.1	8.1	48.7

ABSOLUTE CHANGE

Dec-87

		DOMAIN MAX					
		Day 344	Day 345	Day 344 or 345			PM
		O3	O3	PM2.5NO3	PM2.5OM	PM2.5SO4	2.5 Mass
	Baseline	90.0	122.0	61.4	37.5	26.0	190.0
	50% Red. NOx	185.0	280.0	87.0	40.7	26.0	223.0
	50% Red. VOC	90.0	80.0	35.6	34.3	25.4	166.0
	50% Red. NOX&VOC	104.0	108.0	49.0	35.6	25.6	167.0

		HIGHEST STATION					
		Day 344	Day 345	Day 344 or 345			PM
		O3	O3	PM2.5NO3	PM2.5OM	PM2.5SO4	2.5 Mass
	Baseline	40.8	39.7	20.3	23.7	3.9	116.0
	50% Red. NOx	73.0	62.8	24.5	24.8	3.9	123.0
	50% Red. VOC	33.0	34.1	14.7	22.6	3.7	107.0
	50% Red. NOX&VOC	51.5	49.8	14.5	22.9	3.8	107.0

		AVERAGE OF STATIONS					
		Day 344	Day 345	Day 344 or 345			PM
		O3	O3	PM2.5NO3	PM2.5OM	PM2.5SO4	2.5 Mass
	Baseline	34.7	30.4	18.7	18.0	2.9	86.0
	50% Red. NOx	75.8	72.1	20.5	18.8	3.0	89.0
	50% Red. VOC	21.9	19.2	13.6	17.1	2.8	79.0
	50% Red. NOX&VOC	45.3	42.5	13.3	17.4	2.9	79.0

PERCENT CHANGE

Jun-87

DOMAIN MAX

	DAY 175	DAY 176	Day 175 or 176		PM
	O3	O3	PM2.5NO3	PM2.5OM	PM2.5SO4 2.5 Mass
Baseline, ppb or ug/m3	404.8	350.6	78.1	32.7	100.8
50% Red. NOx	11.5	-15.0	-30.4	2.6	-1.5
50% Red. VOC	-32.8	-34.9	-12.7	-8.9	-0.9
50% Red. NOX&VOC	-16.6	-26.1	-29.9	-6.8	-1.5

HIGHEST STATION

	DAY 175	DAY 176	Day 175 or 176		PM
	O3	O3	PM2.5NO3	PM2.5OM	PM2.5SO4 2.5 Mass
Baseline, ppb or ug/m3	152.2	99.1	26.8	7.4	68.0
50% Red. NOx	20.3	-7.1	-46.3	5.7	0.0
50% Red. VOC	-41.6	-40.6	-6.3	-10.3	0.0
50% Red. NOX&VOC	-3.7	-17.6	-40.7	-6.9	0.0

AVERAGE OF STATIONS

	Day 175	Day 176	Day 175 or 176		PM
	O3	O3	PM2.5NO3	PM2.5OM	PM2.5SO4 2.5 Mass
Baseline, ppb or ug/m3	90.6	85.5	16.8	8.1	53.1
50% Red. NOx	14.5	21.4	-20.2	4.7	1.2
50% Red. VOC	-20.3	-22.5	-7.7	-7.8	-1.2
50% Red. NOX&VOC	-1.3	0.9	-22.6	-4.7	0.0

PERCENT CHANGE

Dec-87

DOMAIN MAX

	Day 344	Day 345	Day 344 or 345		PM
	O3	O3	PM2.5NO3	PM2.5OM	PM2.5SO4 2.5 Mass
Baseline, ppb or ug/m3	90.6	122.0	61.2	26.0	190.0
50% Red. NOx	105.6	129.5	41.7	8.5	0.0
50% Red. VOC	0.0	-34.4	-42.0	-8.5	-2.3
50% Red. NOX&VOC	15.6	-11.5	-20.2	-5.1	-1.5

HIGHEST STATION

	Day 344	Day 345	Day 344 or 345		PM
	O3	O3	PM2.5NO3	PM2.5OM	PM2.5SO4 2.5 Mass
Baseline, ppb or ug/m3	103.9	39.7	20.8	5.2	116.0
50% Red. NOx	78.9	58.2	20.7	4.6	0.0
50% Red. VOC	-19.1	-14.1	-27.6	-4.6	-5.1
50% Red. NOX&VOC	26.2	25.4	-28.6	-3.4	-2.6

AVERAGE OF STATIONS

	Day 344	Day 345	Day 344 or 345		PM
	O3	O3	PM2.5NO3	PM2.5OM	PM2.5SO4 2.5 Mass
Baseline, ppb or ug/m3	34.7	30.4	18.7	5.5	86.0
50% Red. NOx	118.4	137.2	9.6	4.4	3.4
50% Red. VOC	-36.9	-36.8	-27.3	-5.0	-3.4
50% Red. NOX&VOC	30.5	39.8	-28.9	-3.3	0.0

Current Status of VOC Reactivity Research

William Carter
University of California
at Riverside

Presented at:
Photochemical Reactivity Workshop
Durham, North Carolina
May 12-14, 1998

CURRENT STATUS OF REACTIVITY RESEARCH

BACKGROUND

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

RESEARCH AREAS AND UNCERTAINTIES

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

INCREMENTAL REACTIVITY

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

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

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

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

NOT SAME AS OZONE PRODUCTIVITY, THE AMOUNT OF O_3
ATTRIBUTABLE TO NO TO NO_2 CONVERSIONS CAUSED BY
PEROXY RADICALS FORMED FROM THE VOC.

FACTORS AFFECTING INCREMENTAL REACTIVITY

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

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

KINETIC REACTIVITY: FRACTION OF EMITTED MOLECULE
WHICH REACTS.

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

MECHANISTIC REACTIVITY: AMOUNT OF OZONE FORMED
PER MOLECULE REACTING

DIRECT REACTIVITY ("PRODUCTIVITY"): O_3 FORMED
FROM THE PEROXY RADICALS FROM THE VOC.

INDIRECT REACTIVITY: CHANGE IN O_3 FORMED FROM
PEROXY RADICALS FROM THE OTHER VOCs PRESENT.

- EFFECTS ON RADICAL LEVELS AFFECTS HOW MUCH THE OTHER VOCs REACT.
- EFFECTS ON NO_x CONSUMPTION AFFECTS HOW MUCH O_3 IS FORMED FROM A PEROXY RADICAL.

ENVIRONMENTAL FACTORS WHICH AFFECT INCREMENTAL REACTIVITY

NO_x AVAILABILITY IS MOST IMPORTANT SINGLE FACTOR AFFECTING MECHANISTIC REACTIVITIES.

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

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

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

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

MEASUREMENT OR CALCULATION OF ATMOSPHERIC INCREMENTAL REACTIVITY

REACTIVITY CAN BE MEASURED IN ENVIRONMENTAL CHAMBER EXPERIMENTS. BUT THE RESULTS ARE NOT THE SAME AS REACTIVITY IN THE ATMOSPHERE.

- NOT PRACTICAL TO EXPERIMENTALLY DUPLICATE ALL ATMOSPHERIC CONDITIONS AFFECTING REACTIVITY
- CHAMBER EXPERIMENTS HAVE WALL EFFECTS, USUALLY HIGHER LEVELS OF NO_x AND ADDED TEST VOC, STATIC CONDITIONS, ETC.

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

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

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

ENVIRONMENTAL CHAMBER EXPERIMENTS ARE NECESSARY TO TEST THE RELIABILITY OF A MECHANISM TO PREDICT ATMOSPHERIC REACTIVITY.

MECHANISMS FOR REACTIVITY ASSESSMENT

SAPRC-90 MECHANISM

REFLECTS KNOWLEDGE AS OF 1989.

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

HIGHLY SIMPLIFIED REPRESENTATION OF LOW-NO_x CHEMISTRY.

HIGHLY SIMPLIFIED REPRESENTATION OF HIGHER OXYGENATED PRODUCTS.

OVER > 100 TYPES OF VOCs REPRESENTED

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

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

SAPRC MECHANISM UPDATES

SAPRC-93 MECHANISM

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

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

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

UPDATED ISOPRENE CHEMISTRY ADDED

NOW BEING USED IN SEVERAL RESEARCH-GRADE AIRSHED MODELS

SAPRC-97 MECHANISM

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

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

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

CURRENT WORKING MECHANISM AVAILABLE ON THE INTERNET.

SAPRC MECHANISM UPDATES

SAPRC-98 MECHANISM (UNDER DEVELOPMENT)

BASE MECHANISM HAS BEEN COMPLETELY UPDATED.
MANY SMALL CHANGES.

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

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

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

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

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

REPRESENTATION OF ORGANIC PRODUCTS BEING
UPDATED USING PREDICTED PRODUCT DISTRIBUTIONS.

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

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

STATUS OF MECHANISM DEVELOPMENT AND UNCERTAINTIES BY VOC CLASS

ALKANES

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

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

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

ALKENES

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

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

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

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

STATUS OF MECHANISM DEVELOPMENT AND UNCERTAINTIES BY VOC CLASS

AROMATICS HYDROCARBONS

STILL NECESSARY TO USE PARAMETERIZED MECHANISMS.

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

NO MECHANISM CAN SATISFACTORILY FIT ALL CHAMBER DATA FOR BENZENE.

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

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

UNCERTAIN WHETHER PARAMETERIZED MECHANISMS EXTRAPOLATE CORRECTLY TO LOW NO_x CONDITIONS.

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

EXPERIMENTAL REACTIVITY DATA ARE BECOMING AVAILABLE, SIGNIFICANTLY REDUCING UNCERTAINTIES.

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

ATTEMPTS TO IMPROVE PERFORMANCE OF ESTIMATION METHODS ARE UNDERWAY.

STATUS OF MECHANISM DEVELOPMENT AND UNCERTAINTIES BY VOC CLASS

HALOGENATED COMPOUNDS

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

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

STUDIES ARE NEEDED ON SIMPLER SYSTEMS.

NITROGEN-CONTAINING COMPOUNDS

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

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

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

SILOXANES

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

MECHANISM UNCERTAINTY ANALYSIS

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

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

UNCERTAINTY ANALYSIS APPROACHES

FORMAL UNCERTAINTY ANALYSIS

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

UNCERTAINTY ANALYSIS APPROACHES (CONTINUED)

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

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

UPPER AND LOWER LIMIT REACTIVITY ANALYSIS

- CAN BE USED FOR QUANTIFYING UNCERTAINTIES FOR ALL VOCs.
- RELATIVELY STRAIGHTFORWARD TO ESTIMATE UPPER LIMIT REACTIVITIES FOR A GIVEN SCALE. PROPOSED APPROACH HAS BEEN DEVELOPED.
- LOWER LIMIT REACTIVITIES FOR VOCs OF UNKNOWN MECHANISM IS ZERO, SINCE THEY MAY INHIBIT O_3 .
- THIS METHOD GIVES HIGH UNCERTAINTY RANGES. MAY NOT BE ACCEPTABLE FOR REGULATORY USE.
- UNCERTAINTY RANGES FOR SOME VOC CLASSES CAN BE NARROWED BY MECHANISTIC CONSIDERATIONS.

CHEMICAL MECHANISM UNCERTAINTIES

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

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

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

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

REACTIVITY CHANGES DUE TO UPDATING MECHANISM GIVE AN INDICATION OF UNCERTAINTIES

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

TYPES OF ENVIRONMENTAL CHAMBER EXPERIMENTS CURRENTLY USED TO TEST CHEMICAL MECHANISMS

SINGLE VOC-NO_x-AIR RUNS:

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

COMPLEX MIXTURE-NO_x-AIR RUNS:

- TESTS MECHANISMS' ABILITY TO SIMULATE O₃ FORMATION UNDER REALISTIC CONDITIONS
- NOT USEFUL FOR MECHANISM DEVELOPMENT

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

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

DATA NEEDS FOR MECHANISM EVALUATION (NEAR TERM)

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

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

BETTER METHODS NEEDED TO EVALUATE REACTIVITY

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

DEVELOPMENT OF NEW REACTIVITY MEASUREMENT METHODS

PROJECT UNDERWAY TO DEVELOP NEW REACTIVITY MEASUREMENT METHODS.

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

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

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

FLOW SYSTEM POTENTIALLY ADAPTABLE TO VERY LOW VOLATILITY COMPOUNDS

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

DATA NEEDS FOR MECHANISM EVALUATION (LONGER TERM)

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

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

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

AIRSHED MODEL UNCERTAINTIES

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

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

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

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

UNCERTAINTIES IN DISTRIBUTION OF CONDITIONS RELEVANT TO ASSESSING OZONE CONTROL

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

LACK OF ADEQUATE STUDIES OF INCREMENTAL REACTIVITIES IN REGIONAL SCALE MODELS

- IMPORTANT WHEN ASSESSING WHAT IS "NEGLECTABLE" REACTIVITY.

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

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

- MAY NOT BE OPTIMUM FOR ALL CONDITIONS.

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

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

USE MULTIPLE SCALES REPRESENTING THE RANGE OF APPLICABLE CONDITIONS.

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

USE A SCALE OPTIMIZED FOR A RANGE OF CONDITIONS.

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

APPROACHES FOR DEALING WITH DEPENDENCE OF REACTIVITY ON CONDITIONS (CONTINUED)

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

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

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

POLICY ISSUES

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

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

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

INFORMATION AVAILABLE ON THE INTERNET

REACTIVITY TABULATIONS AND UNCERTAINTY CLASSIFICATIONS:

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

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

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

SAPRC-97 MECHANISM:

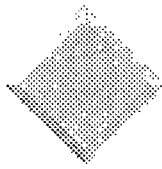
<http://cert.ucr.edu/~carter/saprc97.htm>

CHAMBER DATA BASE FOR MECHANISM EVALUATION (THROUGH 1995):

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

SOFTWARE FOR REACTIVITY CALCULATION AND MECHANISM EVALUATION

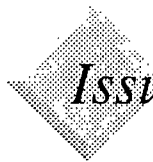
<ftp://cert.ucr.edu/pub/carter/model/>



VOC Reactivity Quantification Methods, Uncertainties and Variabilities

Jim Wilkinson, YJ Yang, M. Kahn, Lewis Qi, Ted
Russell and others
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Issues/Outline

- ❖ What are we trying to do and why?
- ❖ What have we done
- ❖ Available/future methods
- ❖ Uncertainties
- ❖ Variabilities

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What we are trying to do

- ❖ Quantify reactivity of VOCs
- ❖ Understand and quantify uncertainties
- ❖ Understand variabilities
- ❖ Address related issues

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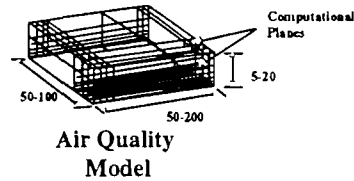
Why

- ❖ Save money
 - Provide incentives to save even more
- ❖ Protect human health
 - Relevant reactivity measures

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Approach(es)

- ❖ Air quality modeling
 - Box modeling
 - Three-dimensional
- ❖ Reactivity quantification
 - Brute force
 - Direct sensitivity analysis
 - ◆ DDM-3D
- ❖ Uncertainty assessment
 - Monte Carlo and other
- ❖ Variability analysis
 - Multiple domains
 - Multiple periods
 - Multiple endpoints



Atmospheric Diffusion Equation

Discretize

$$\frac{\partial c}{\partial t} + L_c(x, t)c = f(x, t)$$

Operator splitting

$$c(t+2\Delta t) = L_{\nu}(\Delta t) L_{\nu}(\Delta t) L_{\nu}(2\Delta t) L_{\nu}(\Delta t) L_{\nu}(\Delta t) c(t)$$

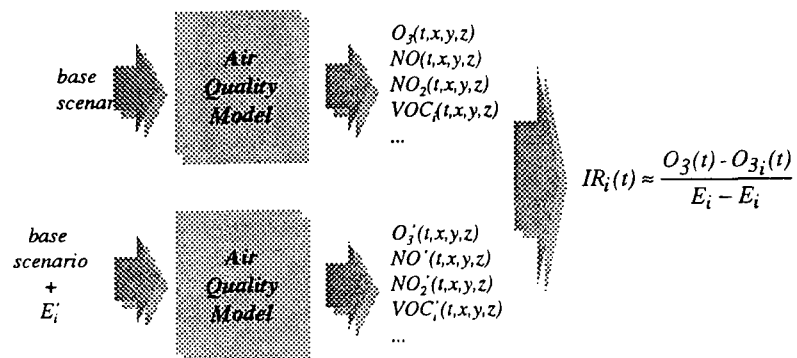
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AQM Reactivity Quantification Methods

- ❖ Brute force
 - Run base case
 - Perturb inventory
 - ◆ Add dE_i of species in emissions
 - ◆ Find $d[O_3]$
 - ◆ Reactivity: $IR_i = d[O_3]/dE_i$
 - ◆ Problems
 - Tedious
 - Numerical errors
- ❖ Direct sensitivity analysis
 - Find $d[O_3]/dE_i$ directly using DDM
 - Multiple reactivities simultaneously
 - Not as prone to numerical errors

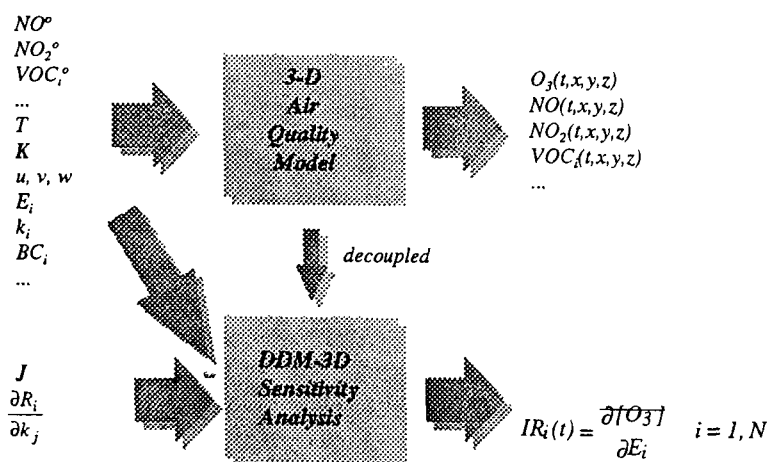
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Brute Force



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Direct Sensitivity (DDM-3D)



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Studies

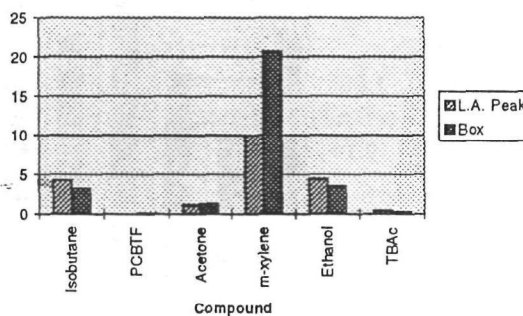
- ❖ California LEV/Clean Fuels Assessment
 - Assess MIR reactivity weighting of exhaust emissions
- ❖ Auto/Oil & NREL reactivity quantification and uncertainty assessment
 - Compare box and airshed model reactivities
 - 3-D modeling of reactivity and 1&3 D modeling of uncertainties
- ❖ National Aerosol Association relative reactivity study
 - Economic assessment of using reactivity in control strategies
- ❖ National Science Foundation
 - Developed and applied DDM-3D, multi-domain analyses
 - 3D Monte Carlo reactivity uncertainty assessment
- ❖ Others
 - Solvent studies, variability analyses, regional domains

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Airshed Vs. Box Model Reactivities

- ❖ Compared alternative fuel MIRs, box model and L.A.-based airshed modeling

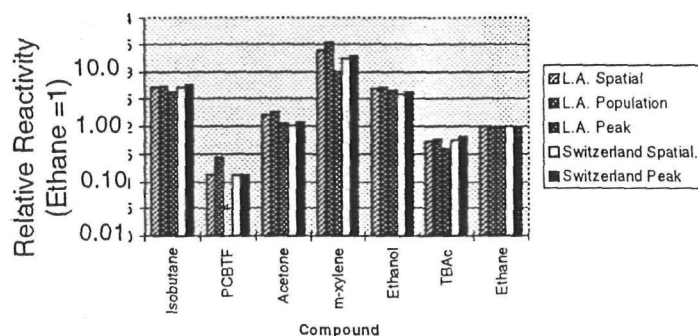
Results usually similar, but aromatics, in particular, can differ.



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Metric Differences

- ❖ Compared peak ozone reactivity Vs. exposure-based reactivities

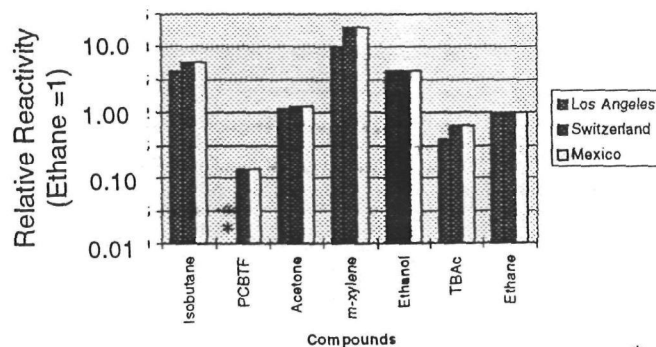


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*Slightly negative

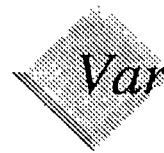
Domain Differences

- ❖ Compared Peak 1-hr reactivities calculated for L.A., Swiss Plateau, Mexico City



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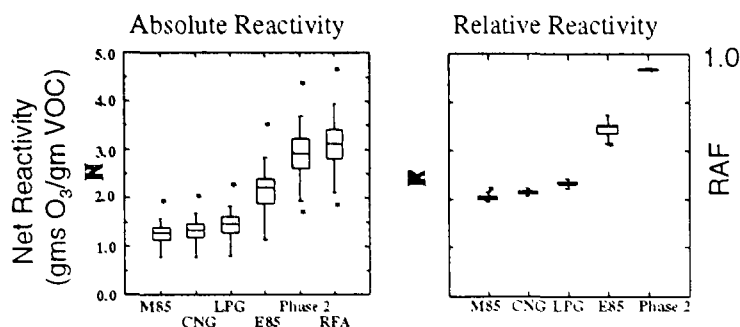
*Slightly negative



Variabilities: Box Model Analysis

- ❖ Compared net reactivity with relative exhaust reactivity (RAF, in each domain)

- Little variability in RAF, lots in net reactivity



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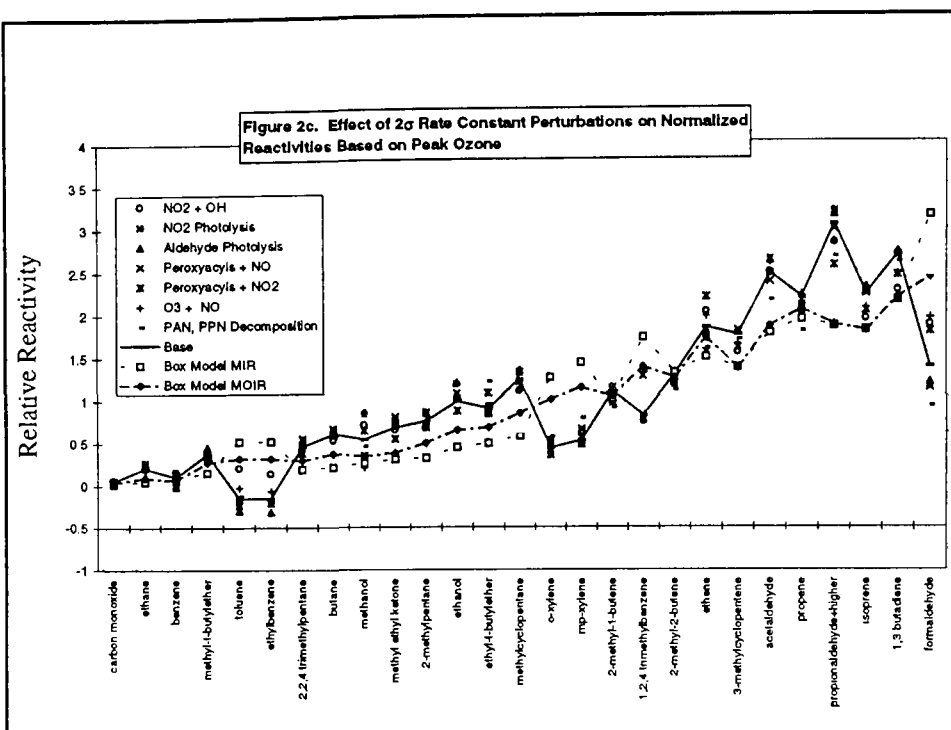
FUEL



Uncertainties

- ❖ Conducted uncertainty analysis using 3-D airshed (L.A. case)
- ❖ Perturbed rate constants and product splits
- ❖ Re-normalized reactivities
- ❖ Found about a 15-30% uncertainty
 - Species dependent

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3D Monte Carlo Reactivity Uncertainty Assessment

❖ 3D Monte Carlo assessment of uncertainties

- Los Angeles basin
- Chemical mechanism and emissions uncertainties
- Direct sensitivity
- Found reactivity uncertainties
 - ◆ Species and metric dependent
 - ◆ Spatial variations in reactivities and uncertainties

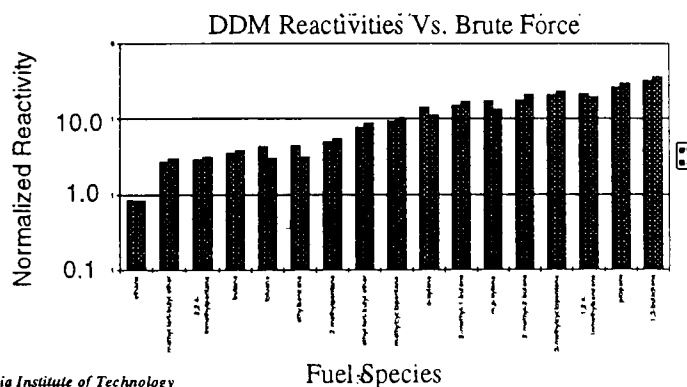
Methods

- ❖ Urban/Regional air quality models
 - Advanced chemistry (SAPRC97+)
- ❖ Direct sensitivity analysis
 - Faster, more accurate
- ❖ Uncertainty analysis approaches
 - Guided Monte Carlo and others

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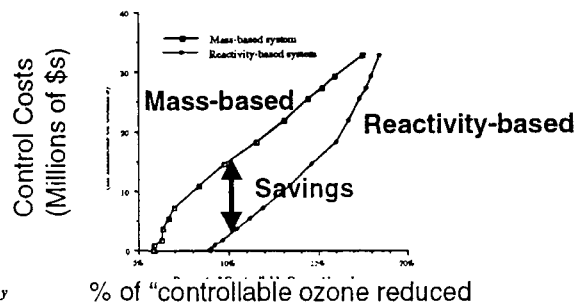
Direct Sensitivity Vs. Brute Force

- ❖ Direct sensitivity provides a more rapid, accurate approach



Economic Assessment (Back to Why)

- ❖ Compared costs of reactivity and mass-based control strategies
 - Mixed integer, non-linear programming of control cost effectiveness in Los Angeles
 - Understates potential savings (reformulations)



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Midway Summary: Use of Reactivity

- ❖ Scientifically compelling
 - Significant differences in ozone impacts
 - Still some issues to resolve
- ❖ Economically compelling
 - Significant economic benefits
 - More to be found if incentives are provided

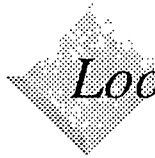
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Gaps in our understanding

- ❖ Regional reactivity assessments
 - Little work on eastern U.S., Texas, etc.
 - Assess variabilities
- ❖ Episodic reactivity Vs. longer term impact
- ❖ More comprehensive uncertainty analysis

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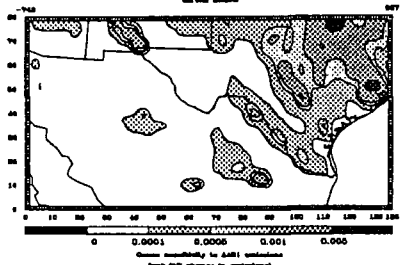
Looming Issues

- ❖ Metric(s) of importance
 - Peak 8-hr: Standard
 - Human exposure: Health
 - Regional exposure: welfare
 - ◆ Most likely of less relevance
 - NO_x limitations

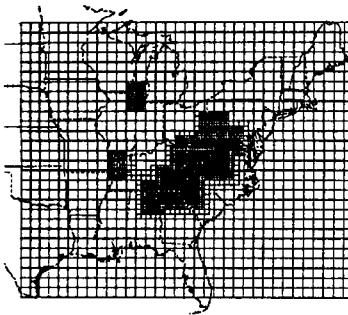
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Regional Reactivity Assessment

Texas-Mexico Border
Sensitivity of ozone to butane
(preliminary study underway)



Eastern U.S.
(To be done)



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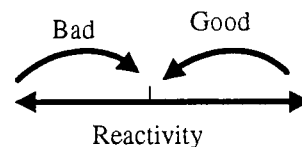
Related Issues

- ❖ Secondary PM formation
 - Can we develop a PM-formation potential scale
 - ◆ Yes
 - Will it be similar to ozone formation potential (reactivity) scale(s)
 - ◆ No

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Exemptions

- ❖ Mistakes have been made
- ❖ Traffic can go both ways
 - Highly reactive ==> less reactive exempt
 - Less reactive ==> marginally reactive exempt
- ❖ Does not account for change in mass emissions
 - Solvent/propellant changes can impact mass emissions
 - ◆ Twice as much of something half as reactive is not a good deal
- ❖ Reactivity scale scientifically more sound
- ❖ Less policy inertia
 - Do not have to “unexempt” a compound
 - ◆ Regulatory uncertainty can be expensive



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Research Needs

- ❖ Regional reactivity assessments
- ❖ Further sensitivity/uncertainty analysis
 - Regional scale
 - Updated chemistry (e.g., SAPRC98?)
 - ◆ Further species mechanism development
- ❖ Assess dependence on metric
 - Peak Vs. exposure
 - Episodic Vs. long term
- ❖ PM impact scale

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Summary

- ❖ Investigated reactivity quantification issues:
 - Fuels, Solvents, Propellants
 - Methods
 - ◆ Air quality models and direct sensitivity analysis
 - Uncertainties
 - Variabilities
- ❖ Uncertainties reasonably small
 - ~30% by species (depending on metric), less by source
- ❖ Variabilities decrease using relative reactivities
- ❖ Scientifically and economically compelling
- ❖ Brightline approach is flawed

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Acknowledgements

- ❖ Jana Milford, Michelle Bergin, Bart Croes, Bill Carter, Basil Dimitriades and Lauri McNair
- ❖ California Air Resources Board, National Science Foundation, National Aerosol Association, Occidental Chemical Company, Coordinating Research Council, Georgia Power, CONACyT, NREL

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Quantification of Uncertainties in Reactivity Estimates for Volatile Organic Compounds

Presented by
Jana B. Milford

Co-authors
Michelle Bergin and Lihua Wang
Department of Mechanical Engineering
University of Colorado, Boulder 80309

Abstract

The research to be presented quantifies uncertainties in air quality model-based estimates of absolute and relative reactivities for volatile organic compounds (VOCs). Monte Carlo techniques have been used to propagate estimates of uncertainty in model inputs and parameters to generate confidence intervals for estimates of VOC reactivity. In this presentation, previously published estimates of reactivity uncertainties due to chemical parameters alone (Yang et al., 1995; 1996a;b; Bergin et al., 1998) will be compared to new estimates that also account for uncertainties in emissions and meteorological conditions for a specific time and location, namely August 27-28, 1987, in California's South Coast Air Basin. For selected aromatic compounds, new estimates of uncertainties attributable to smog chamber-derived reaction parameters will also be presented. The results suggest priorities for future research to reduce modeling uncertainties, but also indicate that the effect of existing uncertainties can be minimized by formulating reactivity policies in terms of relative reactivity estimates, as opposed to absolute reactivities. Implications of modeling uncertainties for a prospective photochemical reactivity policy, and recommendations for additional research, will be discussed.

COMPARISON OF PHOTOCHEMICAL OZONE CREATION POTENTIALS
CALCULATED USING A MASTER CHEMICAL MECHANISM WITH THE MIR
REACTIVITY VALUES FOR UP TO 120 ORGANIC COMPOUNDS

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Atmospheric Processes Research
Meteorological Office
Bracknell
Berkshire
United Kingdom

ABSTRACT

Photochemical ozone creation potentials POCPs for 120 organic compounds have been calculated with a photochemical trajectory model for realistic European conditions. The model employs a Master Chemical Mechanism (Jenkin et al. 1997) containing 2410 chemical species and over 7100 chemical reactions. POCPs provide an estimate of the likely contribution to European regional scale ozone formation over a five day timescale from unit mass emission of each organic compound relative to ethylene. Photochemical PAN creation potentials have also been estimated. The POCP values have been carefully compared with the corresponding MIR incremental reactivities of Carter et al. (1995), developed for the single photochemical day situation appropriate to the Los Angeles airshed. For the vast majority of organic compounds, there is a close functional relationship between POCP and MIR values. Some differences are apparent between the single day and multi-day indices and they provide important insights into the quantification of reactivity. Organic compounds which generate specific highly unreactive organic compounds in their degradation schemes tend to show lower POCPs relative to their MIR values. Such unreactive compounds include: acetone, alkyl nitrates and formate esters. Furthermore, aldehydes, and in particular formaldehyde, show lower POCPs in multi-day situations where OH-degradation predominates over photolysis compared with single day or smog chamber situations. Work is in hand with the Master Chemical Mechanism to improve the representation of the degradation schemes for aromatic hydrocarbons and incorporate the recent mechanistic work by Jeffries et al. (1997) to improve the reliability of the POCP estimates for this important group of organic compounds.

MODELLING OZONE FORMATION FOR POLICY FORMULATION

Models are required to

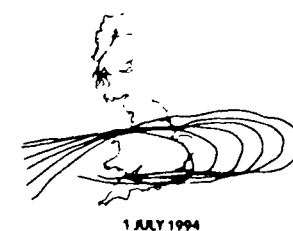
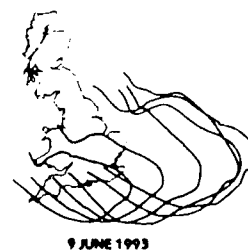
- * quantify transboundary transport
- * define what is needed to meet environmental criteria
- * define the balance between emission controls in the UK and beyond
- * assess the roles of VOC and NO_x controls
- * examine the different VOCs and VOC emitting sectors



The Met Office

95/1033 21

UK MO PHOTOCHEMICAL TRAJECTORY MODEL



BACK TRACK AIR MASS TRAJECTORIES TO A LINE OF ARRIVAL POINTS AT 100 KIL

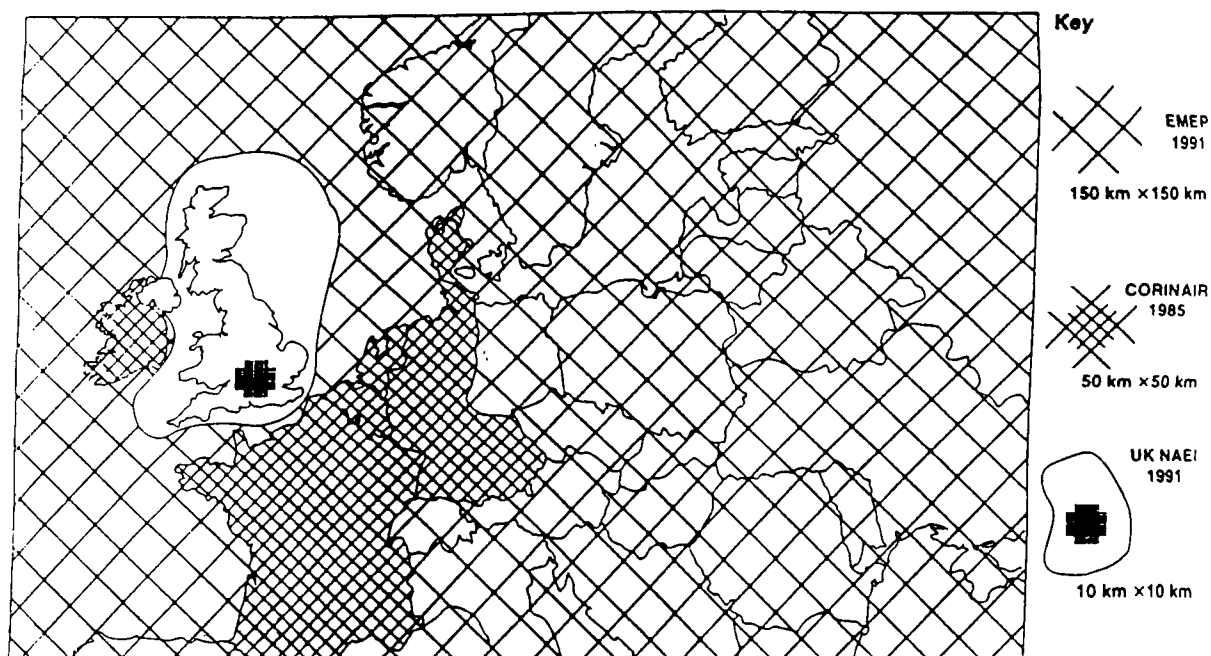


FIGURE 2. A diagrammatic representation of the nesting between the emissions grids employed in the photochemical trajectory model

ORGANIC COMPOUNDS DEGRADED IN MASTER CHEMICAL MECHANISM

ALKANES	22	C1-C12
ALKENES	15	C2-C6
DIALKENES	2	C4-C5
ALKYNES	1	C2
AROMATICS	18	C6-C11
ALDEHYDES	6	C1-C5
KETONES	10	C3-C6
ALCOHOLS	17	C1-C6
ETHERS	10	C2-C7
ESTERS	8	C2-C6
ORGANIC ACIDS	3	C1-C3
CHLOROCARBONS	8	C1-C2
total	120	organic compounds

DEVELOPMENT OF MASTER CHEMICAL MECHANISM

7000 chemical reactions
2500 chemical species
120 emitted organic species

Master Chemical Mechanism development uses:

- * ACCORD for EXCEL as a chemical spreadsheet
- * FACSIMILE as a variable order Gear's method

For example, the butane scheme contains 510 chemical reactions and 186 chemical species (of which 20 are primary emitted species)

Following processes initiate ozone production from the organic compounds :

- * OH radical attack
- * ozone reactions
- * NO₃ radical attack
- * photolysis
- * Cl atom attack

Available on WWW web page:

WWW <http://chem.leeds.ac.uk:80/Atmospheric/MCM>

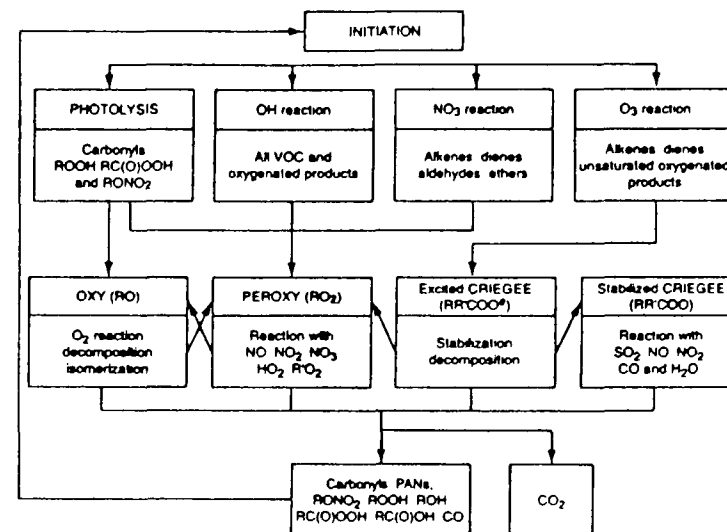


FIGURE 1. Summary of chemistry of organic species considered in the mechanism construction protocol (Jenkin et al., 1997).

DESCRIPTION OF CHAMBER-INDEPENDENT ATMOSPHERIC CHEMISTRY MECHANISMS FROM SMOG CHAMBER DATA

SMOG CHAMBER DATABASES

1. Dual outdoor smog chamber data (University of North Carolina)
2. Indoor teflon chamber (SAPRC)
3. Indoor evacuable chamber (SAPRC)
4. Dual outdoor chamber (CSIRO)

OUTPUT ATMOSPHERIC CHEMISTRY MECHANISMS

- i. Carbon Bond Mechanisms (CBM-IV)
- ii. CAL, SAPRC-90
- iii. Generic Reaction Set

INPUT DATA REQUIRED

- a. concentration measurements
- b. chamber-dependent photolysis rates
- c. smog chamber auxiliary mechanism
- d. evaluated mechanistic data

COMPARISON OF THE MCM WITH CBM-IV MECHANISM

It is concluded that the differences between CBM-IV and the MCM for the estimation of daytime photochemical ozone production are small, within ± 6 ppb in about 100 ppb.

There is a significant difference in the treatment of low- NO_x nighttime chemistry within the MCM.

This close correspondence may not follow for all the secondary products and free radicals. However, this is the reason why the MCM has been developed.

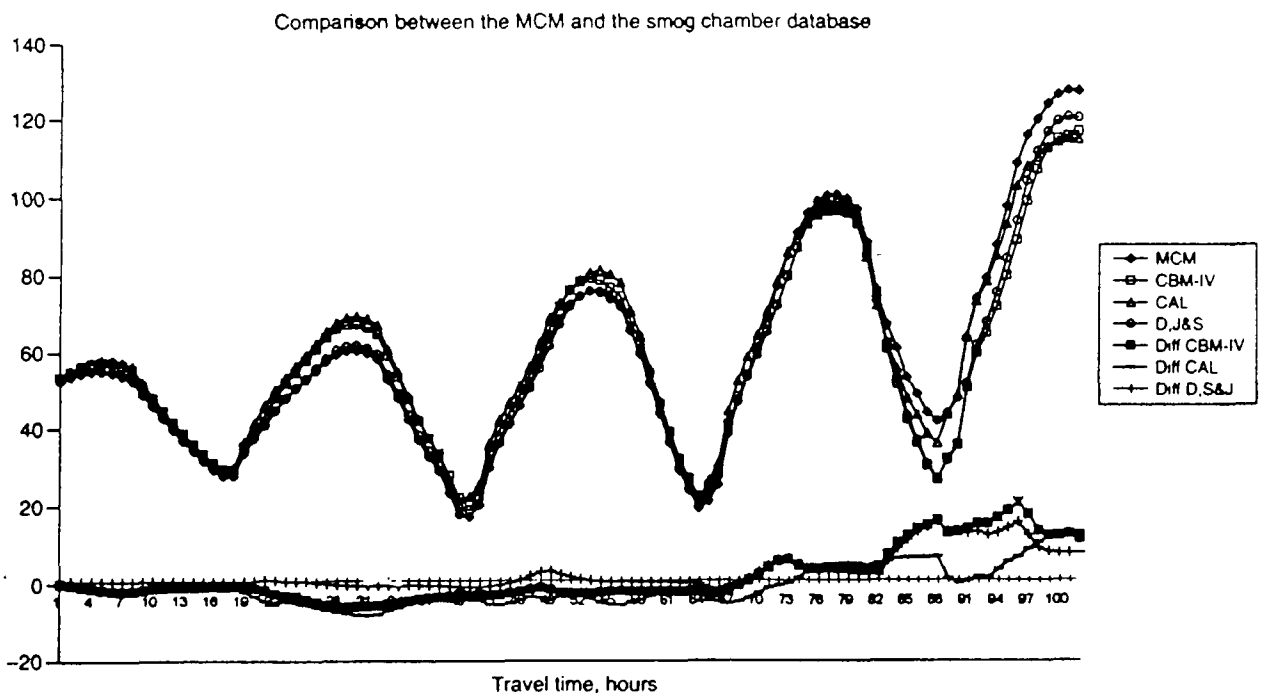
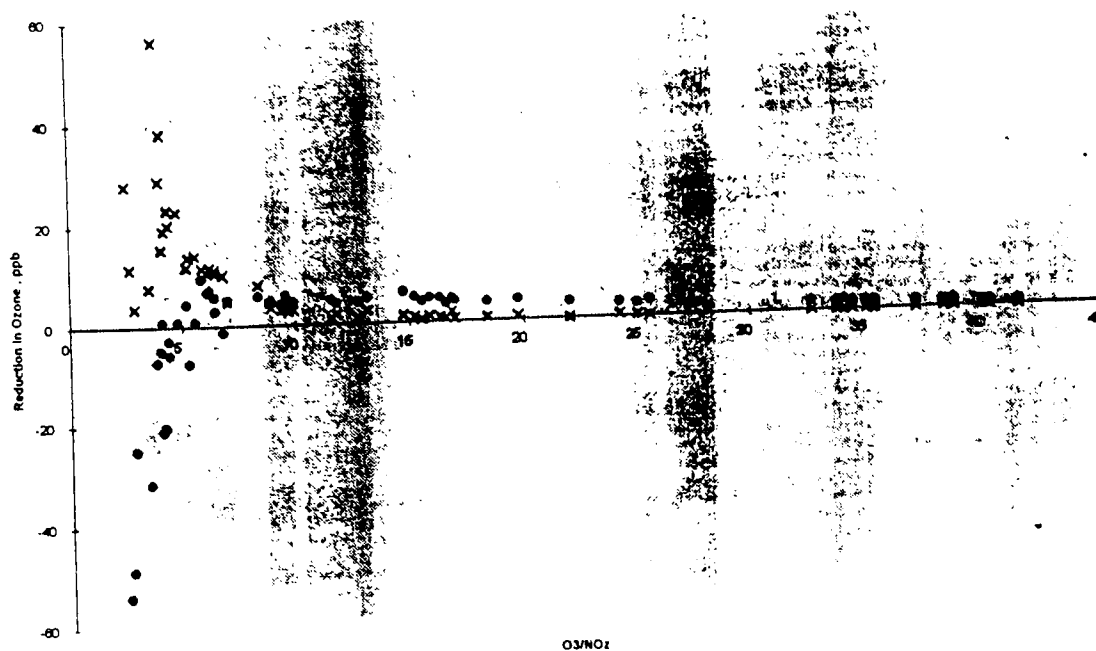


FIGURE 2. Comparison between the explicit chemical mechanisms: MCM and DJ&S and the smog chamber mechanisms: CBM-IV and CAL, and the ozone concentrations produced along the five day trajectory.

97/05/12

Reduction in Ozone for 35% reductions in NO_x and HC emissions plotted against O₃/NO_x



Hydrocarbons and transport of ozone and PAN

1669

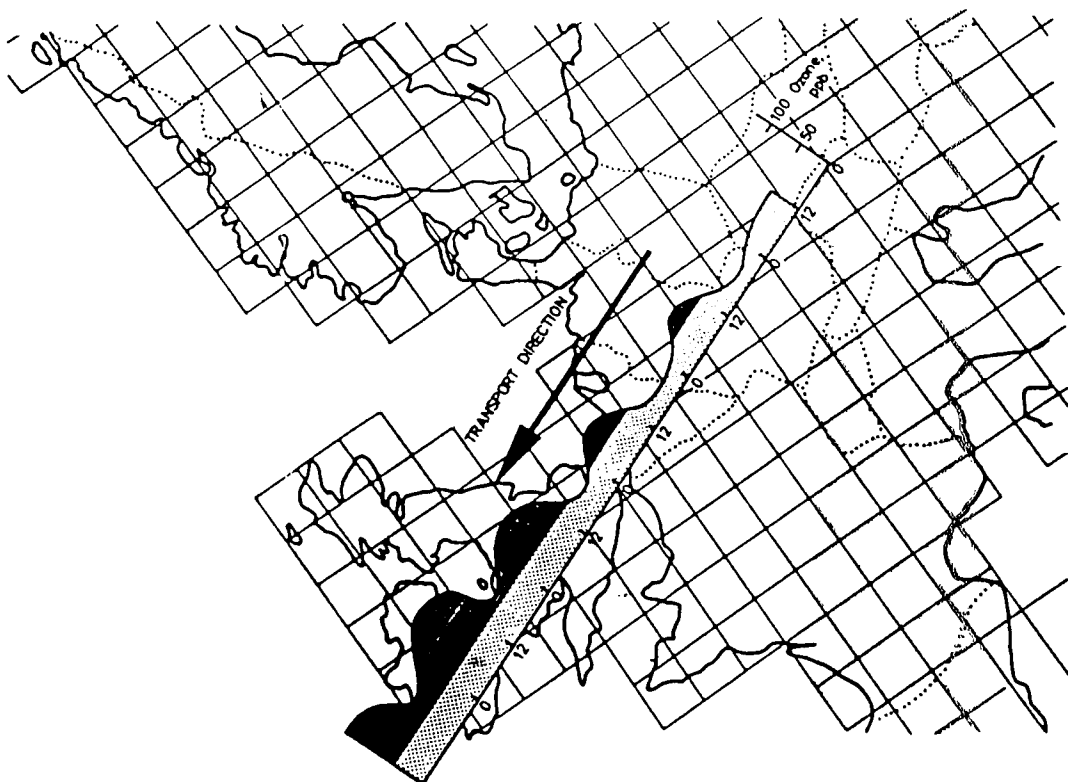


Fig. 2(b). The time development of ozone in the F.R.G.-Republic of Ireland trajectory case.

TABLE 1. POCP and PPCP values for 120 organic compounds determined with the MCM and the UK Photochemical Trajectory Model

Organic compound	POCP	PPCP	Organic compound	POCP	PPCP	Organic compound	POCP	PPCP
Alkanes			Dialkenes			Ketones		
methane	0.6	0.9	1,3-butadiene	85.1	20.8	acetone	9.4	11.9
ethane	12.3	17.3	isoprene	109.2	77.4	methyl ethyl ketone	37.3	44.4
propane	17.6	13.7				methyl-i-butyl ketone	49.0	30.4
n-butane	35.2	31.4	Alkynes			methyl propyl ketone	64.8	52.9
i-butane	30.7	11.7	acetylene	8.6	2.2	diethyl ketone	41.4	47.2
n-pentane	39.5	29.7				methyl-i-propyl ketone	36.4	42.7
i-pentane	40.5	42.7	Aromatics			hexan-2-one	67.2	47.9
neopentane	17.3	6.7				hexan-3-one	69.9	64.1
n-hexane	48.2	44.8	benzene	21.8	4.6	methyl-t-butyl ketone	32.3	24.4
2-methylpentane	42.0	29.4	toluene	63.7	47.8	Alcohols		
3-methylpentane	47.9	66.5	o-xylene	106.3	96.0			
2,2-dimethylbutane	24.1	16.3	m-xylene	110.8	94.6	methanol	13.1	3.0
2,3-dimethylbutane	64.1	63.4	p-xylene	101.0	92.2	ethanol	38.6	61.0
n-heptane	49.4	61.9	ethylbenzene	73.0	44.9	n-propanol	64.3	66.1
2-methylhexane	41.1	31.9	propylbenzene	63.6	34.8	n-butanol	61.2	49.9
3-methylhexane	36.4	40.1	i-propylbenzene	50.0	15.2	i-propanol	14.0	10.0
n-octane	46.3	42.9	1,2,3-trimethylbenzene	126.7	119.1	i-butanol	37.6	17.4
n-nonane	41.4	34.9	1,2,4-trimethylbenzene	127.8	118.5	s-butanol	40.0	44.7
n-decane	38.4	25.8	1,3,5-trimethylbenzene	138.1	122.4	t-butanol	12.3	6.3
n-undecane	38.4	29.1	o-ethyltoluene	89.8	71.8	3-pentanol	42.2	46.3
n-dodecane	35.7	37.2	m-ethyltoluene	101.9	80.8	2-methylbutan-1-ol	40.7	32.6
			p-ethyltoluene	90.6	73.2	3-methylbutan-1-ol	41.2	13.8
			3,5-dimethylethylbenzene	132.0	108.9	3-methylbutan-2-ol	36.6	40.6
			3,5-diethyltoluene	129.5	99.8	2-methylbutan-2-ol	14.2	16.1
						diacetone alcohol	26.2	24.7

Alkenes			Halocarbons			Glycols		
ethylene	100.0	24.8	methyl chloride	0.6	0.7	ethylene glycol	38.2	10.6
propylene	112.3	100.0	methylene dichloride	6.8	3.9	propylene glycol	46.7	50.2
but-1-ene	107.9	82.8	chloroform	2.3	1.7			
cis-but-2-ene	114.6	126.7	cis-dichloroethylene	44.7	20.9	Esters		
trans-but-2-ene	113.2	137.7	trans-dichloroethylene	39.2	17.3			
methylpropene	62.7	34.2	trichloroethylene	32.5	15.7	methyl formate	3.3	1.5
cis-pent-2-ene	112.1	113.8	tetrachloroethylene	2.9	1.9	methyl acetate	4.6	1.9
trans-pent-2-ene	111.7	113.4	methyl chloroform	0.9	0.7	ethyl acetate	21.3	18.7
pent-1-ene	97.7	65.4				i-propyl acetate	21.3	9.6
2-methylbut-1-ene	77.1	65.6	Aldehydes			n-propyl acetate	29.0	24.4
3-methylbut-1-ene	67.1	25.0	formaldehyde	51.9	14.8	n-butyl acetate	24.1	17.6
2-methylbut-2-ene	84.2	100.7	acetaldehyde	64.1	94.0	s-butyl acetate	26.7	21.7
hex-1-ene	87.4	35.1	propionaldehyde	79.8	73.9	t-butyl acetate	6.6	2.3
cis-hex-2-ene	106.9	96.8	butyraldehyde	79.6	61.0	Ethers		
trans-hex-2-ene	107.3	96.6	i-butyraldehyde	61.4	20.8			
styrene	14.2	2.2	pentanaldehyde	76.5	32.7	dimethylether	17.4	3.0
			benzaldehyde	-9.2	-4.0	methyl-t-butylether	16.2	2.3
Cycloalkanes						diethylether	46.7	25.3
cyclohexane	29.0	7.5	Carboxylic acids			diisopropylether	47.6	14.6
cyclohexanone	29.9	11.7	formic acid	3.2	2.1	ethyl-t-butylether	21.4	6.2
cyclohexanol	44.6	11.1	acetic acid	9.7	2.2	Alcohol and Glycol ethers		
			propanoic acid	16.0	21.8			
						2-methoxyethanol	30.0	6.9
						2-ethoxyethanol	38.7	16.6
						1-butoxypropanol	43.6	44.1
						2-butoxyethanol	43.8	24.8
						1-methoxy-2-propanol	36.8	41.2

**IDENTIFICATION OF THE IMPORTANT PARAMETERS
WHICH DETERMINE OZONE FORMING POTENTIAL**

THESE FOUR FACTORS ARE:

MASS EMISSION RATE

MOLECULAR WEIGHT

OH RATE COEFFICIENT

CHEMICAL STRUCTURE

**HOW DOES CHEMICAL STRUCTURE
INFLUENCE REACTIVITY VALUES SUCH AS
POCPs**

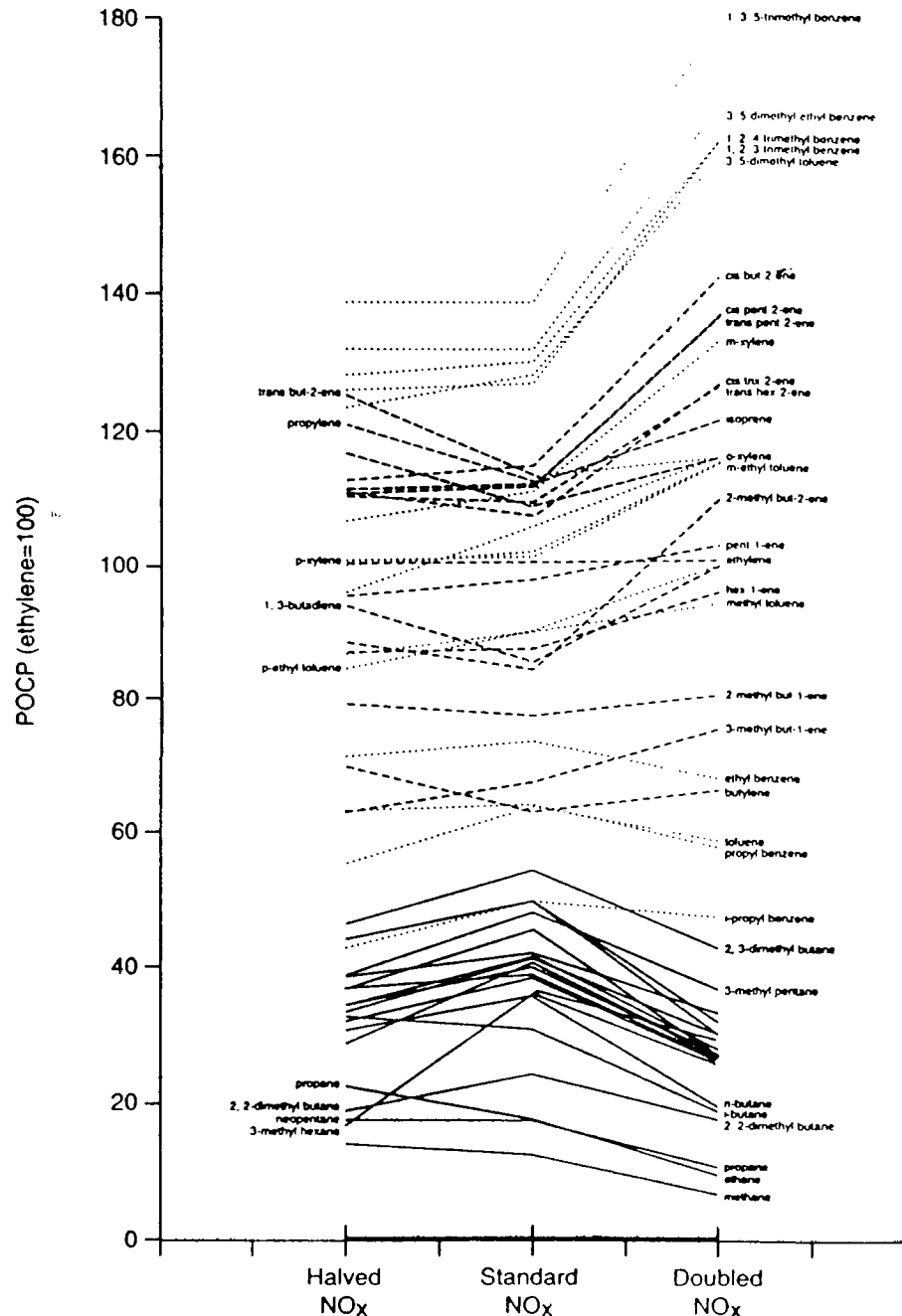
Mainly through the formation of intermediate compounds which degrade much more slowly than the parent compounds.

Examples of unreactive intermediates include :

- * carbon monoxide
- * alkyl nitrates
- * acetone
- * formate esters

FIGURE 4. The POCPs for alkanes, alkenes and aromatic compounds with NO_x emissions halved, standard and doubled.

2-37



LOW REACTIVITY ORGANIC COMPOUNDS ON A BY MASS BASIS

2-methylbutan-2-ol	14.2
styrene	14.2
i-propanol	14.0
methanol	13.1
ethane	12.3
t-butanol	12.3
acetic acid	9.7
acetone	9.4
acetylene	8.5
methylene dichloride	6.8
t-butyl acetate	6.5
methyl acetate	4.6
methyl formate	3.3
formic acid	3.2
tetrachloroethylene	2.9
chloroform	2.3
methylchloroform	0.9
methane	0.6
methyl chloride	0.5
benzaldehyde	-9.2

COMPARISON OF POCP AND MIR REACTIVITY VALUES

POCPs address regional scale ozone formation over the 1-5 day timescale appropriate to Europe.

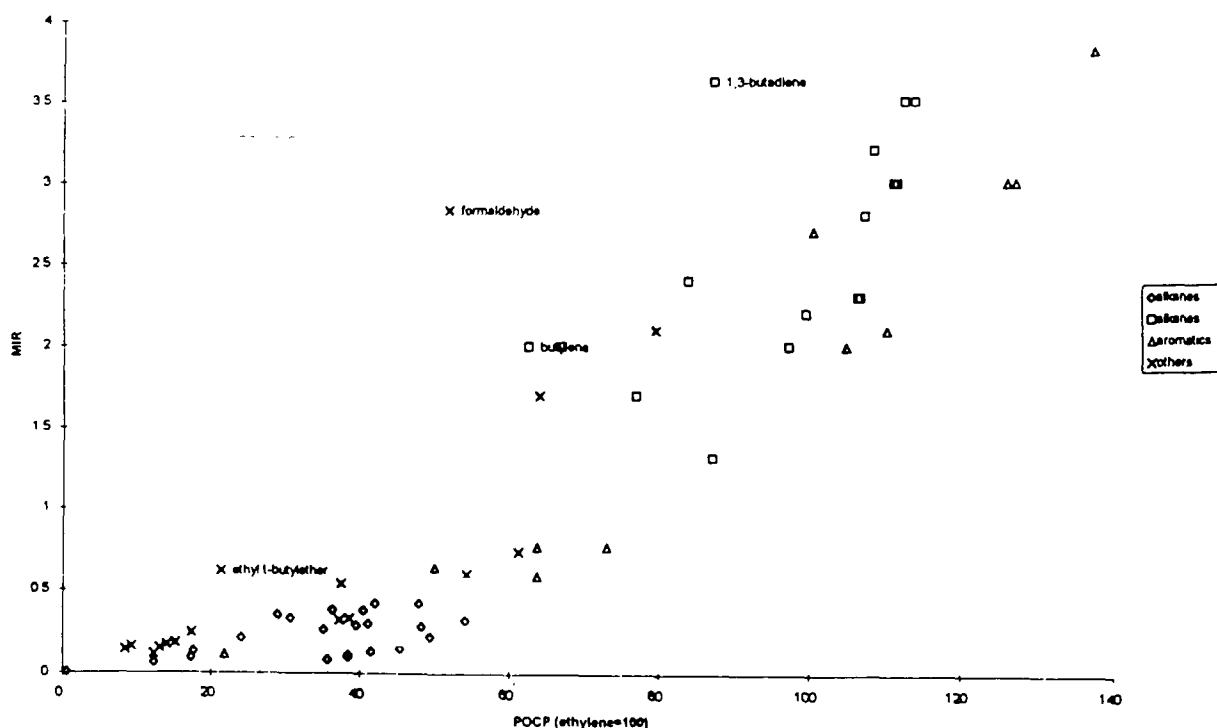
MIR values address urban scale ozone formation.

For the majority of organic compounds the scales are in excellent agreement.

There are some differences:

- * role of formaldehyde
- * 1,3-butadiene
- * butylene
- * ethyl t-butyl ether

FIGURE 3. Comparison between the MIR and POCP reactivity scales for up to 70 organic compounds.



WHAT NEXT WITH POCPs

Expansion of Master Chemical Mechanism to include latest aromatic compound degradation pathway studies of Jeffries and co-workers and Barnes and co-workers.

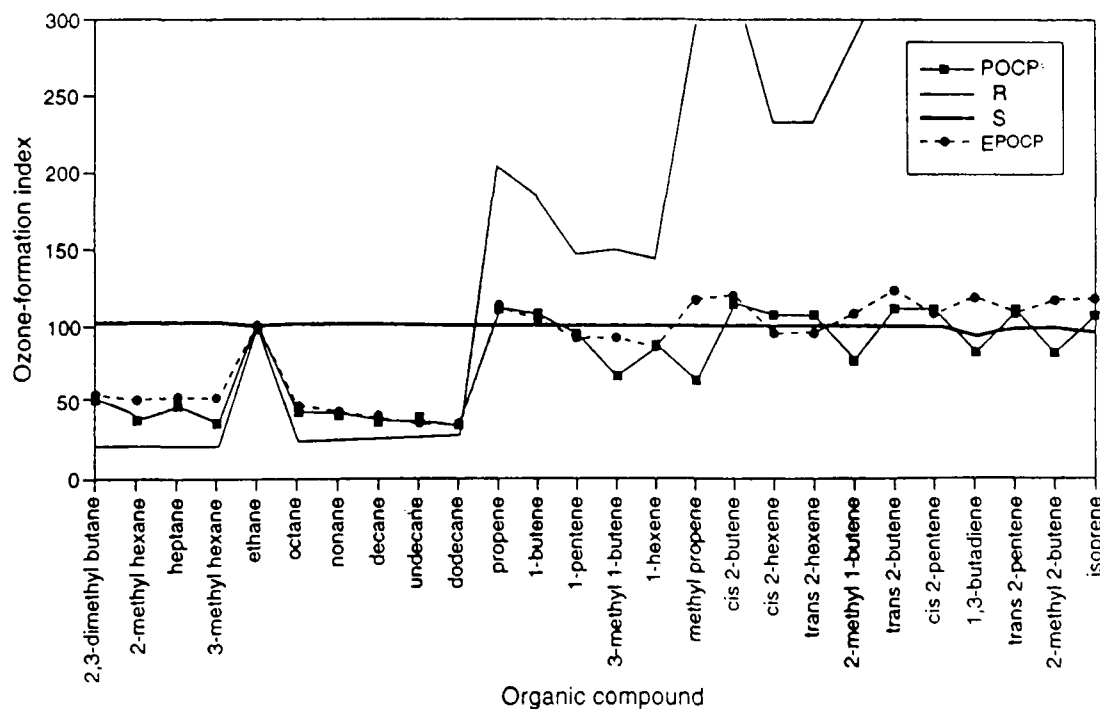
Include an additional 20 organic compounds mainly C₁₀ aromatic compounds making 140 in all.

Expanding the range of oxygenated organic compounds.

Deriving estimation procedures for POCPs.

Derive equivalent of POCPs for large industrial emission sources of organic compounds for controlling downwind ozone formation.

FIGURE 5. Comparison of ozone-formation indices for the reactive alkanes, alkenes and dienes.



UTILITY OF REACTIVITY VALUES INCLUDING POCPs

In the exact limit, no two ozone footprints from different organic compounds can be superimposed.

Single number reactivity values must involve some form of approximation and assumption.

A reactivity value is not a geophysical quantity such as a rate coefficient though it may depend on one or many.

Reactivity values are user-oriented constructs whose calculation depend on understanding of a few environmental processes but also on some policy-oriented choices, such as the spatial scale of interest.

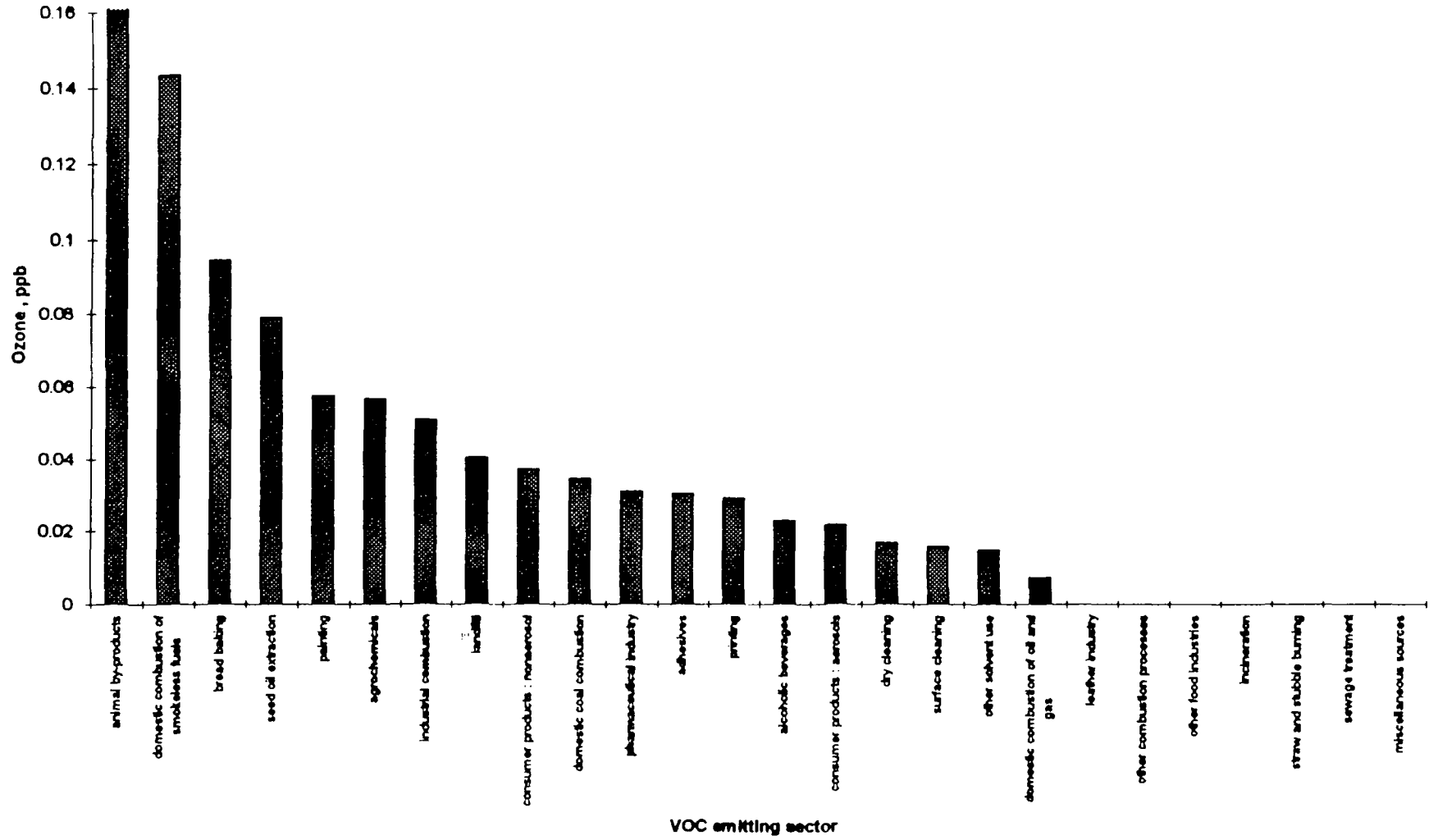
Reactivity values are not subject to observation and testing but are best judged by the insights they give into the role of each organic compound in forming ozone in real situations and their usefulness to policy-makers.

TOP TEN HYDROCARBONS ACCORDING TO INVENTORIES AND POCPs

- | | |
|----|---------------|
| 1 | toluene |
| 2 | n-butane |
| 3 | ethylene |
| 4 | m-xylene |
| 5 | p-xylene |
| 6 | o-xylene |
| 7 | i-pentane |
| 8 | ethyl alcohol |
| 9 | i-butane |
| 10 | propylene |

Together these account for 49% of the ozone forming potential of UK emissions

Ozone reduction in ppb per thousand tonnes per year abated



EPA's Models-3 Framework and the Community Multi-scale Air Quality Model (CMAQ)

Robin L. Dennis

**Atmospheric Modeling Division
National Exposure Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC**

**Photochemical Reactivity Workshop
Durham, NC
May 12-14, 1998**

2-42

EPA/On-Site CMAQ SCIENCE TEAM

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Sharon LeDuc
Sang-Mi Lee
Shawn Roselle
Jeff Young

MEPPS

Bill Benjey
Chris Maxwell
Nick Moghari
Tom Pierce

Project Management

Jason Ching
Robin Dennis
Joan Novak
Ken Schere

Motivation

The complexity of environmental or air quality prediction has increased because we must deal with secondary pollutants, as well as primary ones.

The multi-pollutant nature of the atmosphere is being recognized, also increasing prediction complexity.

Multi-pollutant interactions tell us that we should be thinking and modeling increasingly from a one atmosphere perspective. They also tell us that we need to be thinking multi-scale.

There is greater dependency on the realism of the simulations. We recognize that we need to predict outside today's mix of chemical species to future, very different mixes under conditions of complexity and nonlinearity.

Our Modeling Should Have:

Increased Reliability Entailing Improved Realism in an Expanded Scope, a One Atmosphere Scope

We Came to the conclusion that this necessitated models that:

- **Are as first principles as possible or feasible**
- **Include a full set of interconnected physical and chemical process descriptions**
- **Incorporate a full marriage with prognostic meteorological modeling**

We also came to the conclusion that:

Current Systems Not Expected to Cope

Incrementalism Not Expected to "Get Us There"

No Single Group Can Do It All (Nor should be expected to)

Our Response: Develop a 3rd Generation Modeling System.

This new modeling system is composed of a 3rd Generation Modeling Framework, termed Models-3, and a 3rd Generation Air Quality Model, termed the Community Multi-scale Air Quality Model, CMAQ or Models-3/CMAQ.

Three Pillars of Requirements for a 3rd Generation Modeling System

Science

Increased realism and adaptability

System Framework

Increased Modeling capability

Computing Infrastructure

Increased compute power and flexibility

Umbrella Concept of Community Modeling Is To Permeate

Increased Realism and Adaptability (SCIENCE)

- Up to date science with better or easier integration of new science
(Keep up with the best)
- More complete multidisciplinary; One atmosphere scope
(Integration of "complete" set of physical and chemical processes)
- Better evaluation
(Diagnosis of model processes; diagnostic evaluation)
- More robust and adaptable model structure
(CTM adaptable to different dynamic driver configurations)
- Better modularity to support community modeling

Increased Modeling Capability (SYSTEM FRAMEWORK)

- ◆ Support for the different levels of modularity.
- ◆ Full system available to dispersed scientific community for process study, model/module development, and incorporation of advances.
(Support community modeling at the science level.)
- ◆ Full system available to operational user community for assessment, "easy," controlled execution.
- ◆ Support for levels of interoperability and intercommunication needed to support community modeling.
- ◆ Full execution analysis: verification, visualization, output analysis, process analysis, model evaluation.

SCIENCE

Set of Three Models: CMAQ/ MM5v2/ MEPPS

Designed to be Multi-pollutant and Multi-scale

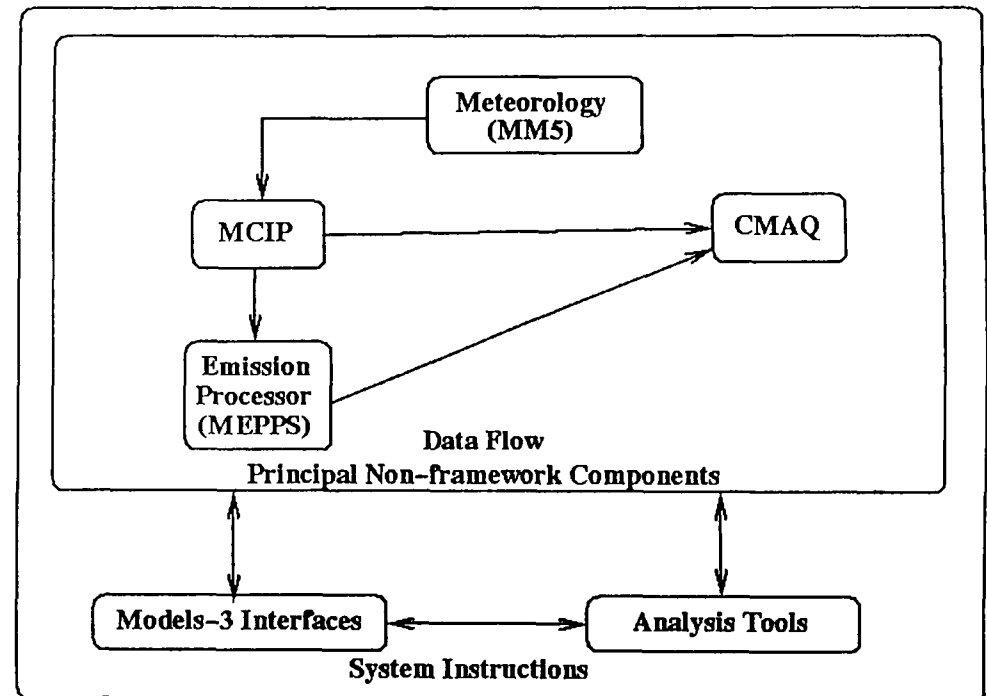
- Ozone, Acidic Deposition (S and N), Nutrients (N), Fine Particles (primary and secondary: sulfate, nitrate, organics), and Visibility
- From Continental to Urban, with embedded Plume-in-Grid

Annual Releases of the Model Set Are Expected for the Next Several Years.

Public Release of CMAQv1.0
June 1998

Major Update and Expansion of Selected Science Options (Given Below) of all Three Models, With a Focus on CMAQ
June 1999 Release

Subsequent Release Dates to be Determined



Meteorological Model: MM5v2

Basic Pedigree

Penn State/NCAR Mesoscale Model Version 5

State-of-the-science prognostic meteorological model

**Started in 1970's; on-going development today;
MM5 is contributed to extensively by the scientific community**

National and international use for operations and research

MM5 Operation

We are using MM5 Version2, the latest release

It is non-hydrostatic (to be able to go down to small grid sizes)

Tested, most applicable set of physics options invoked

One-way nesting (we were first to debug this option) at 108-, 36-, 12-, and 4-km resolutions

4-Dimensional data assimilation (Analysis Nudging) to recreate past meteorology as closely as possible for 108-36-12 resolution

Augmented, adapted output to better serve air quality modeling

MM5 Future Development by Our Group

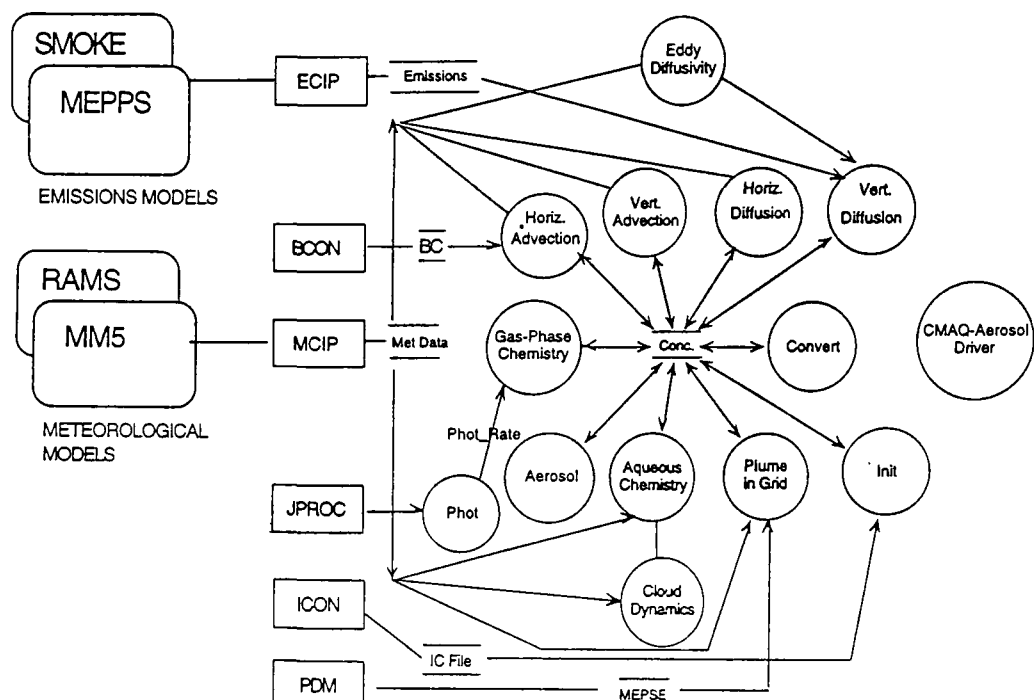
Higher resolution land-use and soil data (Vegeland)

More advanced PBL, microphysics, radiation (Pleim-Xiu with Vegeland)

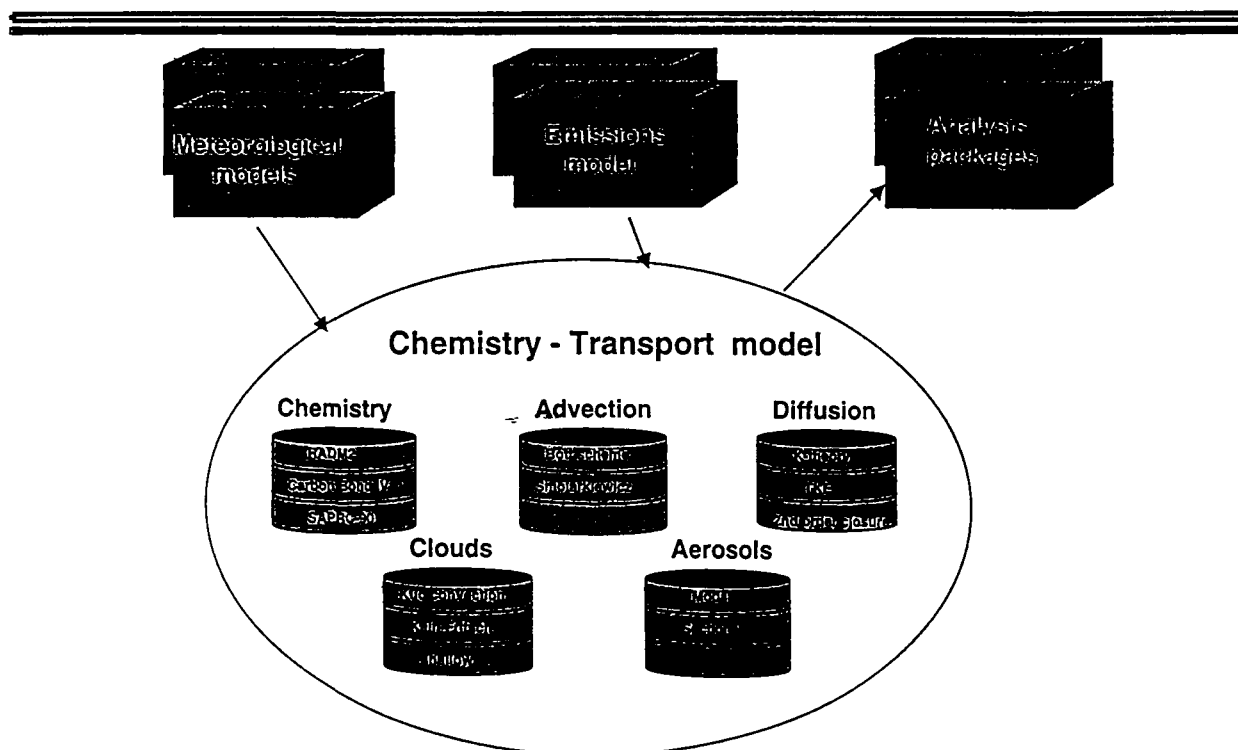
Implementation on workstations and massively parallel computer - CrayT3E

Chemical Transport Model: CMAQ

Model design



CMAQ Adaptability



Science Features -- CMAQv1.0 for June 1998 Release

Generalized coordinate system internal to CTM (to work with any map projection and meteorological driver)

Generalized chemical mechanism reader

Gas-phase chemical mechanisms and solvers

RADM-2+ (Carter isoprene)

CB-IV

QSSA for workstation

SMVGEAR for Cray (vector machine)

Piecewise Parabolic Method (PBM) for advection

Vertical diffusion: K_v (eddy diffusivity)

Horizontal diffusion: K_H (resolution dependent)

Clouds (and precipitation)

Large-scale: grid-resolved at all resolutions

Convective: sub-grid parameterizations at 36- and 12-km

Precipitating

Non-precipitating

Aqueous chemistry (RADM)

CMAQv1.0 for June 1998 Release (cont.)

Particulate Matter

Modal dynamics

3 size ranges

PM-fine

Secondary (S, N, Organics)

Primary (emissions inventory)

PM-Coarse

Primary (emissions inventory)

Chemical speciation tracked

Size dependent dry deposition

Regional Haze: Light extinction; Deciviews

Plume in Grid

Photolysis rates: Look-up table, with cloud attenuation

Implemented on PC/NT; Sun Ultra, Dec Alpha, and SGI (close); and Cray vector supercomputer

Additional Science Features Expected – CMAQ, June 1999 Release

Chemistry: SAPRC

Advection: Bott, ASD (spectral), YAM

Diffusion: Asymmetric Convective Model (ACM)

Surface PBL: Vegeland Pleim-Xiu (PX)

PM: Improved production of organics
Incorporation of sea salt

IC/BC: Stratospheric background (top)

Photolysis: 4-D Implementation

Implementation on massively parallel computer - CrayT3E

MCIP, Meteorology-Chemistry Interface Processor

Features – MCIP for June 1998 Release

Generate coordinate dependent meteorological data (Jacobian) for generalized CTM simulation (traditionally treated in CTM)

- **Maintains modularity of CMAQ regardless of coordinates**
- **Allows consistent links to many meteorological models**
- **Provides meteorologically consistent interpolation methods**

Process meteorological data

- **Window to CMAQ domain**
- **Compute or pass through surface and PBL parameters**
- **Diagnose cloud parameters**
- **Compute species-specific dry deposition velocities (gases)**
- **Output meteorological data in Models-3 I/O API format**

Additional Features Expected – MCIP, June 1999 Release

Link with RAMS (by end of Calendar 1998)

Deposition: CMAQ method (linked to Vegeland_PX land-surface model)

Plans for Future Improvements: CMAQ and MCIP Morphecule Chemical Mechanism

Links to other meteorological models (ETA, RUC, ARPS, WRF)

Additional diffusion options: Hybrid (local/non-local), Transilient

Greater option consistency between MM5 and CTM

Explicit simulation of aqueous phase chemistry in clouds

Particulate modeling: External particle mixtures (particles with same size but different chemistry); better representation of blowing dust.

Improved methods for mass conservation (mass vs mixing ratio)

Deal with mass tracking, source apportionment

Sensitivity analysis packages incorporated

Emissions Model: MEPPS

Models-3 Emissions Processing and Projection System

INPRO/IDA (Inventory Data Analyzer)

QC of source/emissions inventory emissions data

Format conversion to Models-3 I/O API

EMPRO

Modified GEMAP/EMS-95 for point and area sources

SAS-based system, incorporating ARC/Info geographic information system to accomplish spatial allocation of emissions data.

Mobile5a mobile source emissions model

BEIS2 biogenic emissions model

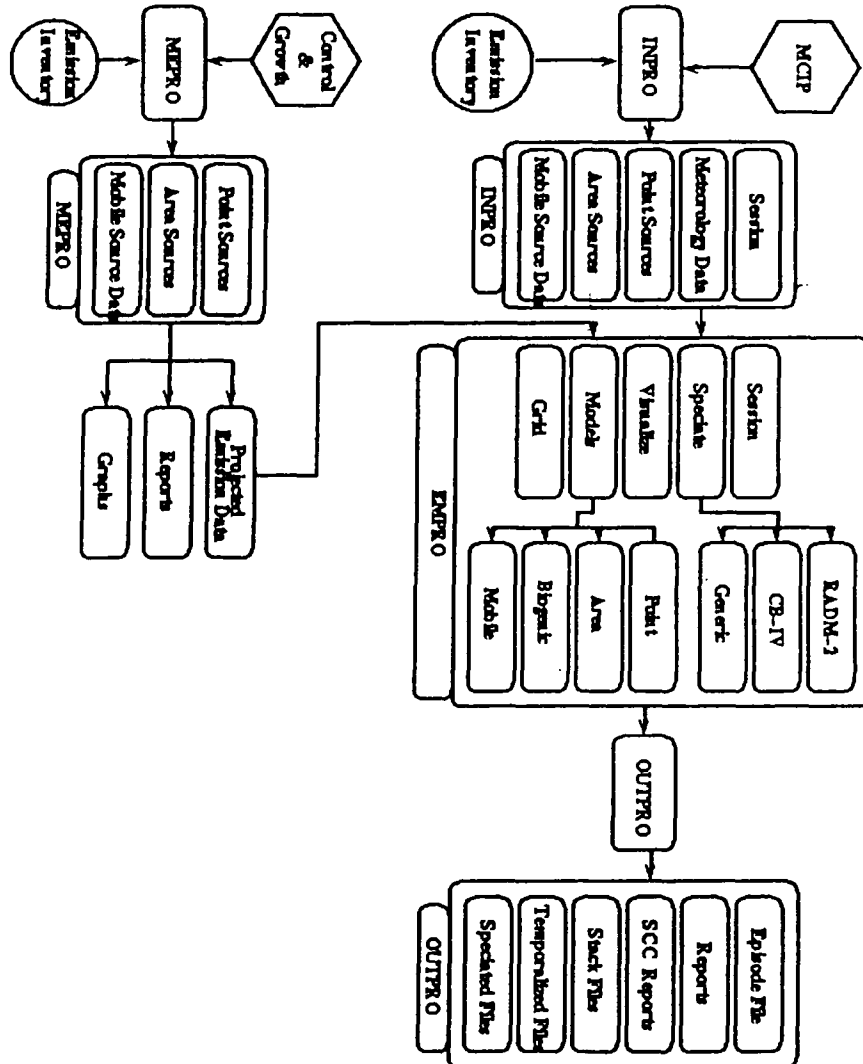
Speciated emissions for RADM-2 and CB-IV mechanisms

ECIP

Linked to MCIP for meteorological data

Calculate plume rise for major point sources

Linked with Plume-in-Grid



MEPRO

Project base year emission data using source-category-specific Economic Growth Analysis System (EGAS) factors for input to EMPRO

Additional Features Expected -- MEPPS June 1999 Release

Mobile5a with PM-fine emissions

BEIS3 biogenic emissions model

Speciation for SAPRC (fixed stoichiometry)

Future Improvements for Emissions

SMOKE emissions processor

Generalized speciation

Link to Morpheus chemical mechanism

108 km: 41x61
 36 km: 67x82
 12 km: 82x100
 4 km: 100x82

Modeling Scales

Horizontal

Nests of 108-km, 36-km, 12-km, and 4-km

Windowing to subdomains from continental to regional

Vertical

30 layers from the surface to the top of the free troposphere

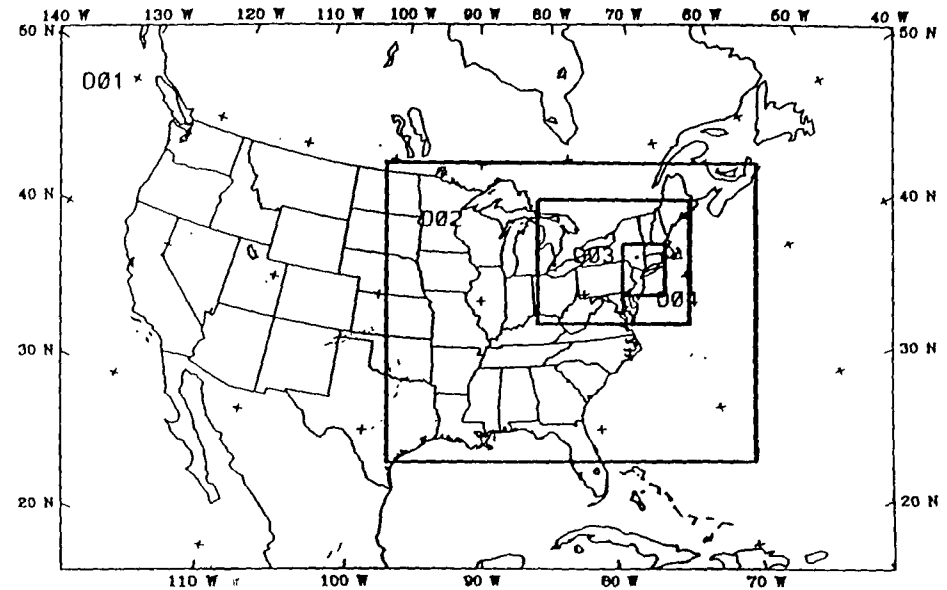
30 layers collapsed to 21 layers, converting the top 18 layers to 9 layers

Temporal

Hourly predictions for 24-hour simulation segments; typically for 5-day simulation periods (episodic)

Hourly meteorological inputs at 36- and 12-km
 15 minute meteorological inputs at 4-km

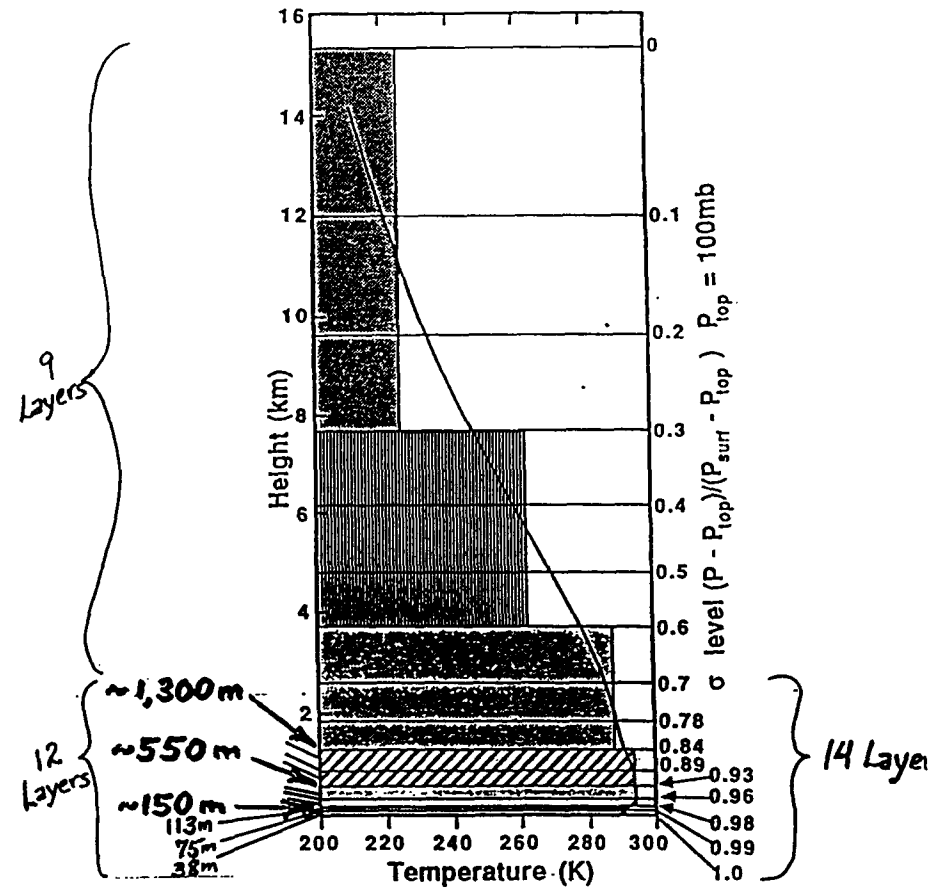
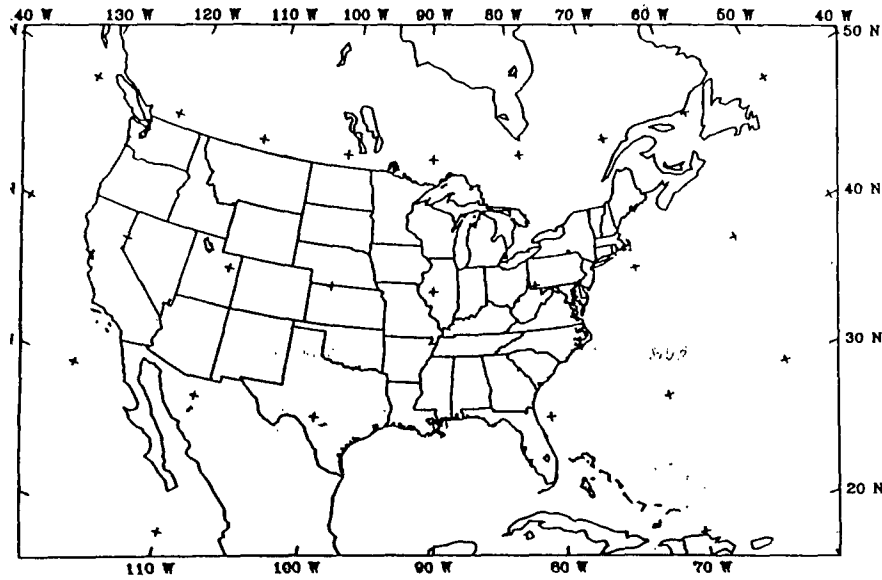
Aggregation (statistically weighted average) of 44 synoptic flow patterns for seasonal and annual averages at the continental scale



121 x 181
36-km
Continental

RADM VERTICAL DOMAIN

2-54



CMAQ MODEL EVALUATION Near Term

Purpose: Acceptance by Regulatory Community

- **Traditional Operational Evaluation - NARSTO NE '95**
 - **O₃ predicted versus measured**
 - **Daily bias & gross error aggregated over all sites**
 - **Accuracy of peak predictions**
- **Time-Space Disaggregated O₃ Statistics - NARSTO NE '95**
 - **Space: type of grid cell based on photochemical Processes**
 - **Time:**
 - * **early morning: titration & inversion breakup**
 - * **daytime: mixing height & dilution; O₃ production**
 - * **nighttime: deposition, surface layer loss**

CMAQ MODEL EVALUATION Long Term

Purpose: Acceptance by Scientific Community

- **Process understanding and scientific uncertainties**
- **Determine best model configuration to reduce uncertainties**
- **Assess value of new measurement information**
- **Diagnostic Evaluation - Nashville SOS '95**
 - **Insight into processes generating O₃**
 - * **OH & NO_x cycle interactions with resulting O₃ production**
 - * **Integrated reaction rate/ mass balance**
 - * **Indicator species**
 - **Sensitivity : CB4 versus RADM2+ chemistry**
- **Sensitivity Analysis - Nashville SOS '95**
 - **Characterize importance of process differences**
 - **Interpretive analysis related to appropriate use of CMAQ**

2-55

SYSTEM FRAMEWORK

Enhanced Modeling Capability

- ❖ Support for the different levels of modularity
- ❖ Full system available to dispersed scientific community for process study, model/module development, and incorporation of advances. (Support community modeling at the science level)
- ❖ Full system available to operational user community for assessment, "easy," controlled execution.
- ❖ Support for levels of interoperability and intercommunication needed to facilitate community modeling
- ❖ Full execution analysis: verification, visualization, output analysis, process analysis, model evaluation.

An Advanced Computer-based Problem Solving and Modeling Environment or Framework With An Effective Human-Computer Interface for Environmental Modeling and Assessment That is Adaptable to a Changing Computing Infrastructure.

Assist Environmental Analysis and Model Development

- Facilitate execution of air quality simulation modeling systems, especially air quality models, and the visualization and analysis of their results.
- Minimize the tedium and chance of error associated with modification of rigid model execution scripts.
- Provide comprehensive data management to assist in storing, accessing, tracking, identifying, and capturing processing history of numerous datasets associated with modeling studies.
- Manage and organize large collections of model executions and associated data.
- Provide cross-platform (a variety of computing platforms) computing of complex modeling studies with distributed data management.

Assist Environmental Analysis and Model Development (cont.)

- Aid the assembly, testing, and evaluation of science process components by facilitating the interchange of process modules and minimizing the chance of incompatible assumptions.
- Facilitate the tailored execution of the modeling system, including customized process analysis.
- Provide the flexibility to change key "global" model specifications such as grid resolution, map projection, or chemical mechanism without rewriting code, thus minimizing error.

Functionality Achieved Via the Following Management Components Incorporated in the Modeling Framework:

Science Manager

Model Builder

Program Manager

Data Manager

Strategy Manager

Study Planner

Tool Manager

Source Code Manager

Framework Administrator

Flexibility for Future Change Achieved by Architectural Layering

ARCHITECTURAL LAYERING: FLEXIBILITY FOR FUTURE CHANGE

	USER INTERFACE	
USER INTERFACE	Management Layer: Data Manager Study Planner Strategy Manager Tool Manager	Science Manager Model Builder Source Code Manager Framework Administrator
Environment Layer: OS, System "Personality"		
Computational Layer: Programs: models, analysis, visualization,...		
Data Access Layer: I/O Applications Programming Interface		
Data Structure/Representation: netCDF, XDR		
Data Storage: File systems & databases		
Physical Device Layer: Disks, networks, printers, machines		

SDC-001

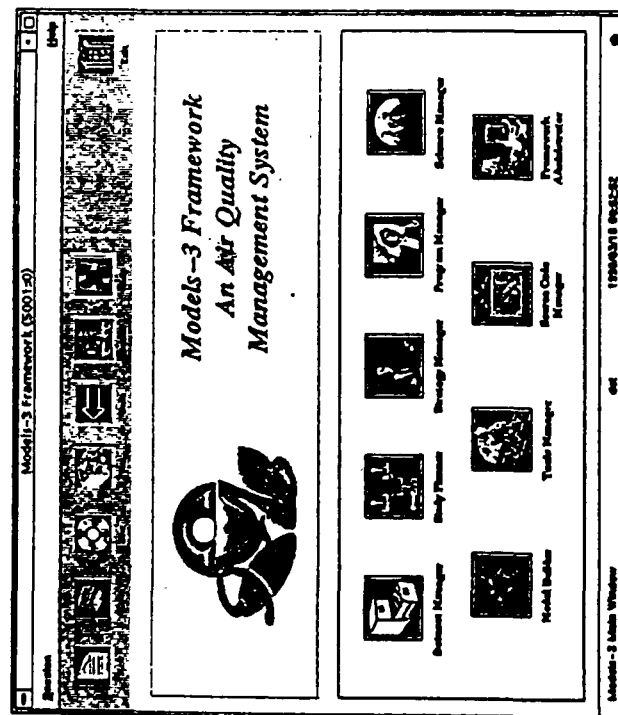
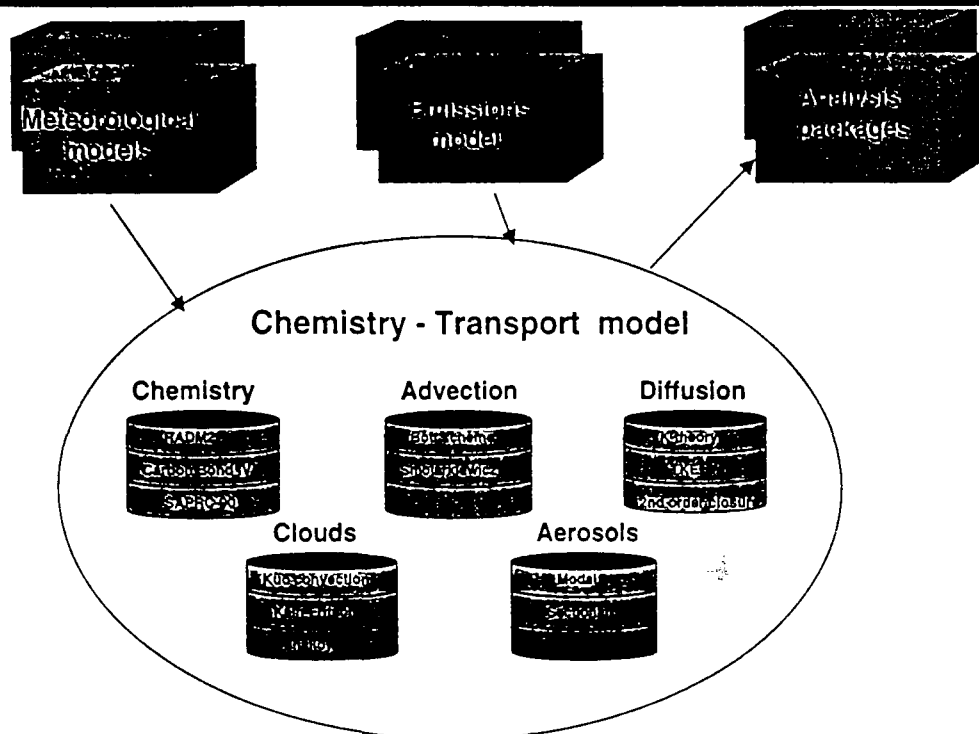


Figure 1-1. Models-3 Main Window

CMAQ Adaptability



Reactivity 05/1/2006

MODELS-3 FRAMEWORK CAPABILITIES

Science Manager

- Define global shared information
 - model domain & resolution
 - coordinate systems & map projections
 - chemical reactions & species

Model Builder

- Select components to create a model specific to the problem
- "Plug & Play" science modules via global data structures
- Customize model components (i.e. redefine chemical reactions)

Program Manager

- Register executable programs into framework
- Identify logical filenames to enable automated program execution via Study Planner

MODELS-3 FRAMEWORK CAPABILITIES (cont.)

Data Manager

- Data access from any networked system
- No need to convert data between computers
- Manage dataset history information
- Uses Federal Geospatial Metadata Standard

Strategy Manager

- Evaluate alternative emissions control options and future years

Study Planner

- Automated multiple-platform execution of a series of interlinked programs/ model/ independent modules
- User control over input parameters

MODELS-3 FRAMEWORK CAPABILITIES (cont.-2)

Tool Manager

- Prepare emission inputs compatible with selected model
- Invoke visualization & analysis tools
 - VIS5D - 3-D analysis & animation
 - PAVE - 2-D analysis & remote viewing
 - IBM DX - specialized analysis tools
 - SAS

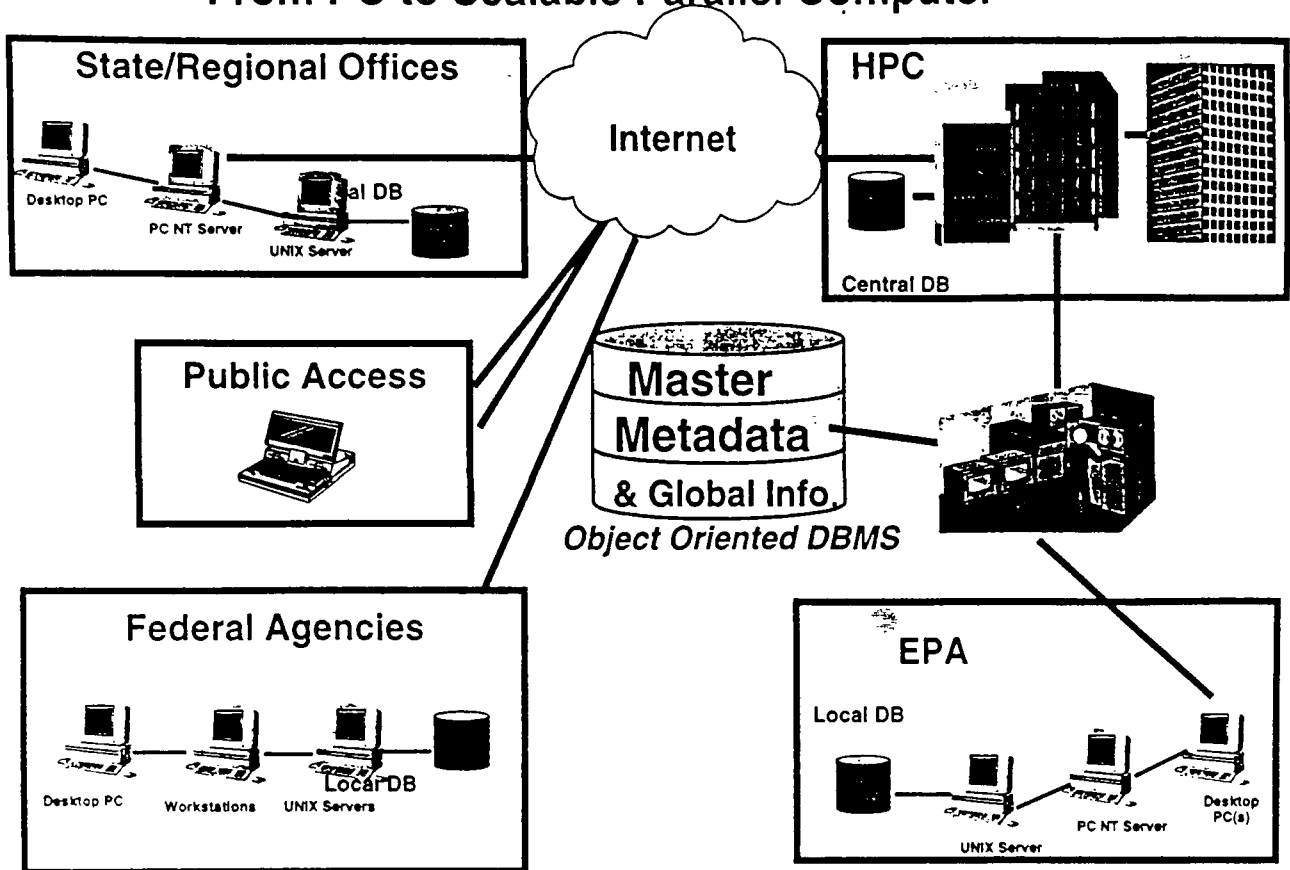
Source Code Manager

- Version control of science code ensures documented software evolution & replication of previous executions
- Facilitates automated building of models from components

Framework Administrator

- Controls integrity of official model versions
- Controls security & access to data/ code
- Provides system maintenance capabilities

Seamless Computing & Data Management From PC to Scalable Parallel Computer



Reactivity 05/17/96

KEY MANAGEMENT LAYER COMPONENT DETAIL

DATA MANAGER

- Data access from any networked computer
 - Metadata in Object-Oriented (OO) DBMS
 - Concurrency control: Multiple users share data access
 - Registering data simplifies search & selection
- No need to convert data between computers
 - eXternal Data Representation (XDR) ... IEEE
 - netCDF ... self-describing files
 - Input/Output Applications Programming Interface Library
- Metadata compliant with FGDC Metadata Standard

KEY MANAGEMENT LAYER COMPONENT DETAIL

STUDY PLANNER

- Automated multiple-platform execution of a series of interlinked programs / models
- Automatic registration of generated output files
- Execution "History" information written on each output file
 - Link to compile time information
 - * science module versions
 - * configuration file, compile environment & date
 - Runtime control information
 - * environmental variables, namelist input, command line
 - * study/plan identification
 - * link to input/output file metadata
 - runtime environment
 - * execution date & time
 - * hardware platform, OS version

SOME FEATURES OF THE MODELS-3/CMAQ SYSTEM THAT SHOULD AID THE SUPPORT OF REACTIVITY CALCULATIONS

Chemical Mechanism Reader

Customizable Process Analysis

Study Planner

Data Manager

Multi-pollutant CTM

Responsibility for Evaluation, Including Diagnostic Evaluation

Meteorological Case Variety and Availability
Expected to be Extensive

Establishing a Community Modeling Capability
Kenneth Galluppi
Univeristy of North Carolina at Chapel Hill

Taken From: Air Quality Community Modeling and Analysis System
Attributes and Implementation
Draft 09/15/97

I. Introduction

Over the past four years, there has been a tremendous growth in the community's utilization of air quality models in the development of emission strategies related to Clean Air Act compliance. For example, the Ozone Transport Assessment Group, OTAG, witnessed model applications growing beyond the four "official" centers to extend to many States, private industries, consulting engineers, and environmental groups. With this exposure, came concerns of public access and consistency in model evaluation, analysis, interpretation, and scientific integrity of the systems and their application. One approach to reducing these concerns is to implement a community modeling and analysis system.

From August 27-29, 1997, a workshop was held in Research Triangle Park to discuss the purposes and needs for models, the benefits of a community modeling approach, and the attributes of and obstacles to developing and implementing such a system. The workshop had fifty participants who represented federal and state governments, industry, and university researchers. This paper is a summary of the background, findings and recommendations from the workshop.

II. Models, Analysis, and Their Applications

There are many approaches to modeling ranging from statistical to comprehensive models based on governing equations of physics and chemistry. Each approach has its strengths and weaknesses in terms of reliability, predictability, and cost. A diversity of modeling approaches serves to check our models for consistency resulting in greater confidence in their application for emission strategy development.

Untangling the physical-chemical relationships required to understand the cause-effects of pollution problems is a daunting task. Over the past decade, the air quality community has been engaged in various developments and applications of comprehensive models in conjunction with complex analysis of observations. Each model or analysis improvement has opened the door to new sets of unexplained observations and hypotheses. Improving our scientific understanding is, and always will be a dynamic process, but remains at the pinnacle of developing sound environmental practices.

It is assumed that the community is committed to the development of scientifically credible models and in building skill in their use for guidance. to discern probable cause-effects and in

develop mitigation and prevention strategies of air quality problems. This commitment stems from the increasing costs of assigning culpability for pollution abatement and prevention. Policies are establishing who pays and how much which opens questions to how reliable is the scientific guidance used for this judgement. The question remains, how does the community develop the best simulation tools for use by both scientists and managers whose common purpose is achieving a sustainable environment?

While the scientific community is engaged in developing new insights into science, the management community is engaged in making decisions based upon the best available science. Most would agree that these are complementary objectives. However, history has shown us that scientific knowledge and new analysis methods are difficult to transfer to a large, diverse, and often an divided management community whose time and funding constraints may inhibit the use of “best” science or its proper application and interpretation.

The development of numerical models and their application to real world problems has enabled mediocre transfers of scientific knowledge and technology utilization. However, the rising costs of environmental protection demands the quicker development of better models and their transfer for use in scientific and management practices. In order to develop low-cost, equitable policies, that the community has confidence in, we need to capitalize on a shared goal to develop the best scientific formulations and learn to apply models in a consistent manner.

The question explored in the workshop is whether the community can enhance these efforts through common, integrated development and application efforts. If so, does this warrant the defining, development and implementation of a community-based modeling and analysis system?

III. What is a Community Modeling and Analysis System (CMAS)?

A Community Modeling and Analysis System (CMAS) is an approach to model development, application and analysis that leverages the community’s complementary talents and resources in order to set new standards for quality of science and reliability of application of air quality models. The resulting comprehensive system forms the foundation which the community, including governments, industry, academia and other stakeholders, participates in the examination of issues and the subsequent development of strategies that meet societal challenges of environmental protection.

A community modeling system is a computerized framework and intellectual process that integrates the research and development findings, and application experiences into a common set of tools and knowledge base. The information and tools in the CMAS are open and readily accessible to everyone. It is called a system because the integration is organized into a wide range of computerized information modules. It is the desire of the CMAS approach to increase productivity and reduce the cost of examining issues and developing alternate scenarios. The cornerstone for accomplishing this is the framework that enables quicker integration of science and techniques and for easier transfer of knowledge and experiences to

the community. The result is peer reviewed, process of providing the best simulation and analysis tools for use in a regulatory setting.

A CMAS is not a single “mother of all models”, but an integrated collection of science modules which can be linked together to form multiple model configurations. The underlying premise is that there is no single group of modules that can claim to be the “best” model. Rather, by changing specific modules one can gain insight into the validity of modeled results. This does not preclude the regulatory community from assigning and locking a prescribed set of modules into being the “regulatory model” for consistency purposes. In fact, there is an advantage to having several “regulatory” models for routine scientific comparisons.

For example, the National Weather Service in its earlier days of weather forecasting, utilized three models for daily comparison of predictions: the complex Limited Fine Mesh (LFM), the 2 variable Baroclinic, and the 1 variable Barotropic models. Although formulated differently, they were compared for consistency. The “simpler” models aided the meteorologist to get a feel for the numerical forecast generated by the LFM, the model of choice. The models are more sophisticated now, but are still cross-checked against models of similar complexity.

How does this freedom of module use potentially impact the regulatory process? Which modules can be utilized and when? Are we adding more confusion to the analysis than before? How can we know when we are getting a “better” simulation”. How do we prevent model “calibration”? These are but a few of the more imposing questions that will inevitably arise and many of which were addressed at the workshop.

IV. Benefits of a Community Modeling System

Increasing productivity, raising confidence in results, interpretation and use, increasing stakeholder buy-in, and reducing costs are all worthy goals of any modeling approach. The CMAS is intended to maximize these benefits through the reduction of overlapping developments, peer review, and ease of development and application. Given a robust and streamlined system design and a peer review process by which the CMAS can be used for development and application, the benefits of a CMAS. The benefits should easily justify the focusing of resources and change in process by which models, tools and techniques are currently developed in the community. There are many benefits to the community. These include:

- a) Implementing scientific advancements into models can be difficult. A modular community system allows for process and formulation changes easier and with less resource. This will enable the community to take advantage of new approaches sooner than ever before.
- b) Model versions and revision levels can be more readily controlled. Further, time to create new revisions will be significantly reduced. A CMAS inherently will have far better

quality assurance procedures when many more are involved in establishing a new version.

- c) With a common framework, model formulations and their applications will be far easier to compare.
- d) New scientists and engineers can be trained in specific areas of expertise since only one framework needs to be learned. Further, over time, there will be a cadre of experts who can share their knowledge with new personnel. This will lead to a dramatic reduction in costs associated with training and continuing education.
- e) Scientists and computer scientists will complement one another without having to learn the other's field. Development groups will be able to better utilize the skills and training of its personnel.
- f) The science and application talents and knowledge will be added to a common base and made available to all. This will enable all problems to be addressed at the best available skill level.
- g) Databases that are utilized by the models and for analysis will be more easily shared which should lead to more thorough quality control, analysis and consistent interpretation.
- h) Analysis techniques and methods can be more readily transferred to the community. This should enable more revealing techniques to be utilized and understood by a larger pool of experts.
- i) A common system will have several levels of use including the management decision maker, scientist/engineer, and model practitioner. A robust CMAS enables each of these specialists to maintain the appropriate level of detail needed to keep their understanding within context, and while at the same time enable each group to communicate more effectively to one another.
- j) User groups and other transfer methods would be implemented to develop a knowledge base.
- k) A peer review process will assure that quality science, application, and analysis are being implemented and put to best use by the community.

V. Attributes of a CMAS

The workshop breakout groups looked at six areas of attributes and implementation issues: science, environmental management, education, support and maintenance, intellectual property, and model application and evaluation. In this draft, each group's listing of attributes is given. In later drafts, the groups' replication of comments will be eliminated. The attributes are characteristics that describe a community modeling and analysis system. In other words, what must a CMAS be able to do to meet the specific perspectives of modeling support?

Group A – Science Workgroup

- a) General enough to minimally integrate the processes required to simulate regional and urban scaled problems.
- b) Incorporates the physical-chemical processes to enable utility for examination of multiple pollutant (ozone, aerosol, acid deposition), air quality problems. Eventually, it must

extend to cross-media where chemical transport crosses media types, for example to water.

- c) Able to produce three dimensional concentration and deposition fields of key chemical and physical species that enable a diagnosis of the cause-effects relationships.
- d) Must be usable by scientists, environmental managers, and stakeholders within the effected communities and regulated industries.
- e) Brings together a working community to examine issues such as the NAAQS, NSR, and deposition.
- f) The science modules must be peer reviewed, relevant processes required for multi-pollutant assessments. Further, the CMAS must be extensible to include alternate formulations of known processes and the inclusion of new science when it becomes available.

Group B – Environmental Management Workgroup

- a) Able to assist the managers by modeling input variations consistent with varying environmental strategies.
- b) Have a high level of quality control to raise confidence of use.
- c) Should be linked to and assist in risk assessment and decision making techniques including social-economics and health risk.
- d) Be able to expose and explain sensitivities and uncertainties in the formulation and their impacts on results, interpretations and utilities.
- e) Responsive to time constraints and adjust formulation accordingly
- f) Must be able to facilitate communication to multiple levels of users from managers, practitioners and public.
- g) Must be able to summarize and explain input scenarios and impacts on results through the use of multiple analysis techniques.
- h) Must be well documented and understandable by multiple levels of users.
- i) Must be reasonable cost to not be prohibitive for any stakeholder to utilize.
- j) The CMAS must be open for all participants to examine. The process to include new modules must be open, peer-reviewed, and well understood.

Group C – Education Workgroup

- a) The community requires a diverse set of expertise to be available to educate and be trained in. This includes: emission engineering, meteorology, computer science, atmospheric chemistry and physics, data analysis, and program and operations management.
- b) Additionally, the community needs to be educated into the impacts on economics, control technologies, risk assessment, population exposure, community and industrial planning, and other environmental concerns.
- c) Good practices in computer science need to be brought to the training program. This includes: systems engineering, database management, programming, graphics/visualization, and system administration.
- d) A thorough program management training must be undertaken that includes: planning and scheduling, science and technology appreciation, resource allocation, communications, and negotiation skill.

- e) Multiple education and training methods must be deployed. Examples include: hands-on, internships, web-based, print, video, satellite, workshops, user groups, and chat rooms.
- f) Various sectors within the community must have better dialog and cross training. These include the scientific, management and practitioner groups, as well as government, industry, environmental, and academia groups.
- g) Guidelines are needed to help establish consistency in personnel skill and training.
- h) Education programs need to be able to expand quickly and be effective to train many users in a relatively short time period.

Group D – Support and Maintenance Workgroup

- a) The CMAS is a common platform for model development and application for both the scientific and regulatory communities.
- b) The system automates as many of the computer operations as practical and makes it easy for code compatibility and code re-use. To the extent possible, CMAS is modular and standardized.
- c) The CMAS is self-documenting and readily available
- d) Acceptability criteria for any change to CMAS will be established. This includes new modules as well as for using in scientific and official regulatory studies.
- e) The CMAS will be supported by a core maintenance group. This group also has responsible for maintaining key databases and datasets that are utilized by the community.
- f) The CMAS and data are open and readily available through several distribution channels.
- g) The core group assigned to maintain the CMAS, implements the procedures for updates, testing and distribution. This include science and computer updates.
- h) The support group is established and overseen by a governing board. The Governing Board is responsible for establishing official policies regarding CMAS and establishing funding support.
- i) Procedures are established by the Board for creating updates to the system and releasing versions for scientific and regulatory use. A proposed schematic linking the institutions involved with CMAS and the procedures that they follow is shown in Figure 1.

Group E - Intellectual Property Workgroup

- a) There are three approaches to making software available that need to be considered: It is accepted that public domain or shareware concept are acceptable only if the code is fully open and accessible.
 - Public Domain: Creator relinquishes all rights to intellectual property and makes software freely available. The code is open.
 - Shareware: Author maintains a copyright on the intellectual property and code but makes it available free or at low cost to promote sharing. The code may be open or closed.
 - Proprietary: The author retains all rights and generally charges a fee for use. The code is usually closed.
- b) The source code for software that affects model results should be available for free. This promotes understanding, review, and trust of the science and its implementation. Related components, such as interfaces and graphical tools, that do not affect the model or

analysis results must be readily available for free or low cost but do not necessarily have to be open.

- c) CMAS tools could also include third party software, such as SAS or Arc/Info, which would remain proprietary. However, regulatory procedures should give a low cost, low resource, alternative.
- d) Value added modules for analysis, graphics, etc. can have license fees, but must be open to scrutiny.
- e) Most credit will be given by reputation and publishing. However, contributed modules should be documented for credit and given proper credit by the users.
- f) There may be liability issues related to deficiencies in best science, bad science, and coding errors. The Governing Board will need to establish procedures for investigating these issues and establishing limits to liability, if any.

Group F - Model Application and Evaluation

- a) The CMAS is managed by a central organization and overseen by a Board of Governors that represents the air quality community stakeholders.
- b) The CMAS center supports, facilitates and maintains the development of a low-cost, open modeling and analysis system. The center does not apply the system.
- c) The CMAS does not preclude outside model developments but serves to promote more involvement in development.
- d) Research interests should be linked to regulatory needs, including time and funding schedules.
- e) All aspects of CMAS must be peer reviewed.
- f) CMAS must be linked to data bases that are readily available, quality controlled and documented. The CMAS management organization can act as a data clearinghouse.
- g) The management center must have sustained support, remain viable, reliable and growing in competence.
- h) In order for applications to be successful, CMAS must provide the following types of tools: a flexible framework, analysis tools, tutorials, technical guidance, and transfer mechanisms such as workshops.
- i) In order for management practices to be improved via a CMAS the following needs must be met: assurance of the best tools, sanctioned regulatory configurations, detailed guidance for use and interpretation, and technical support for all levels.
- j) To improve model evaluation, the CMAS must provide a range of open diagnostic tools that facilitate collaboration. The data and modeled results must be easy to access and with proper guidance, easy to analyze and interpret. Performance evaluation should be understood.

VI. Issues With Implementing a CMAS

There are many obstacles that would prohibit an effective community approach from being implemented, the most obvious being funding support. However, there are many other pressing issues, each of which could inhibit the benefits of a Community Modeling and Analysis System. Whereas, the workshop groups were able to define attributes along six different sets of attributes, the implementation obstacles were much more ubiquitous during

the breakout and plenary discussions. Because of overlap of issues, a consolidated view of the workshops can be presented.

- a) A sustainable funding is critical to achieving a CMAS. To this end, the benefits of a CMAS must be clear and communicated to stakeholders in government, industry, and the public sector. Long term commitments to funding must be identified and put in place. This will be difficult due to funding mechanisms, mix of public and private dollars, and accountability.
- b) A consensus view of the attributes needs to be developed. This will not be straight forward as funding constraints will prevent all attributes from receiving the same attention.
- c) Defining and promoting standards within the community will be difficult. This covers coding and module integration standards.
- d) An agreed upon management structure must be put in place. This includes a Governing Board as well as the CMAS center administration and technical staff.
- e) Guidance and modeling protocols need to be established as to how to utilize a CMAS. This includes guidance for modeling evaluation and peer reviewed acceptance of modules and science.
- f) Setting up a CMAS, management structure, databases, and codes will take time. Additionally, the community will need to change how it performs modeling currently. These changes will take time as well as funds. It is questionable to some whether this resource cost is justified.
- g) The community is accustomed to using certain models and analysis techniques. Establishing credibility for a flexible system will be difficult. The community would need to establish an evaluation program that meets a consensus view of acceptance.

VII. Recommendations

There is general agreement that the benefits of a community modeling system are significant enough to warrant further study and defining. The main recommendation is to form a group of writers to put together a first proposal. This initial draft proposal needs to outline how a Community Modeling and Analysis System can be funded, managed, and leads to improved science and decision practices. The proposal needs to clarify the following points.

- a) Clearly define the CMAS for all to understand.
- b) Clarify the benefits to the various stakeholder groups.
- c) Propose a detailed funding proposal that shows costs to implement and sustain a CMAS Center and future developments. This includes the number and type of positions required and their reporting structure.
- d) Clarify how the development cycles of the regulatory and scientific versions of the community system will work together to assure the best science availability on regulatory timeframes.
- e) Outline how the CMAS would be applied within guidelines, peer reviewed procedures, that enable the best application practices.

- f) Clarify the peer review checks for the science, the CMAS developments, regulatory recommendations, and application guidance.
- g) Clarify potential legal issues involving intellectual property and liability.

It is highly recommended that progress towards defining a CMAS be made quickly and systematically. To this end, the following recommendation are made:

- (a) Groups that have responsibility for achieving progress with Clean Air Act compliance must be briefed about the CMAS proposal. Their buy-in to the concept is extremely important. These institutions include the EPA's Office of Air Quality Planning and Standards (OAQPS), industry and other stakeholder communities, State environmental groups, consultant groups, and academia. These groups must be made aware of the benefits of a community approach and how it would work.
- (b) The Federal Advisory Committee (FACA) looking at new approaches to achieving national air quality standards needs to be briefed about CMAS. FACA should provide guidance as to the needs for a CMAS.
- (c) An outline of the CMAS proposal needs to be circulated as soon as practical to get a wider acceptance to the proposal needs of the community. Accompanying this outline should be a proposal for gaining community buy-in.
- (d) A full proposal outlined above must to be circulated within a wide community audience. The community should have time to comment to the proposal whereby and final proposal to establish a CMAS be written.
- (e) A workshop should be considered for the spring of 1998 that will examine and debate the merits of a CMAS, its feasibility, and funding. The outcome of the workshop would be targeted at gaining a community go or no-go decision and commitments.

Establishing a Community Modeling Capability

Kenneth Galluppi
University of North Carolina at Chapel Hill

Summary of the Air Quality Community
Modeling and Analyze System Workshop
August 27-29, 1997

What is a Community Model and Analysis System (CMAS)?

- Leverage community-wide talents for development and application of modeling and analysis.
- CMAS is computer framework for integrating "best" tools and knowledge.
- Available to all for operational and research needs.

Benefits of CMAS

- Less resources to develop and maintain and evaluate.
- Regulatory and research needs are satisfied and complement one another.
- Operational needs for maintenance and training are a priority.
- Consistency.
- Peer reviewed for all purposes.

CMAS Workshop Groups

- Science
- Environmental Management
- Education and Training
- Support and Maintenance
- Intellectual Property
- Model Applications and Evaluation

Science Workgroup

- Regional and urban scaled problems, for multiple pollutant (O₃, aerosol, acid dep.)
- Usable by science, management and stakeholders.
- Peer reviewed.
- Processes that get to the causes.
- Accommodates robust analysis and alternate formulations.

Environmental Management

- Consistency of formulation and use.
- Decision enhancing analysis.
- High level of quality control.
- Linked to risk-assessment, and other decision making parameters.
- Responsive to regulatory time constraints.
- Facilitate communications.
- Documented, open, no (low)-cost.

Education Workgroup

- Diverse levels of education/training needed: management to practitioner, cross-disciplines including computers.
- Many forms of training to meet all needs.
- Guidelines for training to establish consistency in knowledge and application.
- Timely and affordable.
- Education to link to decisions and impacts.

Intellectual Property Workgroup

- Give proper credit where credit is due.
- Open, peer reviewed and
- Free if it impacts science results, may charge for value added modules, but open.
- If community "owned," are there liability issues?

Support and Maintenance

- Modular, standardized, oriented for code re-use. This includes inputs and analysis tools.
- Well maintained and documented.
- Procedures for making changes and acceptance for scientific and regulatory use.
- Core support group is maintained and overseen by a board.

Application and Evaluation

- Central organization overseen by a Board.
- Maintenance, QA, and training are critical.
- Peer review everything in appli. and eval.
- Facilitate application and developments of an open system but remain neutral.
- Assure best tools, sanctioned versions, guidance for use and interpretation.
- Good set of tools and facilitated collab.

Difficult Issues

- Sustainable funding for support and maint.
- Consensus view of attributes given funding.
- Design and promoting standards is hard.
- Management structure.
- Guidance and modeling protocols a MUST.
- Setting up CMAS takes time and money.
- Establish credibility for flexible approach.

Recommendation for CMAS

- Clarify CMAS and its benefits.
- Detail funding requirements.
- Clarify development and "locking" of science and regulatory versions.
- Guidance procedures for application, peer review, and evaluation.
- Clarify legal issues of a "community" model

ABSTRACT

Emissions Modeling Issues for Reactivity Calculations: State and Status of the Sparse Matrix Operator Kernel Emissions (SMOKE) Modeling System.

Neil Wheeler
Environmental Programs
North Carolina Supercomputing Center

There are a number of scientific and operational criteria for emissions modeling systems to support the use of photochemical grid models to calculate VOC reactivity. These include:

1. The flexibility to support high-resolution chemical mechanisms that are continually changing.
2. The ability to validate that the emissions modeling system is the same as used by other parties.
3. The ability to validate that new mechanisms are properly represented in the emissions modeling system.
4. Sufficient processing speed to allow for the development of multiple emission scenarios, for moderate to long episodes, and potentially complex (large) chemical mechanisms.
5. Designed to be integrated with state-of-the-science meteorological models, photochemical grid models, and analysis tools.
6. Be reasonably easy to use and have a base of technical support for maintenance, technology transfer, and user training.

In this presentation these criteria are discussed in further detail in the context of the Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system. SMOKE was developed as a research prototype for high performance emissions processing under a USEPA cooperative agreement. It has evolved into an operational emissions modeling system under funding from various state and federal agencies. The current state of SMOKE and other currently used emissions modeling/processing systems, and what is needed for each of these systems to support reactivity calculation will be discussed.

Emissions Modeling Issues for Reactivity Calculations

**State and Status of the Sparse Matrix
Operator Kernel Emissions (SMOKE)
Modeling System**

Neil Wheeler

**North Carolina Supercomputing Center
Environmental Programs
Research Triangle Park, NC**



North Carolina Supercomputing Center

Emissions Modeling Issues

- **Flexibility**
- **Validation**
- **Speed**
- **Integration**
- **Ease of Use**
- **Technical Support**



North Carolina Supercomputing Center

Flexibility

**The flexibility to support high-resolution
chemical mechanisms that are
continually changing**



System Validation

**The ability to validate that the emissions
modeling system being used is the same
as used by other parties**



Mechanism Validation

The ability to validate that new mechanisms are properly represented in the emissions modeling system



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Processing Speed

The need for sufficient processing speed to allow for the development of multiple scenarios, for moderate to long episodes, and potentially complex (large) chemical mechanisms



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Integration

Designed to be integrated with state-of-the-science meteorological models, photochemical grid models, and analysis tools

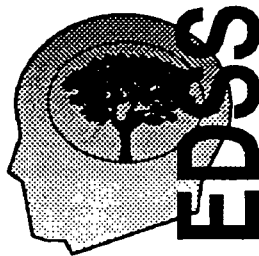


Ease of Use and Support

The system must be reasonably easy to use and have a base of technical support for maintenance, technology transfer, and user training



Sparse Matrix Operator Kernel Emissions (SMOKE) Modeling System



North Carolina Supercomputing Center

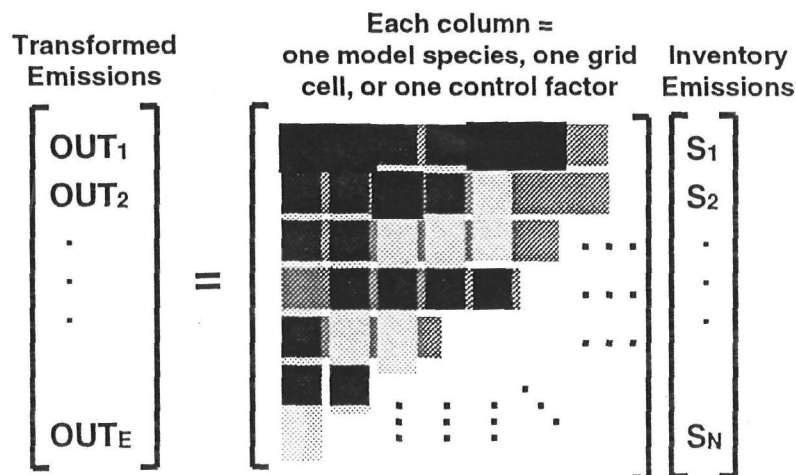
SMOKE - Concepts

- **Traditional Emissions Processing Paradigms**
 - Self-contained records describing sources
 - Admirably suited to 1970's-vintage machines with minuscule available memories and tape-only storage
 - Passing of redundant data
 - No exposed parallelism
- **Factor based tasks - linear matrix operations**
- **Sparse matrices**
- **Re-arrange the order of multiplications to avoid redundant computations**
- **Uses the Models-3/EDSS I/O API**
- **Integrated within EDSS**



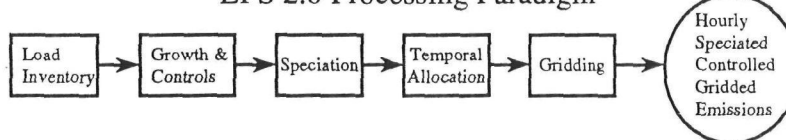
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SMOKE Sparse Matrices

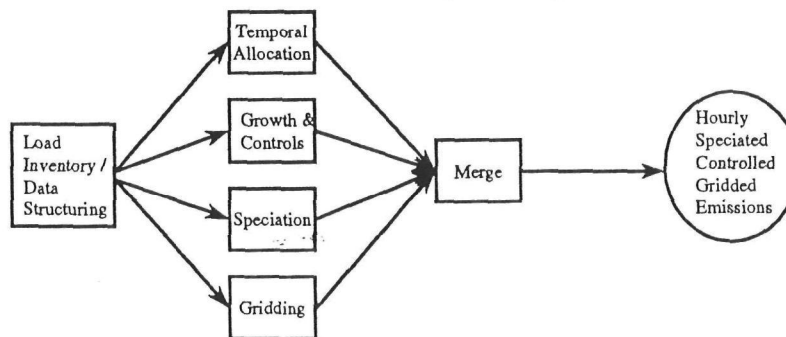


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EPS 2.0 Processing Paradigm

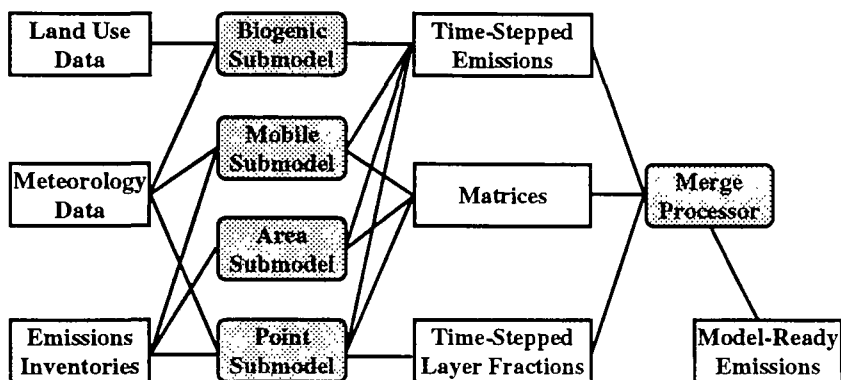


SMOKE Processing Paradigm



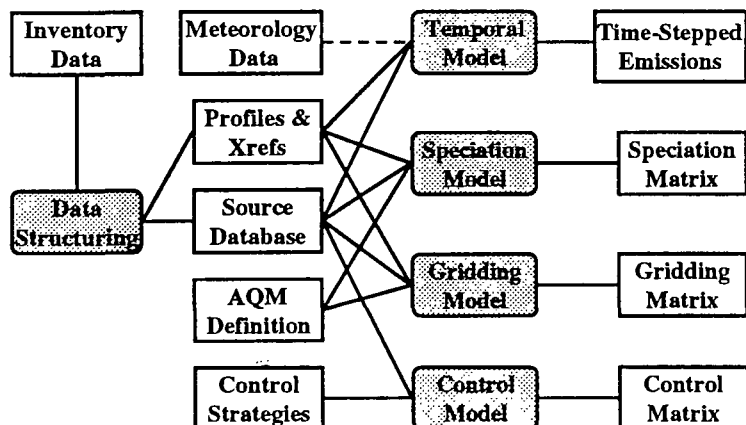
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SMOKE Submodels and Dataflows



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Structure of SMOKE Submodels



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SMOKE Features

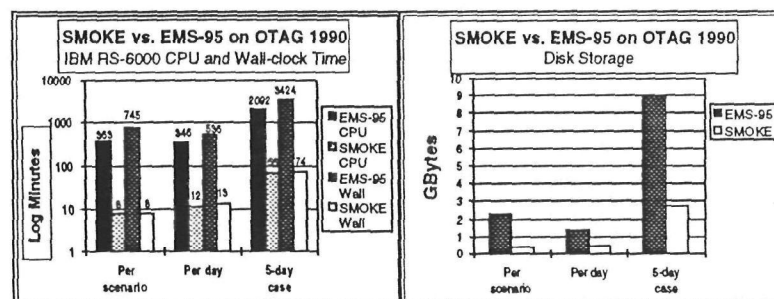
- Inputs: EPS 2.0 or EMS-95
- Outputs:
 - Models-3 (CMAQ) / EDSS (MAQSIP)
 - UAM-IV / UAM-V / CAMx
 - SAQM with converter
- Machine Independent I/O API (M-3/EDSS)
- Multi-day runs
- Approximately 30 times faster than EPS or EMS-95
- 70% less disk space than EMS-95



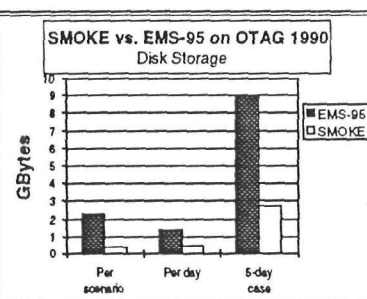
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SMOKE

Speed



Disk Space



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Status of SMOKE

- Operational Prototype
- Validation
 - EMS-95 (OTAG)
 - EPS 2.0 (North Carolina)
 - BEIS2
- Current Applications
 - Season Model for Regional Air Quality (SMRAQ)
 - North Carolina Regional and Urban Modeling
- Availability
 - Publicly released February 1998
 - <http://envpro.ncsc.org/products/smoke>



SMOKE - Future Needs

- Enhanced support for new species
- Enhanced sorting of profiles/cross references
- Run-Time Dimensioning
- Control-Related Enhancements
- Enhanced Error Handling
- Integration with a Chemical Mechanism Reader
- Enhanced Quality Assurance
- Improved User Interface
- Improved input format
- Integration with inventory development



Work Plans and Level of Effort



Further Information

**Neil Wheeler
(919) 248-1819
wheeler@ncsc.org**

**<http://envpro.ncsc.org>
<http://envpro.ncsc.org/EDSS/>
<http://envpro.ncsc.org/products/smoke/>**



Scientific and Operational Criteria for the Use of Eulerian Models to Compute Reactivities

May 12, 1998

U.S. EPA
Photochemical Reactivity Workshop
Regal University Hotel
Durham, NC

Harvey Jeffries
Environmental Sciences and Engineering
University of North Carolina
Chapel Hill, NC

Scientific and Operational Criteria

Background

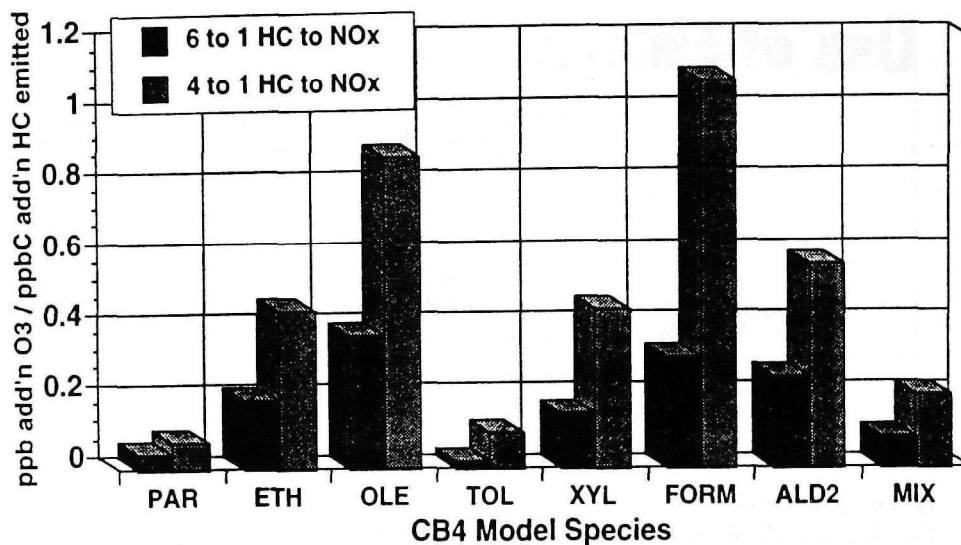
“Reactivity” is a sensitivity, or change in a system’s state relative to a change in the system’s input.

It has been clearly established from theory and experimental evidence that:

The reactivity of an organic compound in the atmosphere is a strong function of both the compound’s unique properties and the conditions of the ambient environment in which it is reacting.

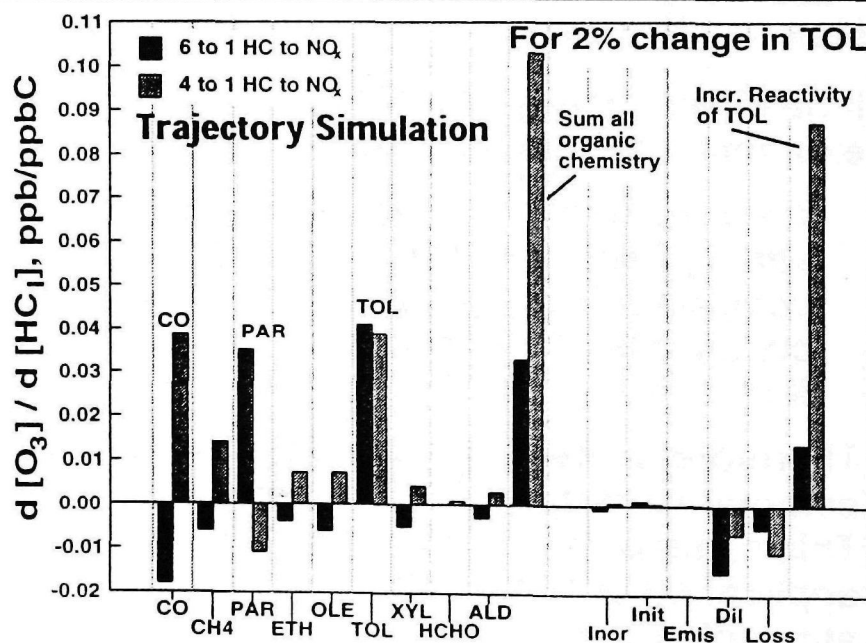
Therefore, there is not a single reactivity per compound, but instead a continuum of reactivities. This same phenomenon prevents the direct application of “smog chamber” reactivities to the atmosphere.

Peak Ozone Sensitivity



Harvey Jeffries

All VOCs Contribute To O₃



Harvey Jeffries

Background, cont.

Such understanding raises questions about the use of a “bright-line” test or about a “national exemption”.

Basil Dimitriadis described this problem as,

All these methods of using the reactivity concept in regulatory organic emissions programs have varying merits and difficulties.

Scientific issues associated with obtaining a valid, acceptably accurate measure of an organic compound's reactivity presents a common difficulty.

Background, cont.

Given the newest national standards and goals, focusing only on role of VOCs in ozone formation is not acceptable.

Instead, VOC reactivity needs to be expanded to include the atmospheric compositional effects that a VOC would have on:

- Peak one-hour ozone and 8-hour ozone
- PM_{2.5} formation
- Regional Haze
- HAPS formation
- Nitrate deposition

Conceptual Model of VOC reactivity shows complexity

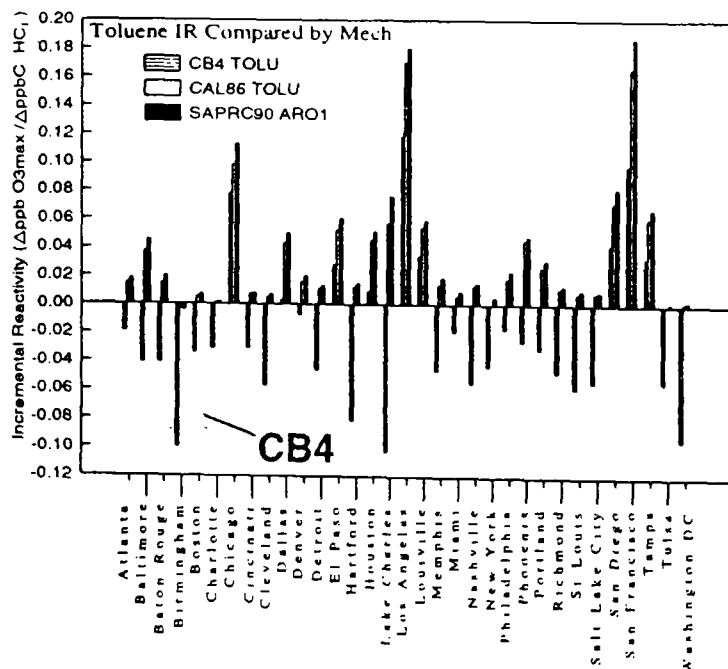
Background, cont.

Previous efforts to deal with this complexity have centered around trying to find “standard conditions” which would ideally produce a “universal reactivity scale”, for example, manipulate ambient NO_x conditions, to produce maximum ozone response (the MIR scale). To use these scales for policy, one must argue their relevance to natural-use environments.

An alternative method is to assess all impacts of a real-world VOC emissions change scenario for a set of well-simulated regional and urban conditions and to include the VOC's projected use conditions.

Modern, community-based Eulerian Air Quality Models can meet these requirements.

Different Mechanisms, Different Sensitivities

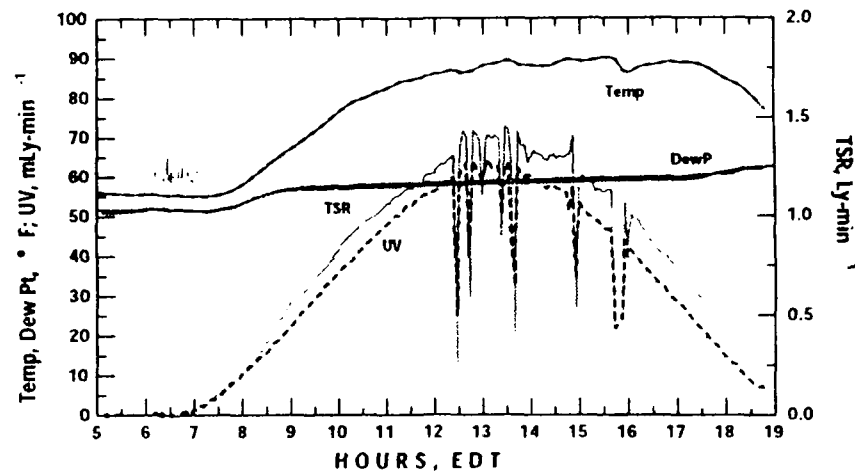
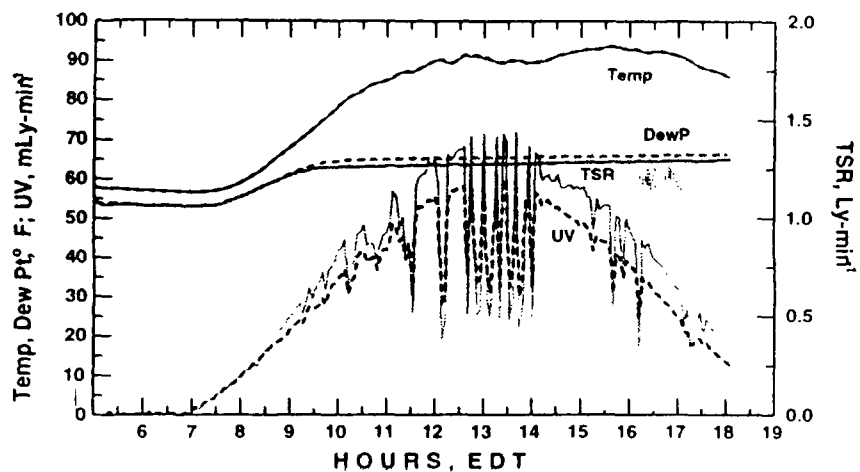
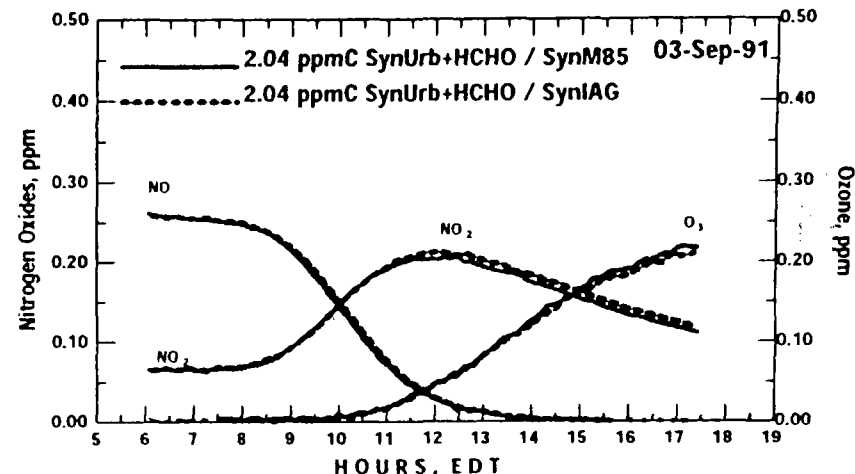
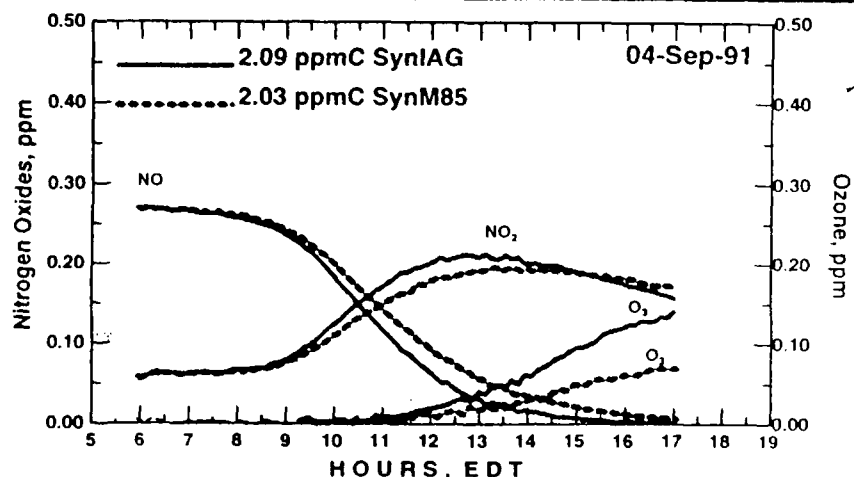


Harvey Jeffries

M85 Less Reactive Than Ind.Avg.Gasoline

...But, Not When Mixed with Urban Air

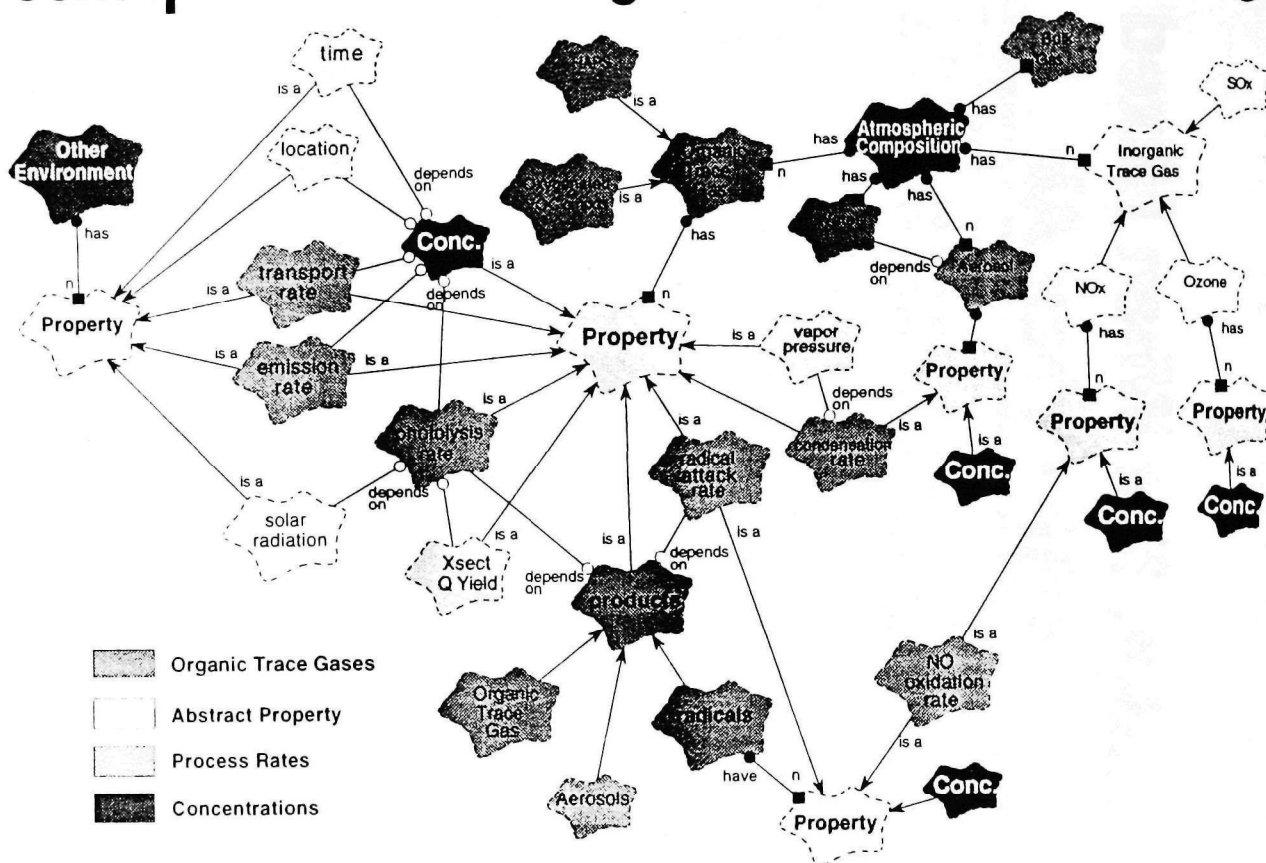
2-89



Harvey Jeffries

Harvey Jeffries

Conceptual Model of Organic Trace Gas Reactivity



see 4-100 and Operational Criteria

Purpose

To identify and describe the attributes of a modeling system that can compute a VOC's (or a mixture of VOCs') impacts on atmospheric composition.

To compare these attributes with those of existing modeling systems.

To identify significant work that needs to be done to use this modeling system to evaluate possible strategies that incorporate VOC reactivity.

Components

Simulate Target VOC's Chemistry

**Simulate Target VOC's Emissions
(also Replaced VOC's Emissions)**

**Simulate Environments including
Target VOC**

**Evaluate Atm. Compositional
Changes**

I will discuss each of these in detail.

AT-0002

Technical and Operational Criteria

Simulate VOC Chemistry

All reactivity calculations require the use a chemical simulation model to establish the radical and chemical environment in which the VOC reacts.

If the reaction mechanism and reaction parameters for the target VOC are not available, a kinetics and chamber study must be undertaken to produce these items. This would be the responsibility of the party wanting to assess the reactivity of the target VOC.

This target VOC chemistry must be integrated with a chemical reaction mechanism for the regional and urban atmospheric environment.

Particle and HAPS formation are new data requirements.

AT-0002

Simulate VOC Emissions

To have accurate estimates of a target VOC's effects on atmospheric composition, we must have a accurate simulation of the emissions of the VOC, resolved in both space and time within the test domains. This would also be the responsibility of the party wanting to assess the reactivity of the target VOC.

Further, the expected growth in emissions over the requested deferment period must be provided. In addition, the decrease in any displaced emissions already in the existing base and future case model inventories must be specified.

North Carolina

Scientific and Operational Criteria

Simulate Environments

Eulerian models permit our most advanced and most accurate simulations of urban, regional, and global atmospheric chemical environments.

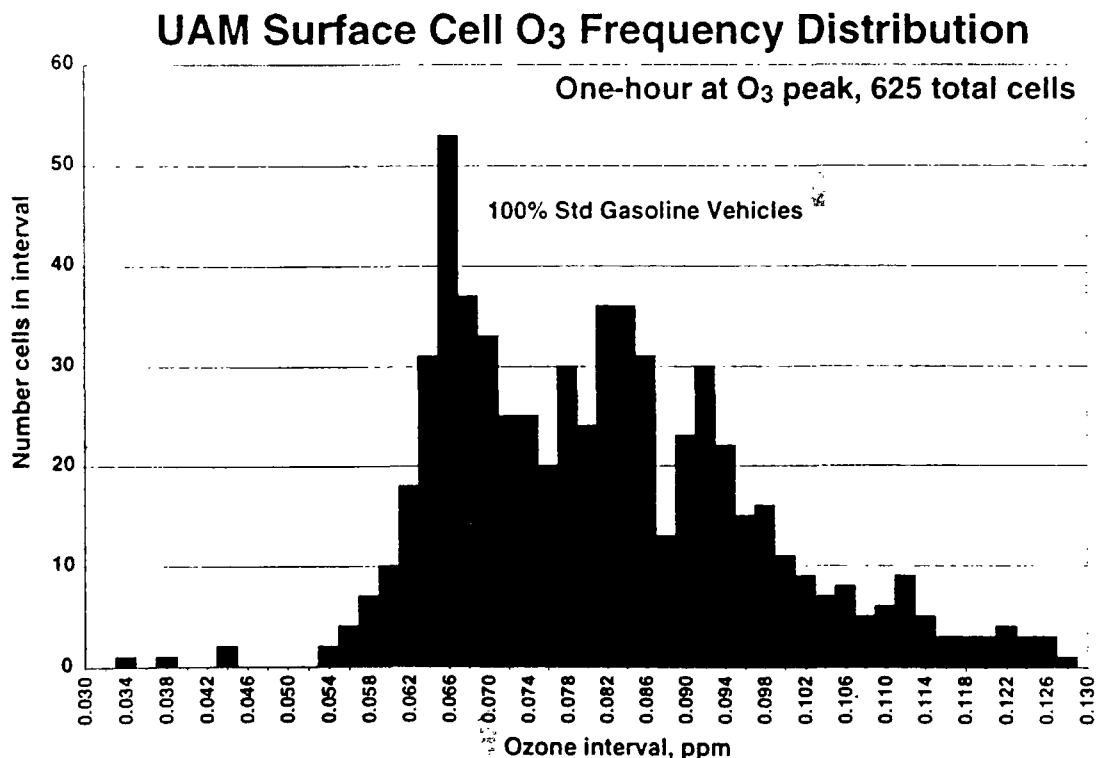
For reactivity assessments, we want to perform “best operational practice” model simulations of 3 to 5 “well-simulated” and “well-understood” regional and urban domain test cases. Ideally, a test case that represents a significant market for the target VOC would be included.

The responsibility for the creation and maintenance of these test cases rests with the EPA and the States. States and industries share responsibility to run tests.

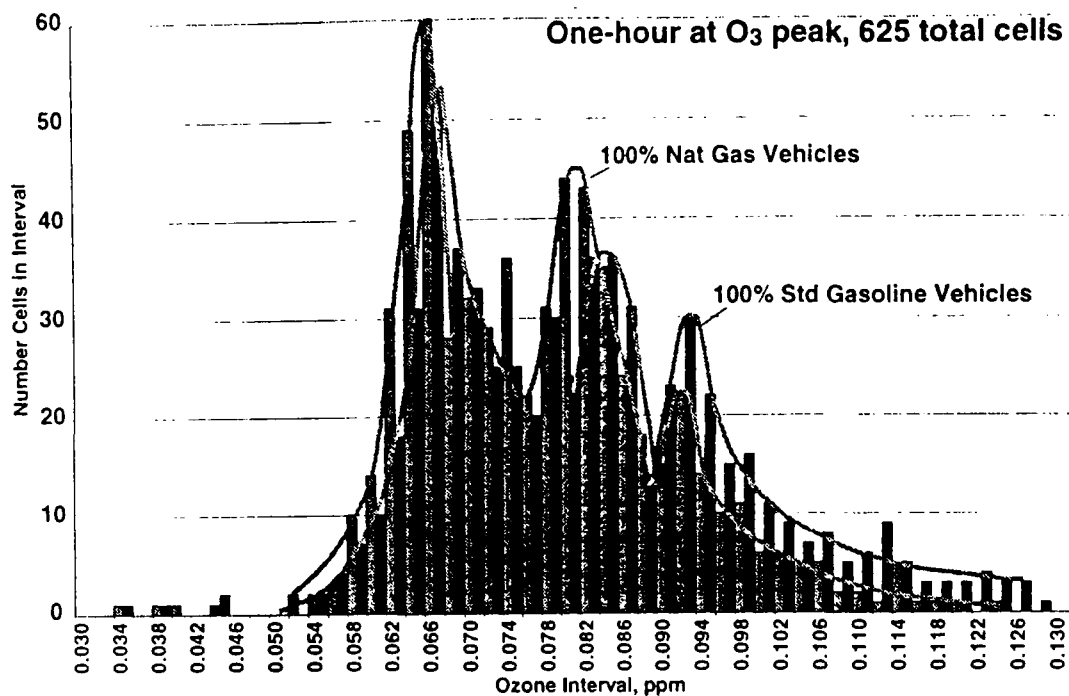
Evaluate Simulation Results

A variety of ways exist to assess atmospheric compositional impacts. I prefer those that indicate the entire range of results, e.g., changes in frequency of predicted concentrations. (Need some example results to test meaningful ways of analysis).

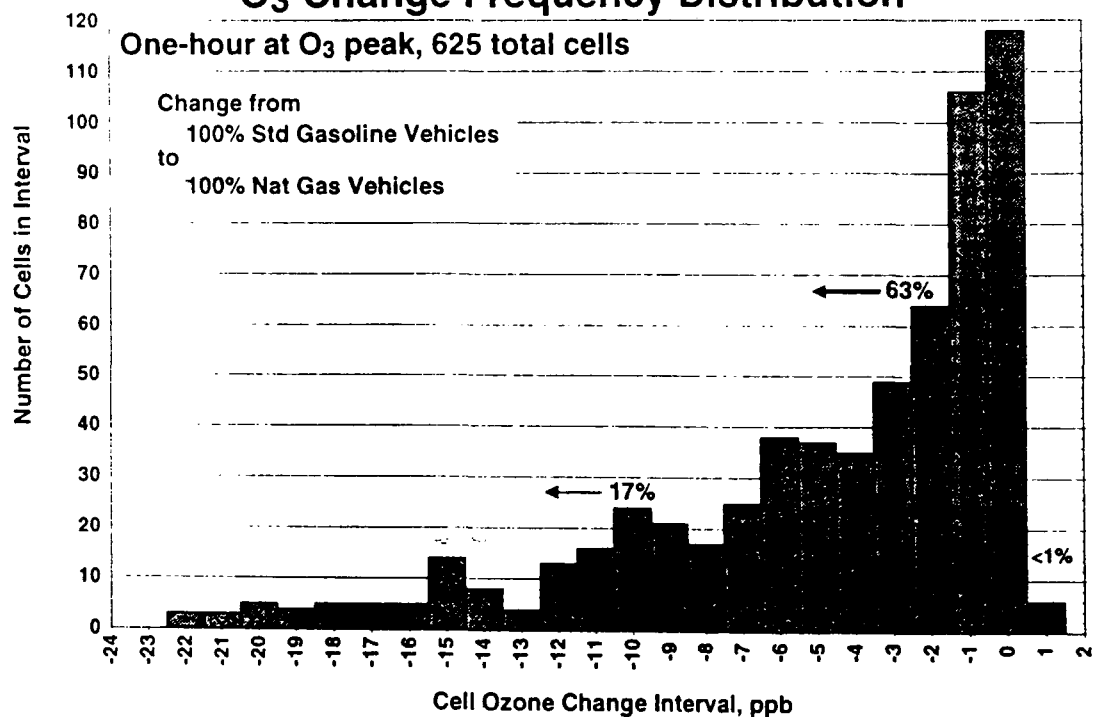
.The impact could be classified as:
 always negative impact outcomes
 non-detectable outcomes
 always positive impact outcomes, and
 mixture of outcomes.



UAM Surface Cell O₃ Frequency Distribution



UAM Surface Cell O₃ Change Frequency Distribution



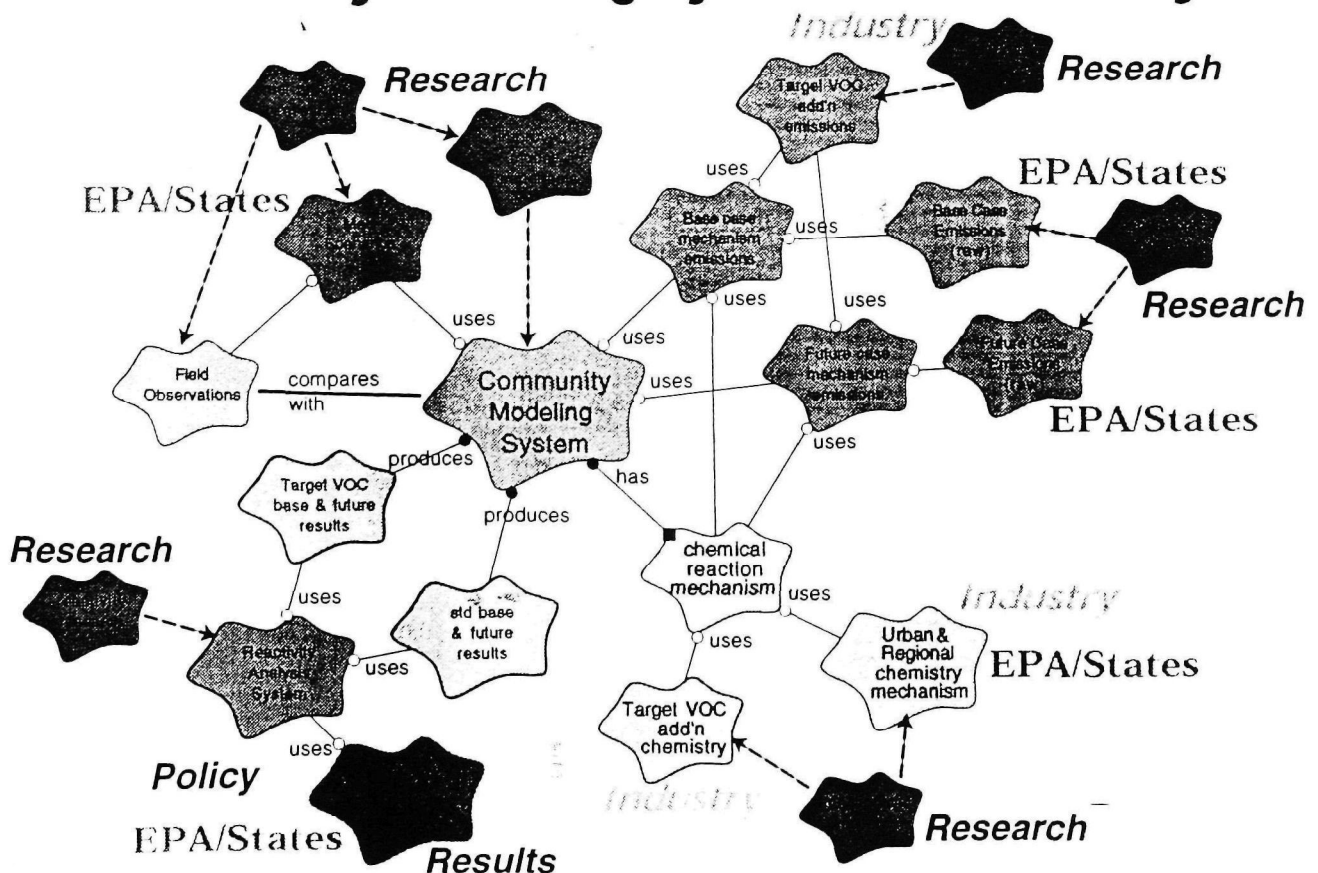
Evaluate Results, cont.

For always negative outcomes, the “proposed use” should not be permitted and the VOC should be controlled.

For non-detectable and always positive outcomes, the “proposed use” should be permitted for a renewable, fixed-time period.

For a mixture of outcomes, the “proposed use” might be permitted for a renewable, fixed-time period, if the adverse effects are “tolerably small” compared to the costs and other societal benefits.

Community Modeling System for Reactivity



Work Needed

Major Research Topics

Fundamental VOC chemistry, target VOC chemistry, analytical methods, synthesis of products for further testing, better coordinated observations for challenging models, ambient measurement of VOC products.

Major Modeling System Improvements

Rapid emissions processing system, sensitivity computational subsystem, reactivity results display and analysis system.

Major Modeling Data Set Needs

Nested-grid, regional and urban emissions inventories, nested-grid regional and urban meteorological scenarios.

Education and Technology Transfer Needs

Full educational and reactivity modeling technology transfer package, support for a Community Modeling User's Group.

February 1993

Work Needed

Major Research Topics

1. Chemistry of major organic classes in regional and urban air are still uncertain and require further research work to determine reaction products and pathways.
2. Chemistry of targeted VOCs most likely not well known and will require further laboratory and chamber study to determine reaction products and pathways.
3. Items 1 and 2 require advances in analytical methods for multi-functional products.
4. Items 1 and 2 require synthesis of gram quantities of stable intermediate oxidation products to permit positive identification, calibration, and for important parameters (e.g., rate constants, absorption cross sections) to be determined.
5. Observed meteorological and chemical data are still weak at challenging modeling predictions and improvements in *sets* and *combinations* of observations are needed to evaluate models more fully.
6. More ambient measurements of oxygenated VOCs and reaction products are needed to confirm model predictions.

Major Modeling System Improvements

1. A community-based, rapid emissions processing system that accommodates easy changes in source specification and that improves on spatial and temporal allocation is needed. System also needs to accommodate new variable parameter reaction mechanisms such as Carter's SAPRC computed stoichiometry and Jeffries' morpheus reaction mechanisms. System should also provide for costs and savings of various reactivity-related control programs.
2. A community-based model sensitivity computational subsystem needs to be integrated into the Community Air Quality Model that will permit rapid generation of model sensitivities to emissions and parameter changes. This will aid in the exploration of a large number of reactivity-based control measures without requiring large amounts of computational time.
3. A community-based reactivity results display and analysis system is needed that manages the post-processing of model results generated as part of a reactivity scenario. This system can also produce output relevant to policymakers needs.

Major Modeling Data Set Needs

1. Nested-grid, regional and urban emissions inventories suitable for reactivity analysis.
2. Nested-grid, regional and urban meteorological scenarios that span 6—15 days for NE, SE, TX, CA, and other local areas.

Education and Technology Transfer Needs

1. Manuals, short test simulations, software installation guides are needed. A series of short training courses for industrial, state, and local regulators are need.
2. Support for a Community Modeling User's Group.

CLEAN AIR ACT 1990

SECTION 183(e)

(2) STUDY AND REPORT —

(A) STUDY.—The Administrator shall conduct a study of the emissions of volatile organic compounds into the ambient air from consumer and commercial products (or any combination thereof) in order to—

(i) determine their potential to contribute to ozone levels which violate the national ambient air quality standard for ozone; and...

REQUIREMENTS OF 183(e)—

1. Ambient air validity
2. Contribution to ozone levels that violate the NAAQS
 - A. Includes from 80 ppbv O₃ and up
 - B. Includes ambient availability, not just content
3. Determine potential

“INCREMENTAL REACTIVITY FOR THE PAINT INDUSTRY”

PRESENTATION TO:

EPA PHOTOCHEMICAL REACTIVITY WORKSHOP



May 12-14, 1998

Durham, North Carolina

By

Edward D. Edwards, *Ownership*

Robert Wendoll, *Director of Environmental Affairs*

DUNN-EDWARDS CORPORATION

CLEAN AIR ACT 1990

SECTION 183(e)

(3) REGULATIONS TO REQUIRE EMISSION REDUCTIONS.—

(A) IN GENERAL.—Upon submission of the final report under paragraph (2), the Administrator shall list those categories of consumer or commercial products that the Administrator determines, based on the study, account for at least 80 percent of the VOC emissions, on a reactivity-adjusted basis, from consumer or commercial products in areas that violate the NAAQS for ozone.

COMMENTS:

This section requires analysis of regulations on the same reactivity adjusted basis that matches the study.

OZONE FORMATION POTENTIAL OF VARIOUS VOCs

A useful definition of reactivity is that of incremental reactivity, defined as the amount of ozone formed per unit amount (as carbon) of VOC added to a VOC mixture representative of conditions in urban and rural areas in a given air mass (Dodge, 1984; Carter and Atkinson, 1987, 1989b; Carter, 1991),

$$\text{Incremental reactivity} = \frac{\Delta[\text{ozone}]}{\Delta[\text{VOC}]}$$

where $\Delta[\text{ozone}]$ is the change in the amount of ozone formed as a result of the change in the amount of organic present, $\Delta[\text{VOC}]$ (note that Carter and Atkinson [1989b] used the quantity $\Delta[\text{ozone}] - [\text{NO}]$) rather than $\Delta[\text{ozone}]$ under conditions where the maximum ozone was not attained and NO was not fully consumed). This concept of incremental reactivity corresponds closely to control strategy conditions, in that the effects of reducing the emission of a VOC or group of VOCs, or of replacing a VOC or group of VOCs with other VOCs, on the ozone-forming potential of complex mixture of VOC emissions are simulated.

—Source: *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, A Report to Congress, 1992, The National Academy of Sciences, pps. 153-154

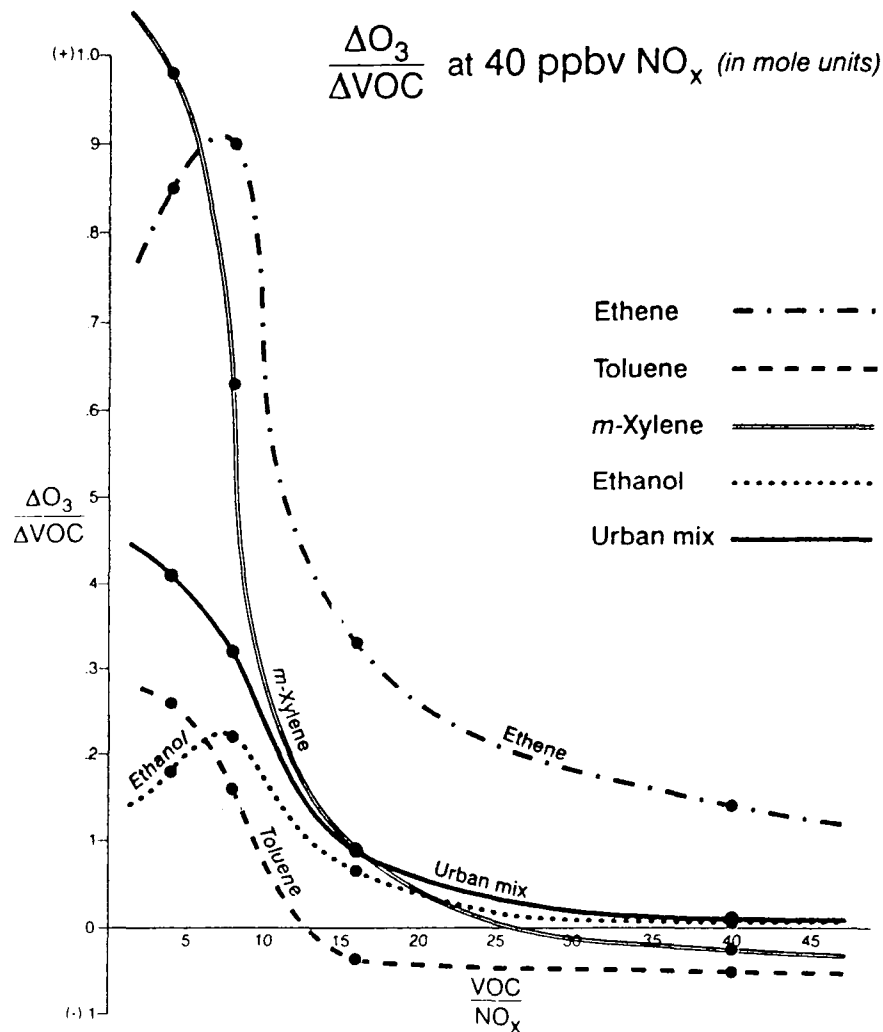
TABLE 5-4 Calculated Incremental Reactivities of CO and Selected VOCs as a Function of the VOC/NO_x Ratio for an Eight-Component VOC Mix and Low-Dilution Conditions

Compound	VOC/NO _x , ppbC/ppb			
	4	8	16	40
Carbon monoxide	0.011	0.022	0.012	0.005
Ethane	0.024	0.041	0.018	0.007
<i>n</i> -Butane	0.10	0.16	0.069	0.019
<i>n</i> -Octane	0.068	0.12	0.027	-0.031
Ethene	0.85	0.90	0.33	0.14
Propene	1.28	1.03	0.39	0.14
<i>trans</i> -2-Butene	1.42	0.97	0.31	0.054
Benzene	0.038	0.033	-0.002	-0.002
Toluene	0.26	0.16	-0.036	-0.051
<i>m</i> -Xylene	0.98	0.63	0.091	-0.025
Formaldehyde	2.42	1.20	0.32	0.051
Acetaldehyde	1.34	0.83	0.29	0.098
Benzaldehyde	-0.11	-0.27	-0.40	-0.40
Methanol	0.12	0.17	0.066	0.029
Ethanol	0.18	0.22	0.065	0.006
Urban mix ^a	0.41	0.32	0.088	0.011

^aEight-component VOC mix used to simulate VOC emissions in an urban area in the calculations. Surrogate composition, in units of ppb compound per ppbC surrogate, was ethene, 0.025; propene, 0.0167; *n*-butane, 0.0375; *n*-pentane, 0.0400; isooctane, 0.0188; toluene, 0.0179; *m*-xylene, 0.0156; formaldehyde, 0.0375; and inert constituents, 0.113.

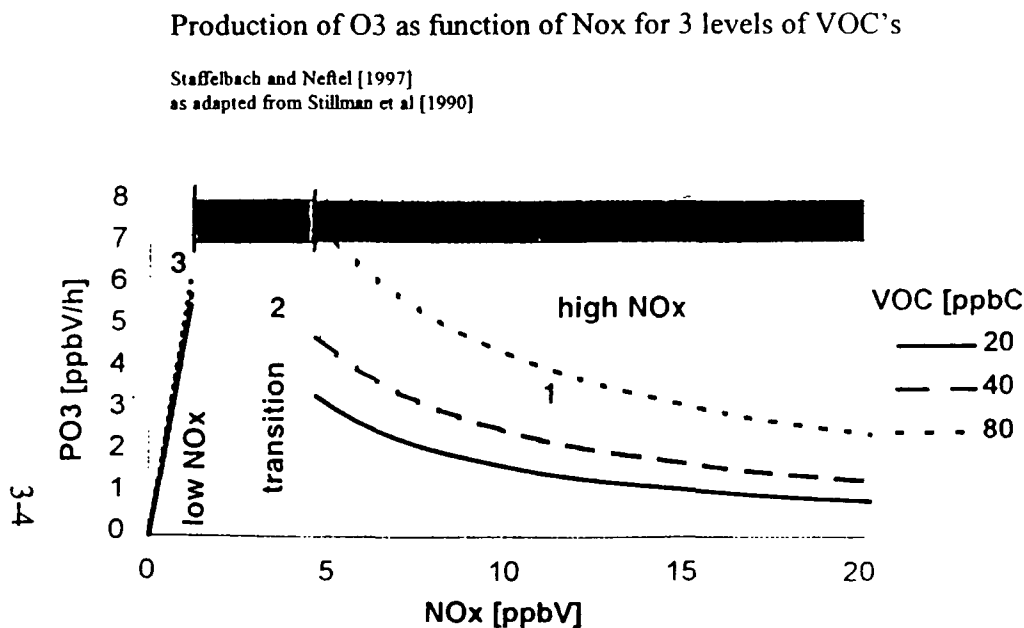
Source: Adapted from Carter and Atkinson (1989b).

Calculated Incremental Reactivities



Source: Adapted from Carter and Atkinson (1989)

From: *Rethinking the Ozone Problem in Urban and Regional Air Pollution*



For Incremental Reactivity,

We need to look at both slopes and the transition area

Species data must be from ambient air shed chamber work

This yields production and loss as incremental reactivity,
not mechanistic reactivity

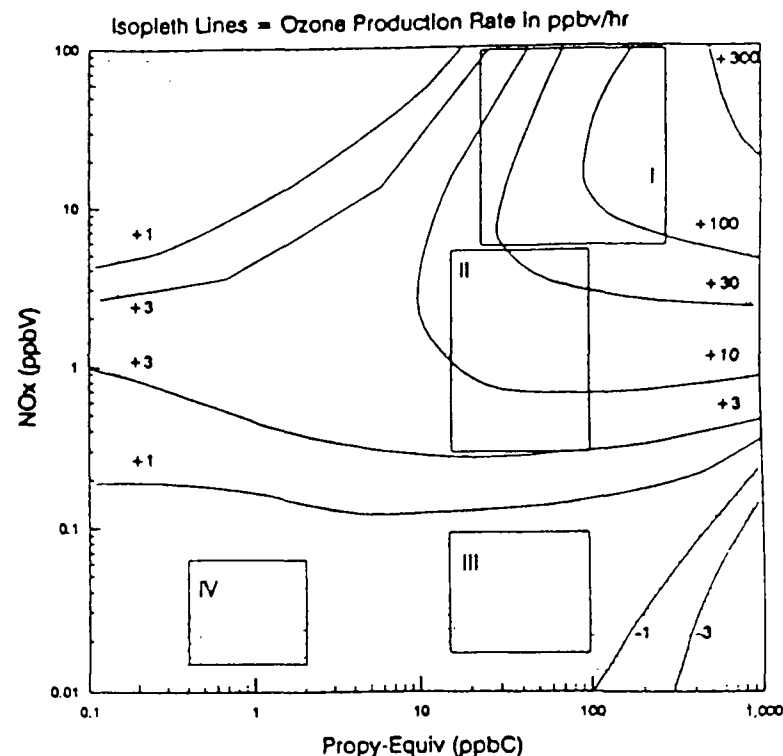
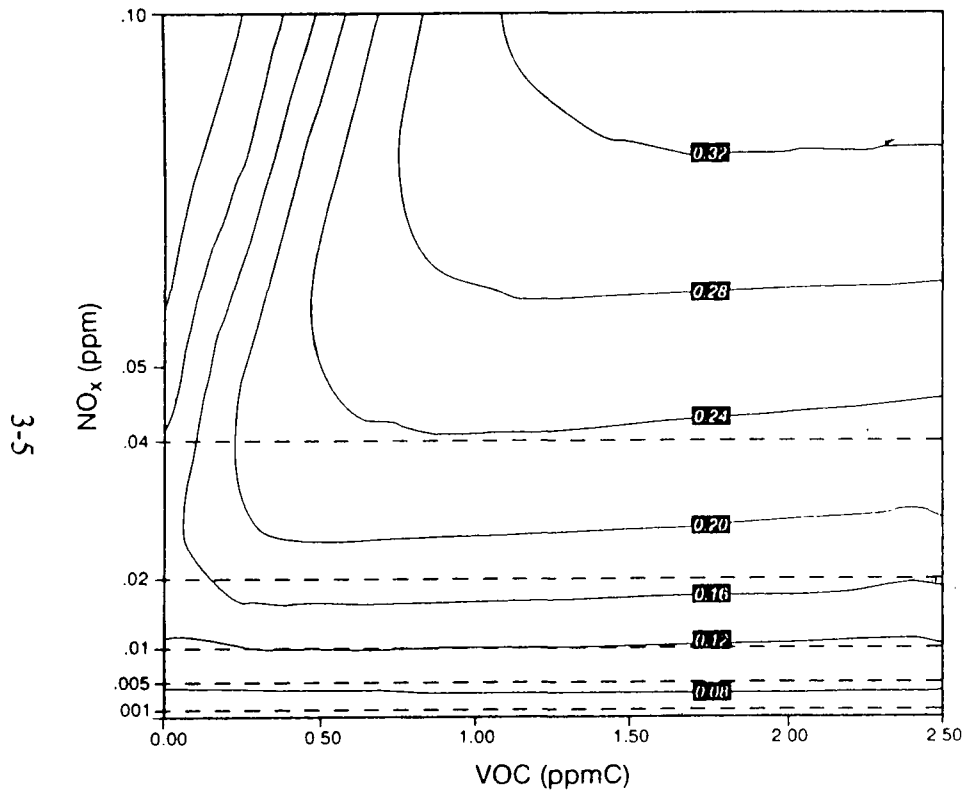


Fig. 16. Summary of hydrocarbon/NO_x regimes. The four rectangles indicate the typical total [Propy-Equiv]_{surf} and NO_x concentration ranges observed at I, urban/suburban sites; II, rural sites in the eastern United States; III, remote sites in the tropical forests of Brazil; and IV, remote sites in the marine boundary layer. Isopleth lines are used to indicate model-calculated net rates of ozone photochemical production (in units of ppbv per hour) at midday as a function of assumed NO_x and propylene concentrations. The calculations were carried out using the photochemical box model and methodology described by Chameides et al. [1987] with rate constants from Gery et al. [1989] and DeMore et al. [1990]. The model adopted a temperature of 290 K, a dew point of 285 K, a solar zenith angle of 30°, a CO concentration of 85 ppbv, a CH₄ concentration of 1.85 ppmv, and an O₃ concentration of 25 ppbv. The shaded area in the figure denotes the concentration regions for which photochemical processes were calculated to produce a net loss of ozone.

Suggested NO_x levels for Incremental Reactivities Chamber Studies Simulating Ambient Air



• The dotted lines indicate the following NO_x levels: .001, .005, .01, .02, & .04

Source: FW. Lurmann, Sonoma Technology, Santa Rosa, Calif. (1990)
From *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, Figure 6-2 page 171

INCREMENTAL REACTIVITY

1. Can reasonably simulate ambient air with appropriate chamber work.
2. Is based upon measured ozone forming potential of VOCs in simulated ambient air.
3. Determines a VOC's "contribution to levels that violate the NAAQS" for all ozone levels required by NAAQS starting at 80 ppbv (8-hour average).
4. Is speciated.
5. Can validate the slopes of ozone isopleths generated by SIP model.
6. Can be used to validate a SIP modeling process that simulates attainment at two points rather than the current one point method.
7. Can distinguish between naturally clean air and ozone attainment that results from VOC reductions only (important to determining ozone transport potential).
8. Provides BRIGHT LINE regulatory distinction by VOC species by air shed.

9. Provides PALE LINE regulatory distinction by VOC species by air shed to reduce overall reactivity.
10. Provides improved graphical basis for decision between VOC + NO_x controls vs. NO_x only controls.
11. Can be validated for all air sheds.
12. Provides for seasonal control strategies through temperature and sunlight variables.
13. Provides for speciated VOC regulation that declines as reactivities reach zero or become negative.
14. Reduces the discrepancy between container VOC content and reactive emissions to allow one adjustment factor by product type.
15. Fits into a CTG framework.
16. Is better than a preemptive Federal approach.

PROPOSAL AND REQUIREMENTS

1. Requires a new large chamber available to Government, Industry and Academia
2. Chamber to be built that meets the requirements of the CAA of 1990 Section 183(e)
3. A reactivity engine and a peak 1 hr/ 8 hr simulator that are in public domain and the best currently available
4. Support by one or more major regional or local Air Management Districts
5. Support by Paint Companies affected by the District(s)
6. A peer reviewed process developed under NARSTO
7. Joint Funding by Districts, Government and Industry
8. EPA incorporate Incremental Reactivity into the SIP process

CLEAN AIR ACT 1990

SECTION 183(e)

(3) REGULATIONS TO REQUIRE EMISSION REDUCTIONS.—

(C) USE OF CTGS.—For any consumer or commercial product the Administer may issue control techniques guidelines under this Act in lieu of regulations required under subparagraph (A) if the Administrator determines that such guidance will be substantially as effective as regulations in reducing emissions of volatile organic compounds which contribute to ozone levels in areas which violate the national ambient air quality standard for ozone.

COMMENTS:

Incremental reactivity, with a CTG is far more effective in reducing ozone for each air shed than a national mass-based regulation.

EPA Photochemical Reactivity Workshop
May 12-14, 1998
Durham, North Carolina

Presenter

The Solvents Council of the Chemical Manufacturers Association. Jonathan Kurland of Union Carbide Corporation will make the presentation on behalf of the Solvents Council.

Title of Presentation

CMA Research Initiatives

Abstract

The Chemical Manufacturers Association (CMA) is a Washington D.C. based trade association with over 200 member companies that collectively produce approximately 90 percent of the basic industrial chemicals produced in the United States. The CMA Solvents Council represents the major U.S. manufacturers of hydrocarbon and oxygenated organic solvents.^{1/}

The Solvents Council recognizes (1) the need to better understand the role that individual ozone precursors (including solvents) play in forming ground-level ozone and (2) the potential benefits of designing regulatory systems that take into account differences in the ozone-forming potential of different precursors. For this reason, the Council has been involved in both research and public policy discussions about the concept of photochemical reactivity.

This presentation will briefly summarize the activities of the Council in both the research and public policy arenas, including the following:

- The work being sponsored by the CMA Ethylene Glycol Ether and Propylene Glycol Ether Panels to examine the kinetics and photochemical oxidation mechanism of glycol ethers.
- The Council's support for the HONO work being conducted by Dr. William Carter.
- The Council's perspective on the Reactivity Research Advisory Committee (RRAC) established by the California Air Resources Board (CARB).
- The approach developed by the Council and submitted to CARB for taking uncertainty into account in reactivity-based programs.

1. The following companies are members of the Solvents Council: ARCO Chemical Company; BP Chemicals, Inc.; Celanese Ltd; The Dow Chemical Company; Eastman Chemical Company; Exxon Chemical Company; Phillips Chemical Company; Shell Chemical Company; Sun Company; Union Carbide Corporation.

CMA Research Initiatives

Barbara Francis
Chemical Manufacturers Association
Jonathan Kurland
Union Carbide Corporation

EPA Photochemical Reactivity Workshop
May 13, 1998

Chemical Manufacturers Association (CMA)

- Trade Association
- Over 200 member companies
 - Collectively produce approximately 90% of the basic industrial chemicals produced in the U.S.

Solvents Council

- Represents the major U. S. producers of hydrocarbon and oxygenated solvents
- Addresses environmental issues that affect both users and producers

Solvents Council Members

- ARCO Chemical Company
- BP Chemicals, Inc.
- Celanese Ltd.
- Dow Chemical Company
- Eastman Chemical Company
- Exxon Chemical Company
- Phillips Petroleum Company
- Shell Chemical Company
- Sun Company
- Union Carbide Corporation

Atmospheric Reactivity Task Group

- Includes both scientists and policy specialists
- Active in:
 - Policy issues
 - Research

Policy Activities

- Participates in developing a regulatory framework for reactivity
- Provided comments to CARB for dealing with the uncertainty in MIR values in regulations
- Presented an alternative model for categorizing complex hydrocarbons, such as mineral spirits, naphthas, Stoddard Solvent, etc.

Research Interests

- CARB Reactivity Research Advisory Committee
- Chemical Mechanism Studies
 - Reactivity studies on glycol ethers
 - Support for better reactivity estimation methods
- Environmental fate

Reactivity Research Advisory Committee

- Participation on RRAC of the California EPA Air Resources Board (CARB)
 - Choice of significant compounds for MIR determination by Dr. Carter under his contract with CARB
 - Advice on prioritization of CARB research
 - Support for HONO work by Dr. Carter

Ethylene Glycol Ether and Propylene Glycol Ether Panels Research Activity

Kinetics and Mechanism of Photochemical Oxidation of Glycol Ethers

- 2-Butoxyethanol and 1-Methoxy-2-propanol
- Work by Dr. Roger Atkinson
 - Kinetics and products of oxidation
 - k_{OH} and products of the reaction of the ethers with $HO\cdot$ in air with NO_x
 - Soon to be published
- Work by Dr. William P. L. Carter
 - Smog chamber runs
 - Mechanism and kinetics derived from Atkinson's studies
 - Calculation of MIRs

Principal Factors Determining the MIR

- The rate of reaction with $HO\cdot$
 - If the compound is unreactive this is the dominant term. Very reactive compounds will be completely consumed.
- Direct reactivity
 - The more oxidations of NO to NO_2 by peroxy radicals, the more ozone production
- Effect on $HO\cdot$ concentration
 - Compounds that generate free radicals by photolysis will increase the concentration.
 - Reactions of alkylperoxy radicals with NO to make alkyl nitrates instead of NO_2 and $RO\cdot$ reduce the concentration.
- The effect on NO_x concentration
 - Formation of alkyl nitrates removes NO_x

Ethylene Glycol Ether and Propylene Glycol Ether Panels Research Activity

Determination of Nitrate Yields in Photooxidation

- Work to be done by Dr. Paul Shepson at Purdue University
- Oxidation of ppm levels of glycol ethers in air with NO_x
 - PTFE-coated chamber
 - Controlled hydroxyl radical source by photochemical initiation
- Determination of nitrate yields by
 - gas chromatography
 - pyrolysis of RONO₂ to RO· and NO₂
 - determination of NO₂ by chemiluminescence
 - no calibration needed to quantify molar yield of nitrate
 - speciation requires further work
 - GC/MS or synthesis of authentic samples

HONO Work by Dr. William P. L. Carter

- Purpose: To support better estimation of MIRs when direct experimental data is lacking, and avoid use of arbitrary default values
- Objective: Obtain direct reactivities to make possible a scheme for estimating MIR values that considers by SAR or other means k_{OH} , direct reactivity and indirect reactivity.
 - Direct reactivity is the NO to NO₂ conversions during oxidation of a compound. The current Carter scheme for upper limit MIRs lumps the direct and indirect reactivity.
 - HONO yields HO and NO upon photolysis.
 - In a flow system, radical generation loses its importance and the direct reactivity can be determined.

Related Work

- Other CMA Panels
 - sponsor chemical-specific work
- Individual members of CMA acting independently
 - atmospheric chemistry and kinetics of specific chemicals

Other Interests Areas of CMA

Environmental Fate

- Low-vapor-pressure (LVP) Compounds
 - Volatility as well as reactivity influences ozone formation.
- Down-the-drain Factor
 - The EPA inventory of consumer product emissions recognizes that some VOC largely go into wastewater and are biodegraded at a POTW.

Summary

- CMA is committed to involvement in these issues.
- CMA is active in reactivity research and policy development.
- CMA is interested in related issues.
- We want to play an active role in future activities.

Acknowledgments

CMA Staff

Atmospheric Reactivity Task Group

CSMA Position on the Importance of Relative Reactivity

D. Douglas Fratz
Director of Scientific Affairs
Chemical Specialties
Manufacturers Association
Washington, DC

Presented at the
EPA Photochemical Reactivity Workshop
May 12-14, 1998
Durham, North Carolina

Good morning. I am Doug Fratz, Director of Scientific Affairs for the Chemical Specialties Manufacturers Association in Washington, DC. CSMA represents manufacturers of formulated chemical products for household, institutional, commercial and industrial consumers. These products include cleaners, disinfectants, pesticides, polishes, automotive products, and aerosols of all types. I'd like to talk to you today about CSMA's positions on the importance of relative reactivity to ozone attainment strategies.

Importance of Reactivity

- **History of CMSA Support**
- **Importance to Ozone Attainment Strategies**
- **CSMA Research on Reactivity**
- **Future Research Needs**

In presenting our current positions, I'll also review the history of our industry's support for reactivity; the many ways in which reactivity is important to cost-effective ozone attainment; some studies CSMA has sponsored over the past 10 years; and some concepts for future research that we believe is still needed.

History of CSMA Support

- 1988 - CARB Consumer Products Program
- 1990 - 183(e) of Clean Air Act
- 1991 - CARB/South Coast Conference, Irvine
- 1993 - Support for VOC Exemptions
- 1994 - California SIP Hearings

We began urging the consideration of reactivity in 1988 in relation to the California ARB regulations on consumer products, which began with underarm products. We also helped develop Section 183(e) of the Clean Air Act of 1990 on Consumer & Commercial Products, a section which contains requirements for EPA to consider reactivity in relation to those products. I gave a talk at the 1991 Irvine conference on reactivity, supporting the consideration of reactivity for consumer products. Around 1993, we began supporting EPA exemptions for negligibly reactive VOCs, urging that standard criteria and protocols be promulgated. In 1994, we were successful in getting the California Air Resources Board to include the potential to consider reactivity in the consumer products element of the State Implementation Plan.

History of CSMA Support

- 1995 - EPA Report to Congress - Chapter 3
- 1996 - Reactivity Principles to CARB
- 1997 - Proposed CARB Reactivity-Based Compliance
- 1998 - Proposed CARB Regulatory Language

In 1995, EPA's Report to congress on Consumer & Commercial Products was finally completed. We worked closely with EPA to assure that they met their statutory requirements to consider reactivity under 183(e). Chapter 3 of the report and the regulatory prioritization process EPA conducted met those mandates. By 1996, we were working again with California on reactivity, putting forth the principles we believed were essential to establishing reactivity-based compliance options for consumer products, as allowed in the SIP. Since 1997, we have also participated in ARB's Reactivity Research Advisory Committee. In 1997, we outlined the specific elements of a consumer products reactivity program, and this year we have developed specific draft regulatory language upon which a voluntary reactivity compliance option can be based.

CSMA Policy Positions

• EPA VOC Exemptions Program

- Ethane Criteria
- Mass-Based Criteria
- Standard Criteria & Procedures
- Expeditious Review

Now, I'd like to review our current positions on reactivity related issues. We support retaining ethane as the standard for exempting VOCs as negligibly reactive. There is no need to reproduce the 1977 experiment that provides the basis for choosing ethane. We may need to inventory some exempted VOCs for use in modeling, but there is no need to subject them to controls. We favor mass-based, as opposed to mole-based, comparisons for VOC exemptions. All ozone attainment inventories, controls and strategies to date have been mass-based. We support EPA developing standard criteria and procedures for exemptions. And we support expeditious reviews of exemption petitions. Our industry has relied on these exemptions to meet regulatory standards, and they are essential to our meeting the ozone reduction goals being placed upon us.

CSMA Policy Positions

• Consideration of Relative Reactivity in Ozone Attainment

- Alternative to Mass-Reduction
- Regulatory Prioritization
- Increased Cost-Effectiveness
- Cost Effectiveness Based on Cost Per Ozone Reduction Benefits

We believe that consideration of relative reactivity is essential in many other aspects as well. In particular, it is an important alternative to simple mass based VOC reductions. We support allowing regulated parties to use reactivity reductions to partially or fully meet their VOC mass reduction goals. This would result in increased cost-effectiveness in moving toward ozone reduction goals. Finally, we support all regulatory analyses of ozone attainment options being based on cost per ozone reductions, not precursor reductions. This would put all VOC controls, and even NOx controls, on an even playing field.

CSMA Policy Positions

• Reactivity Positions for Consumer Products

• Principles

- Optional
- Sound Science/Stable/Flexible
- Cost Effective/Efficacy Maintained
- Existing Provisions/Enforceable

These are the principles we proposed in California in 1996. Reactivity considerations must be optional, to allow companies to determine whether reactivity or mass-reductions are more cost-effective. Our VOCs already are of low reactivity. Mandatory reductions would not make sense. The reactivity values assigned to VOCs must be based on sound science, and be both stable (so *manufacturers will use them*) and flexible (to *encourage continued research*). The program must encourage cost-effectiveness, and allow manufacturers to make products that are both safe and effective. We believe that all of the provisions related to the mass-based standards, such as the various exemptions, must be maintained. Obviously, the program must also be enforceable.

CSMA Policy Positions

• Reactivity Positions for Consumer Products

• Policy Position

- Optional
- Product-By-Product Ozone Equivalence
- Maintain Exemptions
- Scientifically Determined MIRs
- All Products

We reiterated these same positions in our updated policy positions over the past year, and added a few more specific ones. In particular, we believe the most sound program would assure product-by-product equivalence of ozone impact, or equivalence by groups of products. We would like to see a program that could benefit all consumer products, and be adapted for other industries as well.

CSMA Consumer Products

- **Reactivity-Based Compliance Option and Credit Program**
 - **Equivalent Ozone Impact on Product-By-Product Basis**
 - **Official List of Reliable MIRs**
 - **Over-Reduction Credits Transferable between Products**

This year, we developed a specific proposal for a reactivity-based, voluntary compliance option for consumer products in California. Our program is a relatively simple one. It is designed to assure ozone equivalence on a product-by-product basis. It would be based on a list of VOCs with reliable MIR values. VOCs without reliable MIRs would not be allowed to be traded, and have to meet mass-reduction goals. We are proposing, however, that excess reductions credits for one product be usable for products which can't meet their reduction goals. This adds further flexibility. We are not proposing any complex schemes to address uncertainty. Only reliable MIRs would be used. What is often overlooked is that mass-based reductions also demonstrate high uncertainties regarding ozone reduction. In consumer products, we already have generally minimized VOC content for cost reasons. Mass reduction reformulations usually require different VOCs. These might be 3 times more reactive, or 3 times less reactive, than those they replace. The 30% uncertainty for reactivity is small when compared to this 300% level of uncertainty. But even these large uncertainties will even out over 100s of products.

CSMA Research on Reactivity

- **1988 - UAM Study on Underarm Products in California**
- **1993 - UAM Study on Pesticides, Disinfectants, Air Fresheners in New York**
- **1997 - Impact of Consumer Products on California Air Quality**

Now, I'd like to review some of the reactivity studies we've done over the past decade. All have been modeling studies on the effects of consumer product emissions on ozone formation. The three studies are: a 1988 study on underarm products in California; a 1993 study on pesticides, disinfectants and air fresheners in New York; and, a study completed just last year entitled, "Impact of Consumer Products on California Air Quality". All of the modeling in these studies was done by Dr. Gary Whitten.

1988 UAM Study

• Underarm Products in California South Coast AQMD

- 0.06% VOC Inventory
- No Measurable Impact
- 0.2ppb
- One Third as Reactive

The first study, way back in 1988, looked at the impact of underarm antiperspirants and deodorants in the Los Angeles basin. These products represent only about 0.06% of their VOC inventory, and are mostly composed of ethanol, simple hydrocarbons, and other low-reactivity VOCs. The modeling showed that even eliminating all emissions would have no measurable impact on peak ozone--less than 0.2ppb, primarily because of their low reactivity. This study may have been done before its time. It was spectacularly unsuccessful in convincing California not to regulate. Underarm products remain targeted for an 80% reduction that our industry still hasn't figured out how to meet.

1993 UAM Study

• Pesticides, Disinfectants, Air Fresheners New York City Metropolitan Area

- 0.1% Ozone - 1990
- 0.25% Ozone - 1997
- No Measurable Impact
- One Third as Reactive

We are not an industry that gives up, however, and our second study was more successful with similar findings. This time, we looked at household pesticides, disinfectant and air fresheners in New York City. The ozone contribution here was 0.1% in 1990, 0.25% in 2007. Again, the low reactivity contributed to the unmeasurable ozone impact. This study convinced New York to promulgate only reasonable standards for these products.

1997 Study - Sierra Research

• “Impact of Consumer Products on California’s Air Quality”

- **Inventory**
- **MIR-Weighted Inventory**
- **UAM Sensitivity Runs**

Our final study, completed last year by Sierra Research, was a multi-phase study looking at the inventories and reduction goals of the 1994 California SIP. The study included correcting the VOC emissions inventory for consumer products; creating a reactivity-weighted inventory for all VOC sources; and, doing Urban Airshed Modeling to determine the ozone benefits of the additional VOC reductions for which consumer products were targeted in the SIP. Both South Coast and Sacramento UAM runs were done.

1997 Sierra Research Study

• Consumer Products Inventory corrections

- **Non-emitted VOCs**
- **Survey Errors**
- **Industrial/Agricultural Products**

The inventory corrections for consumer products included removing non-emitted VOCs, most of which were those biodegraded in waste water treatment. This correction was made by EPA in its consumer and commercial products inventory, but has never been made by California. The study also corrected errors in consumer products survey data, mostly non-VOC ingredients that were misreported as VOCs. And, products that were industrial, agricultural, or otherwise double-counted in other VOC inventories were removed. The result was a change in the total VOC emissions inventory for consumer products in California from 265 tons/day to less than 215 tons/day.

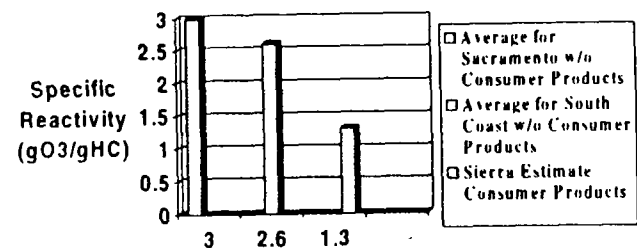
1997 Sierra Research Study

• MIR-Weighting of Inventory

- Specialization of Inventory
- MIR Estimates
- Less Than One Half as Reactive

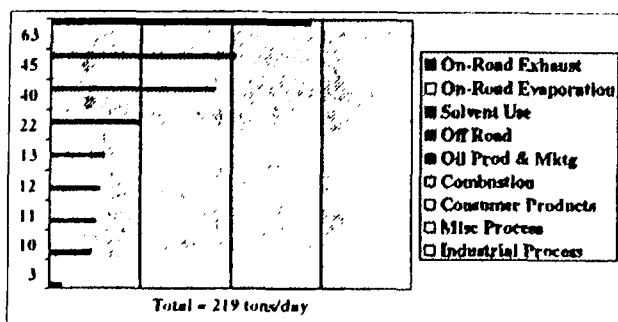
The reactivity-weighting was done for all VOC sources in the 1994 SIP inventory. MIR estimates were used to create an MIR-weighted inventory. The consumer products VOC inventory was found to be less than half as reactive as the overall inventory.

MIR Values for Consumer Products and Other VOC Sources



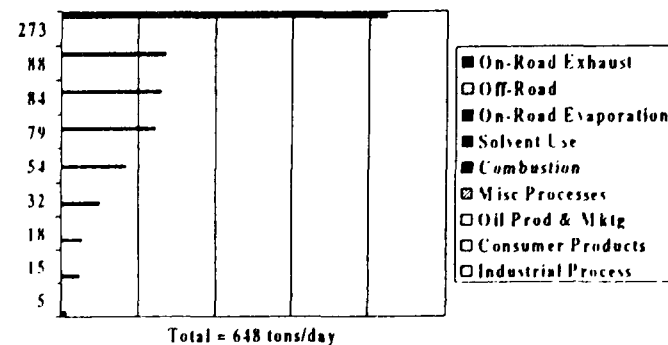
This slide shows how consumer product reactivity compares to the overall 1990 VOC inventory in California. Consumer products emissions average an MIR of 1.3. The average for other emissions was found to be 2.6 in South Coast and 3.0 in Sacramento.

1990 Sacramento VOC Emission Inventory



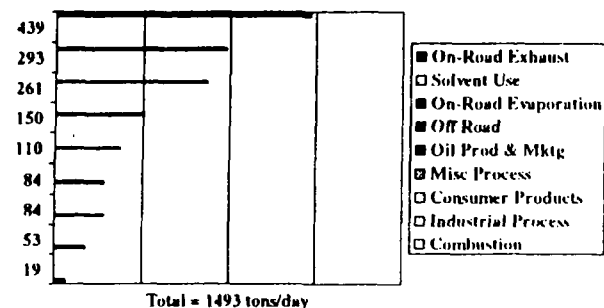
This slide, which I hope you can read, shows the 1990 Sacramento inventory by VOC tonnage. The emissions inventory is dominated by on-road exhaust, on-road evaporation, solvent use, and off-road emissions. Smaller, but still seemingly significant contributions occur from oil production, combustion, consumer products, miscellaneous processes, and industrial processes.

1990 Sacramento Ozone Forming Potential Inventory



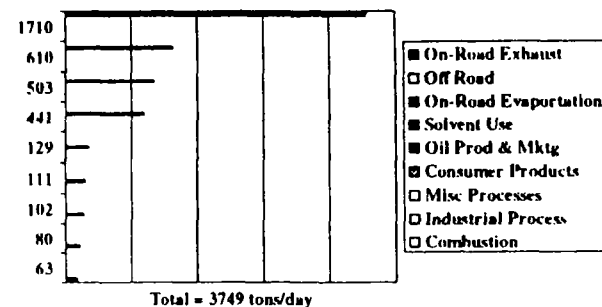
Here is that same Sacramento inventory that is MIR-weighted. On-road exhaust now dominates the ozone production inventory, with off-road also increasing its contribution. All of the other sources, including consumer products, now represent a much smaller portion of the inventory, and can be seen to be making a much smaller contribution to ozone formation.

1990 South Coast VOC Emissions Inventory



Here is the same inventory, this time for South Coast. Once again, on a VOC tonnage basis, on-road exhaust is closely followed by solvent use, on-road evaporation, and off-road, with others making smaller contributions to VOC emissions.

1990 South Coast Ozone Forming Potential Inventory



And, once again, in the MIR-weighted inventory, we see the actual ozone contribution of on-road exhaust and off-road increase significantly, while the contributions of other sources, including consumer products, go down proportionately. Consumer products here contributed only less than 3% of ozone formed. We believe that this type of analysis could provide a valuable tool in prioritizing ozone precursor reductions. The MIR-weighting technique, however, can only look at VOCs; the use of airshed modeling could allow this consideration to include NO_x as well.

1997 Sierra Research Study

• UAM Sensitivity Runs

- SCAQMD and Sacramento
- 30% and 85%/38% Reductions
- Peak Ozone Remained within 1-Hour Standard

Our study also included UAM sensitivity runs by Dr. Whitten. These runs were using the uncorrected VOC inventories in the SIP, even though we knew consumer product emissions were overestimated. Both South Coast and Sacramento runs were done, with the base case being the 30% reduction in consumer product emissions currently in the regulations, and the test case being the additional reductions targeted in the SIP of 85% for South Coast by 2010, and 38% in Sacramento by 2005. (The SIP actually targeted a 55% reduction for consumer products in 2005, but only used 38% in the modeling for Sacramento.) The results were that even without any further reductions in consumer products emissions, the 120 ppb 1-hour peak ozone standard was met in both South Coast and Sacramento.

UAM Runs

Effects of Consumer Product Controls South Coast - 2010

One-Hour Peak Ozone

• 85% Controls	• 122.3
• 30% Controls	• 124.9
• One-Hour Standard	• 125

The slide shows the results of the South Coast modeling runs. The modeling with all reductions targeted in the SIP, including 85% for consumer products, resulted in peak ozone of 122.3 ppb. Without further consumer product reductions beyond the 30% already in regulation in 1994, the peak result was 124.9 ppb, still under the 125 ppb monitoring limit.

UAM Runs

Effects of Consumer Product Controls Sacramento - 2005

	<u>One-Hour Peak Ozone</u>
• 38% Controls	• 124.2
• 30% Controls	• 124.5
• One-Hour Standard	• 125

Likewise, here are the data on peak ozone in the Sacramento run. In this case, the additional consumer product reductions in 2005 resulted in only a 0.3 ppb increase in peak ozone, remaining below the 125 ppb monitoring standard. Additional consumer product regulations were found not to be necessary to attain the ozone standard on which the 1994 California SIP is based.

1997 Sierra Research Study

• UAM Sensitivity Runs

- Reasons for Low Peak Ozone Impact
 - Low Reactivity
 - Emissions Geography

So in both South Coast and Sacramento, no additional controls on consumer products still result in levels less than 125ppb in 2010 and 2005, respectively, if all other VOC and NOx reductions in the SIP are made. The two reasons why this result occurred were determined to be that, first, the low reactivity of the consumer product emissions, and, second, where the emissions occur geographically. They are distributed in the grids of the model by population, which does not allow them to contribute ozone formation proportionally in the areas of peak ozone formation.

Reactivity - Future Directions

- Continued VOC Exemptions
- Reactivity-Weighted Trading
- Cost-Effectiveness on Ozone Basis

These are our recommendations for future directions in ozone attainment policy. First, we support continued exemptions for negligibly reactive VOCs. Second, we support the establishment of broad-based reactivity-weighted trading programs. Finally, we support the use of cost-effectiveness analyses based on ozone reductions instead of precursor reductions in looking at regulatory options.

Future Research Needs

- Identification of Negligibly Reactive VOC
- Improved Precursor Inventories
 - Tonnage
 - Speciation
- Chamber Studies to Establish Additional, Reliable MIRs
- Chemical Mechanisms Studies
- Reactivity Estimation Protocols
- UAM Sensitivity Runs
- UAM Cost-Effectiveness Optimization Runs

Right now our scientific knowledge is many years ahead of our regulatory policies, but we do have suggestions for further research. Research is needed for identifying more negligibly-reactive VOCs. Research is needed to improve precursor inventories, both in terms of tonnage and speciation. Chamber studies are needed to establish additional MIR values. Chemical mechanisms studies are needed to improve both MIR determinations and the computer models. Sensitivity runs, like those we did in the Sierra Research study; could help to evaluate regulatory options. In addition, similar computer modeling of regulatory options should be run routinely to optimize the cost-effectiveness of the regulatory options being considered for ozone controls, both those for VOCs and NO_x.

Conclusions

- **Reactivity Consideration Essential**
- **CSMA Supports Reactivity-Based Compliance Options for Consumer Products**
- **Additional Research Needed**

In conclusion, CSMA and the consumer products industry continue to believe that the consideration of reactivity is essential to ozone attainment policy. We support continued VOC exemptions as well as cost-effective, voluntary, reactivity-based, compliance options. We also believe that continued research is needed. The best incentive for encouraging our industry to fund research, however, would be to see ozone attainment policies change in response to the many years of research that has already been accomplished. Thank you.

Reactivity Concerns

**Philip J. Ostrowski
Occidental Chemical**

**Photochemical Reactivity Workshop
May 13, 1998**

5/11/98

Summary

- **Regulations based on multiple day reactivity should be used for the best long term scientific approach**
- **More data is needed to properly implement reactivity regulations**

5/11/98

2

Summary

- **For the interim**
 - Old VOC exemptions must continue to be used
 - No new exemptions of marginally reactive compounds
 - Use the reactivity of methane as a cut off for new exemptions to avoid long term mistakes

5/11/98

3

Summary

- **There are practical concerns on the enforcement side of reactivity regulations**

5/11/98

4

Current Two Tier VOC System

- **VOCs are treated equally**
 - VOCs differ significantly in O₃ formation potential
 - Sources are not encouraged to use VOCs with low reactivity

5/11/98

5

Current Two Tier VOC System

- **Exempt compounds are treated equally**
 - Exempt compounds differ significantly in O₃ formation potential
 - Sources are not encouraged to use exempt compounds with low reactivity

5/11/98

6

Reactivity Regulations

- **Reactivity based VOC regulations make sense for the long term**
 - Sources will be encouraged to use materials which have low reactivity
 - Reactivity must be based on weight since most emissions are measured by weight
 - Air quality should improve

5/11/98

7

Reactivity Regulations

- **Reactivity regulations must be flexible.**
 - Relative ranking for the one day box model has in some cases changed significantly over time
 - Need flexibility to accommodate better data (up or down)

5/11/98

8

Reactivity Regulations

- **Reactivity regulations must have scientific input**
 - Need scientific community consensus for values of reactivity
 - Uncertainty must be addressed
 - Need periodic review as more information becomes available

5/11/98

9

Current Reactivity Thinking

- **Box model**
- **One day episodes**
- **Absolute reactivity differs in different air shed**
- **Relative ranking is about the same in all airsheds so regulations are possible**

5/11/98

10

Current Reactivity Thinking

- **What makes sense in California may not work for other parts of the country**
 - **LA has little influence from upwind sources**
 - **LA has unusual weather and geography**
 - **Weather includes lots of sunshine and a persistent high that causes inversions**
 - **Mountains add to the trapping of pollutants**

5/11/98

11

National Reactivity Regulations

- **Need regional models East of Mississippi**
- **Cities in the Northeast corridor are affected by transport of ozone and precursors from upwind sources**

5/11/98

12

National Reactivity Regulations

- Use multiple day reactivity, compared on an integrated O₃ scale
 - The relative reactivity ranking of some compounds in multiple day episodes shows significant differences versus the one day box model
 - Incorrect reactivity could encourage use of the wrong chemical

5/11/98

13

National Reactivity Regulations

- Second highest one hour average O₃ is not reliable for measuring trends
 - Compounds should be compared on an integrated O₃ scale
- Relative reactivity scales must be developed for multiday events using an integrated O₃ scale
- More Data is Needed

5/11/98

14

For the Interim

- **Old VOC exemptions must continue to be used**
 - Without the old VOC exemptions non compliance would soar
 - Sources may revert back to old highly reactive compounds
 - Time must be allocated to switch from two tier to reactivity systems

5/11/98

15

For the Interim

- **No new exemptions of marginally reactive compounds**
 - Mistakes could be made with excess use of the wrong compound
 - Multiday reactivity will increase or decrease the relative reactivity of compounds

5/11/98

16

For the Interim

- **No new exemptions continued**
 - **Compounds in the EPA VOC exemption petition queue may have different relative rankings in multiday reactivity evaluations**
 - **Some of these compounds will have increased relative reactivity**

5/11/98

17

For the Interim

- **No new exemptions continued**
 - **More VOC exemptions could encourage widespread emissions of a compound which may adversely impact air quality**
 - **Marginally reactive exempt compounds can be used to replace exempt compounds with much lower reactivity**

5/11/98

18

For the Interim

- **Use the reactivity of methane as a cut off**
 - This approach should eliminate mistakes since methane has very low reactivity

5/11/98

19

Enforcement Policy

- **Complex analytical issues must be dealt with**
 - Laboratory Methods
 - GC Mass Spec
 - Method 24
 - Variability issues
 - Theoretical composition versus actual
- **Production Records use**

5/11/98

20

Categorization of Low Reactivity Compounds

**John G. Owens
3M Chemicals
St. Paul, MN USA**

It is recognized that all organic compounds which volatilize into the atmosphere do not contribute to the formation of tropospheric smog. Some compounds have low reactivity with respect to common atmospheric removal mechanisms such as photolysis and reaction with hydroxyl radicals. These low reactivity compounds are stable enough to become well dispersed throughout the troposphere prior to the onset of their decomposition. As a result, these organic materials are incapable of contributing to the production of ground level ozone.

As compounds are considered for exemption from VOC regulations, it would be useful to first categorize them based upon their reactivity. Those which are shown to have low reactivity will not contribute significantly to ground level ozone regardless of their ozone yield during decomposition. These materials could be considered for exemption from VOC regulations without need for further information. Compounds of higher reactivity have the potential to add to ground level ozone during their decomposition. These higher reactivity compounds could be selected for further study to determine the ozone production from their atmospheric oxidation. Such categorization could streamline the exemption process and focus resources on the study of compounds which have the greatest potential to impact smog formation.

Categorization of Low Reactivity Compounds

John G. Owens

3M Chemicals

Criterion for VOC Exemption

- $k_{\text{OH}}(x) < k_{\text{OH}}(\text{C}_2\text{H}_6)$
(compound x is atmospherically longer lived than ethane)
- $k_{\text{OH}}(\text{C}_2\text{H}_6) = 0.24 \times 10^{-12} \text{ cm}^3/\text{molecule-s}$
which translates into an atmospheric lifetime of approximately 0.24 years
- Additional criteria being being developed such as ozone production during tropospheric decomposition
- Reactivity of compounds in recent exemption requests have been very close to and in some cases higher than ethane

Very Low Reactivity Compounds

- Some compounds are very low in reactivity
 $k_{\text{OH}}(\text{x}) \ll k_{\text{OH}}(\text{C}_2\text{H}_6)$
and do not photolyze in the lower atmosphere
e.g. saturated, halogenated compounds
- Compounds with sufficiently low reactivity will be well dispersed throughout troposphere during decomposition
- Oxidation of these compounds does not contribute measurably to ground level smog regardless of O_3 yield.

Categorization of Low Reactivity Compounds

- Useful to establish a criterion which distinguishes between :

I. Compounds with reactivity relatively close to ethane

i.e. more likely to contribute to smog formation and smog chamber studies necessary

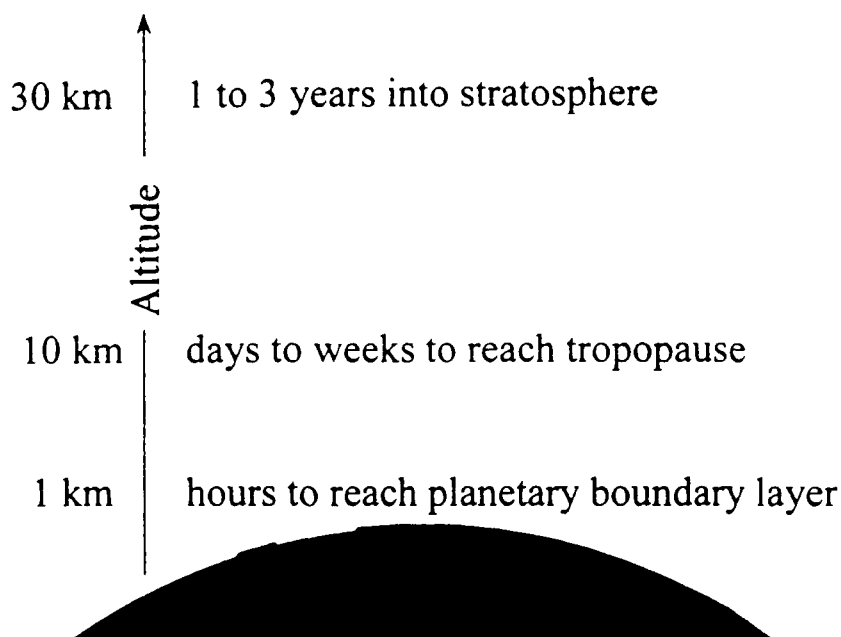
Vs.

II. Compounds which are significantly less reactive than ethane

i.e. clearly will not contribute to smog formation and k_{OH} and photolysis data is sufficient

Transport Times for Chemical Species in the Atmosphere

The longer a compound survives in the atmosphere, the greater the proportion transported to high altitudes by diffusion and convection.



Categorization of Low Reactivity Compounds

- further clarify VOC definitions
- focus resources on evaluation of compounds which are more likely to be contributors to smog formation
- streamline exemption process
- provide benefit to chemical users

EPA Photochemical Reactivity Workshop, May 12-14, 1998, Durham, NC

Presenter:

Daniel B. Pourreau, Ph.D., Coatings Development Manager, ARCO Chemical Company.

Title of Presentation:

Impact of a Molar Ethane Standard on the Number and Type of VOC-Exemptible Compounds; Practical and Environmental Implications.

Abstract:

Since 1977, the USEPA has granted several industry petitions to exempt specific organic compounds on the grounds of "negligible photochemical reactivity". Most of the early exemptions were granted on the basis of kinetic reactivity data, that is the rate of hydrogen abstraction by atmospheric OH radicals. The compound's hydrogen-abstraction rate constant, k_{OH} , expressed in molar units was typically compared to that of ethane. Compounds with k_{OH} constants lower than ethane were considered "negligibly reactive" and appropriately exempted from VOC regulations.

More recent petitions have been granted on the basis of both kinetic and mechanistic data. The reason for relying on mechanistic reactivity was the realization that several compounds with negligible kinetic reactivity had significant ozone yields when irradiated in the presence of other more reactive gases and NO_x pollutants. Mechanistic reactivity is defined as the incremental amount of ozone formed when a compound is added to a polluted atmosphere under well defined conditions.

The compounds' maximum incremental reactivity, or MIR, expressed on a weight basis has been the published standard since the EPA's Report to Congress in 1995 and was the basis for the exemption of Acetone from VOC regulations. Here, the "cutoff" between reactive and "negligibly reactive" compounds was the MIR of ethane on a per gram basis.

Since then, the EPA has received several petitions from industry to exempt other compounds based on MIR data. Because of this and concerns about possible future petitions, EPA is now considering a tightening of the MIR standard by requiring that compounds be less reactive than ethane on a per mole basis.

We will present evidence that shows that the number of useful compounds that meet the current gram-based MIR standard is limited and that the proposed mole-based standard would severely limit the number of useful VOC-exempt compounds available to industry. The impact this policy change would have on the industry's ability to meet current and future VOC regulations will also be discussed.

Introduction - Title Slide

Good Morning. First, I'd like to thank the EPA for calling this workshop and giving Industry the opportunity to participate. ARCO Chemical also has a petition before the EPA to exempt a new solvent from VOC regulations. I will, however, not discuss this petition today, only to the extent that it illustrates how such low reactivity materials can provide immediate and substantial environmental benefits by replacing more reactive VOCs still in use today.

The main thesis of my presentation is that the EPA's proposal to adopt a new, stricter standard based on the photochemical reactivity of ethane on a per mole basis would virtually eliminate all viable substitution candidates. The impact of such a decision would be two-fold:

1. It would strengthen the Industry's opposition to further mass-based VOC limitations and,
2. it would favor substitution to environmentally persistent halocarbons.

Neither would achieve anywhere near the environmental benefits which would result from the exemption of a handful of solvents which meet the EPA's current gram-based exemption criterion.

Slide 1

Let me start by illustrating the magnitude of the challenge we face today. Based on recent Industry analyses, the US Coatings, inks, and adhesives industries alone consume close to 5 billion pounds of solvent per year, despite all the regulatory efforts to decrease their usage. As you'll see later on, there are many reasons why solvents continue to be popular tools in these industries.

Slide 2

Low VOC technologies such as water and powder have made significant strides in the past few years but are still not suitable for many applications and often lag in performance compared to solvent-based systems. For example, you still cannot powder coat a bridge nor can you repaint it with water in cold and damp weather. These are realities we have to deal with.

Abatement technologies have also been very helpful in reducing the amount of solvent emitted into the atmosphere. But solvent recovery is not often practical and incineration generates NOx.

For these reasons, the EPA should continue to encourage the development of low reactivity solvents and their use in place of many of the more reactive and toxic solvents still in use today.

Slide 3

By far the most popular solvents in these industries are aliphatic and aromatics hydrocarbons and oxygenated solvents such as esters, ketones, and alcohols. Halogenated solvents, which are still popular in the cleaning industries because of their high solvency and low flammability account for less than 1% of solvent usage in the coatings industry.

Slide 4

The reasons for choosing hydrocarbon and oxygenated solvents are numerous.

The best solvents have intermediate solvency. Strong enough that they reduce resin viscosities effectively but not so strong that they strip primer coatings or attack the substrate. This is one of the reasons strong solvents such as methylene chloride are almost never used in the coatings industry.

Waterborne coatings also require solvents to stabilize the paint formulation and improve film formation. Here, the best solvents are oxygenated solvents such as glycol ethers and N-Methyl-pyrrolidone. Hydrocarbons and halogenated solvents are not useful here because they are essentially insoluble in water.

Different coating operations also require different drying or evaporation rates. Fast solvents are used in air-dried systems, slower solvents under bake conditions. Most often, blends of solvents are used to tailor the dry time to the specific operation and optimize the performance and appearance of the coating.

Another reason for choosing solvent-borne systems is that their dry times are independent of environmental conditions. This is not the case with waterborne systems that dry much slower under cold and damp conditions.

Most solvents used today have relatively low toxicities. Solvents such as benzene are no longer used and those solvents listed as Hazardous Air Pollutants are strictly regulated by OSHA in the workplace and by State and Federal Environmental Protection Agencies. Many companies have already reformulated their products with non-HAP solvents such as Cypars, P-series glycol ethers, alcohols, and esters.

These solvents are also inexpensive. Because paint is sold by the gallon and solvents by the pound, low density is a distinct benefit. Halogenated solvents, in contrast, have high densities and are relatively expensive on a volume basis.

Another advantage of non-halogenated solvents is that emissions can be incinerated. They typically have good fuel value and no corrosion issues related to halo-acid formation. The coil coating industry, for example, is effectively using solvent incineration as an abatement and energy producing tool.

Finally, non-halogenated solvents typically have low environmental persistence. Since they do not contain halogens, they have zero ozone depleting potential and low acid rain contributions. They rapidly oxidize in the atmosphere to water and carbon dioxide which has relatively low global warming potential.

Slide 5

I'd like to expand a little more on this point with this table which compares the ozone depleting and global warming potentials of the major halogenated solvents and the average of several halogenated and non-halogenated solvents. As you can see, the atmospheric lifetimes of halogenated solvents are typically measured in months whereas non-halogenated solvents typically oxidize in the matter of days.

Since the global warming potential of a solvent is a function of its atmospheric lifetime, its ozone depleting potential, and its total infrared absorbance relative to carbon dioxide it is easy to see why halogenated solvents are likely to have a greater impact on global warming than their non-halogenated counterparts.

Slide 6

Which brings me back to the challenge we face today:

Replacing close to 5 billion pounds of solvent per year with substitutes that generate less tropospheric ozone yet do not have a lot of health and environmental baggage attached to them.

This graph provides a clue as to how we might achieve that. Of the top 20 solvents used in the coatings industry today, only a handful contribute significantly more than their actual emissions to tropospheric ozone formation. These are the aromatics, and to a lesser extent, some of the higher members of the ketone, alcohol, and glycol ether families.

Clearly, one way to significantly reduce ozone formation would be to develop policies that encourage substitution of these highly reactive VOCs with less reactive ones. And to a certain extent, the EPA's current policy does that.

Slide 7

By exempting VOCs with incremental reactivities less than ethane on a per gram basis, the EPA has given Industry the incentive to develop and use low reactivity solvents such as acetone and PCBTF. Petitions for several other solvents with similar or lower reactivities are before the EPA today. Granting these petitions could result in immediate and substantial environmental benefits which are illustrated here.

With additional exempt solvents, current ozone levels could potentially, with time, be reduced by 88%, assuming that all exempt solvents had reactivities equal to ethane on

a per gram basis. In fact, some of the petitioned solvents have reactivities less than half that of ethane so ozone reduction opportunities of over 90% are conceivable.

Which brings us to this key question:

If such substantial benefits are achievable using ethane on a per gram basis as the cutoff between exempt solvents and VOCs, why not make the standard stricter? Why not go to ethane on a per mole basis?

Slide 8

The reason you do not benefit from using a molar ethane cutoff is that you drastically reduce the number of viable exempt substitutes for more reactive VOCs. As this graph illustrates, the number of practical non-halogenated solvents which meet the current MIR standard on a per gram basis is approximately ten. Going to a mole standard reduces this number to one.

Given the wide range of properties required from today's coating formulations, having 10 viable substitutes for high reactivity VOCs is a minimum. Having one is essentially useless.

Another potential impact of this new proposed standard is that it would favor halogenated solvents. As I illustrated earlier, halocarbons have limited use today in coatings, inks, and adhesives and have relatively high atmospheric persistence. A stricter ethane standard would have relatively little impact on the number of exemptible halogenated solvents and could drive Industry to turn to these solvents to meet the new and more stringent mass-based VOC limits. This could have a negative impact on worker health, acid rain, global warming, and stratospheric ozone depletion.

Slide 9

I'd like to leave you with a real life example of how low reactivity solvents can be used to replace more reactive and toxic ones. What we have done here, and for several other coating formulations, is taken a conventional high solids formulation and replaced the solvents with lower reactivity and non-HAP alternatives. We then calculated the ozone impact of each formulation on a pounds ozone per pound of solids applied basis. Finally, we compared these solvent-based formulations to a standard waterborne formulation.

Slide 10

This slide graphically illustrates that reformulating conventional solvent-borne systems with low reactivity and non-HAP solvents can significantly reduce the ozone impact and toxicity of these formulations. In this particular case, we were even able to lower the ozone yield and HAP content of the solvent-borne system below that of the waterborne

system.

You will notice, however, that the low ozone formulation has the same solvent content as the conventional system. Without VOC exemptions, there would be no incentive for industry to go to this type of formulation.

Worse yet, if the EPA goes to a mole based ethane standard or suspends further exemptions, Industry will have the incentive but no tools to reformulate with.

Slide 11

In conclusion, we urge the EPA to continue exempting VOCs based on their reactivity relative to ethane on a per gram basis. The status of exempt solvents can always be revisited at a later date in light of newer and better science. It would counterproductive, however, to wait for the outcome of what will likely be a lengthy and complicated process to reap the benefits that can be achieved today, with the current policy.

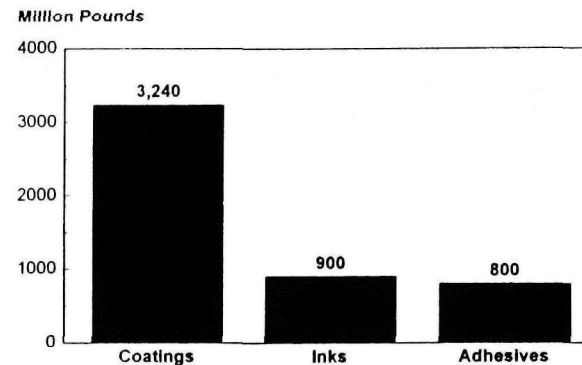
Thank you for your time.

Impact of a Molar Ethane Standard on the Number and Type of VOC-Exemptible Compounds; Practical and Environmental Implications.

EPA Photochemical Reactivity Workshop
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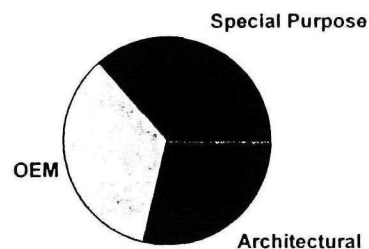
Daniel B. Pourreau, Ph.D.
Coatings Development Manager
ARCO Chemical Company

1997 US Solvent Usage by the Coatings, Inks, and Adhesives Markets



- Solvents continue to be widely used

1996 US Solvent Usage in Coatings by End Use

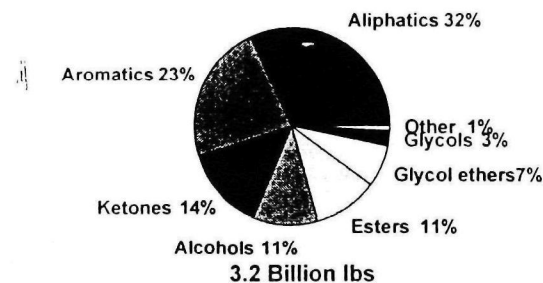


3.2 Billion lbs

Kusumgar, Nerfi & Growney, 1997

- Powder limited to larger volume OEM operations
- Waterborne coatings have performance limitations
- Abatement not practical in architectural & special purpose sectors
- Incineration generates NOx

Hydrocarbons and Oxygenated Solvents Popular



Kusumgar, Nerfi & Growney, 1997

- Hydrocarbons and oxygenated solvents account for >99% of usage
- Halogenated solvents account for <1% of coating solvent usage

Reasons Why Hydrocarbon and Oxygenated Solvents are Popular Coating Solvents

- **Physical and Solubility Properties**
 - Intermediate solvency for coating resins
 - Some can stabilize resins in water
 - Range of evaporation rates
 - Dry times independent of conditions
 - Low cost per gallon
- **Environmental, Health, & Safety**
 - Can be incinerated
 - Relatively low toxicities
 - Low environmental persistence
 - No ozone depleting potential
 - Low acid rain contribution
 - Low global warming potential

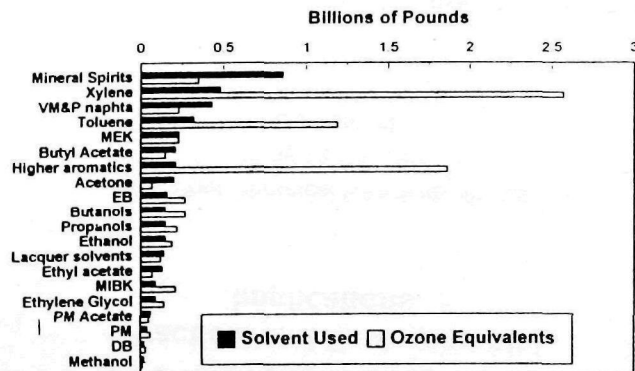
Impact of Atmospheric Lifetime on the Global Warming and Ozone Depleting Potential of Solvents

	Average Atmospheric Lifetime, days	Pounds CO ₂ per Pound Solvent	Ozone Depletion vs. CFC-11	Global Warming Relative to CO ₂
Major Halocarbon Solvents				
Methylene Chloride	131	0.53	> 0	28
Chloroform	200	0.37	> 0	15
Carbon Tetrachloride	50 years	0.29	1.1	> 2,000
1,1,1-Trichloroethane	6 years	0.66	0.1	> 360
Perchloroethylene (PERC)	130	0.53	> 0	unknown
Other Halocarbon Solvents (Avg. of 24)				
	229	0.84	>0	>15*
Non-halocarbon (Avg. of 13)				
	26	2.60	none	2-3

References

- 1 1994 Report of the Scientific Assessment Working Group of Intergovernmental Panel on Climate Change
 - 2 Kirk Othmer Encyclopedia of Science and Technology, 4th Ed
- *Based on the relative lifetime and CO₂ equivalents of chloroform

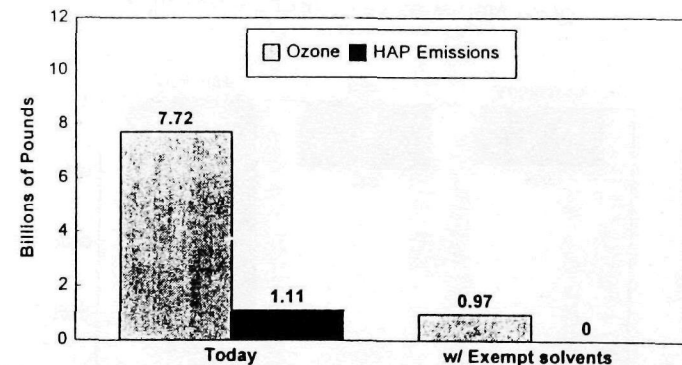
Top 20 Coating Solvents: Volume & Tropospheric Ozone Impact



- Top 20 coating solvents account for 92% of usage
- Aromatics generate the most tropospheric ozone

Based on Carter MIR data & KN&G Solvent study

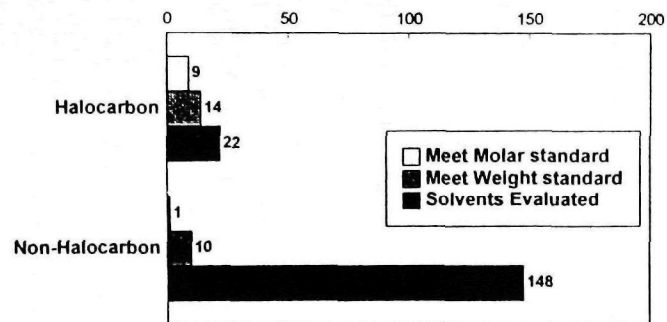
Potential Environmental Benefits with Ethane Cutoff on a Weight Basis



- >88% reduction in ozone possible
- Major HAP reductions also achievable

Assumes replacement of top 20 solvents with non-HAP solvents with MIRs equal to ethane on a weight basis

Impact of a Molar Ethane MIR Cutoff on the Type and Number of Available Exempt Solvents



- Stricter standard would drastically limit the number of exempt hydrocarbon and oxygenated solvents
- Substitutions would be limited to exempt halocarbons

Based on Carter MIR data

Wood Clearcoats

Components	MIR lbs ozone/lb solvent	High Solids 2K system	lbs ozone	High Solids 2K system w/ TBAC	lbs ozone	Waterborne Lacquer*	lbs ozone
Acrylic Resin	215			215		315	
Urethane crosslinker	222			222			
Flow Additive							
EB	2.31					83	192
DB	1.87						
EEAC	2.33	175	408			28	62
Xylene	7.05	55	388				
Toluene	5.12	179	916				
PMA	1.08	93	100	215	25		
TBAC	0.16			289	46		
Water							
Total wt		1000	1813	1000	276	850	244

System Properties
% Solids
lb solvent/lb solids
lb HAP/lb solids
lb ozone/lb solids

Conventional 2K PU
50%
1.0
3.5
10%

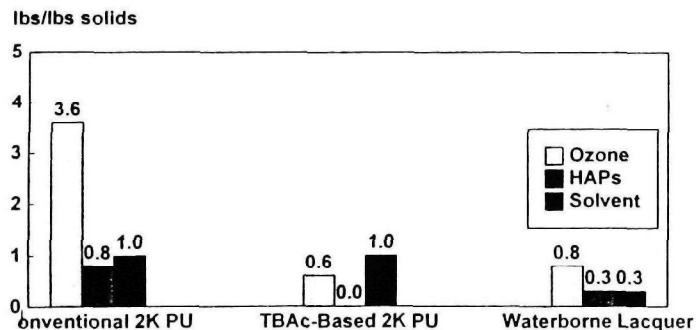
TBAC-Based 2K PU
50%
1.0
1.5
10%

Waterborne Lacquer*
50%
0.3
1.5
10%

*Rohm & Haas CL-204 Wood Clear Formulation

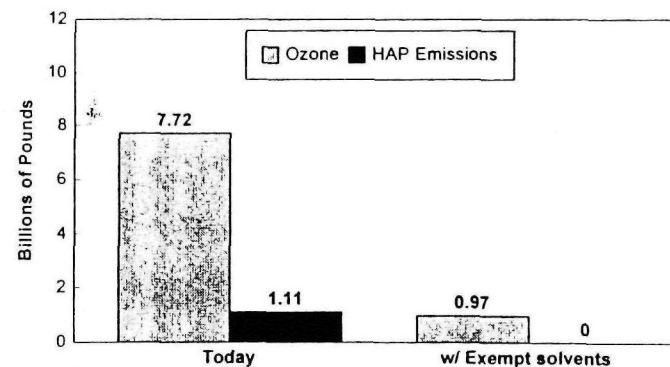
Wood Coatings

Two-component Urethanes vs Waterborne Lacquer



- Ozone impact of TBAC-based wood coatings lower than waterborne
- HAP content lower than waterborne & conventional
- Ease of use and durability superior to waterborne

Potential Environmental Benefits of Current EPA Policy



- >88% reduction in ozone possible
- Major HAP reductions also achievable

Assumes replacement of top 20 solvents with non-HAP solvents with MIRs equal to ethane on a weight basis

General Industry Concerns With the Process
Remarks by Donna Carvalho
Pennzoil Products Company

Good Morning, my name is Donna Carvalho. I am here representing Pennzoil Products Company. I am here today to offer an industry perspective on the need for further photochemical reactivity research. Pennzoil Products Company, through its subsidiary, Magie Brothers Oil Company, currently has a delisting petition before the Agency. I will not be discussing that petition except as it relates to why clear science is needed.

Pennzoil applauds this EPA effort to identify research needs and partners. We also welcome the opportunity to have this forum for policy discussions. As EPA seeks to determine what research is necessary, we offer the following suggestions:

First, we ask EPA to focus whatever process is adopted for photochemical reactivity decisions to that purpose only. This process does not need to be a substitute program for new source review, prevention of significant deterioration, global warming or the hazardous air pollution program. We recognize that the final process may impact each of these other programs; however, we believe that any negative impact will be very small while the positive impact could be significant as state and federal agencies and industry rightfully focus on controlling those VOC emissions that are most volatile and reactive.

Second, we suggest that EPA recognize that it does not have to have 100% surety to delist a chemical. Whatever scientific approach is adopted should combine scientific excellence with realistic and **timely** policy making. States inherently recognize the tension between what knowledge is available and what can and should be controlled when they exempt certain materials from control requirements. Your counterparts in EPA will be doing the same when they finalize the VOC consumer product rule. As proposed, this rule exempts materials with a particular vapor pressure, or where the vapor pressure is not known, with a carbon-number cutoff. These various rules combine what the regulator knows about the materials being regulated with what can be realistically and cost-effectively controlled.

Third, as members of industry, we suggest that EPA develop and adopt an easily understood "cookbook" type of approach to making photochemical reactivity decisions. As discussed in more detail later, our preference is that this approach would include giving deference to volatility issues. Other alternatives might include a carbon number cutoff, use constraints, and/or magnitude or volume of use considerations.

Finally, Pennzoil offers the following specific comments. First, we would prefer that photochemical assessments be made on a per-gram basis rather than a per-mole basis. Second, we would also recommend a reactivity scale that looks at ozone formation over a period of time.

I will now discuss each of these suggestions and recommendations in more detail. As noted initially, the research and final decision-making process that is developed out of these workshops should be focused solely on defining photochemical reactivity. The final method for determining photochemical reactivity should be consistent with other programs to the greatest extent possible,

but should not replace other programs. Trying to address other pollution concerns with a process for determining whether a chemical is photochemically reactive or not will only make an already complicated process more complex and time-consuming. There are already numerous other EPA programs which have been developed to control hazardous and non-hazardous VOC emissions. The goal of the research coming out of the workshop should be to determine which chemicals participate in ozone formation and which do not. Once this group has established the process that answers that question and that question only, then other EPA programs fill the gap to determine what and how emissions are to be controlled.

Having an overly broad process is a real concern for us. I mentioned earlier that Pennzoil has a delisting petition before the Agency. This petition is the culmination of nearly 20 years of tests and research. One of the initial tests done in 1982 indicated that the product which is the subject of the petition had essentially the same photochemical reactivity as ethane. However, at that time, EPA expressed to us reluctance to act on the findings because of the uncertainty regarding what Congress would be doing with hazardous air pollutants within the context of the then proposed Clean Air Act. That question took another eight years to answer. Recently, EPA has said in its perc delisting whether the product is hazardous or not is not a factor to be considered when making its VOC delisting decisions. Even though EPA's current position would not help or hinder our petition, we think this position is the correct one and should be maintained. Other air pollution concerns should not play a role in determining if the material is photochemically reactive or not. Rather, the other EPA programs in place will address other concerns.

As noted earlier, we do not believe that limiting the scope of the program will negatively impact these other programs. Instead, controls can be directed to those VOCs which actually merit control.

Pennzoil also believes that the Agency should identify realistic research goals and decision-making frameworks. This is what combining scientific excellence with realistic and **timely** policy making means. The Agency must decide what method or methods will reasonably satisfy it. As part of this decision-making, EPA should determine which method or methods get the best information it can have for the most reasonable cost. Pennzoil has tested its materials several different ways. Other companies who do not have our resources may not be able to make a twenty-year investment in evaluating their products under changing tests or reactivity scales.

Our preference is that EPA adopt a relatively simple, easy to understand, "cookbook" method. Our history with the Agency shows that we have tested our materials in various manners and conditions. When it became apparent that the Agency preferred one scale over another, we ensured that our testing results included those scales. However, industry should not have to continue to try and hit a moving target. One company should not be evaluated under one set assumptions one day and another company evaluated under different assumptions the next. The Agency's goal today should be to develop a simple method that can be understood and easily performed.

In this light, Pennzoil would urge the Agency to reconsider looking at volatility as a surrogate for photochemical reactivity and/or as an initial screening measure. After all, you are determining if something is a "**volatile organic compound**". It seems counterintuitive that non-volatile or negligibly volatile chemicals are nonetheless "**volatile organic compounds**"

Unlike reactivity scales which are developed after time-consuming and sometimes costly chamber tests are performed, volatility is easy to determine. Further, there is already substantial EPA precedence for using volatility to determine control requirements. As noted earlier, your counterparts in EPA are expected to issue any day now a consumer products rule that will exempt products with a volatility of less than 0.1 mm/Hg at 20 degrees C. Where vapor pressure is unknown the Agency will exempt products with more than 12 carbons. Similarly, most states exempt the storage and/or use of low volatility products from control requirements in EPA-approved SIPs. Given the industry familiarity with these types of tests and controls, EPA should determine whether it can build and/or improve upon a process which uses volatility. Neither EPA nor industry should have to spend time and effort determining if something is "photochemically reactive" when in some cases, the emissions will be exempted from control requirements anyway. Unfortunately, even if there are no control requirements, there are costs associated with identifying and quantifying the low volatility emissions. Further, the facilities may be unnecessarily paying to obtain and maintain a Title V permit.

Another option for EPA to consider is using volatility as the screening tool. Other easily understood, uniform tests (whether chamber tests or modeling) could be required if one cannot pass the screen.

Finally, to the extent that EPA adopts a uniform process where chamber tests are conducted and results are modeled, we offer the following specific recommendations. First, such tests should compare the tested material with ethane on a per-gram basis. The basic reason for determining if a compound is photochemically reactive is to determine if it is a "volatile organic compound" which must be controlled. Under all the regulatory programs of which we are aware, VOC emissions are controlled on a weight basis (usually pounds per hour or tons per year). For paints, coatings, and consumer products, where solvent substitution is often the most effective approach for reducing VOC emissions, VOC limits are set on a grams per liter basis. Where solvent substitution is used as a control strategy, the substitutions are made on a volume basis, which is fairly close to a weight basis and has nothing to do with the molecular weight of the compounds. The VOC control program and the process for determining if a compound is or is not a VOC should be consistent. EPA has publicly announced that, in making decisions about VOC exemptions, it will compare compounds to ethane on a gram-basis. EPA should continue to follow this policy.

Similarly, whatever reactivity scale is finally decided to be appropriate should model ozone formation over a period of time and not just look to peak occurrences. Again, we suggest this for consistency with the new ozone control requirements. The systems for determining ozone attainment now take into account the fact that ozone develops over a period of time and is affected by weather and other local conditions. When comparing tested materials to ethane, one should look to see what happens to both materials over time and differing conditions. If the results are basically the same, the material should be exempted.

Pennzoil hopes that these remarks will give you an industry perspective on these issues. We too want to see a process developed where all the players will know what is expected to make enlightened and accurate photochemical reactivity decisions. Thank you for this opportunity to speak.

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TITLE: A GLOBAL 3-D RADIATIVE-DYNAMICAL-CHEMICAL
MODEL FOR DETERMINING LARGE-SCALE IMPACTS
OF ATMOSPHERIC OZONE PRECURSORS

PRESENTER: Dr. Eduardo P. Olaguer
The Dow Chemical Co.

ABSTRACT

The Dow Chemistry-Climate Model (DOWCCM) is a new 3-D modeling tool that utilizes sophisticated methods for simulating radiative transfer, photochemistry, and geophysical fluid dynamics in order to compute large-scale atmospheric impacts of ozone precursors. These large-scale impacts include global and regional ozone formation potentials, global warming potentials, ultraviolet actinic flux changes, tropospheric oxidation capacity changes, and changes in global atmospheric circulation. DOWCCM combines an 11-wave, spectral meteorological model with a grid, chemical transport model to enable the simultaneous prediction of the general circulation and chemical composition of the atmosphere from 0 to 79 km. The current photochemical scheme incorporates up to 136 gas phase and heterogeneous reactions involving about 40 species, including those pertaining to methane oxidation. Work is now in progress to expand the tropospheric chemical mechanism to include non-methane hydrocarbons and oxygenated species such as acetone. The DOWCCM employs a fourth-order, positive-definite Bott scheme similar to that used in Models-3 to simulate tracer advection. Also incorporated in the model is a parameterization for convective venting of tracers from the boundary layer to the free troposphere. The DOWCCM is very computationally efficient (approximately 1 CPU minute is required per model day on a Cray T90), yet it successfully simulates the basic features of the general circulation and of total column ozone, and precisely predicts the atmospheric lifetime of methyl chloroform. Future versions of DOWCCM may contain nested regional models within a global framework.

Reactivity Calculations with the Regional Atmospheric Chemistry Mechanism

William R. Stockwell

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The gas-phase chemical mechanism is one of the most important components of an air quality model. The Regional Acid Deposition Mechanism, version 2 (RADM2) (Stockwell et al., 1990) is used in a number of air quality models including the MODELS3/CMAQ modeling system. Many new measurements of mechanism parameters have become available after the RADM2 mechanism was completed 8 years ago. We have used these measurements to create a successor to the RADM2 mechanism, the Regional Atmospheric Chemistry Mechanism (RACM) (Stockwell et al., 1997).

The RACM mechanism has a reasonably complete set of explicit inorganic reactions that include 21 chemical species. The revisions to the RADM2 inorganic chemistry for the RACM mechanism were relatively small. The RACM organic chemistry was highly revised from RADM2. The most important revisions included a reevaluation of the yields of aldehydes and ketones from alkanes, the yield of HO from the ozonolysis of alkenes, revised branching ratios for the reactions of acetyl peroxy radicals with NO and NO₂, a revised aromatic oxidation scheme, new oxidation schemes for isoprene and terpenes and the addition of the reactions of NO₃ radical with organic peroxy radicals. The reactions of organic peroxy radicals with NO₃ radical and the revised branching ratios for the reactions of acetyl peroxy radicals with NO and NO₂ lead to predicted PAN concentrations by RACM that nearly 40% lower than those predicted by RADM2 under similar conditions. The RADM and RACM mechanisms have been tested against environmental chamber data and the agreement is good for O₃, NO_x and hydrocarbons.

We have applied the RACM mechanism to ozone reactivity calculations for biogenic emissions and highly oxygenated compounds for rural European conditions. We believe that the new scientific data included in the RACM mechanism make it a better mechanism for the determination of incremental reactivities than the RADM2 mechanism. The new RACM mechanism should replace the RADM2 mechanism in any future development of comprehensive Eulerian air quality models.

References

- Stockwell, W.R., F. Kirchner, M. Kuhn, and S. Seefeld, A New Mechanism for Regional Atmospheric Chemistry Modeling, *J. Geophys. Res.*, 102, 25847-25879, 1997.
- Stockwell, W.R., P. Middleton, J.S. Chang and X. Tang, The Second Generation Regional Acid Deposition Model Chemical Mechanism for Regional Air Quality Modeling, *J. Geophys. Res.*, 95, 16343-16367, 1990.

Requirements for Chemical Mechanisms for Eulerian 3-D Regional Atmospheric Chemistry Models

- 1. Predict concentrations of O₃, H₂O₂, ROOH, PAN, HNO₃, H₂SO₄..**
- 2. Mechanism must give accurate predictions over chemical concentrations ranging from clean to moderately polluted.**
 - Peroxy radical reactions are important**
- 3. Mechanisms must be valid for multiday simulations.**
 - Nighttime chemical species such as NO₃ are important.**
 - Less reactive species which are subject to long range transport are important.**

The Regional Atmospheric Chemistry Mechanism (RACM)

A completely revised version of the RADM2 mechanism of *Stockwell et al.* [1990]

Mechanism Includes:

- 237 reactions**
- 17 stable Inorganic species**
- 4 inorganic intermediates**
- 32 stable organic species
(4 are primarily of biogenic origin)**
- 24 organic Intermediates**

The Regional Atmospheric Chemistry Mechanism 1996

Includes:

- Detailed and explicit inorganic chemistry
- Lumped organic chemistry

4

Type	Number
Alkanes	5
Alkenes (including biogenics)	7
Aromatics	3
Carbonyls	9
Organic Peroxides	3
Organic Acids	2
Organic Nitrate and PANs	3

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Regional Atmospheric Chemistry Mechanism Highlights

- Rate constants and product yields updated to recent laboratory measurements
- New mechanism for biogenic compounds:
(Isoprene, α -pinene and d-limonene)
- Alkane decay:
The relative ratio of the yields of aldehydes to ketones was significantly reduced
- NO₃ - unbranched alkenes reactions:
Nitrate production now included.
- Ozonolysis of alkenes:
HO production has a much greater yield.
- Aromatic chemistry improved
- PAN production significantly reduced:
 - New rate constants for peroxyacetyl nitrate chemistry (PAN)
 - RO₂ + RO₂ reactions revised
 - RO₂ + NO₃ reactions added
- Tested against environmental chamber data

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Statewide Air Pollution Research Center Smog Chamber Experiments for Testing of RADM Mechanism

Description	Identification Numbers
Propane	EC216
n-Butane	EC178, EC305, EC306
Ethene	EC142, EC143
Acetaldehyde	EC254
Toluene	EC340
Toluene + n-Butane	EC331
m-Xylene	EC344, EC345
Multi-Component	EC231, EC232, EC233, EC237, EC238, EC241, EC242, EC243, EC245, EC246

Statewide Air Pollution Research Center Multi-Component Smog Chamber Experiments

Components

NO_x
n-Butane
2,3 Dimethylbutane
Ethene
Propene
t-2-Butene
Toluene
m-Xylene
HCHO
CO

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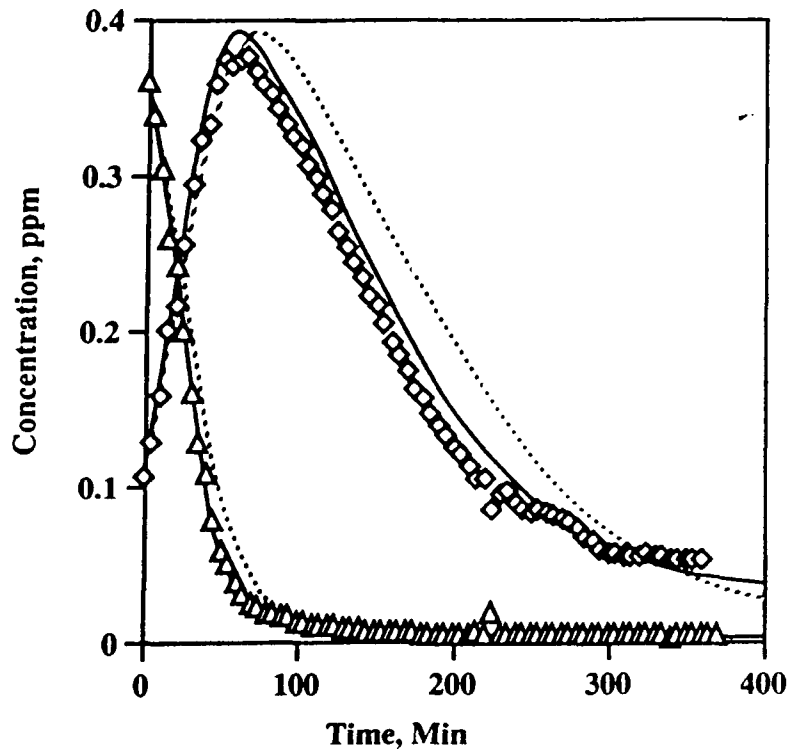
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NO_x

SAPRC environmental chamber
experiment EC-237



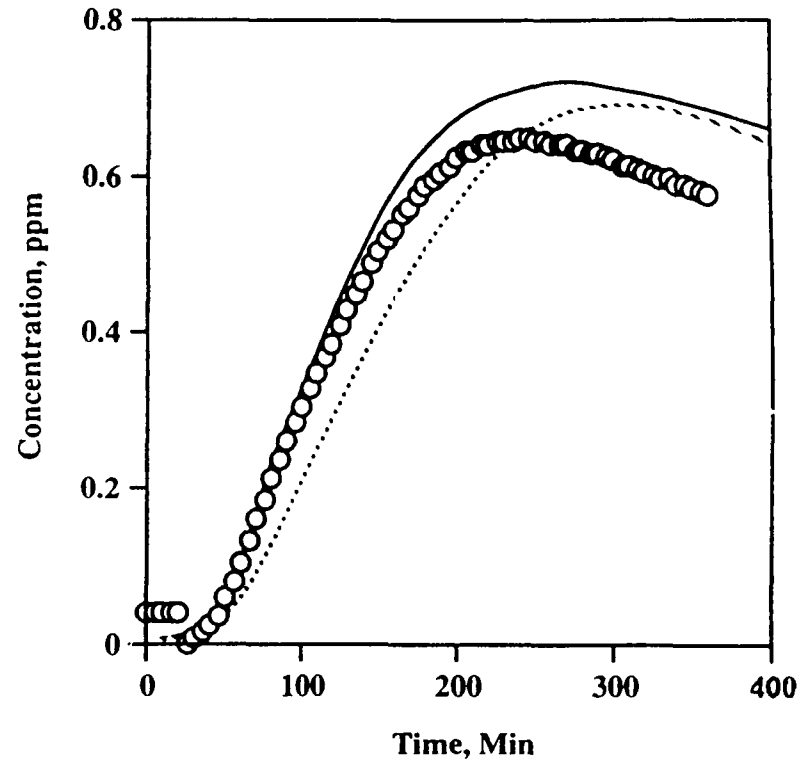
- ◇ Experimental values of NO₂
- △ Experimental values of NO
- RACM simulations; dotted lines
- RADM2 simulations

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Ozone

SAPRC environmental chamber
experiment EC-237

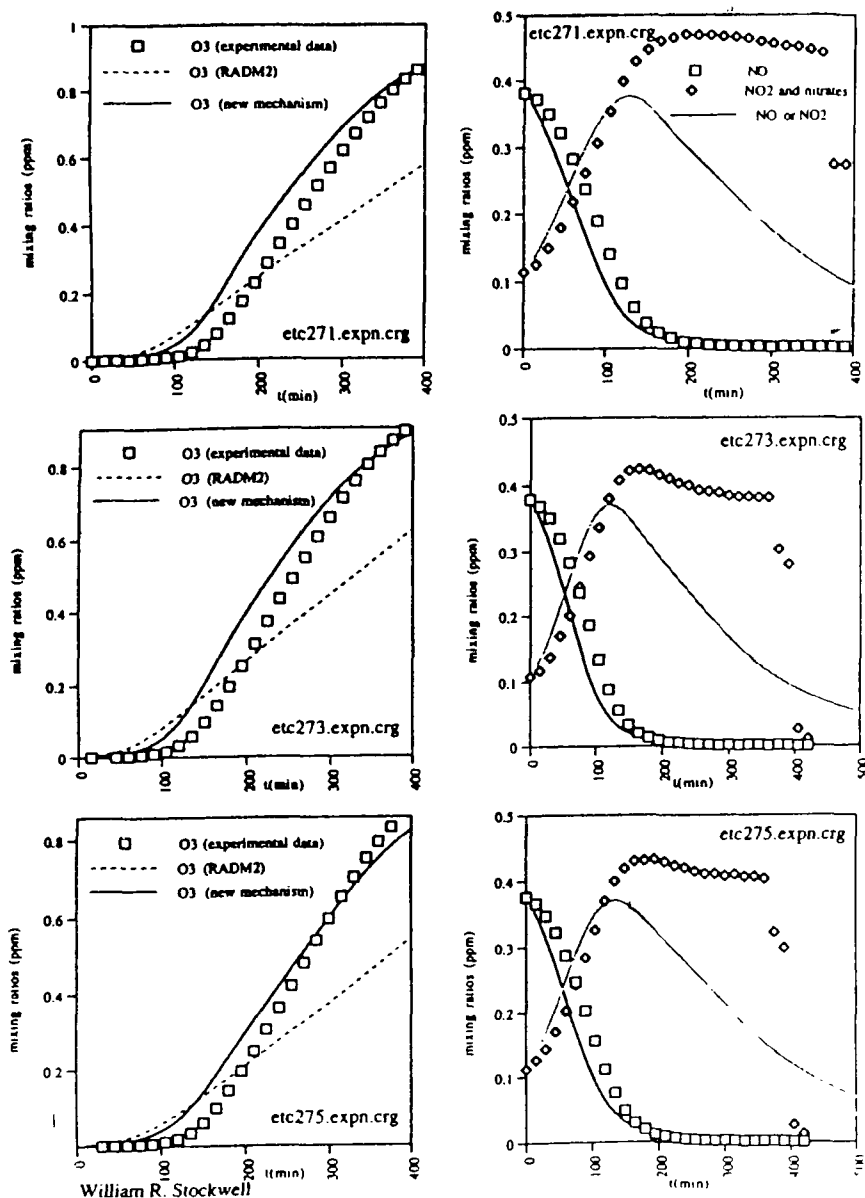


- Experimental values of O₃
- RACM simulations; dotted lines
- RADM2 simulations

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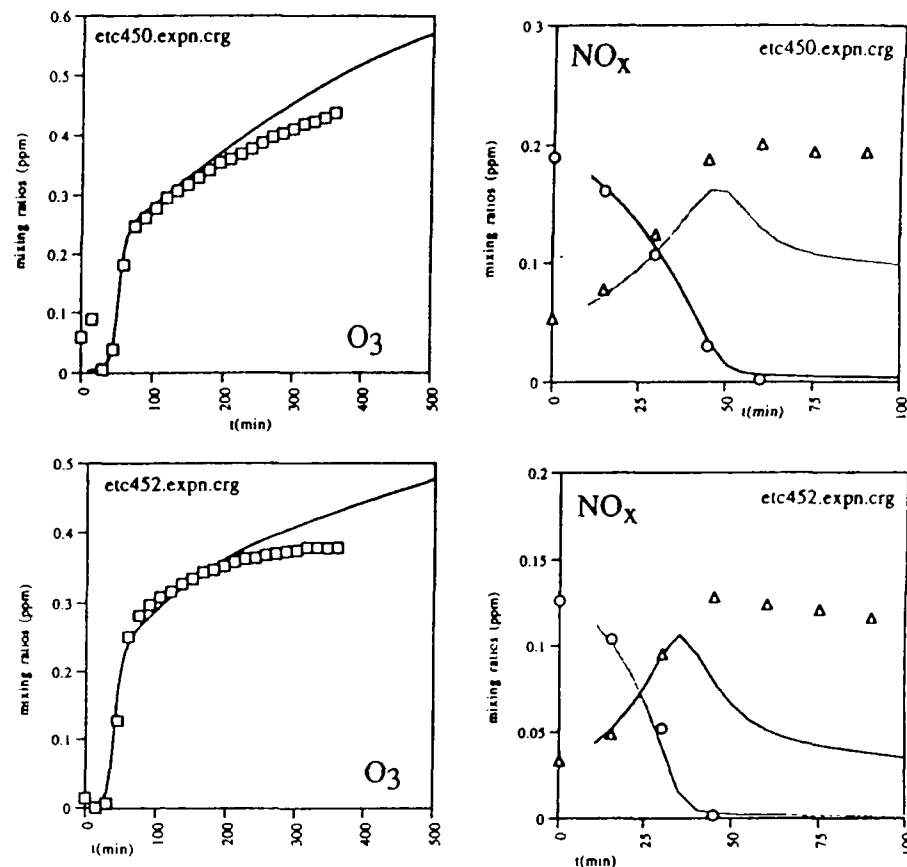
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Comparison of Simulation and Smog-Chamber Run for Isoprene



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Reactivity Calculations with the Regional Atmospheric Chemistry Mechanism
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Comparison of Simulation and Smog-Chamber Run for d-Limonene

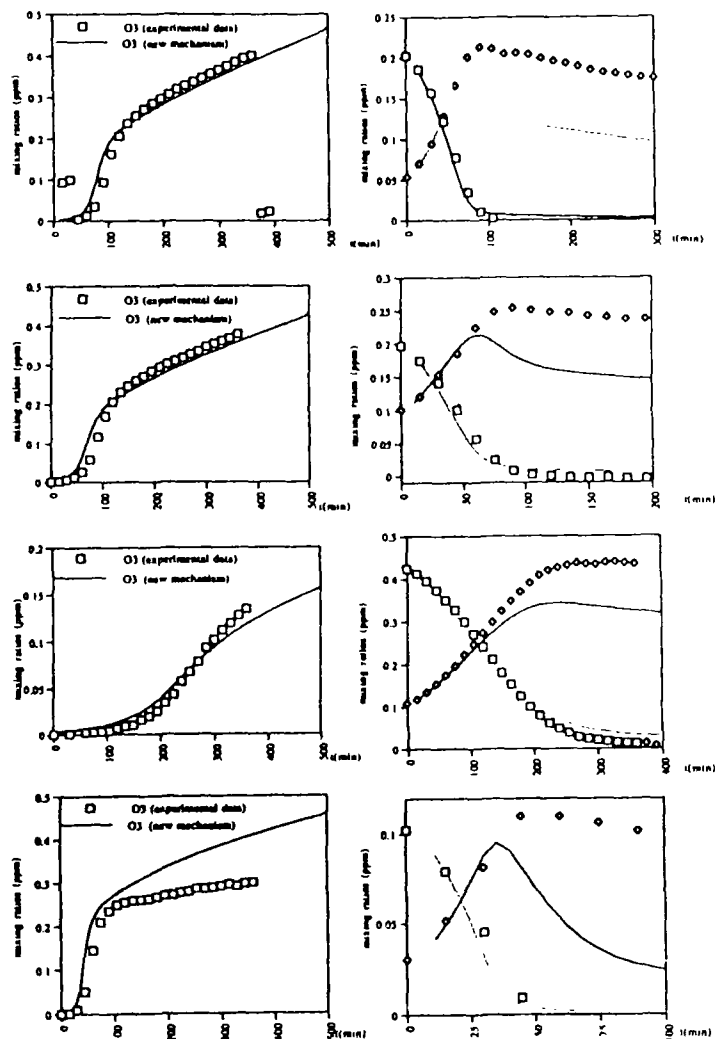


the experimental data are given by the following symbols: squares represent ozone, circles NO and triangles the sum of NO₂ and nitrates
the lines represent the simulation results for the corresponding species but the NO₂ line represents only NO₂ (without nitrates)

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Comparison of Simulation and Smog-Chamber Run for α -Pinene

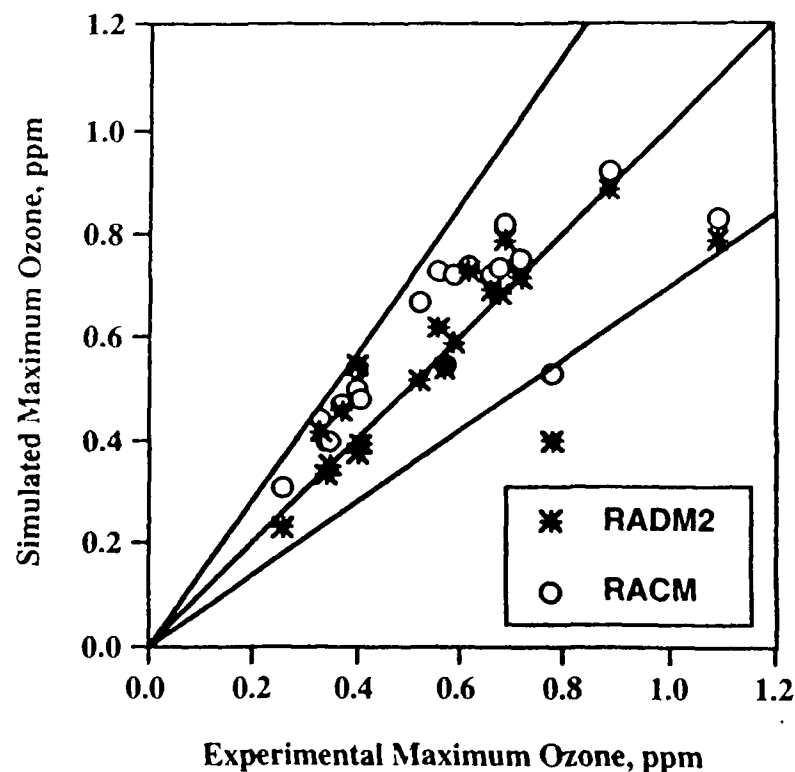


the experimental data are given by the following symbols: squares represent ozone, circles NO and triangles the sum of NO₂ and nitrates
the lines represent the simulation results for the corresponding species but the NO₂ line represents only NO₂ (without nitrates)

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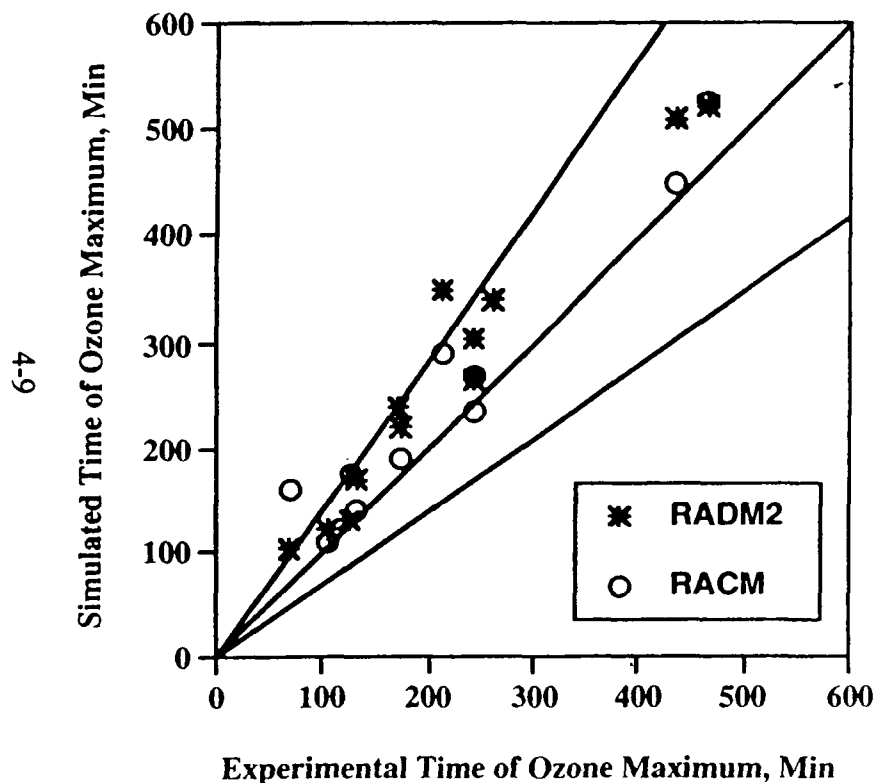
Maximum ozone concentrations predicted by RACM and RADM2 mechanisms plotted against SAPRC experimental values.



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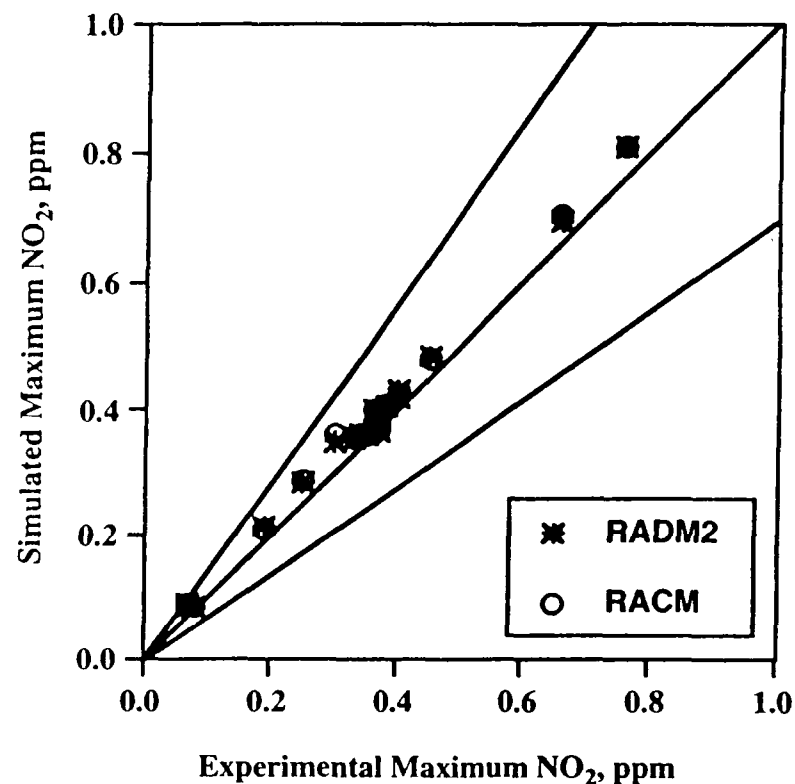
Time of the maximum of the ozone concentrations predicted by RACM and RADM2 mechanisms plotted against SAPRC experimental values.



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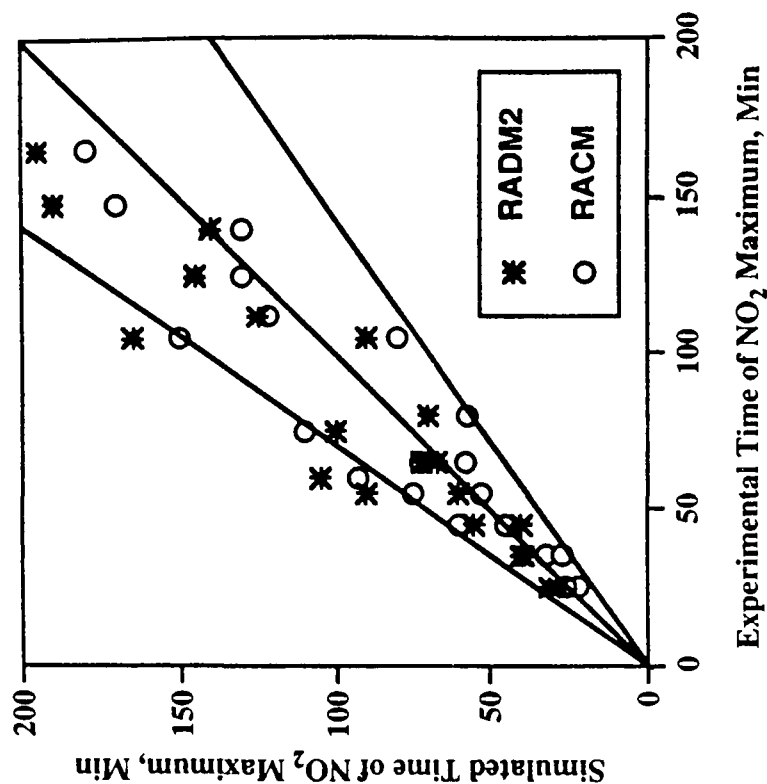
Maximum NO₂ concentrations predicted by RACM and RADM2 mechanisms plotted against SAPRC experimental values.



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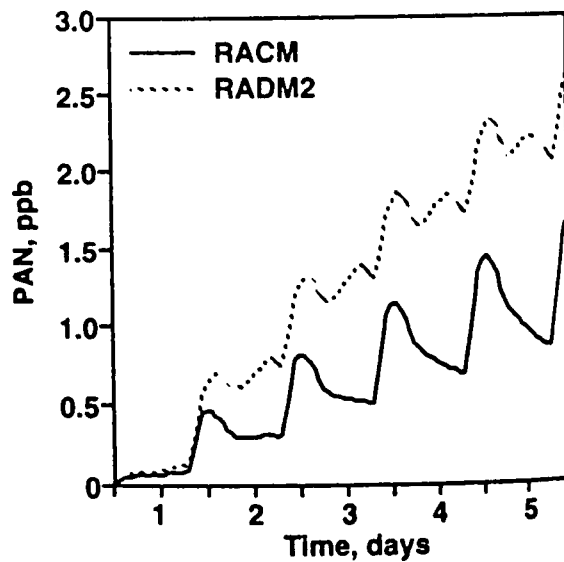
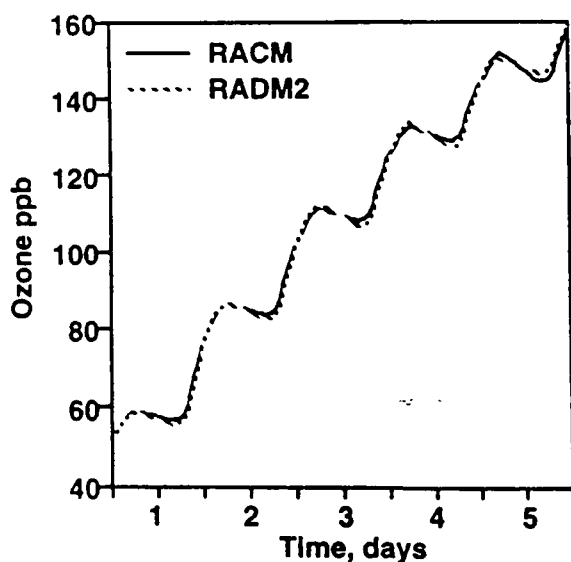
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Time of the maximum of the NO₂ concentrations predicted by RACM and RADM2 mechanisms plotted against SAPRC experimental values.



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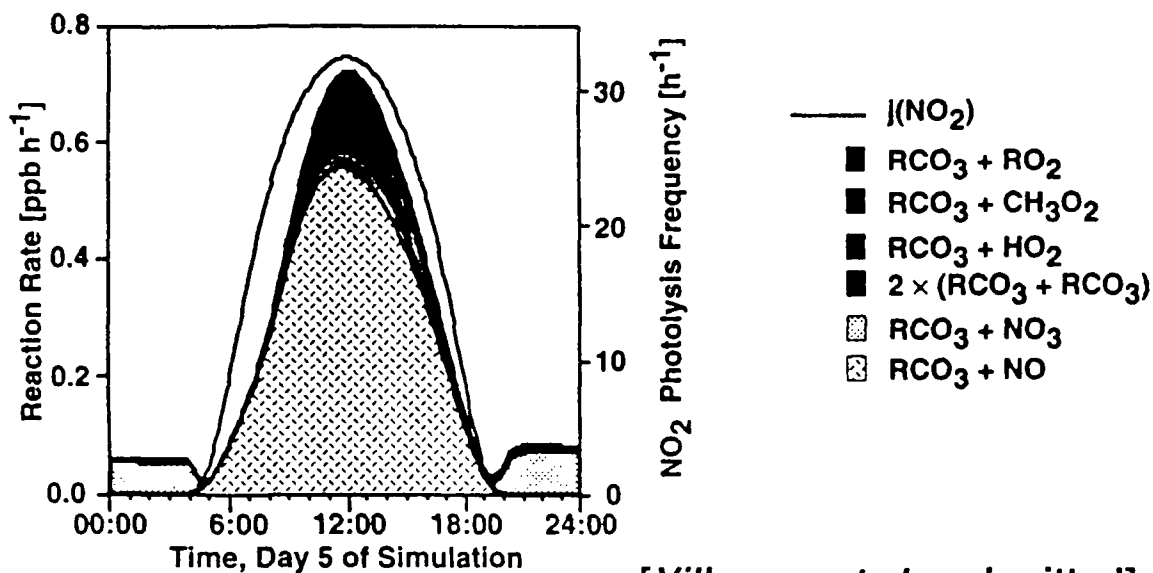
Effect of Revisions on Ozone and PAN



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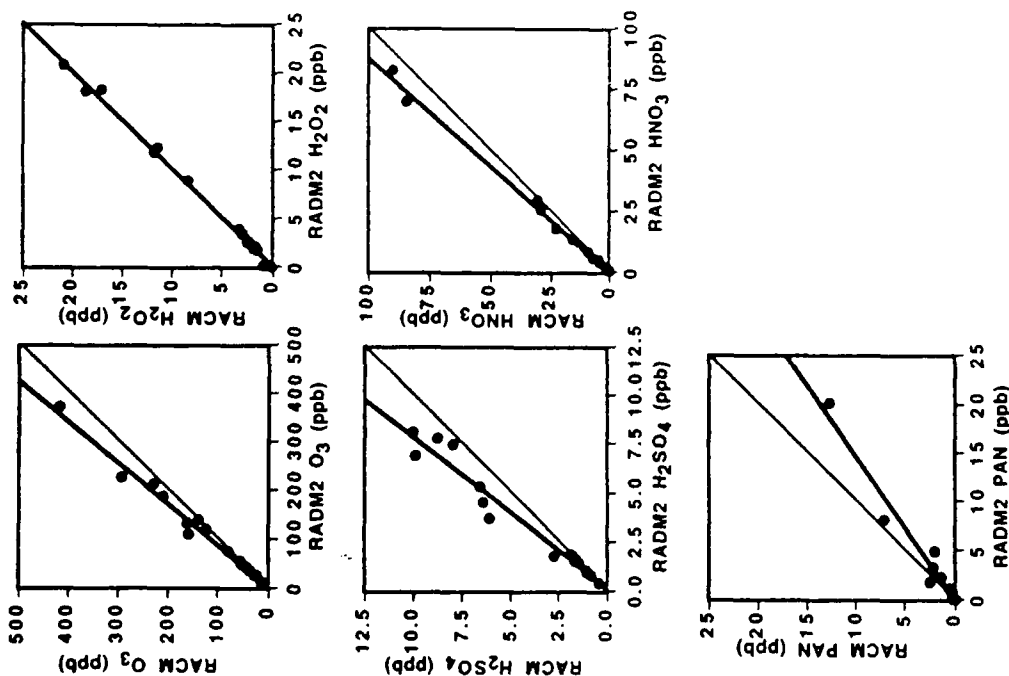
Fate of RCO_3 Radicals in RACM

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[Villenave et al., submitted]

The maximum concentrations of O_3 , H_2O_2 , H_2SO_4 , and HNO_3 and the PAN concentrations at noon on the second day for the RACM and RADM2 mechanisms for 18 different scenarios.



The dark black line is the best fit line and the thin black line is the 1-1 line of perfect agreement.

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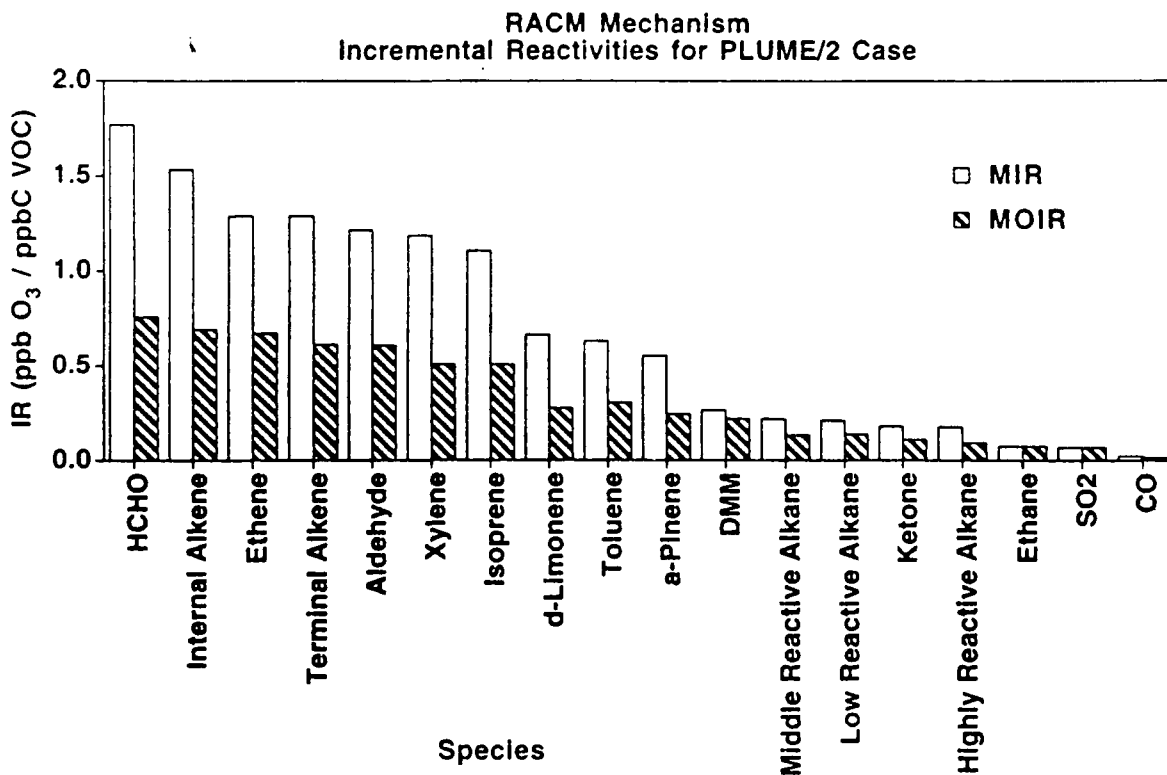
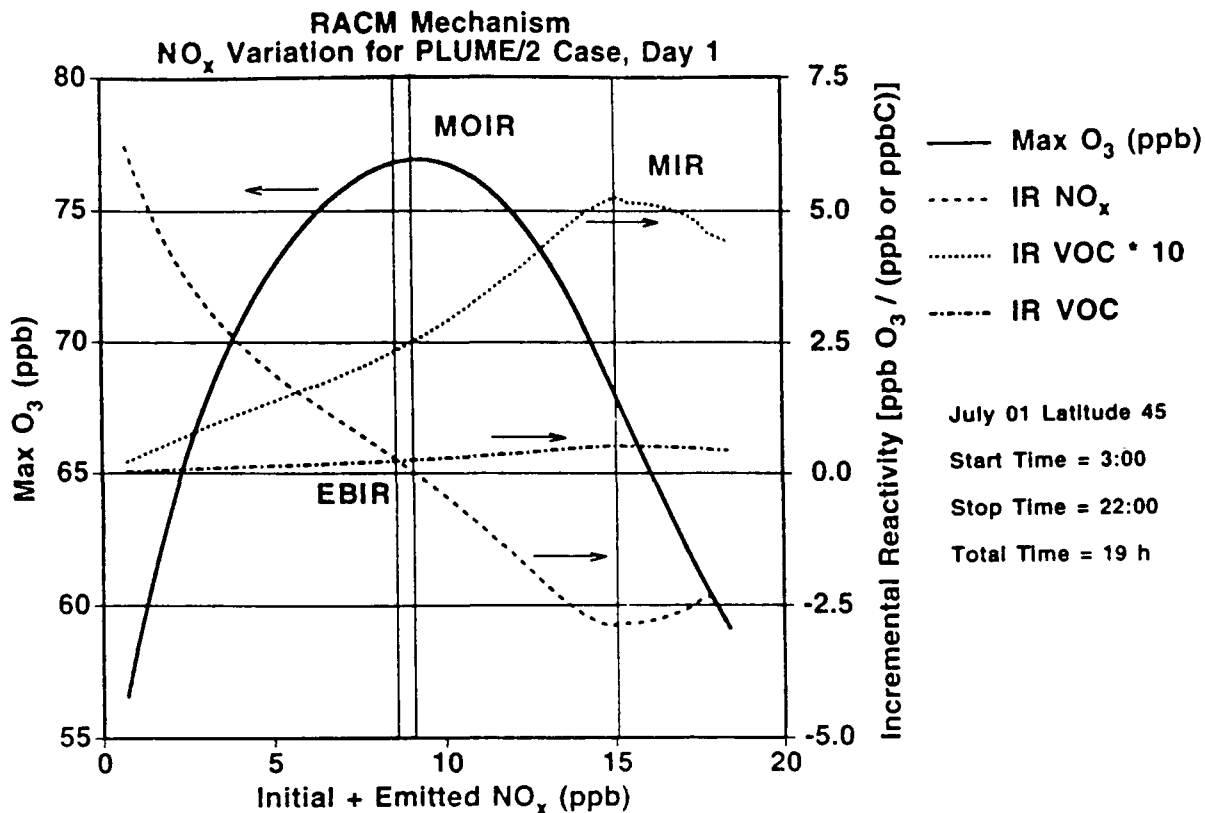
Correlations between the RACM and RADM2 mechanisms for calculated maximum concentrations of O₃, H₂O₂, H₂SO₄, and HNO₃ and the PAN concentrations at noon on the second day for the 18 scenarios.

Species	Slope	Intercept (ppb)	Variance (r ²)
O ₃	1.168	- 4.619	0.983
H ₂ O ₂	1.004	- 0.274	0.996
H ₂ SO ₄	1.243	0.009	0.957
HNO ₃	1.141	- 0.015	0.996
PAN	0.661	0.040	0.966

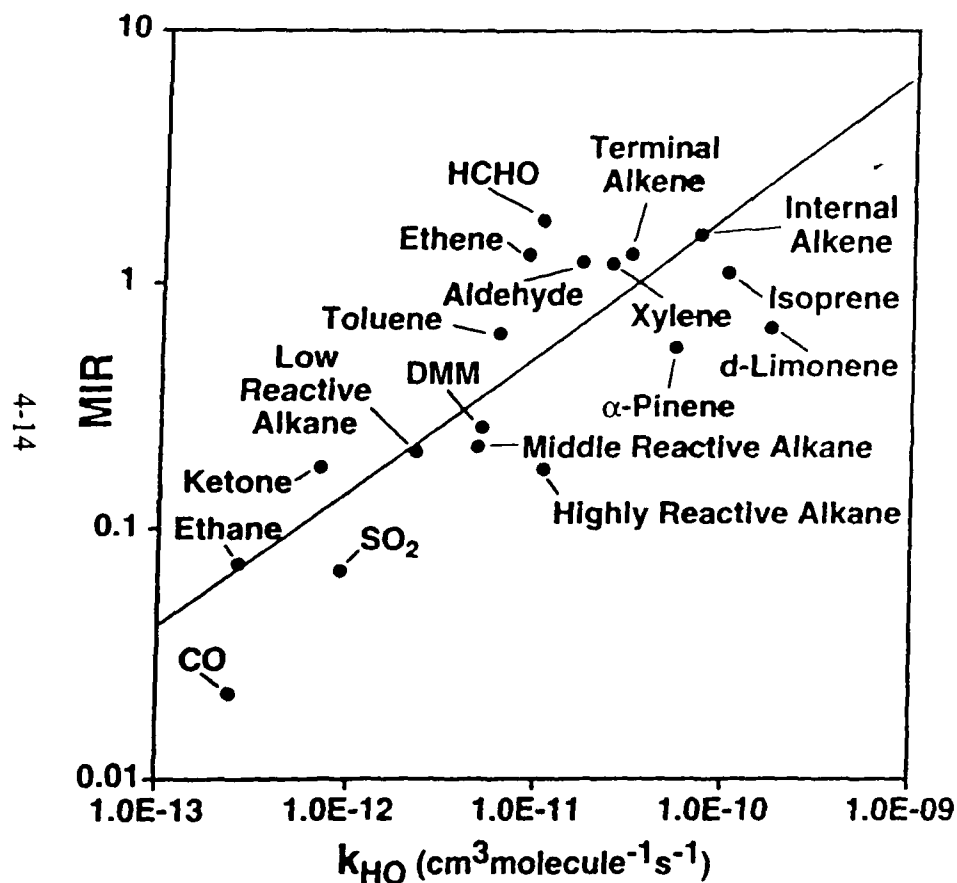
Initial Conditions for Incremental Reactivity Calculations

Start Time (Local Hour) 3:00
End Time (Local Hour) 22:00
Temperature (K) 298.15
Pressure (mbar) 1013.25
Photolysis Frequencies July 01, Latitude 45°

Initial Concentrations		Emission Rates	
Species	(ppb)	Species	Emissions (ppb min ⁻¹)
O ₃	50	NO _x	Varied
H ₂ O ₂	2.0	SO ₂	5.18 x 10 ⁻⁴
NO	0.2	CO	5.65 x 10 ⁻³
NO ₂	0.5	Ethane	2.41 x 10 ⁻⁴
HNO ₃	0.1	Low Reactive Alkane	2.94 x 10 ⁻³
HCHO	1.0	Medium Reactive Alkane	7.70 x 10 ⁻⁴
CO	200	Highly Reactive Alkane	4.52 x 10 ⁻⁴
CH ₄	1700	Ethene	4.56 x 10 ⁻⁴
H ₂	500	Internal Alkene	1.88 x 10 ⁻⁴
	(%)	Terminal Alkene	2.19 x 10 ⁻⁴
H ₂ O	1.0	Toluene	5.72 x 10 ⁻⁴
O ₂	20.9	Xylene	5.19 x 10 ⁻⁴
N ₂	78.1	HCHO	1.39 x 10 ⁻⁴
		Aldehyde	3.62 x 10 ⁻⁵
		Ketone	5.02 x 10 ⁻⁴



Maximum Incremental Reactivity (MIR) vs k_{HO}



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Reactivity Calculations with the Regional Atmospheric Chemistry Mechanism
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Conclusions

- We strongly recommend the RACM mechanism for use in atmospheric chemistry models over the RADM2 because the RACM chemistry is based upon more recent and reliable data.
- Compared with the RADM2 the RACM predicts concentrations:
 - somewhat greater for O_3 , H_2SO_4 and HNO_3
 - almost the same H_2O_2
 - significantly less PAN.
- The extended RACM has been applied to ozone incremental reactivity calculations for rural European conditions.
- We have estimated incremental reactivities of isoprene, terpenes and dimethoxymethane.

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Reactivity Calculations with the Regional Atmospheric Chemistry Mechanism
Fraunhofer Institute for Atmospheric Environmental Research (IFU)

Hydrocarbon reactivity and ozone production in urban pollution according to the Stockwell et al., (1990) reaction mechanism

Chris J. Walcek
State University of New York at Albany

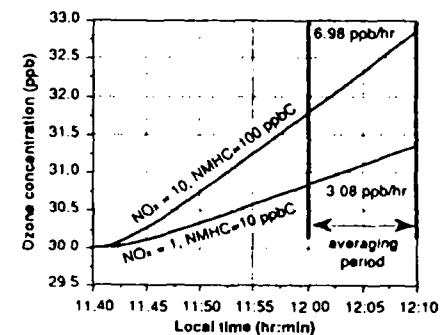
Abstract- A method for ranking the ozone production potential for various classes of reactive hydrocarbons is presented. Using the Stockwell et al.,(1990) chemical reaction mechanism ("RADM2"), ozone production efficiencies for 14 classes of emitted hydrocarbons included in the mechanism are quantified over a wide range of background NO_x and hydrocarbon concentration regimes. O_3 production efficiencies are calculated by running a box model initialized with specified concentrations for a 2-day period under fixed sunlight and meteorological conditions, after which NO_x is oxidized and ozone production ceases. Individual organic compound concentrations are then perturbed by 1 ppb, and the resulting changes in O_3 after 2 days are compared with the base simulation. For some ranges of NO_x and organic compound concentrations, the additional ppb of O_3 produced from each additional ppb of organic compound is somewhat constant, but there are some compounds under some chemical conditions for which the additional ozone production potential is highly variable. Despite these variations, net ozone production from each class of organics is approximately correlated with the corresponding reactivity of the organic compound with HO radical, although there are some broad violations of this correlation. HO reactivity may only crudely be an indicator of ozone production potential under many conditions for some classes of organic compounds.

Hydrocarbon reactivity and ozone production in urban pollution according to the Stockwell et al., (1990) reaction mechanism

Chris Walcek
State University of New York at Albany

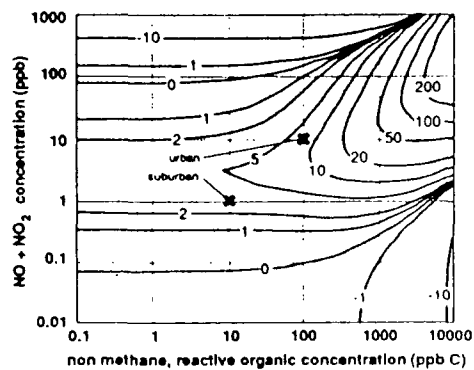
1. Simple method for calculating "ozone production efficiency"
2. Detailed description of a couple "cases"
3. Generalized results for wide range of NO_x and hydrocarbon concentrations
4. Conclusions

Ozone concentration change in air parcel, calculated using Stockwell et al., (1990) mechanism



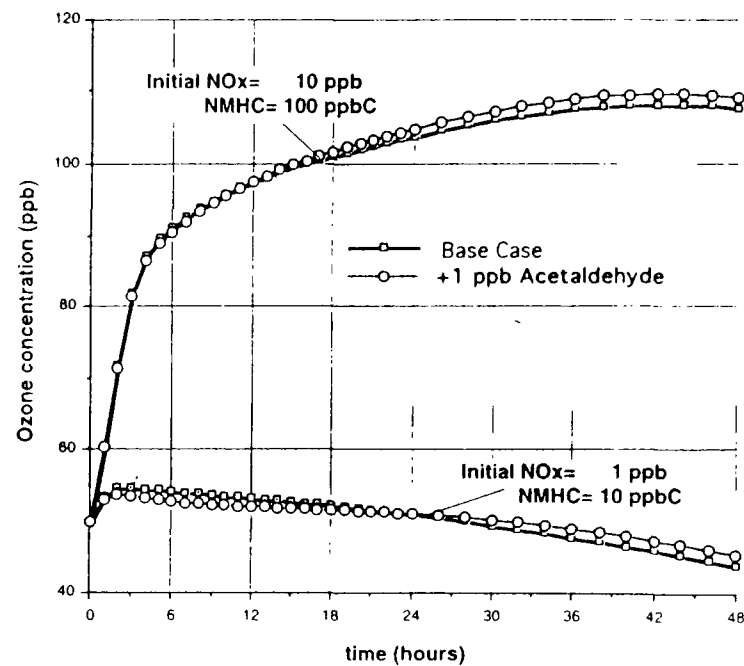
noon conditions,
50% clear-sky photolysis rates
20 °C, 50% Rh; 1.8 ppb isoprene

Ozone formation rates vs concentrations of NO_x and hydrocarbon concentrations

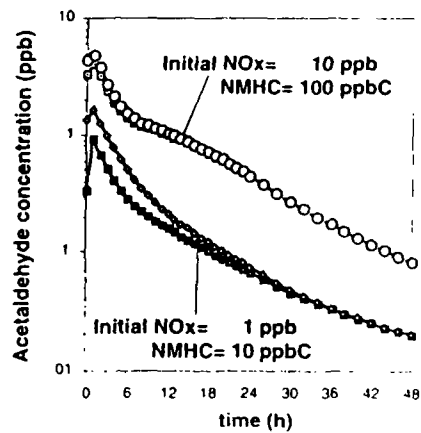
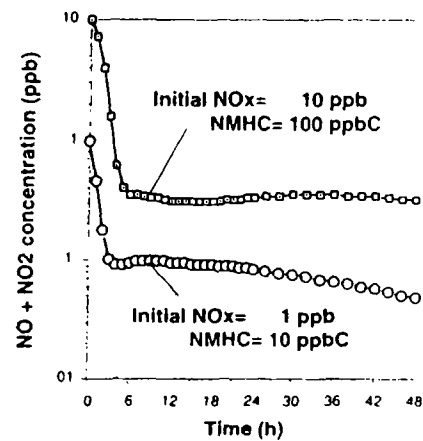


noon conditions
 April, 40° north
 50% clear-sky photolysis rates
 20 °C
 50% Rh
 1.8 ppb isoprene

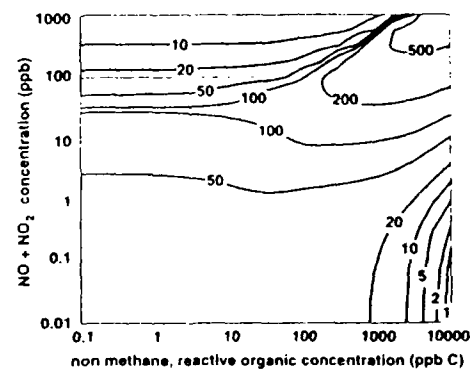
Ozone concentration (ppb) vs time



NO_x and Organic concentration vs. time

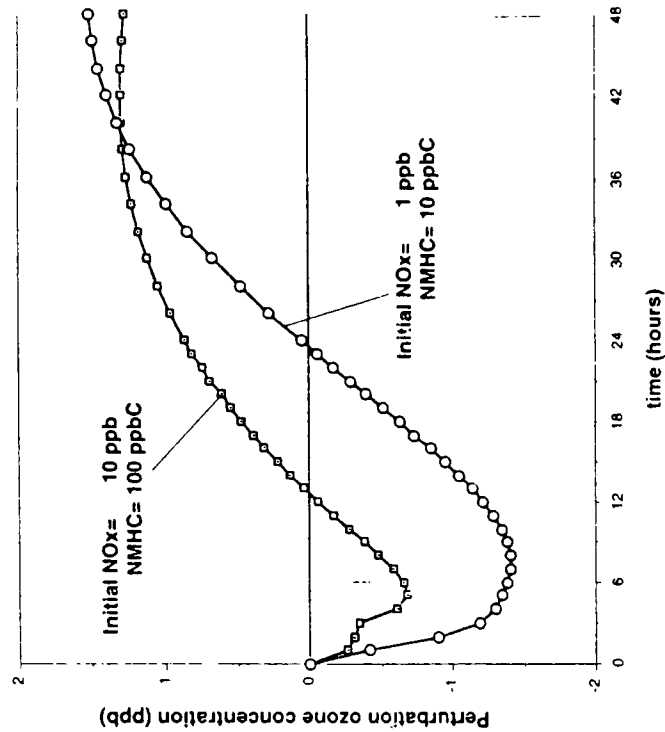


Accumulated ozone after two days
continuous noon conditions
Chemistry only
Stockwell et al., (1990) mechanism

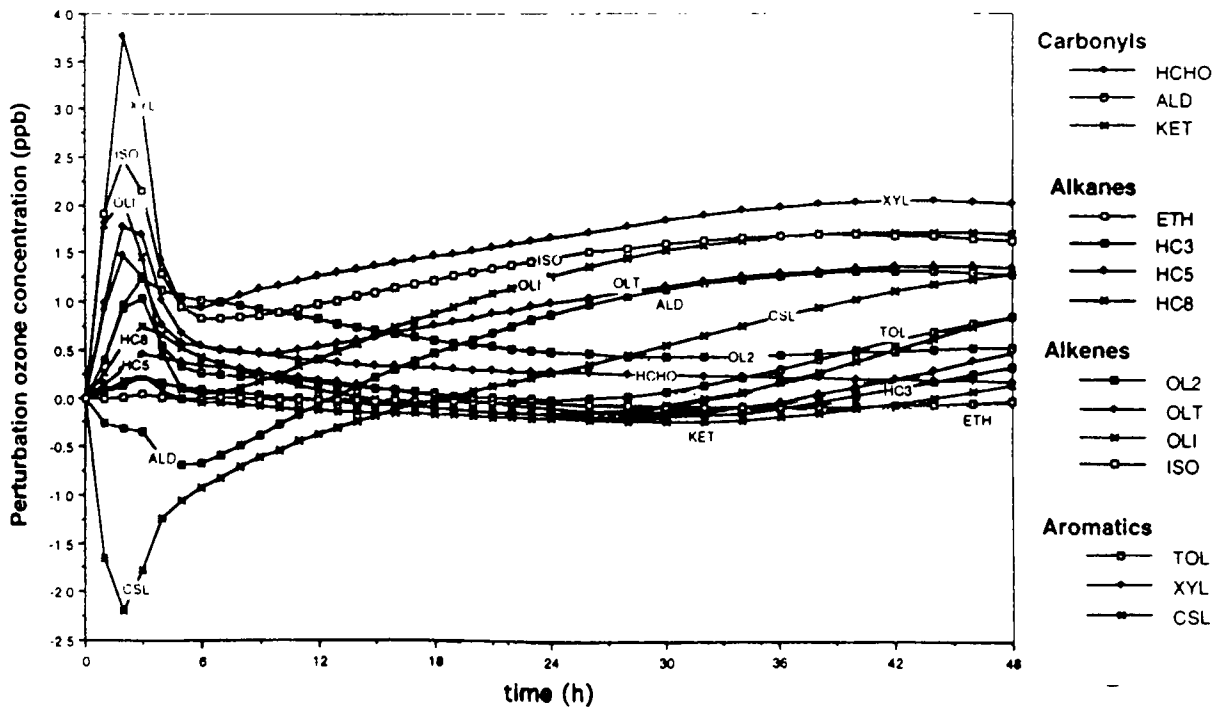


grey area denotes <50 ppb
(initial concentration)

Change in ozone (ppb) concentration due to 1 ppb change in acetaldehyde



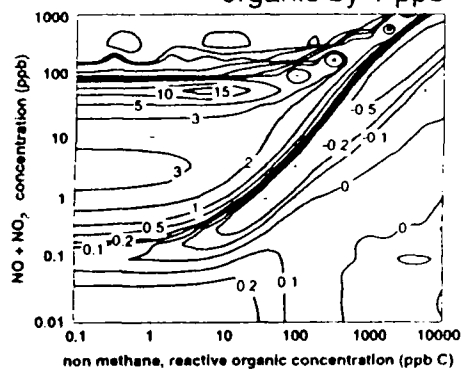
Perturbation ozone concentration induced by 1 ppb increase in various hydrocarbon
Initial NO_x=10ppb; Initial NMHC=100ppbC



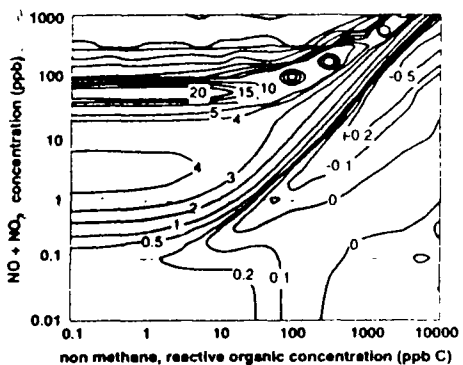
Aromatics

Change in accumulated ozone (ppb) after two days due to change in initial specified organic by 1 ppb

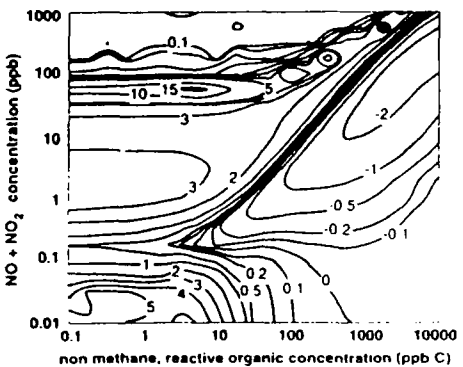
Toluene
(& less reactive)
TOL



Xylene
(& more reactive)
XYL



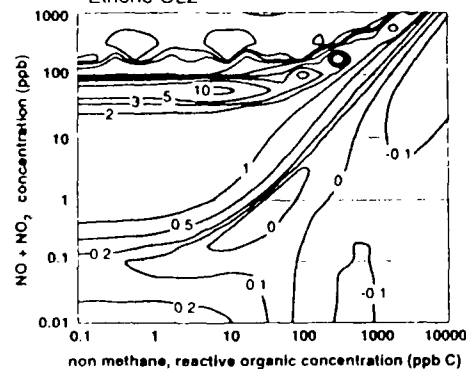
Cresol
(& other
hydroxy-substituted)
CSL



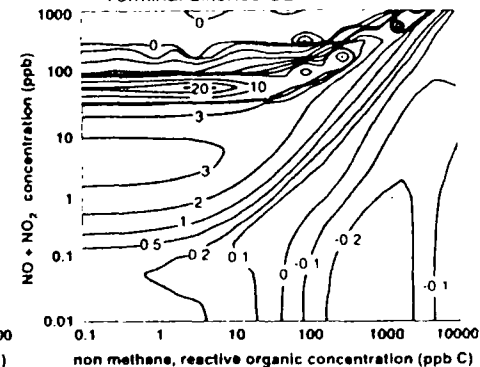
Olefins (Alkenes)

Change in accumulated ozone (ppb) after two days due to change in initial specified organic by 1 ppb

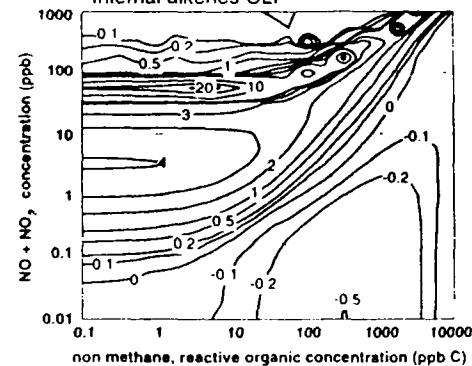
Ethene OL2



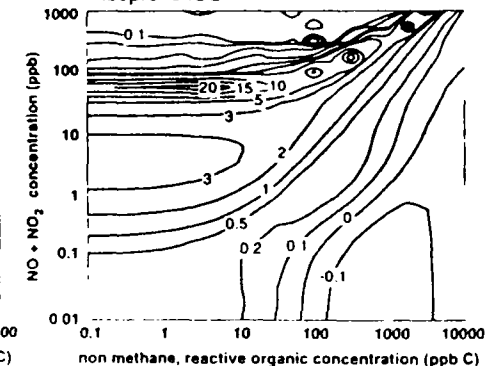
Terminal alkenes OLT



Internal alkenes OLI



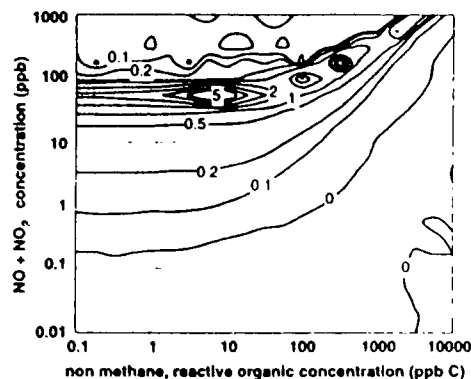
Isoprene ISO



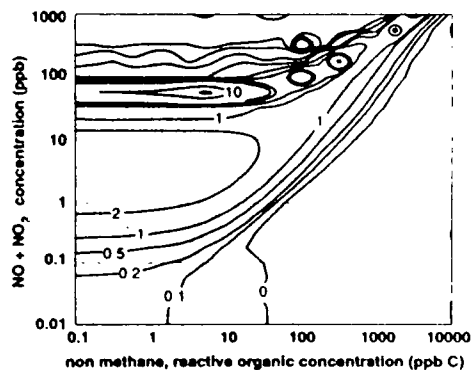
Carbonyls (aldehydes)

Change in Accumulated ozone (ppb) after
two days due to change in initial specified
organic by 1 ppb

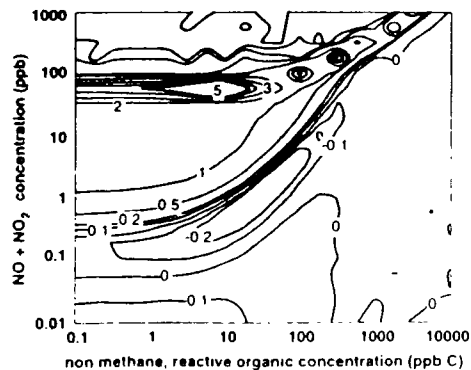
Formaldehyde
HCHO



Acetaldehyde
(& higher ald)
ALD



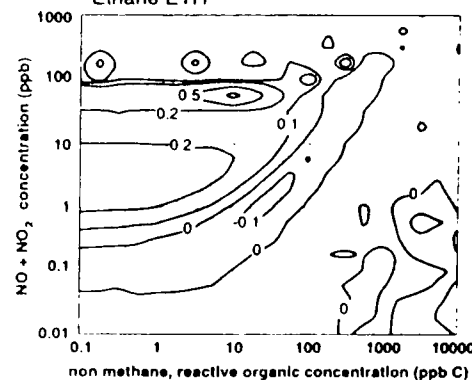
Ketones
KET



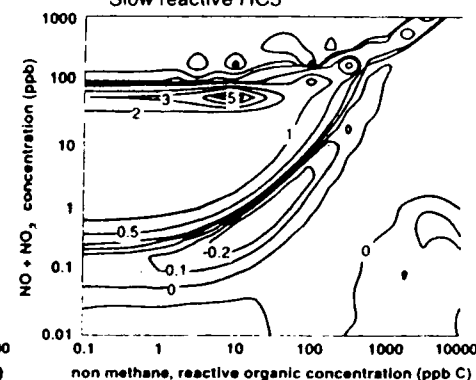
Alkanes

Change in accumulated ozone (ppb) after
two days due to change in initial specified
organic by 1 ppb

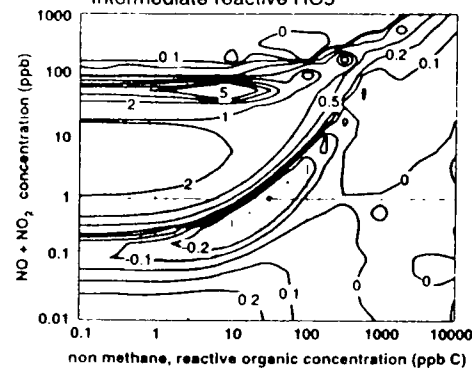
Ethane ETH



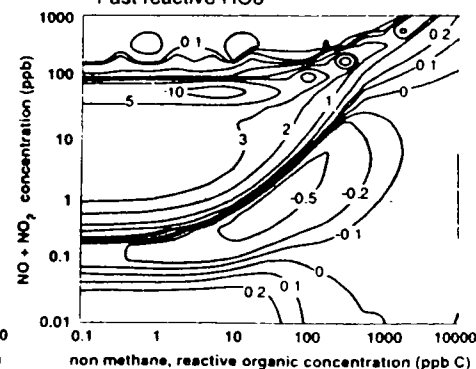
Slow reactive HC3



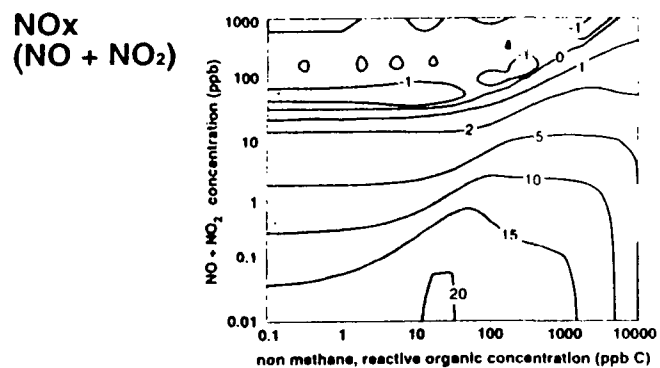
Intermediate reactive HC5



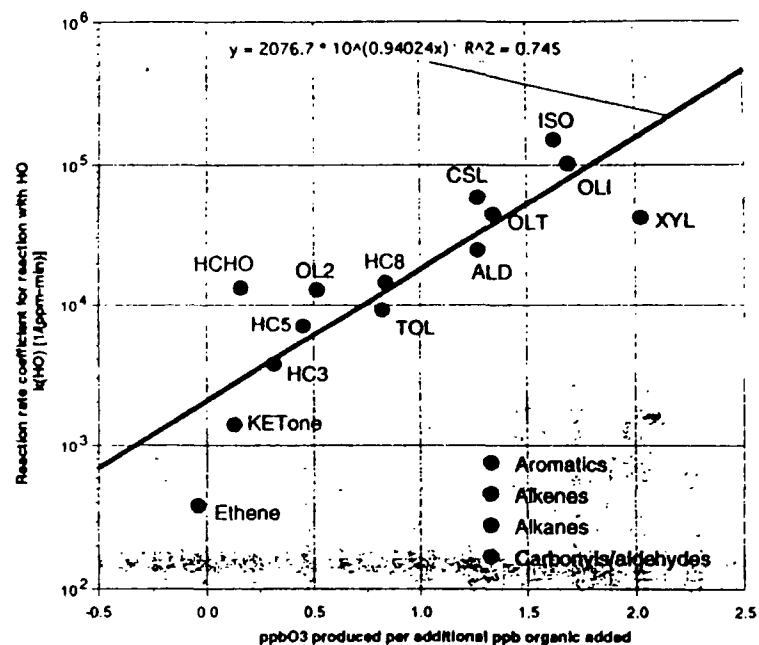
Fast reactive HC8



Change in Accumulated ozone (ppb) after two days due to 1 ppb change in initial NO_x



Ozone "production efficiency" from hydrocarbons
in the Stockwell et al., (1990) mechanism
initial conditions: 10 ppb NO_x, 100 ppb(C) organic
after 48 hours, continuous noon conditions

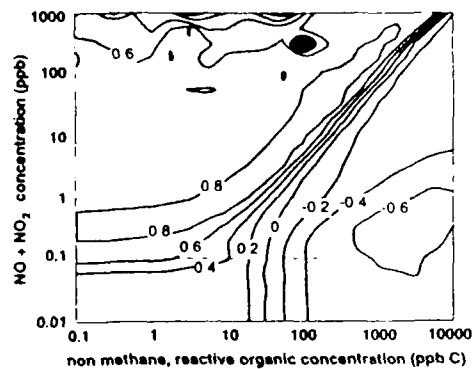


Correlation coefficient (r) between

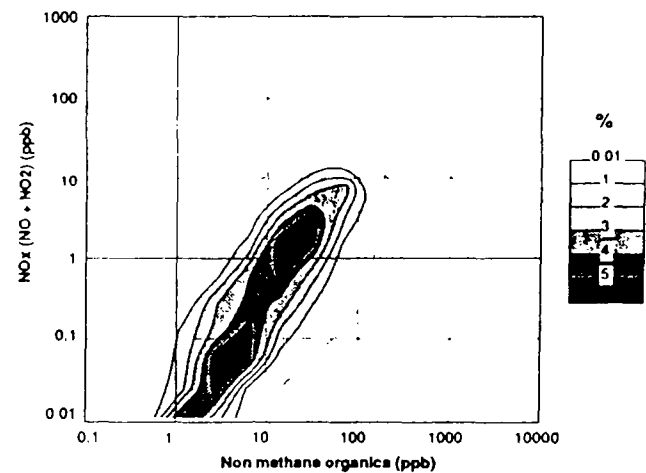
(a) change in accumulated ozone (ppb)
due to 1 ppb change in all organics

vs.

(b) log (rate coefficient for reaction of
each organic with HO)



Joint probability distribution:
NO_x and nonmethane hydrocarbon concentrations
% probability of observing concentration per 1/3 log₁₀
concentration range
900 - 950 mb, Northeast U. S., 21-24 April 1981
(RADM 35x38 domain)



MULTI-DAY OZONE FROM LOW-REACTIVITY VOC's

by

Gary Z. Whitten

Systems Applications International

Overview

- Concern for downwind areas
- New technique based on UAM
- Compares candidate VOC to ethane
- Provides incremental impacts

UAM-BASED TECHNIQUE

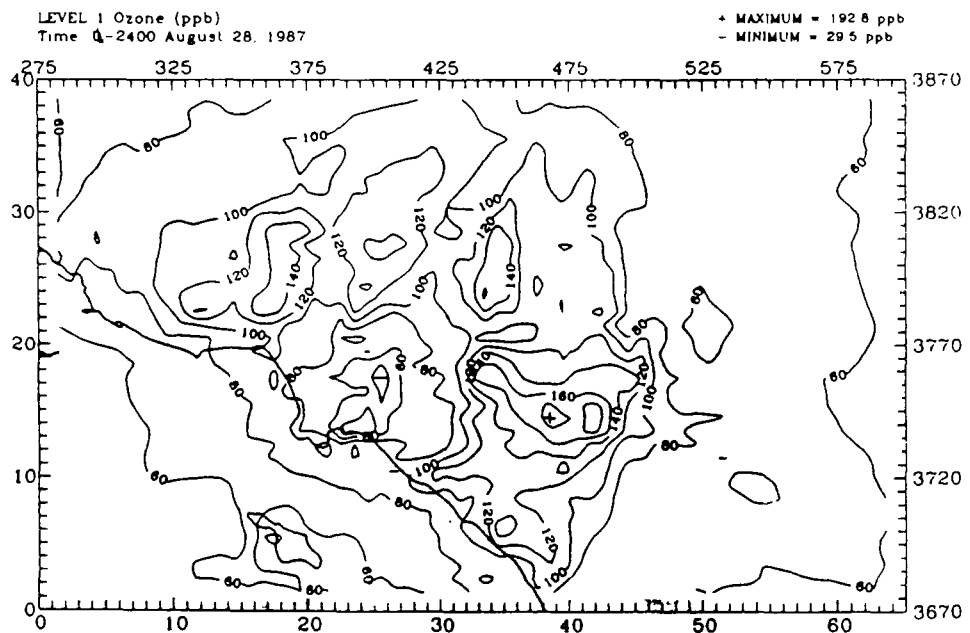
- VOC increment added to upwind cells
- Uses "back" trajectory from final peak cell
- 100 tons ethane for base case
- Spread over 9 cells over 1 hour
- Use explicit chemistry for ethane and candidate VOC

Example Candidate VOC

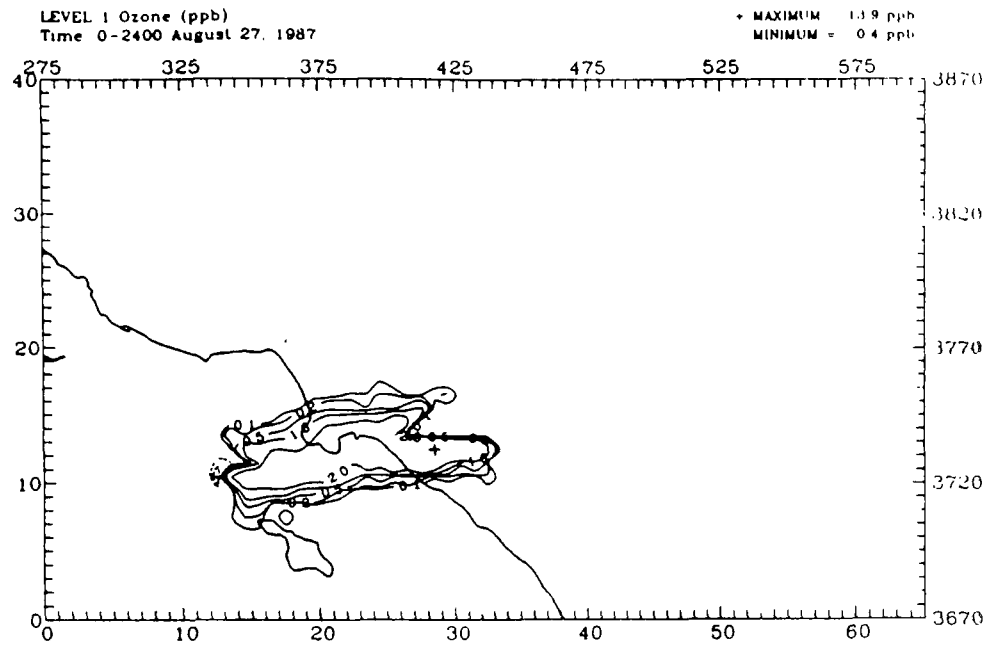
- 1-bromopropane
 - Same k_{OH} by weight as ethane
 - Molecular k_{OH} 4 times faster
- Chemistry assumed to be like propane
 - Molecular k_{OH} same as propane

UAM Results

- 1st day both nearly 14 ppb impact
 - Not at main peak (cloud not there yet)
- 2nd day impacts differ
 - ethane 4 ppb (on peak of 190)
 - candidate only 2.3 ppb
- 2nd (off peak impacts)
 - ethane 7.8 ppb
 - candidate 4.8 ppb

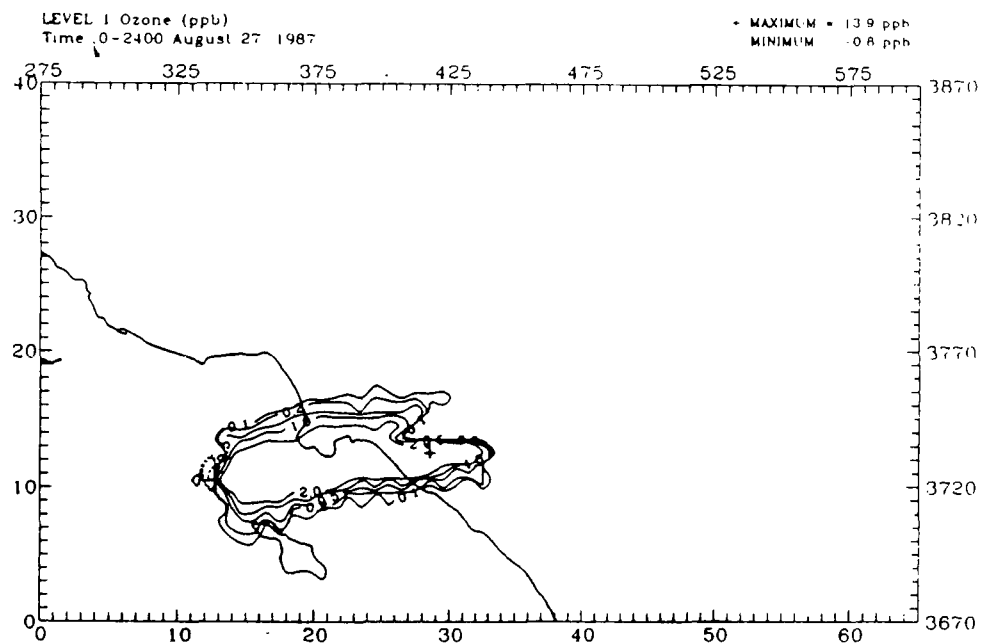


UAMPLT Tue Mar 26 12 10 08 1986



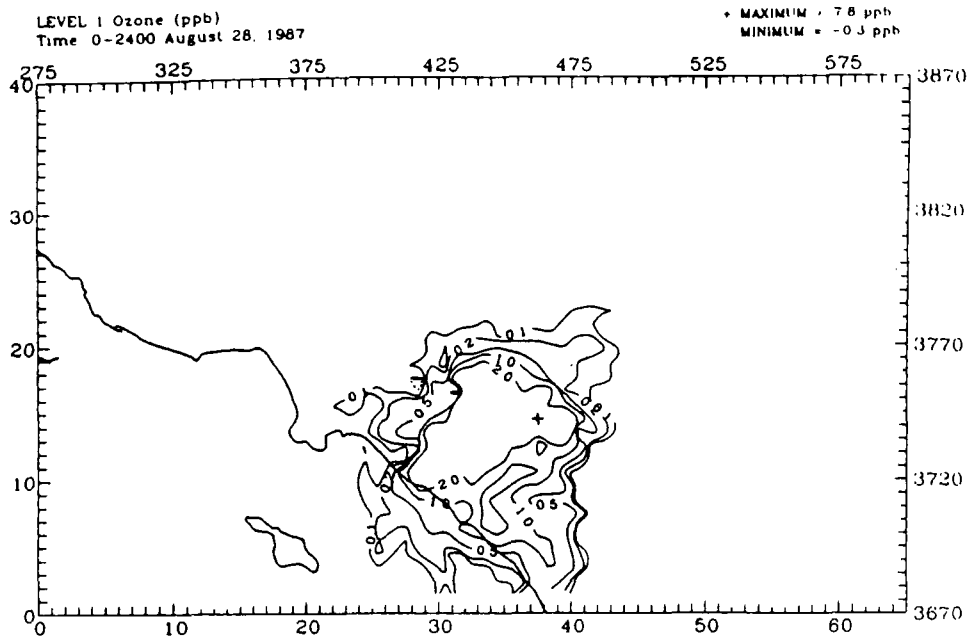
Difference in Maximum Simulated Ozone Concentrations
August 27, 1987 (Simulation 100 ton ethane minus base)

UAMPLT Wed Mar 27 08 33 10 1986



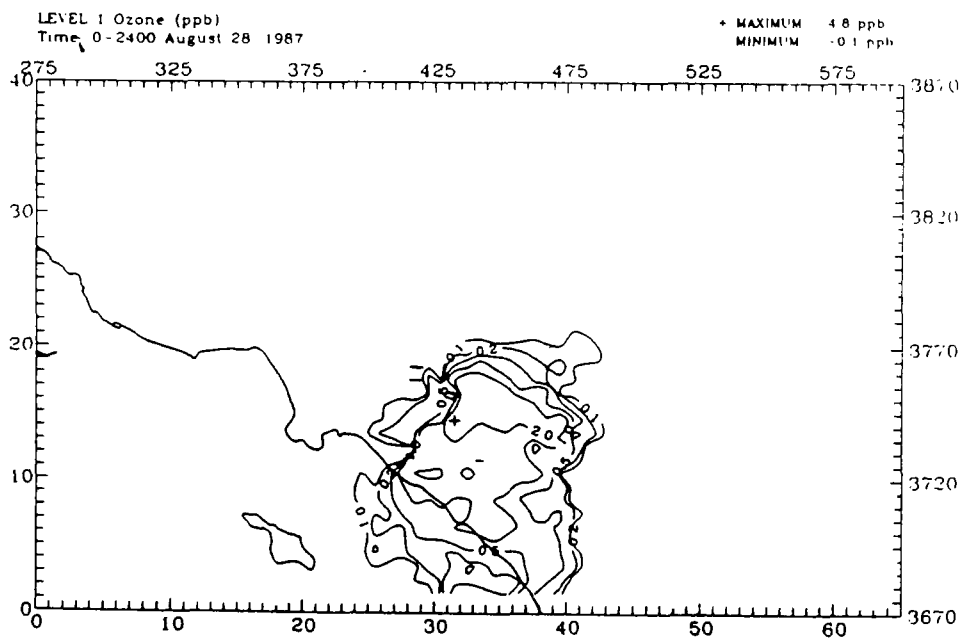
Difference in Maximum Simulated Ozone Concentrations
August 27, 1987 (Simulation 100 ton bromopropane minus base)

UAMPLIT Tue Mar 26 12 10 08 1986



Difference in Maximum Simulated Ozone Concentrations
August 28, 1987 (Simulation 100 ton ethane minus base)

UAMPLIT Wed Mar 27 08 33 11 1986



Difference in Maximum Simulated Ozone Concentrations
August 28, 1987 (Simulation 100 ton bromopropane minus base)

Abstract

Computing Volatile Organic Compound Reactivities with a 3-D AQM

Zion Wang
University of North Carolina
at Chapel Hill

In many urban areas, selective VOC control on reactive VOCs is much more advantageous over indiscriminate control. This raises the need for identifying reactive VOCs. One of the currently used methods to quantify VOC reactivity is by measuring how changes in VOC emissions in an airshed affect ozone formation in the same airshed with the EKMA modeling method. However, due to simplifications in the dispersion component of the model and in the ambient conditions and emissions inputs, the use of three-dimensional photochemical models to obtain reactivity data is desirable. This study attempts to use a three-dimensional photochemical model to compute the reactivity data for a few VOC species. The study also examines how different parameterization techniques impact reactivity calculations.

Box Modelling of NO_x and VOCs to Determine Emission Reduction Strategies

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Abstract:

Measurement data from the Canadian National Air Pollution Surveillance monitoring network was used to provide initial conditions for a series of sensitivity runs of a box model of local chemistry. The sensitivity runs were used to determine the factors having the greatest impact on ozone concentrations at 15 sites in urban centres in Canada. Sensitivities to NO_x were either zero or negative, indicating that the measurement sites were likely VOC limited and subject to NO_x titration of ozone. Decreases in model Nox at these sites led to increases in ozone production by the model. Sensitivities to total VOC and ten major unoxxygenated VOC classes were positive, indicating that reductions in VOCS would result in decreases in ozone concentrations. Specific VOC classes had a much greater effect than others, with internal-bond alkenes and higher aromatics having the greatest impact on ozone production.

Model Description:

The photochemical model employed had three main components:

- (1) **A gas-phase chemical mechanism** (Makar et al, 1998) used as input for the model chemical calculations. The mechanism employed has been under development for several years at AES, and is intended as a replacement for the regional model mechanism of ADOM. The major revisions to the species of the previous mechanism include:
 - the inclusion of three additional PAN-like species
 - the inclusion of CO and C₂H₆ as advected, non-constant variables of the system
 - the separation of higher alkanes into C₄-C₅ and C₆-C₈ species
 - the separation of higher alkenes into terminal and internal double bond species
 - the separation of higher aromatics into di and tri substituted species
 - the inclusion of species-specific RO₂s and R(O)O₂s
 - the inclusion of six (previously one) higher carbonyls
 - the inclusion of formic acid, acetic acid, and C₁-C₃ alcohols
 - the inclusion of HNO₄ as an advected species.

The new mechanism has 251 reactions, compared to the ADOM mechanism's 114. Some of the more important revisions include:

- All reactions retained from the ADOM model have rate constants updated according to the most recent data for those reactions.
 - Inclusion of specific RO₂+RO₂ reactions and their products
 - NO₃ + RO₂, NO₃ + R(O)O₂ reactions included
 - Much greater detail in the formation of oxygenated products from the original nonoxygenated VOCs. Aside from the greater speciation, the formation of products of higher alkanes, alkenes, and aromatics has been altered to incorporate recent laboratory studies on these species. The aromatic mechanism now includes the highly reactive broken ring products and dicarbonyls known to form after the initial oxidation by OH, O₃ and NO₃.
 - A more detailed isoprene mechanism, including the formation of MACR and MVK and MPAN has been included.
 - Higher Terpenes have been included as a separate species.
 - All photolysis rates have been updated according to the most recent information available.
- (2) **A one-dimensional radiative transfer subroutine.** This model (Yung, 1976) was used to calculate the intensities of light as a function of wavelength at each site for which the model was applied. The radiative transfer model made use of the US Standard Atmosphere (1976) for ozone and total column number density information. Solar zenith angles were calculated using the latitude, longitude, local time and time zone of each site for which calculations were performed. The resulting solar intensities were used to calculate photolysis rates for the chemical model.
- (3) **A numerical solver** to solve the system of differential equations resulting from the chemical mechanism. The solver used here was that of Kahaner et al (1989), a variation on the predictor-corrector code of Gear (1971). The same solver was set up by the author of the current work for use as the numerical driver in the AES CREAMS box model.

As input data, the model made use of the NAPS database. The National Air Pollution Surveillance database includes time coincident NO_x and VOC measurements made at several sites across Canada, from 1986 until the present. A subset of 15 sites was used in the current study. VOC measurements include standard testing for 175 different species. These were lumped into the model speciation using the reactivity weighting method of Middleton et al, (1990).

Unfortunately, until 1996, the NO_x data was usually only reported to the nearest 10 ppbv. In addition, the records contain only a total NO_x expressed as NO₂. The lack of more detailed NO_x data presents an important confounding factor to the conclusions of the study, as is noted below.

Methodology:

A model run of an individual record would take place through the following stages:

- (1) A measurement record, consisting of the site latitude, longitude, time (year, month, day, start hour, end hour, time zone), NO₂, NO, NO_x, O₃, CO, SO₂, and VOCs was read in by the model.
- (2) Most of the NAPS records did not have NO reported as a separate variable, and the NO_x and NO₂ concentrations were usually equal. Initial concentrations of NO₂ and NO were calculated using the following stages:
 - (a) If NO_x was reported, and NO_x=NO₂ in the record, then it was assumed that the NO concentrations were less than the 5 ppbv, and the model mechanism was used to generate an initial NO concentration by assuming a steady state with the other model variables. The same process was used if only NO_x was reported (a smaller number of stations reported NO_x, and zero NO₂ and NO).
 - (b) If both NO₂ and NO values were reported, those values were used as initial conditions.
- (3) Following initialization of NO_x, the model was run forward in time for one hour to initialize the other variables. If the site was located in a city, the concentrations of NO, NO₂, CO, SO₂ and the unoxxygenated VOCs were held constant during this initialization, simulating the replenishment of these variables by emissions. If the site was considered to be rural, then all variables aside from methane, water vapour, oxygen and the total number density were allowed to vary with time. Table 1 gives a listing of the stations, and their categorization as rural or urban. This procedure allowed the generation of initial concentrations for the other model species (eg. oxygenated hydrocarbons, organic peroxides, hydrogen peroxides, radicals, etc.). These were used as initial values these species in the sensitivity runs which followed. The idea here was to allow the chemical model to "spin up" slightly, to avoid the sensitivity calculations being affected by the initial conditions for the unmeasured species.
- (4) Twenty-five sensitivity runs were then performed on each record. For urban runs, the concentrations of NO and the ten unoxxygenated VOCs {ethane (C₂H₆), propane (C₃H₈), C₄-5 alkanes (C₄AK), C₆-8 alkanes (C₇AK), ethene (C₂H₄), terminal bond alkenes (as propene; PRPE), internally bonded alkenes (as trans-2-butene; BUTE), toluene (TOLU), di-substituted aromatics (DARO) and tri-substituted aromatics (TARO)} were held constant at the measured (or calculated, as was often the case for NO) values, once again in an attempt to mimic the emissions dominated regions. For rural runs, all species were allowed to vary with time, the above species having their initial concentrations taken from the measurements.

The twenty-five runs consisted of

- A Base run: 1 hour integration as described above.
- Two NO_x runs: NO increased and decreased by 25%, relative to the base run.

- Two Total VOC runs: the hydrocarbons listed above all increased or decreased by 25%, relative to the base run.
 - Two individual VOC runs for each of the ten VOCs listed above, with increases and decreases of 25%, relative to the Base run.
- (5) The output data from the runs were used to calculate sensitivities of ozone concentrations to the given perturbation by fitting the three data points (+25%, base, -25%) values to a parabola, then calculating the resulting derivative of ozone with respect to percent change in the particular variable).

The concentrations of biogenic hydrocarbons were not affected by the sensitivity runs; isoprene and alpha-pinene were treated like the other unoxxygenated VOCs, but no sensitivities were calculated.

The resulting output was a list of sensitivities of ozone towards each of the perturbed variables, in units of change of ozone concentration per percent change in the parameter from its measured concentration ($\Delta O_3 / \Delta \text{variable}$; units (ppbv/%)). Positive sensitivities indicate that a decrease in the variable will result in a decrease in ambient ozone concentrations. Negative sensitivities indicate that a decrease in the variable will result in an increase in ozone concentrations.

Results:

The records were analyzed in two groups: cases for which ozone concentrations were greater than 70 ppbv (G70) and cases for which ozone concentrations were less than 50 ppbv (L50). Here, only the summer (July and August) $O_3 > 70$ ppbv cases will be examined in detail.

The results for these records are shown in Figures 1 to 7. Figure 1 shows the sensitivity of model ozone towards changes in NO. Regional differences are apparent in these stations. Stations in Windsor, Toronto, Hamilton and Sarnia all show that decreases in local NO concentrations would lead to increases in ozone concentrations. This probably indicates the effects of local ozone titration; if the NO concentration was decreased, then ozone concentrations close to the emissions sources would increase due to a reduction in importance of the $NO + O_3$ removal pathway. In Simcoe and Stouffville, this effect is less apparent. In the three west coast stations (Coquitlam, Surrey, Langley), changes in the NO concentration had little effect on the ozone concentration.

Figure 2 shows the effect of changes in total VOCs. For all sites, sensitivities are positive; VOC reductions result in ozone decreases. The greatest reductions as a function of percent change in the local VOC concentration are for Coquitlam, Sarnia and Windsor (note: the Coquitlam value is the result of only three records, and must be considered less statistically significant than the other cases). Figure 2 shows that a 25% reduction in total VOCs would result in a reduction in ozone concentrations during episodes of about 15 ppbv ($0.6 \text{ ppbv/\%} \times 25\%$).

Figures 3 and 4 show the sensitivities towards the two VOCs which had the greatest impact on ozone concentrations out of the ten for which sensitivities were calculated. They show the effects of targeting particular VOCs for emissions reduction.

Figure 3 shows the sensitivity to BUTE; the internally bonded alkenes. Urban Ontario values are between 0.05 and 0.25 ppbv/%. Simcoe, Stouffville, Surrey and Langley have virtually no change. Coquitlam values are very sensitive to changes in BUTE.

Figure 4 shows Tri-substituted aromatics, with sensitivities of about 0.03 ppbv/% being typical.

The remaining species have progressively smaller effects on the ozone concentration. In decreasing order of importance, they are: Toluene, Di-substituted aromatics, C6-8 Alkanes, terminal-bond alkenes, ethene, C4-5 Alkanes, Propane and Ethane.

These results suggest that targeted reductions of internal-bond alkenes, followed by higher aromatics would have the biggest effect on local ozone concentrations in most of southern Ontario. Certain VOCs (those with both high reactivity and high concentrations) result in much of the RO₂ formation leading to ozone production.

Figures 5 - 7 show the sensitivities grouped according to region and plotted relative to each other. The greatest impacts of VOC controls are seen in the urban regions of Ontario, Sarnia and Windsor in particular, followed by Toronto. Impacts of reductions are smaller in Simcoe, Stouffville and the Vancouver sites other than Coquitlam. The latter has a high sensitivity to BUTE as in the Ontario sites, but this may be due to small sample size (three records).

In addition to the summer ozone episode cases, sensitivities were also calculated for spring episodes (April to May). The relative results were similar to the summer episodes for most stations, but the magnitudes of the sensitivities were smaller. For example, the Junction Triangle station's sensitivity to total VOCs was about 0.075 ppbv/% in the spring versus 0.25 ppbv/% in the summer. NO sensitivities at the same site were also lower in spring versus summer, -0.25 ppbv/% versus -0.4 ppbv/%. The same pattern of sensitivities for individual VOCs was noted as for the summer cases; sensitivities tend to be highest for internally bonded alkenes, with aromatics following in importance.

The spring data included a single record from Edmonton. Although statistically insignificant, it is interesting to note that the NO sensitivity was still negative, and that the pattern of VOC sensitivities has changed. Di-substituted aromatics have the greatest impact on ozone concentrations, followed by toluene, propene and the C6-C8 alkanes. Further episode measurements would be required to determine whether this reflects true regional differences in the ozone production due to hydrocarbons.

A large number of records with ozone less than 50 ppbv were examined to see if the sensitivities of ozone production due to NO_x or VOCs differed between ozone episodes and non-episode scenarios. The sites show the same pattern as for the summer cases, with negative NO sensitivities, positive VOC sensitivities, with butene followed by the higher aromatics leading the VOC sensitivity magnitudes. The magnitudes are smaller than for ozone (>70 ppbv) episodes (eg. Windsor VOC sensitivity 0.25 versus 0.5 ppbv/%); VOC controls will have a smaller impact on non-episode situations than during episodes. Figure 22 shows the sensitivities for the Rocky Point site at Coquitlam, BC,

with negative NO sensitivities and positive VOC sensitivities, internally bonded alkenes (BUTE) being the most important of the latter.

Discussion:

The results from these tests suggest the following:

- (1) At the sites for which ozone episode data was available, decreasing local NO concentrations would lead to increases in ozone. Provided that this was not a result of model setup (see below), this would suggest that NO_x reduction strategies in the vicinity of urban areas would actually lead to local increases in the ozone concentrations.
- (2) At all sites, reductions in the total VOC loading resulted in immediate local ozone decreases. These reductions in ozone concentrations were greatest for a total, across the board VOC cut, but more detailed work showed that specific VOCs (in order of precedence: internally bonded alkenes, tri-substituted aromatics, di-substituted aromatics, and toluene) probably make up most of the VOC effects. These VOCs are both sufficiently reactive and have sufficiently high concentrations to have a significant local impact on ozone production.
- (3) The direction (if not the magnitude) of the sensitivities was the same for cases in which the ozone concentration was less than 50 ppbv. This would suggest that a strategy in which different components of the reactive mix are targeted for reductions at different times seems unnecessary. The same VOC reduction strategy may be used regardless of whether an ozone episode is taking place; VOC reductions during low ozone days will not have adverse effects.

Two confounding factors should be noted at this point.

NO_x concentrations, and NO_x sensitivities. As was mentioned above, the NO₂ and NO concentrations in the NAPS database were usually reported only to the nearest 10 ppbv, and usually total NO_x was reported as NO₂. The strategy of determining NO concentrations from the use of steady-state may have led to errors in the sensitivities in two ways; through lack of accuracy in the original measurements, and through the use of steady-state to generate NO concentrations, followed by perturbations from that steady-state to generate sensitivities.

Assumption of local emissions via constant NO and VOCs. Another source of uncertainty (for the urban sites) is the assumption of a local emission source (ie. the concentrations of NO and unoxxygenated VOCs being held constant; the level being changed for sensitivity calculations). The effect of these uncertainties can only be resolved with more accurate measurement data and further model runs, as discussed below.

Conclusions and Plans for Future Work:

The work performed here indicates that the NAPS sites studied have positive sensitivities of ozone production with respect to VOCs, and negative sensitivities with respect to NO_x. NO_x reductions at the given sites could lead to increases in local ozone.

VOC reductions will reduce local ozone, and specific VOCs (internally bonded alkenes, followed by aromatic compounds) can be targeted as having the greatest local impact on ozone production.

It should be noted that significant uncertainties exist in the NO_x conclusions, due to the limitations on the measurement accuracy and the assumptions in the use of the measurements. The following steps are recommended for future work to resolve these uncertainties:

- (1) The use of more accurate NO_x data (ie. both NO and NO_2 resolved, with ppbv or better accuracy) from measurement intensives (eg. Pacific 93, NARSTO). These can be used to test the effect of the NAPS data being reported in 10ppbv intervals; the intensive data can be degraded in the same fashion as the NAPS data, and the resulting model output compared to that resulting from the true NO_x initial conditions.
- (2) The effect of the "emissions" boundary condition can easily be tested with the current data set and model; all species can be made time variables with the measurement data providing an initial condition only.

References

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- Kahaner, D., C. Moler, and S. Nash, 1989: Numerical Methods and Software, Prentice-Hill, Englewood Cliffs, New Jersey.
- Makar, P.A., S-M. Li, P.B. Shepson and J. Bottenheim, 1998: The AES Gas-Phase Mechanism for Tropospheric Chemistry: Theoretical Formulation: AES Internal Report, Atmospheric Environment Service, Downsview, Ontario (In preparation).
- Middleton, P., W.R. Stockwell, and W.P.L. Carter, 1990: Aggregation and analysis of volatile organic compound emissions for regional modelling. *Atm. Env.*, 24A, pp 1107-1133.
- Yung, Y.L., 1976: Numerical Method for Calculating mean intensity in an inhomogeneous Rayleigh-scattering atmosphere. *J. Quant. Spec.* 16, pp755-761.

Tables:

1. NAPS stations included in this study.

Figures:

1. Sensitivity of model ozone with respect to changes in NO, Summer $\text{O}_3 > 70$ ppbv episodes.
2. Sensitivity of model ozone with respect to changes in Total VOCs, Summer $\text{O}_3 > 70$ ppbv episodes.
3. Sensitivity of model ozone with respect to changes in BUTE; internally bonded alkenes, Summer $\text{O}_3 > 70$ ppbv episodes.
4. Sensitivity of model ozone with respect to changes in TARO; tri-substituted aromatics, Summer $\text{O}_3 > 70$ ppbv episodes.
5. Sensitivities of model ozone with respect to NO_x and VOCs, Southern Ontario Stations outside Toronto, Summer $\text{O}_3 > 70$ ppbv episodes.

6. Sensitivities of model ozone with respect to NO_x and VOCs, Toronto stations, Summer O₃ > 70 ppbv episodes.
7. Sensitivities of model ozone with respect to NO_x and VOCs, West Coast Stations, Summer O₃ > 70 ppbv episodes.

Table 1.

NAPS #	ST. NAME	NEAREST CITY	PROV.	CITY/ RURAL (C/R)
30118	Roy Building	Dartmouth	N. Scotia	C
60204	UIC Building	Windsor	Ontario	C
60403	Evans & Arnold	Toronto	Ontario	C
60413	Elmcrest Rd.	Toronto	Ontario	C
60418	Junction Triangle	Toronto	Ontario	C
60422	33 Edgar Ave.	Toronto	Ontario	C
60424	Bay and Grosvenor	Toronto	Ontario	C
60512	Beasley Park	Hamilton	Ontario	C
61004	Centennial Park	Sarnia	Ontario	C
62601	Experimental Farm	Simcoe	Ontario	R
63201	Hwy 47 & Hwy 48	Stouffville	Ontario	R
90130	10255-104 th st.	Edmonton	Alberta	R
100111	Rocky Pt. Park	Coquitlam	B.C.	C
100127	Surrey East	Surrey	B.C.	R
101301	Langley Central	Langley	B.C.	C

Figure 1.

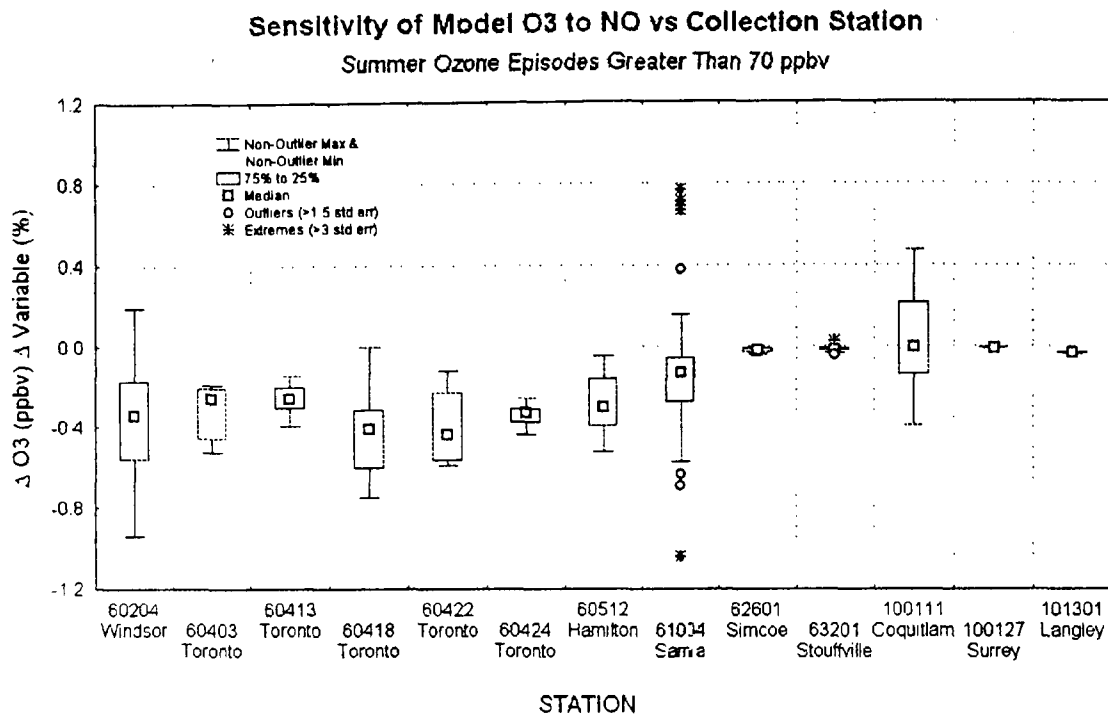


Figure 2.

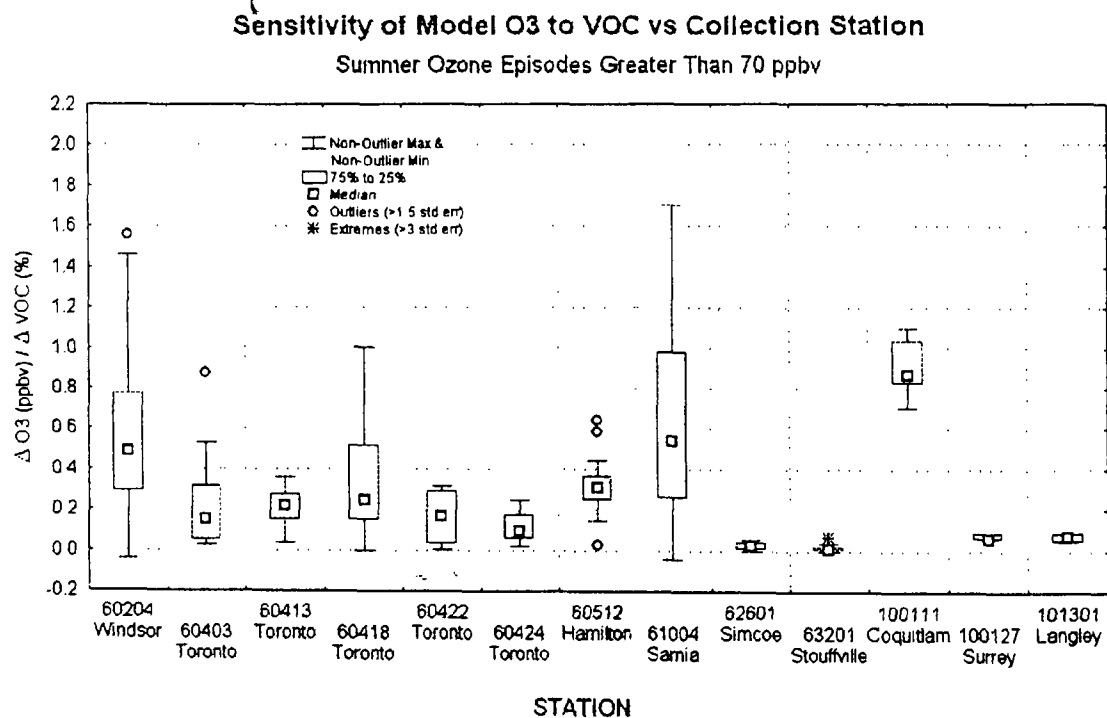


Figure 3.

Sensitivity of Model O3 to BUTE vs Collection Station
Summer Ozone Episodes Greater Than 70 ppbv

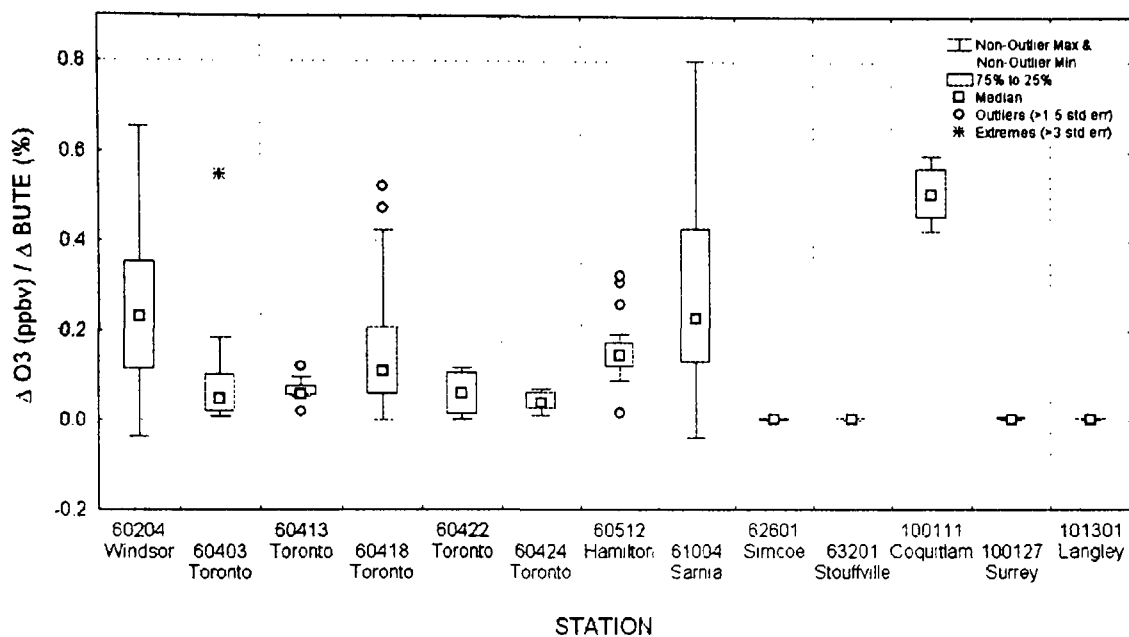


Figure 4.

Sensitivity of Model O3 to TARO vs Collection Station
Summer Ozone Episodes Greater Than 70 ppbv

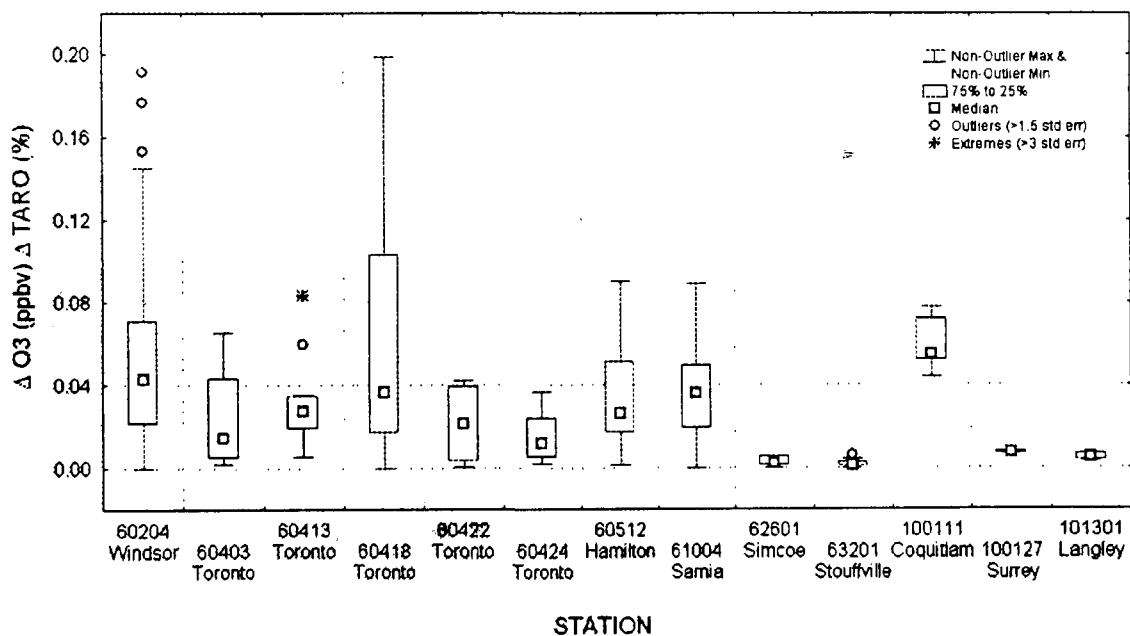


Figure 5.

Sensitivities of O₃ Production to NO_x and VOC
Summer Ozone Episodes Greater Than 70 ppbv

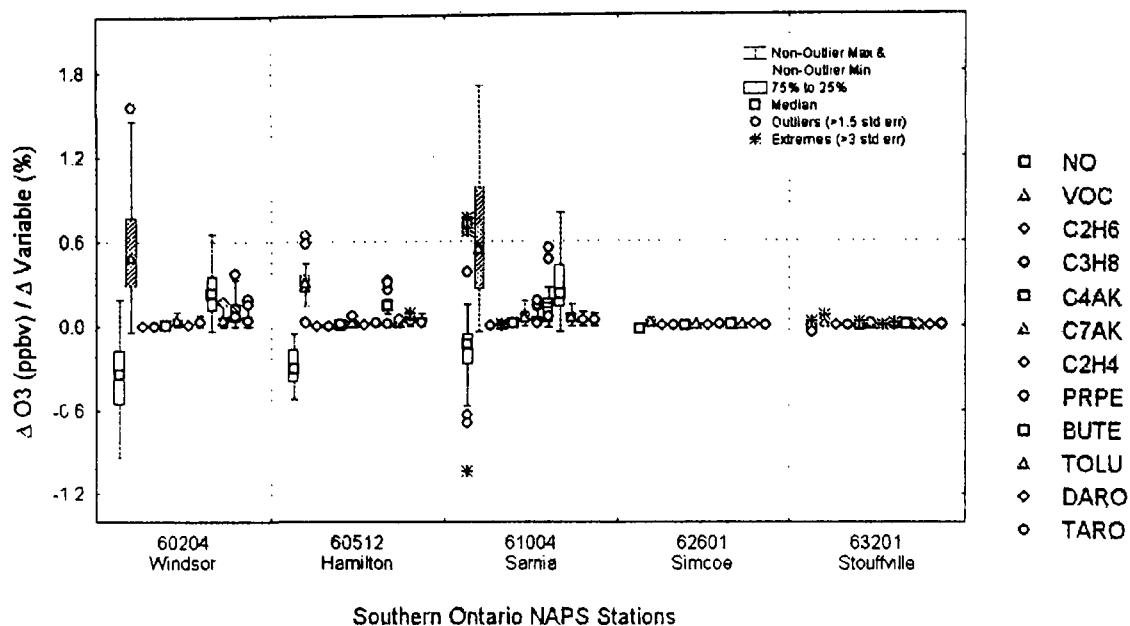
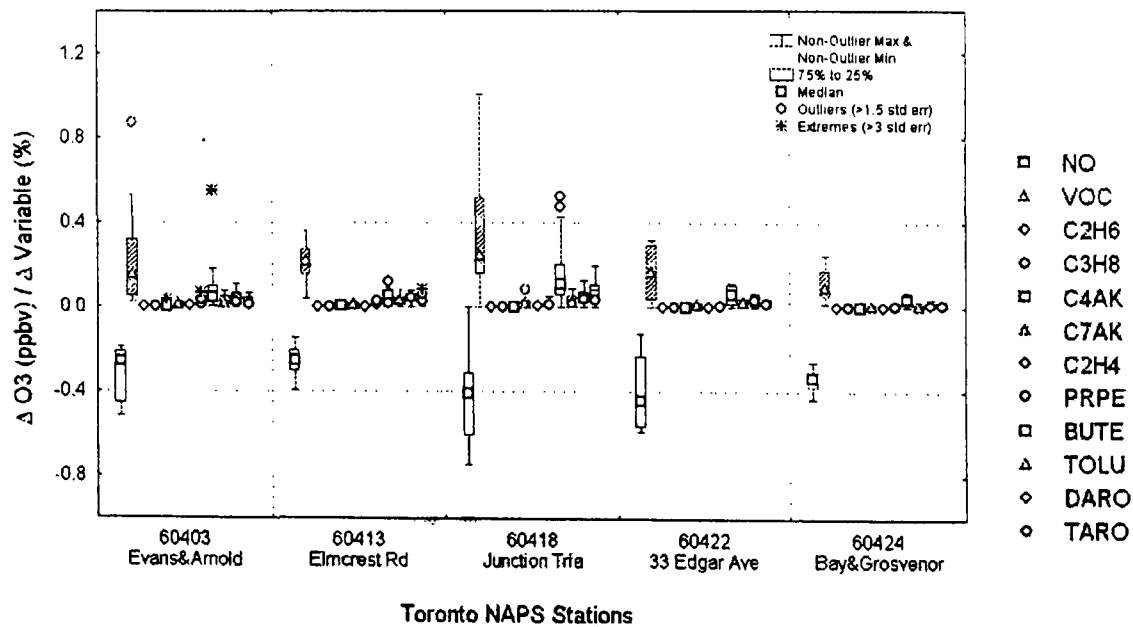
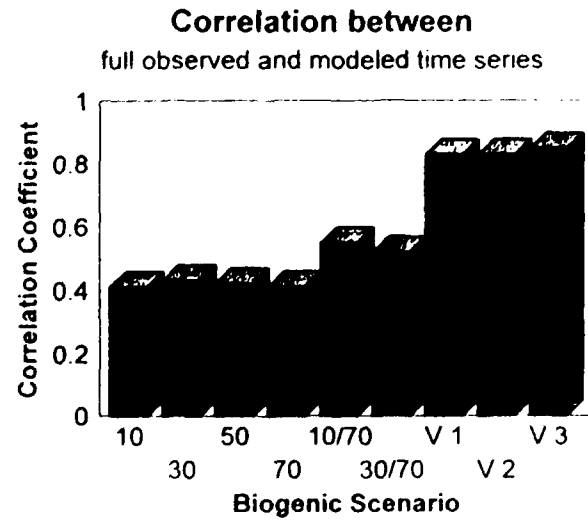


Figure 6.

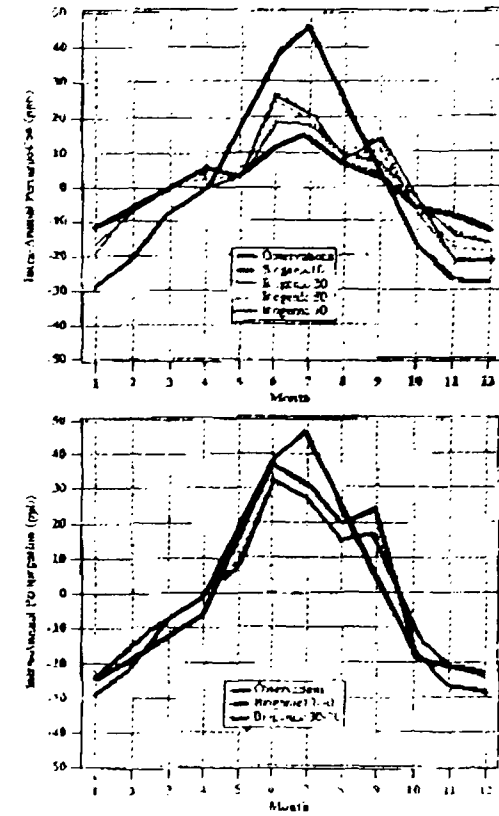
Sensitivities of O₃ Production to NO_x and VOC
Summer Ozone Episodes Greater Than 70 ppbv



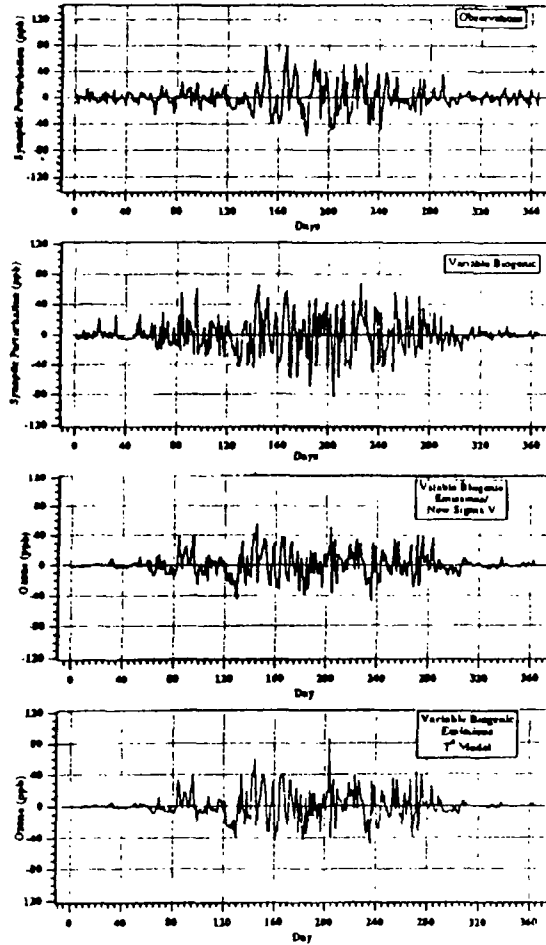
Comparing the full time series



Comparing the intra-annual perturbation

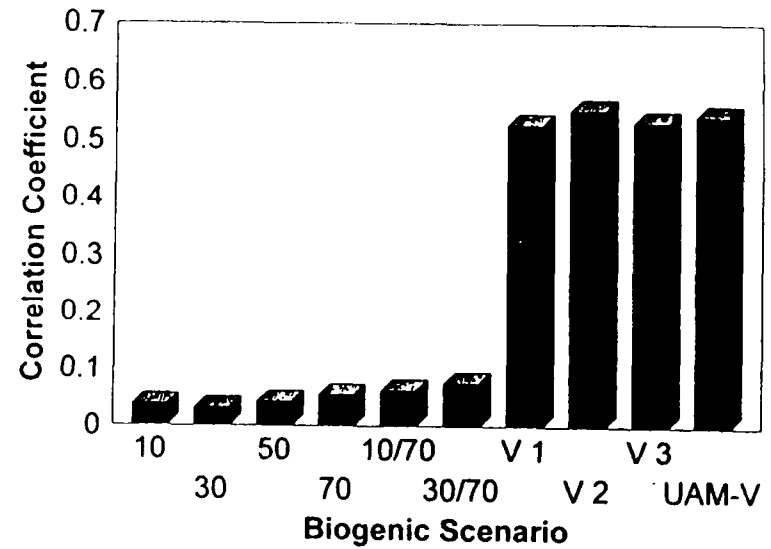


And the synoptic perturbation

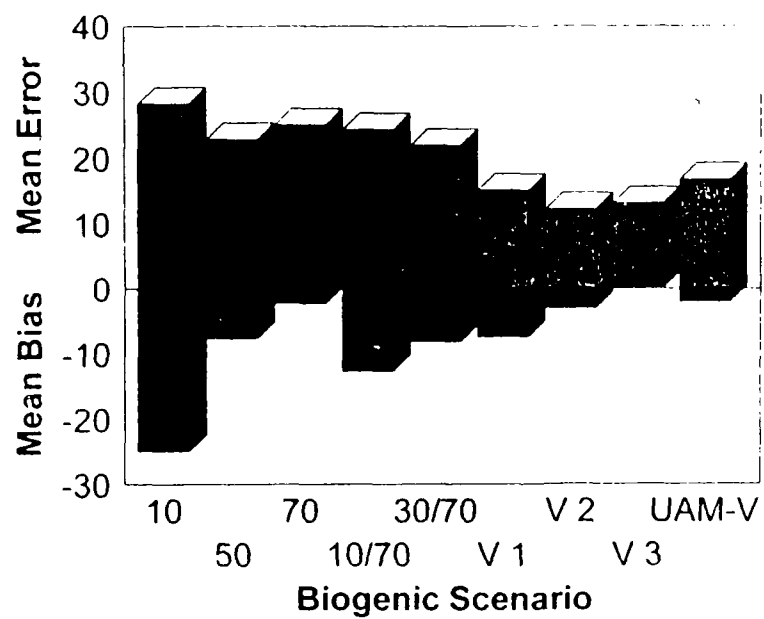


Comparative statistics...

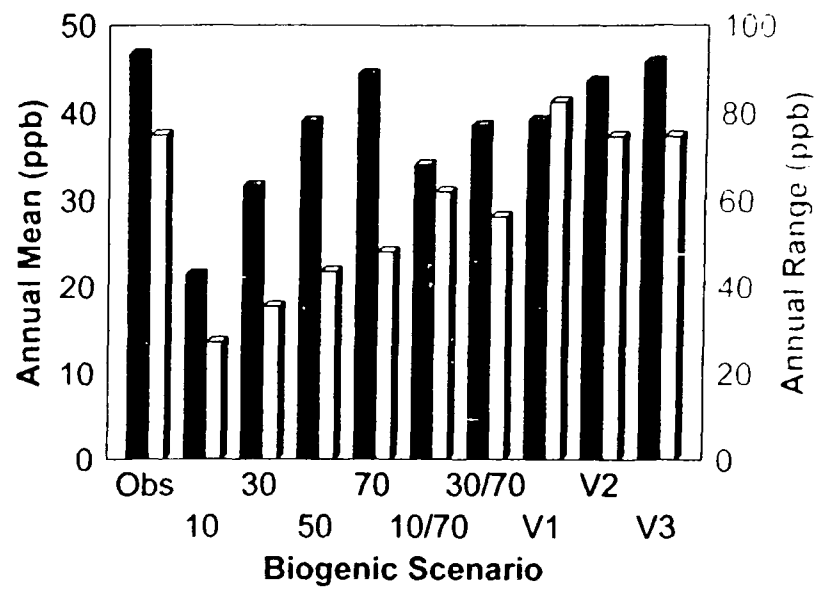
Correlation Analysis of Synoptic Term



Error Analysis



Comparative Statistics



Conclusions

- ☐ Shows promise as an approach for developing a “modeled ozone climatology”
 - applications in weight-of-evidence component in SIP
- ☐ Model performance seems good
 - need to ensure that we’re not “getting the right answers for the wrong reasons”
- ☐ Demonstrates the importance of modeling the time dependence of biogenic VOC emissions
 - gives an indication of the temperature dependence that is well known for ozone in the Northeast

Abstract

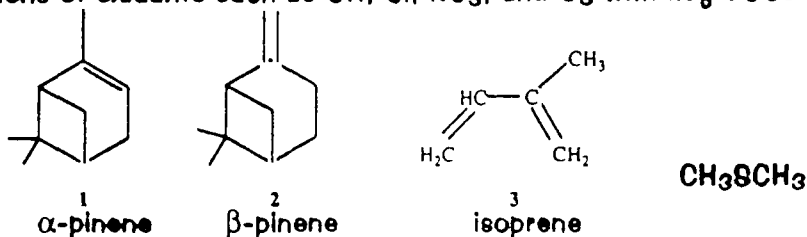
TVA's Research In Tropospheric Ozone Mitigation and Contribution of Natural Hydrocarbons to VOC Reactivity

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Atmospheric Sciences & Environmental Assessments
Environmental Research and Services
Tennessee Valley Authority
Muscle Shoals, AL 35662-1010

The Tennessee Valley Authority has, through its partnerships with OtNr federal and state agencies, universities, and private sector participants, Contributed substantially to the knowledge base concerning tropospheric ozone. Particularly through participation in the Southern Oxidants Study (SOS), its field studies and related modeling efforts, new information concerning the formation of ozone in plumes from urban areas and point sources of precursor NO_x and VOC emissions has been developed. This information is critical in diagnosing whether reductions in NO_x emissions, VOC emissions, or both are most effective in reducing the likelihood of exceedances of the NAAQS for ozone. These efforts have also provided new insight on whether emissions of NO, from all sources produce ozone at the same efficiency when mixed with VOCs found in ambient air. TVA and its SOS collaborators have also found that, in the Southeast during the "high ozone" season, natural hydrocarbons and specifically isoprene are the major source of VOC reactivity in ozone formation processes in non-urban areas. Urban area VOC emissions are clearly important for ozone mitigation in populated areas, but different strategies may be required for urban and rural areas especially in light of the new 8-hour NAAQS for ozone.

Computational Studies of Oxidant Reactions of Volatile Organic Compounds Relevant to the Formation of Tropospheric Ozone: David A. Dixon, Thom H. Dunning, Jr., Michel Dupuis

- Volatile organic compounds or VOCs play a key role in the global carbon cycle
 - the direct formation of carbon monoxide CO from their oxidation by radicals and ozone.
 - primary seed compounds leading to the formation of aerosols which provide reaction sites and act as carriers of condensed active species
- Develop a fundamental molecular understanding of the oxidation of VOC's by using advanced computational electronic structure methods on high performance computing systems.
- Calculate the thermodynamic and kinetic information needed to predict degradation mechanisms. Provide both novel insights and chemically accurate data. Provide spectroscopic information for identifying key intermediates.
- Develop a base capability in the modeling of rates and mechanisms of oxidation processes of importance to the Atmospheric Chemistry Program. Such a capability can be used to help guide further experiments and to extend limited experimental data into new domains.
- Reactions of oxidants such as OH, Cl, NO₃, and O₃ with key VOCs

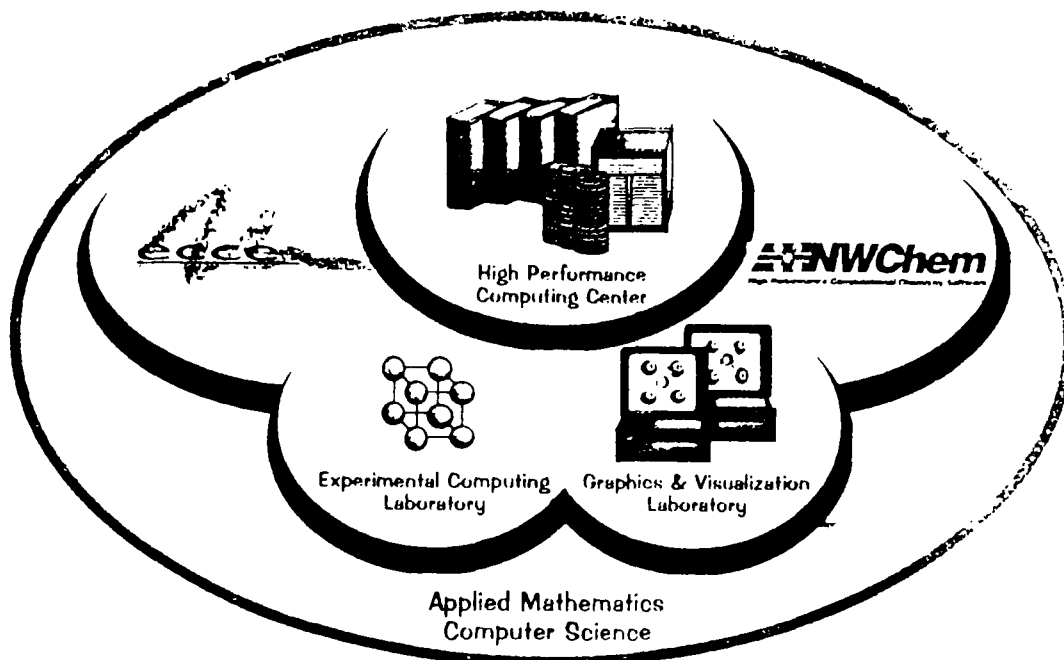



TM&S Capabilities and Interest Relative to Atmospheric Chemistry

- Reliable predictions of thermodynamic properties of atmospheric compounds and intermediates including radical species, including predicting molecular structures.
- Reliable prediction of kinetics of important atmospheric chemistry reactions (rate constants from ab initio molecular theory, variational transition state theory, tunneling effects).
- Models of reaction mechanisms and pathways.
- Thermodynamics of cluster formation.
- Global warming potentials (infrared intensity calculations).
- Predictions of excited state chemistry.
- Focus on aerosol formation from natural and anthropogenic sources.
- Expertise in stratospheric chemistry, tropospheric degradation processes, cluster formation, and global warming potential predictions.
- Expertise in algorithm development and software implementation on massively parallel computers for development of high performance, portable, and scalable software.

EMSL Molecular Science Computing Facility

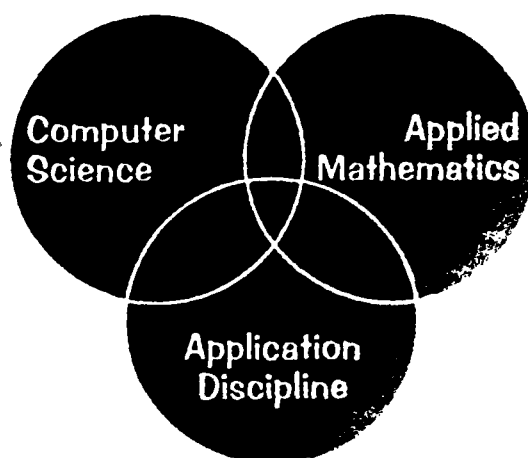
A DOE National Scientific User Facility



 Molecular Science Computing Facility

 High Performance Computing
Pacific Northwest National Laboratory

Multidisciplinary Teams for HPCSI Software Development



Application Discipline

- theories
- approaches

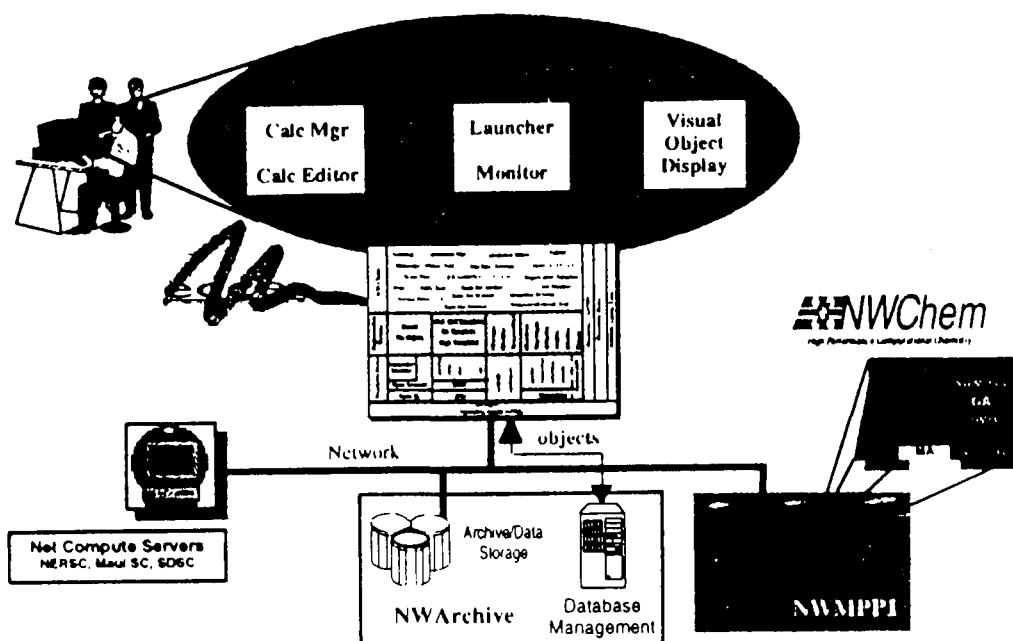
Applied Mathematics

- numerical analysis
- mathematical algorithms

Computer Science

- software methodology
- software tools

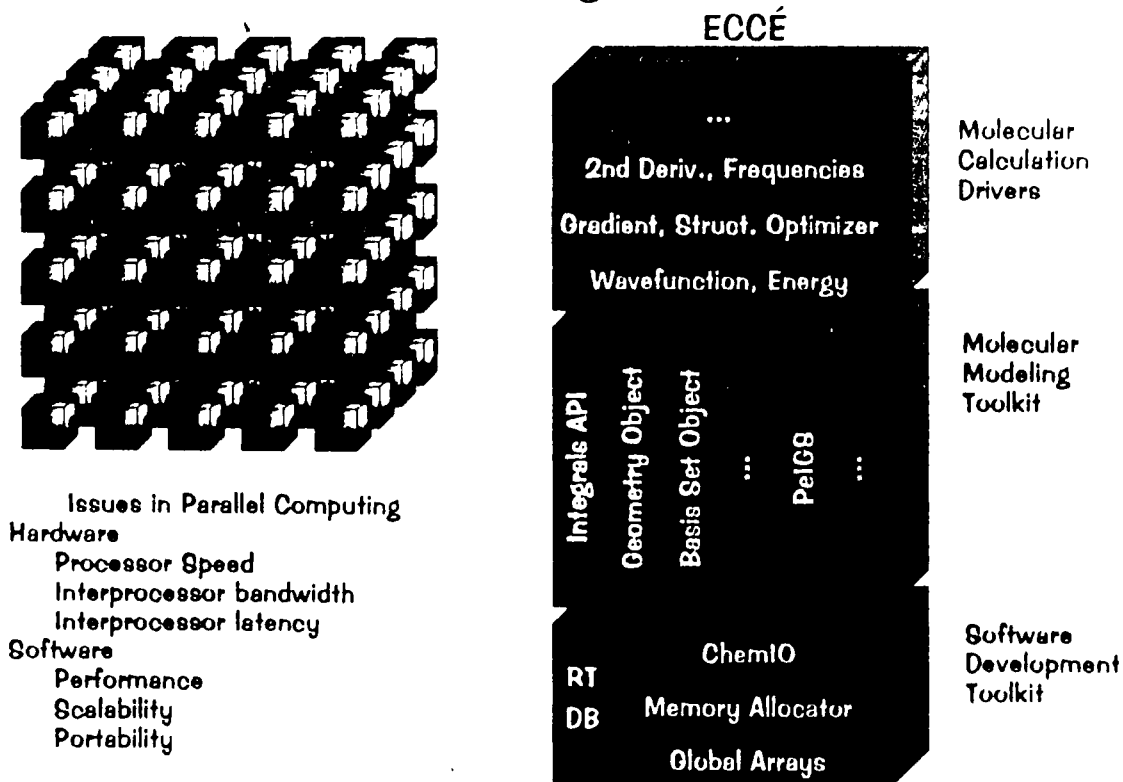
Molecular Science Software Distributed Computing Model



Molecular Science Computing Facility

Theory, Modeling & Simulation

NWChem Molecular Modeling Software Architecture



Environmental Molecular Sciences Laboratory

Current NWChem Functionality

Quantum Mechanical Capabilities:

- Hartree-Fock energies, gradients, and second derivatives.
- Multiconfiguration self consistent field (MCSCF) energies and gradients.
- Density functional theory at the local and nonlocal levels (with N^3 and N^4 formal scaling) energies and gradients.
- Many-body perturbation theory (MP2-MP4) energies plus MP2 gradients.
- Coupled cluster [CCSD and CCSD(T)] energies.
- Single and multireference configuration interaction energies.
- Segmented and generally contracted basis sets including the correlation-consistent basis sets under development at EMSL.
- Effective core potential energies, gradients, and second derivatives.

Classical Mechanical Capabilities:

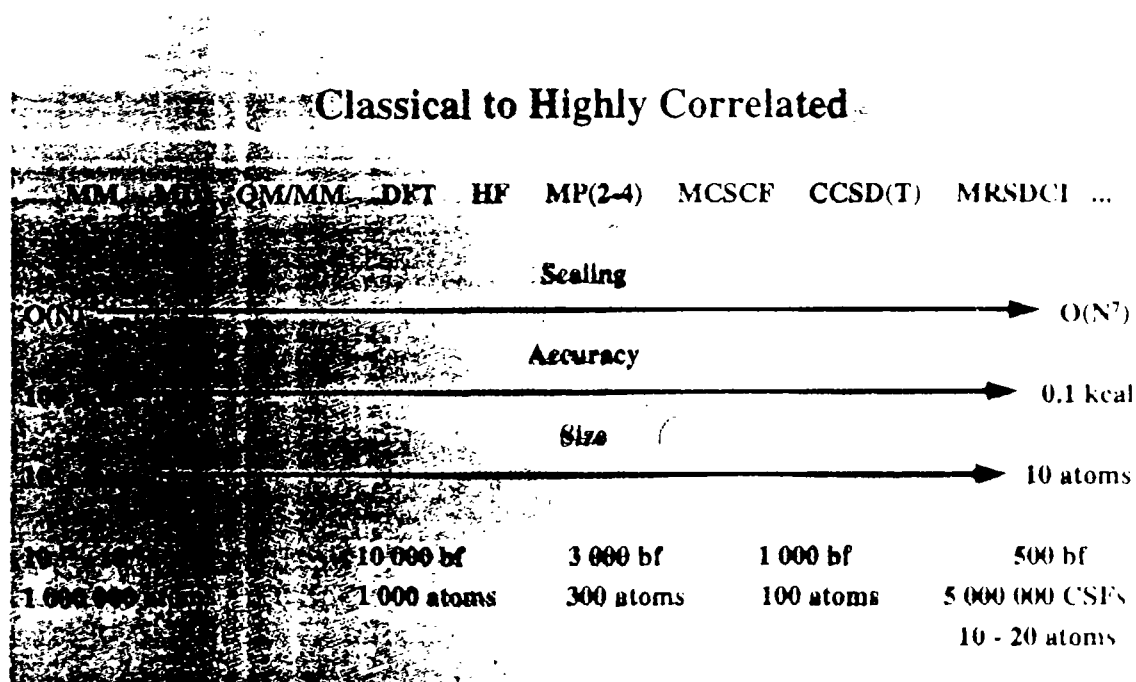
- Energy minimization
- Molecular dynamics simulation
- Free energy calculation
- Supports variations such as: multiconfiguration thermodynamic integration or multiple step thermodynamic perturbation, first order or self consistent electronic polarization, simple reaction field or particle mesh Ewald, and quantum dynamics

High Performance Computational Chemistry

Environmental Molecular Sciences Laboratory

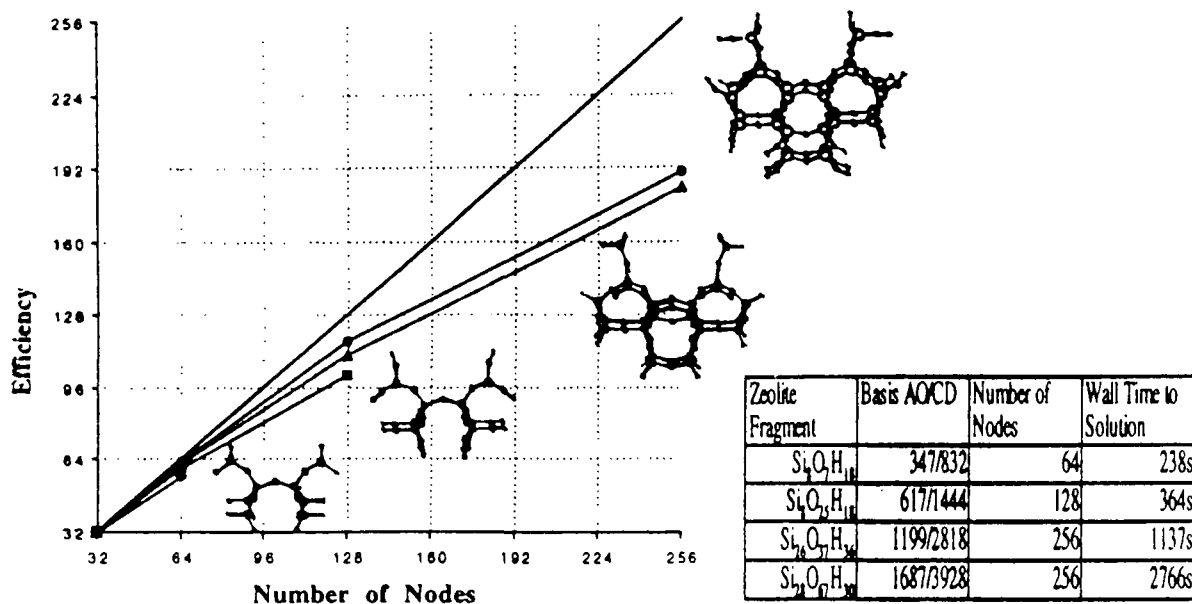
Pacific Northwest National Laboratory

Current NWChem Functionality Targets



High Performance Computational Chemistry

Measured Parallel Efficiency for NWChem - DFT on IBM-SP; Wall Times to Solution for Full SCF Convergence



High Performance Computational Chemistry

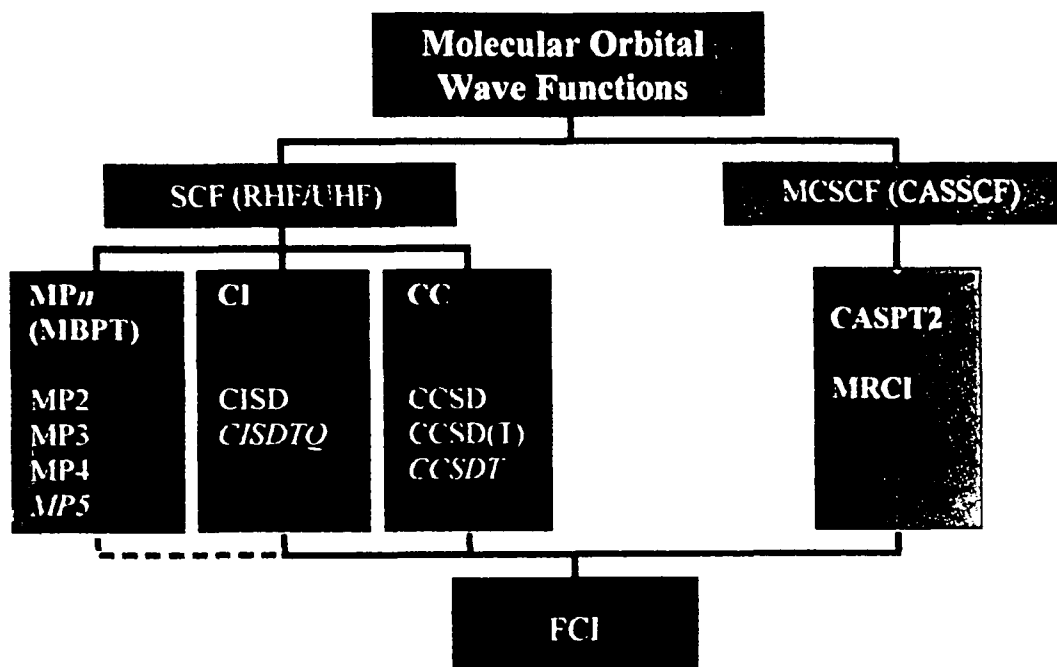


Theory, Modeling & Simulation

Required Accuracies for Chemical Systems: Separations and Catalysts

- Absolute Rates (Speedup for Catalysts): Impact on Rates
 - Factor of 10 @ 25°C is $\Delta E_a = 1.4$ kcal/mol
- Relative Rates/Equilibrium Constants (Selectivity for Catalysts and Separations): Impact on Selectivity
 - Change from a 50:50 mixture to a 99:1 mixture @ 25°C
 $K_{eq} = 1$ changes from $K_{eq} = 100$
 $\Delta G = 0$ to $\Delta G = 2.8$ kcal/mol
- There is a clear requirement for accuracy in the computational results. How is this accomplished?

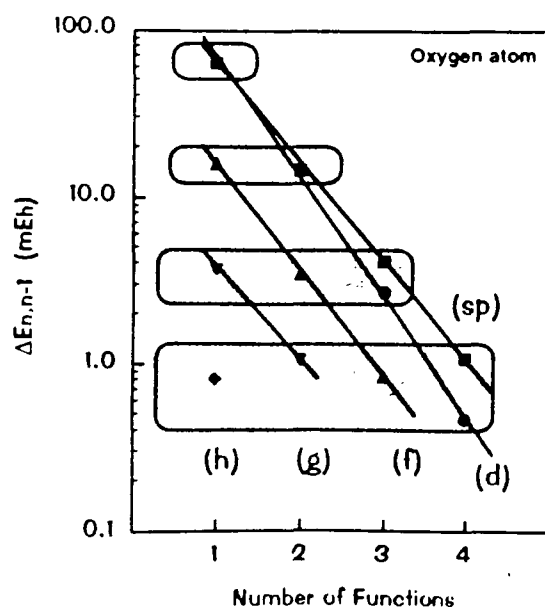
Expansion of the Many-Electron Wave Function : Methods of Electron Correlation



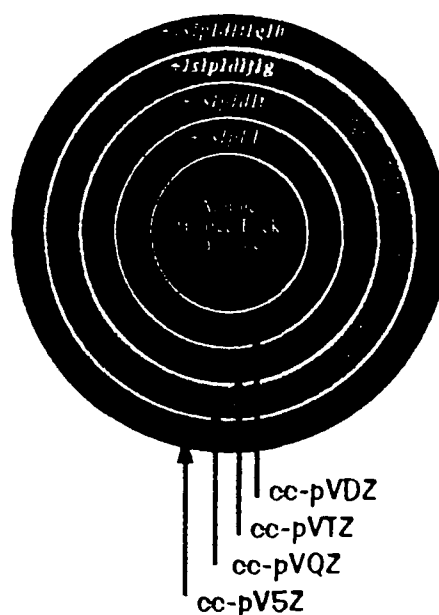
How to best represent the molecular orbitals:

Correlation Consistent Basis Sets

How important are different types of Gaussian functions?



Functions are added in correlation consistent shells





- $\Sigma D_\infty(\text{CH}_4) = 419.60 \text{ kcal/mol}$
- $\Sigma D_\infty(\text{CH}_4) = 420.71 \text{ kcal/mol}$ including core correlation and spin orbit effects
- $\text{ZPE} = 27.09 \text{ kcal/mol}$.
- $\Delta H_f(\text{CH}_4) = -17.1 \text{ kcal/mol}$ at 0 K
- Experimental value of $-16.0 \pm 0.1 \text{ kcal/mol}$
- Use of larger $\Delta\text{ZPE} = 27.71 \text{ kcal/mol}$ (Grev et.al.): $\Delta H_f(\text{CH}_4) = -16.5 \text{ kcal/mol}$
- $\Sigma D_\infty(\text{CH}_4) = 419.2 \text{ kcal/mol}$ by exponential extrapolation.
- $\Delta H_f(\text{CH}_4) = -15.6 \text{ kcal/mol}$ based on $\Delta\text{ZPE} = 0.5\Sigma v_i$
- Use of the Grev value for ΔZPE gives $\Delta H_f(\text{CH}_4) = -15.0 \text{ kcal/mol}$.

Organic Thermochemistry & Kinetics

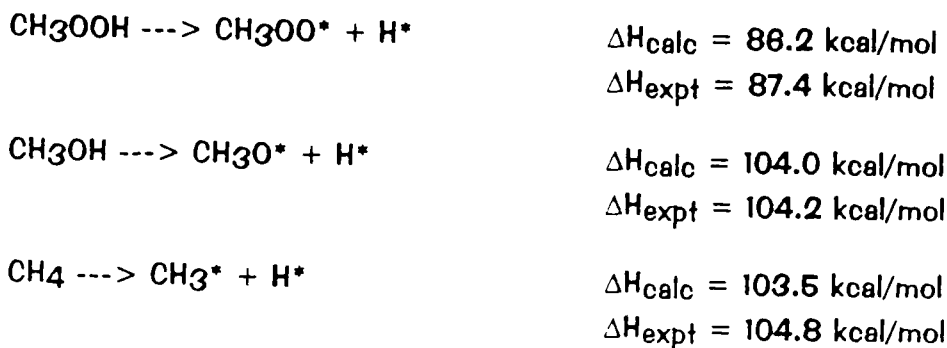
- Estimates of computer time required for CCSD(T) calculations with cc-pVQZ basis sets. Estimates are based on an algorithm that scales as N^6 , rather than the N^7 formal scaling.

Molecule	Time (1 Tflop)	Time (100 Tflop)
C_6H_6	1 min	0.6 sec
C_8H_{18}	40 min	25 sec
$\text{C}_{16}\text{H}_{34}$	40 hr	25 min
$\text{C}_{24}\text{H}_{50}$	600 hr	6 hr

- Kinetics: Probably requires augmented cc basis sets: $\sim 10 \times$ per point at the aug-cc-pVQZ level

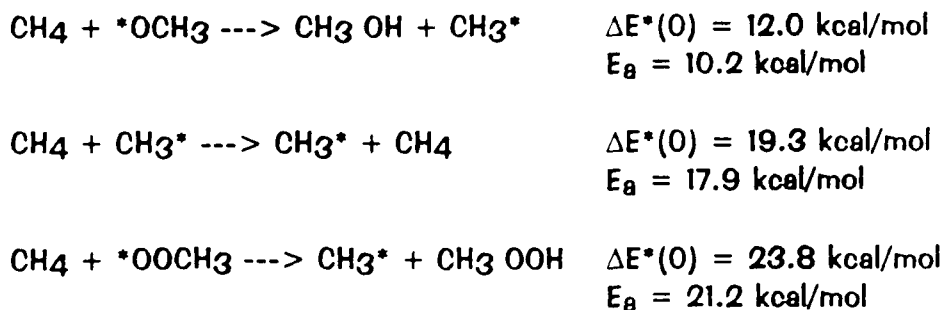
Organic oxidation reactions: Thermodynamics

- Geometries optimized at the MP2/DZ+P level and final energies calculated at the PMP4/TZ2PF (spin projected) level.

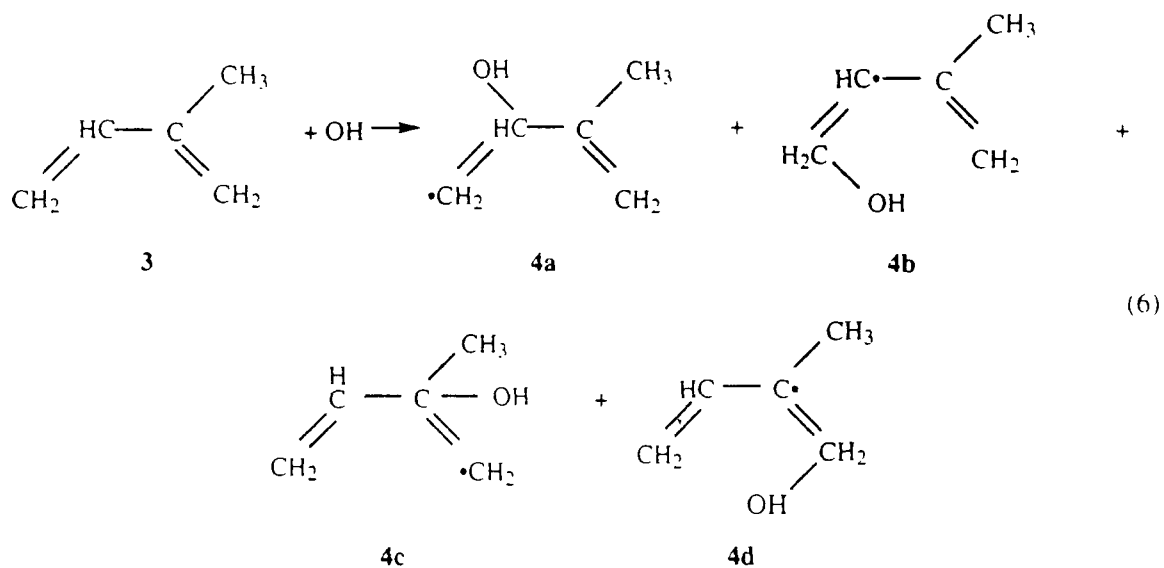


Organic oxidation reactions: Kinetics

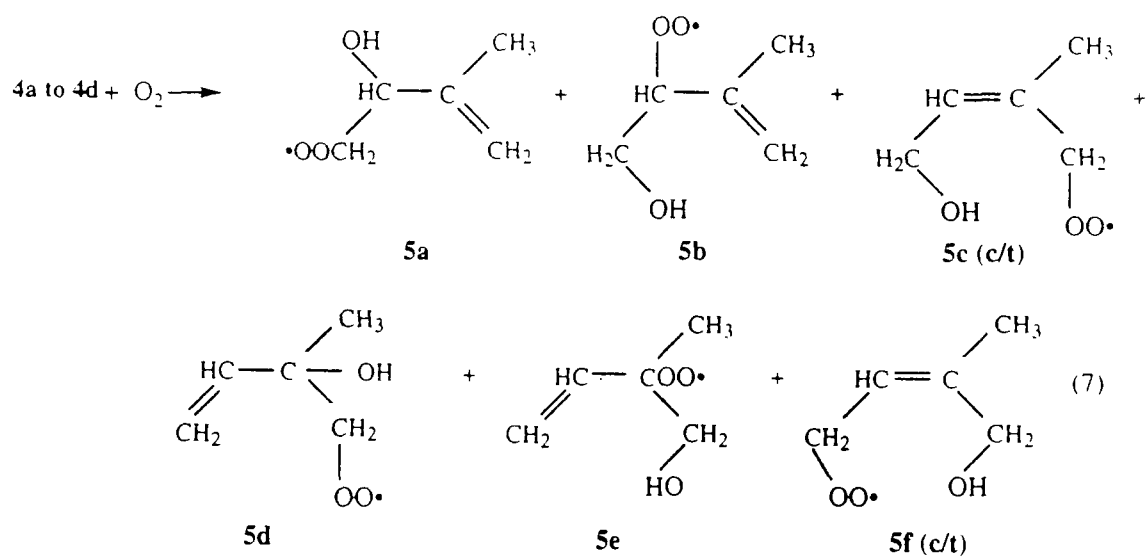
- Calculate for the following prototypical reactions
 - the barrier heights, $\Delta E^*(0)$, and activation energies.
 - E_a , from transition state theory with a Wigner tunneling correction
- Geometries optimized at the MP2/DZ+P level and final energies calculated at the PMP4/TZ2PF (spin projected) level.



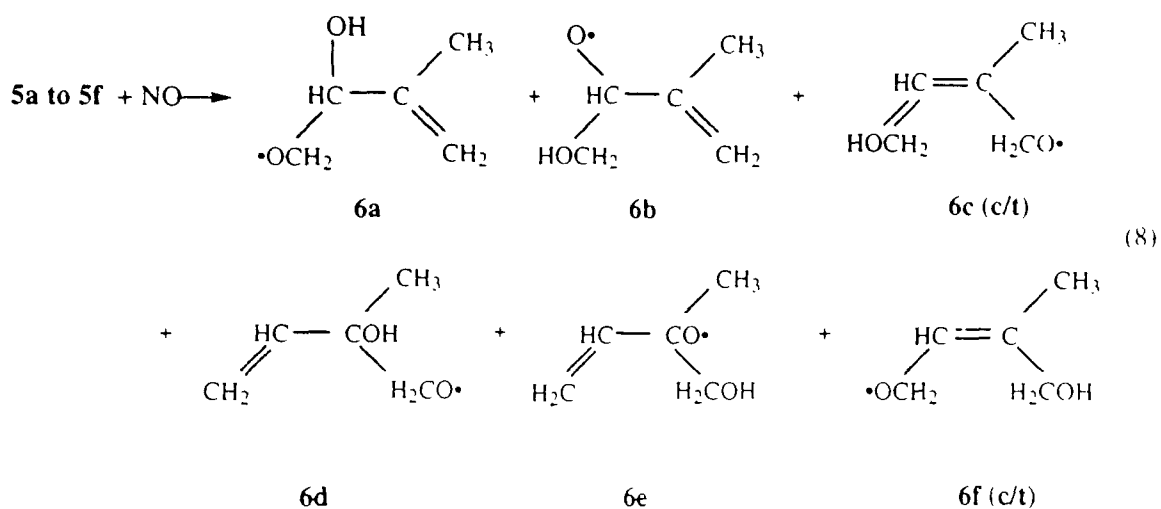
Isoprene Chemistry: 1



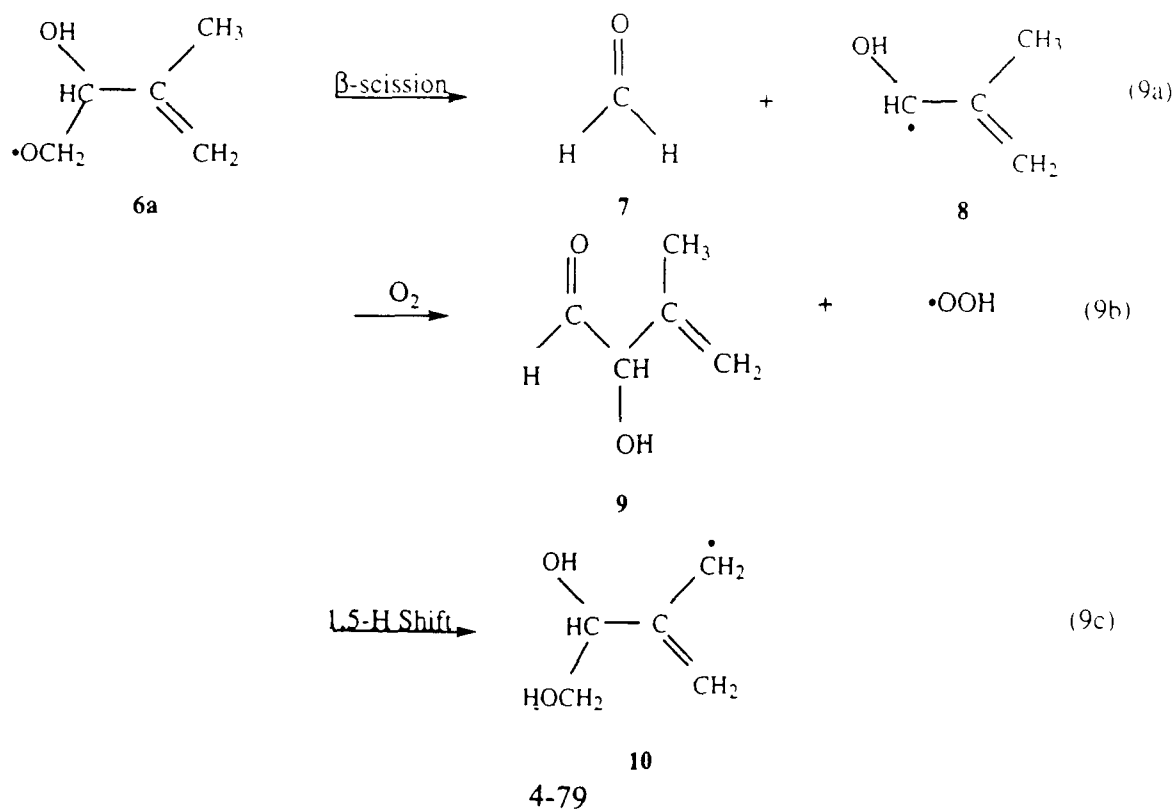
Isoprene Chemistry: 2



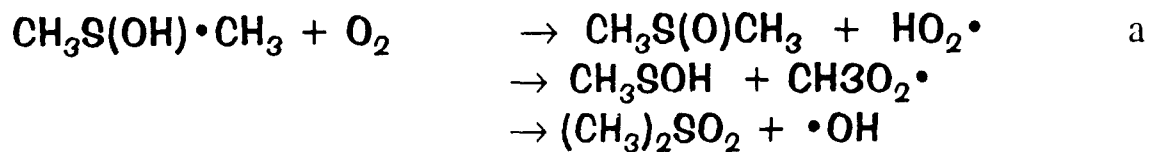
Isoprene Chemistry: 3



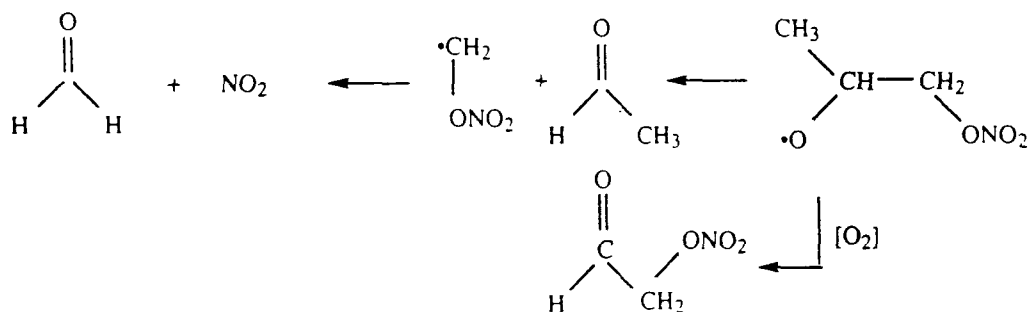
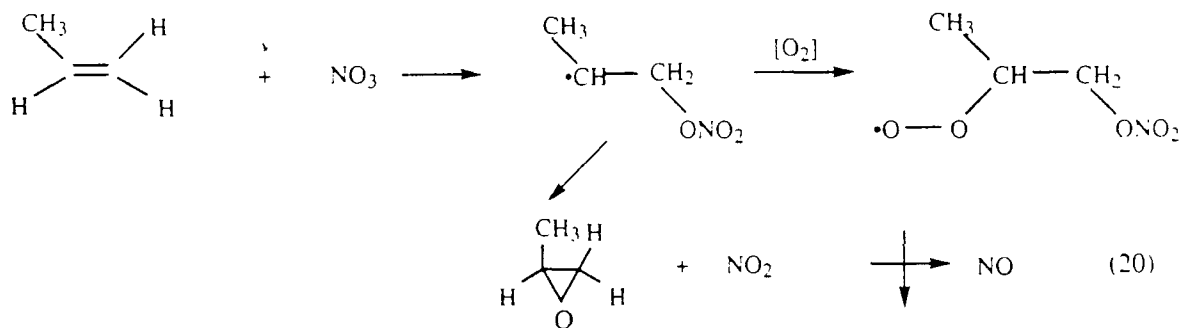
Isoprene Chemistry: 4



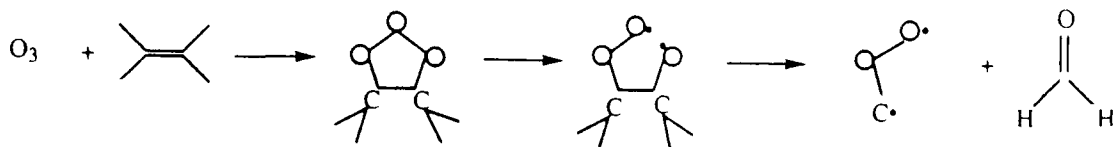
S(CH₃)₂ Chemistry



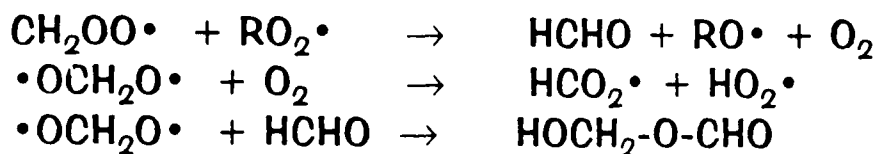
NO₃ (Nighttime) Chemistry



Ozonolysis



Criegee Intermediate Reactions



Theory, Modeling & Simulation

Unimolecular Decomposition of $\text{CH}_3\text{CH}_2\text{O}\cdot$

Method	ΔE	$\Delta E(298)$	ΔE^\pm	ΔE_0^+
MP2/TZ2PF	10.93	7.1	23.17	20.6
PMP2/"	11.15	7.3	16.32	13.7
MP48DQ/"	14.80	11.0	24.19	21.6
PMP48DQ/"	14.98	11.1	19.35	16.8
MP48DTQ/"	13.18	9.3	22.90	20.3
PMP48DTQ/"	13.35	9.5	18.21	15.6
QC18D/"	15.78	11.9	22.04	19.5
QC18D(T)/"	15.50	11.7	20.54	17.7
CC8D/"	16.13	12.3	22.40	19.8
CC8D(T)/"	15.58	11.7	20.85	18.3
CC8D(T)/aug-ccTZVP	15.51	11.6	19.53	17.0
BP/DZVP2	20.63	18.1	20.71	18.1
B3LYP/DZP	17.87	14.5	19.98	16.8
B3LYP/TZ2PF	15.13	11.7	18.13	14.9
Expt		13.1(NASA/JPL/94)		21.6(BaH)

Energies in kcal/mol, Geometry at MP2/TZ2P level except for NLDFT

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Unimolecular Decomposition of $\text{CH}_3\text{CH}_2\text{O}^\bullet$ Rates

RRKM, High Pressure limit, 298K, N_2 collision partner, $s = 4.2 \text{ \AA}$, $\sigma = 250 \text{ K}$

Method	$E_a(\text{kcal/mol})$	$\log A(s^{-1})$	$k(s^{-1})$
QCISD/TZ2PF	18.3	13.7	1.2
QCISD(T)/TZ2PF	20.3	13.7	0.041
CCSD(T)/TZ2PF	18.9	13.7	0.46
CCSD(T)/aug-cc-VTZ	17.7	13.7	3.2
Expt	21.6	15.0	0.14

Tunneling estimate for an imaginary frequency of $642i$ with a Wigner correction based on the reverse reaction: 1.4 @ 298 K, 1.46 @ 277 K

BaH, *Int. J. Chem. Kinet.* 11, 977 (1979)

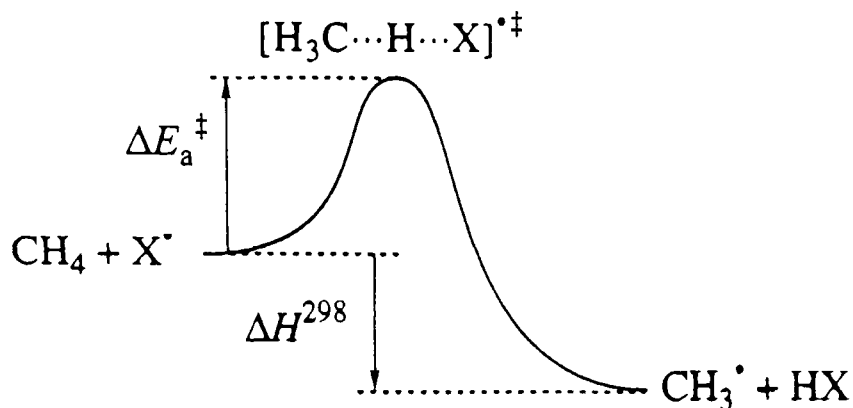
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Benchmark Calculations for Abstraction of H from CH_4

- $\text{CH}_4 + \text{OH}^\bullet \longrightarrow \text{CH}_3^\bullet + \text{H}_2\text{O}$
 - Model for hydroxyl radical decomposition of alkanes in troposphere
- $$\text{RH} + \text{OH}^\bullet \longrightarrow \text{R}^\bullet + \text{H}_2\text{O}$$
- Reactions have low activation energies leading to alkanes having short atmospheric lifetimes.
 - $\text{CH}_4 + \text{Cl}^\bullet \longrightarrow \text{CH}_3^\bullet + \text{HCl}$
 - Atmospheric sink for Cl atoms which participate in the destruction of ozone.
 - $\text{CH}_4 + \text{H}^\bullet \longrightarrow \text{CH}_3^\bullet + \text{H}_2$
 - Simplest reaction of a radical with a hydrocarbon.
 - Potential importance in the combustion mechanism of simple hydrocarbons.

Computational Model

- Abstraction of H from CH₄



- What does the TS structure look like?
- What is the overall reaction enthalpy, ΔH^{298} ?
- What is the barrier height, ΔE_a^{\ddagger} ?

Kinetic Parameters From Transition State Theory

- rigid rotor, harmonic oscillator
- 1 free internal rotor
- Wigner tunneling correction

$$E_a = 4.32 \text{ kcal/mol} \quad 200 \leq T \leq 420 \text{ K}$$

$$A = 1.47 \times 10^{-11} \text{ cc/molecule} \cdot \text{s}$$

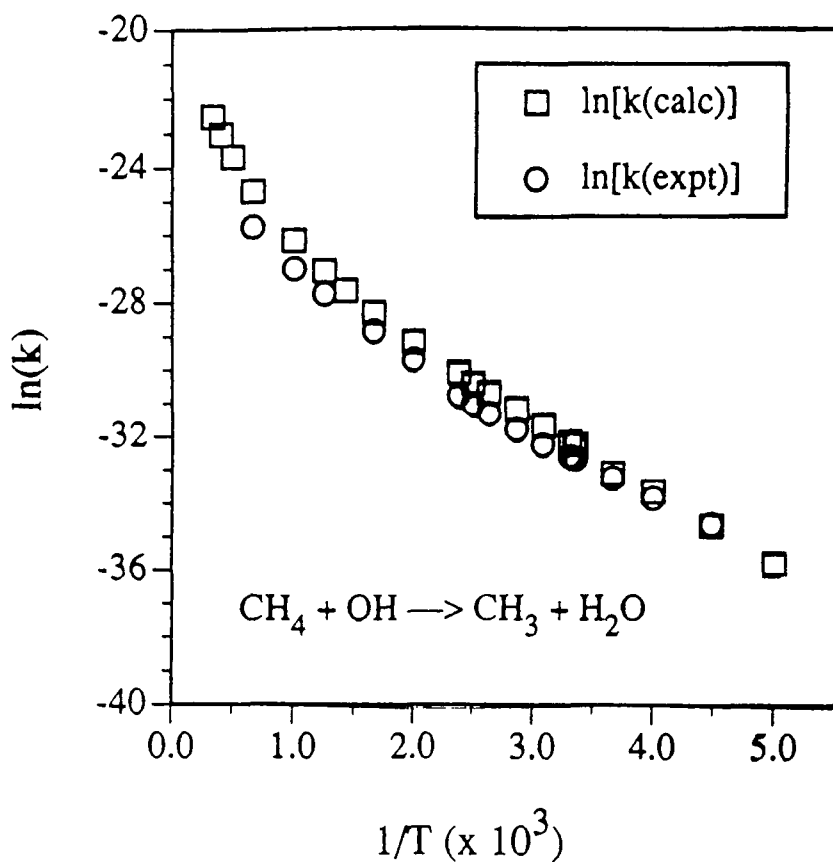
$$E_a = 5.56 \text{ kcal/mol} \quad 200 \leq T \leq 3000 \text{ K}$$

$$A = 1.16 \times 10^{-10} \text{ cm}^3/\text{molecule} \cdot \text{s}$$

Experimental values

$$E_a = 3.6 \text{ kcal/mol} \quad 200 \leq T \leq 400 \text{ K}$$

$$A = 2.9 \times 10^{-12} \text{ cm}^3/\text{molecule} \cdot \text{s}$$



HFC-23 and HFC-236fa Reactions with OH

HFC-23 = CF_3H & HFC-236fa = $\text{CF}_3\text{CH}_2\text{CF}_3$

<u>Molecule</u>	<u>k(298) expt</u>	<u>k(298) calc</u>
HFC-23	2.4×10^{-16}	6.9×10^{-16}
HFC-236fa	3.4×10^{-16}	6.1×10^{-16}

Experimental values from DeMore's work at JPL
Rate constants in $\text{cm}^3/\text{molecule}\cdot\text{sec}$

ATMOSPHERIC CHEMISTRY OF ORGANIC COMPOUNDS

Roger Atkinson

Photochemical Reactivity Workshop

May 12-14, 1998

Tropospheric VOC Removal Processes

The tropospheric removal or transformation processes for VOCs are:

Physical Removal Processes

Dry deposition

Wet deposition

Chemical Removal Processes

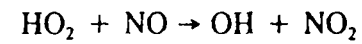
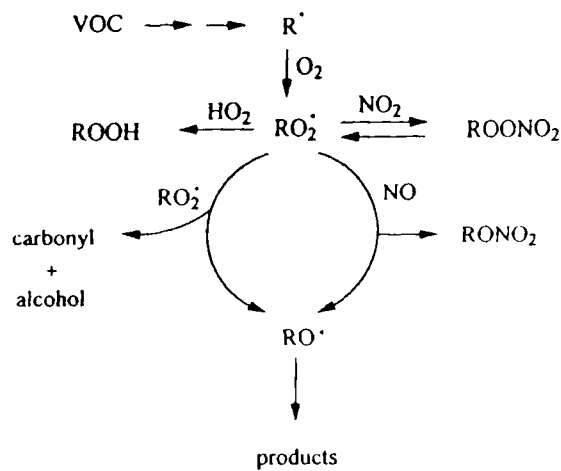
Photolysis

Reaction with ozone (O_3)

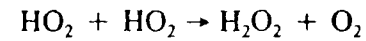
Reaction with the hydroxyl (OH) radical

Reaction with the nitrate (NO_3) radical

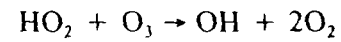
Net photochemical formation of O_3 *versus* net photochemical loss of O_3 in the troposphere depends on the rate of



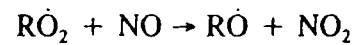
versus



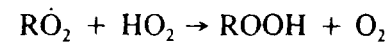
and



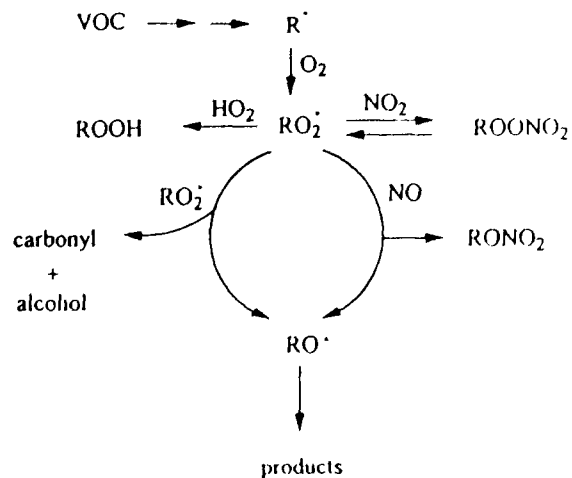
and also by the rate of



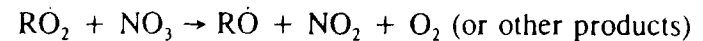
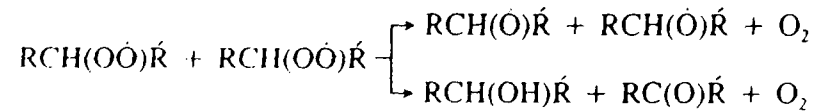
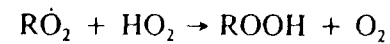
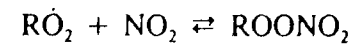
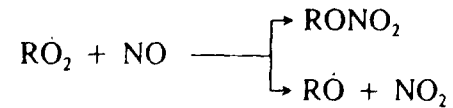
versus



Organic Reactions (general)



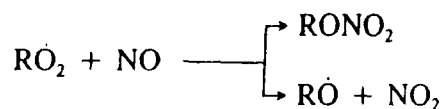
Peroxy Radical Reactions



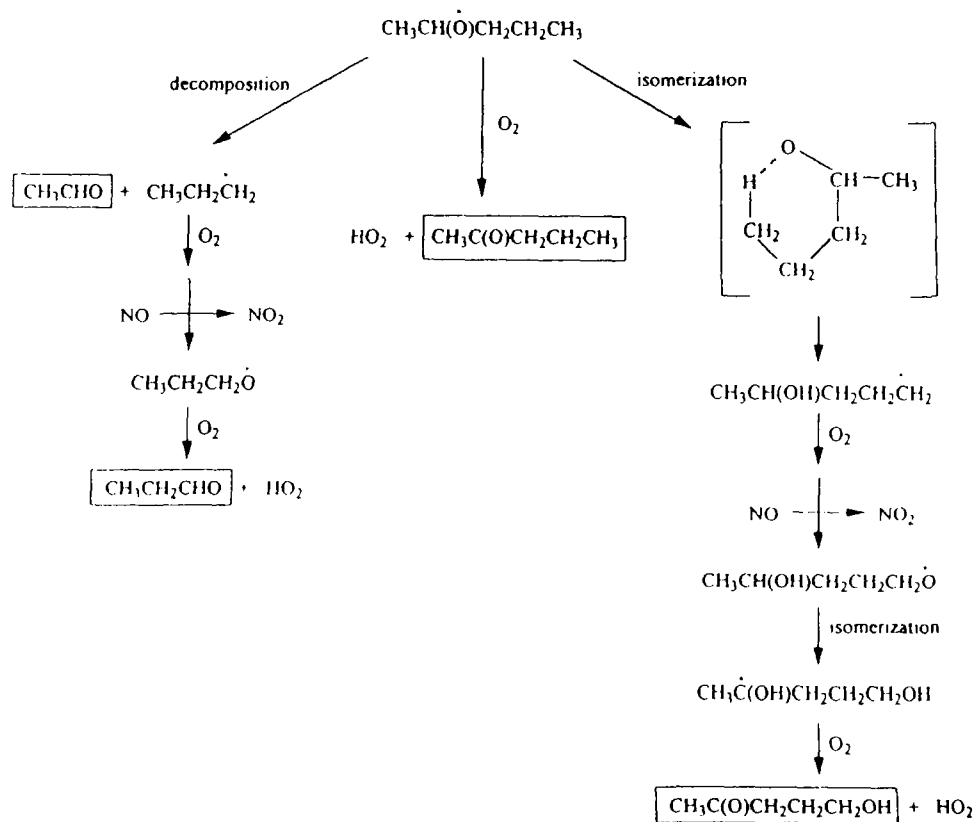
- Reactions of organic peroxy radicals.
- Organic nitrate formation.
- Reactions of alkoxy radicals.
- Wet and dry deposition of VOCs and of their reaction products.

- There is a need for kinetic and product data for the reactions of a wide variety of organic peroxy radicals with NO, HO₂ radicals and NO₃ radicals.

Organic Nitrate Formation



- The nitrate yields increase with increasing pressure and with decreasing temperature.
- Data are available for 18 secondary alkyl radicals formed from alkanes and for 4 other alkyl and β -hydroxyalkyl radicals formed from alkanes and alkenes (mainly at room temperature and atmospheric pressure).

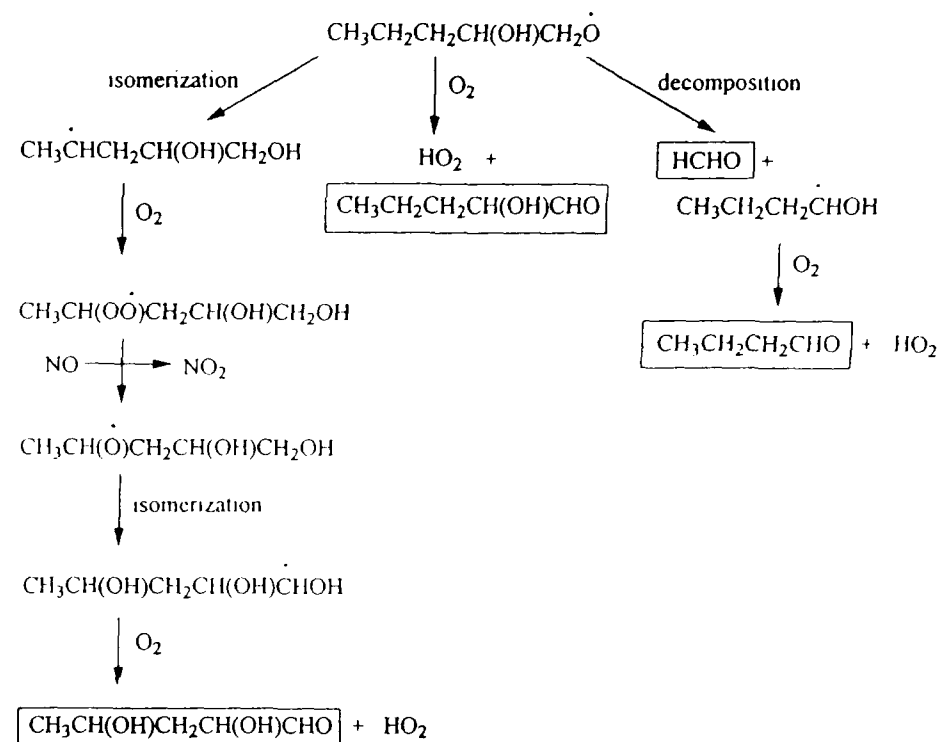


OH and NO₃ Radical Reactions with Alkanes and Alkenes

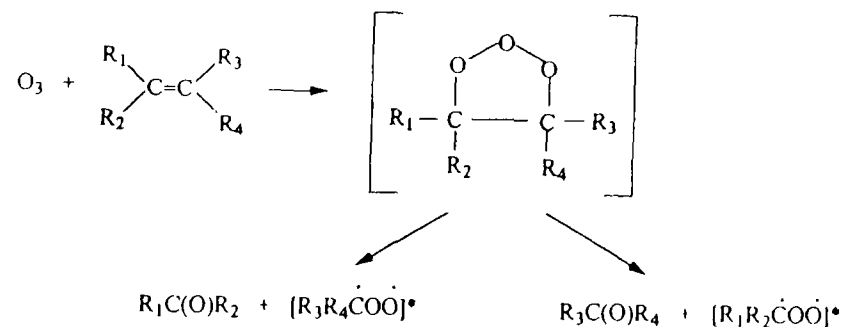
- The initial reactions lead to the formation of alkyl or substituted-alkyl (\dot{R}) radicals, which then add O₂ to form $\dot{R}O_2$ radicals.

- The present knowledge and uncertainties in the OH radical-initiated reactions of alkanes and alkenes are:

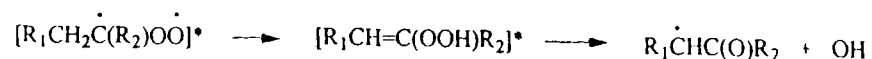
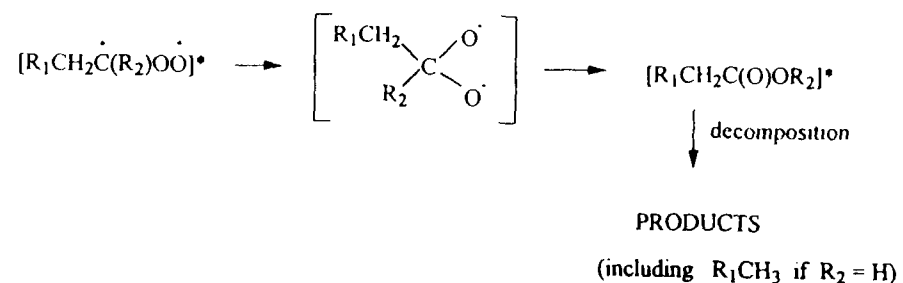
- $RONO_2$ formation from $\dot{R}O_2 + NO$
- $\dot{R}O_2 + RO_2$, $\dot{R}O_2 + HO_2$ and $\dot{R}O_2 + NO_3$ reactions
- Reactions of alkoxy and hydroxyalkoxy radicals:
 - Reaction with O₂ (if α -H atom present)
 - Decomposition
 - Isomerization through a 6-membered transition state



- Isomerization reaction has been observed from alkane and alkene reactions; quantification of the resulting hydroxycarbonyl and dihydroxycarbonyl products is now required.
- The products and mechanisms of the NO_3 radical reactions are not well understood; in part because these reactions occur in the essential absence of NO and hence $\text{RO}_2 + \text{HO}_2$ and $\text{RO}_2 + \text{RO}_2$ reactions are important and, especially in laboratory systems, ROONO_2 are important intermediate reservoir species.

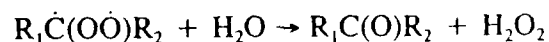


followed by reactions of the biradicals



Areas of uncertainty:

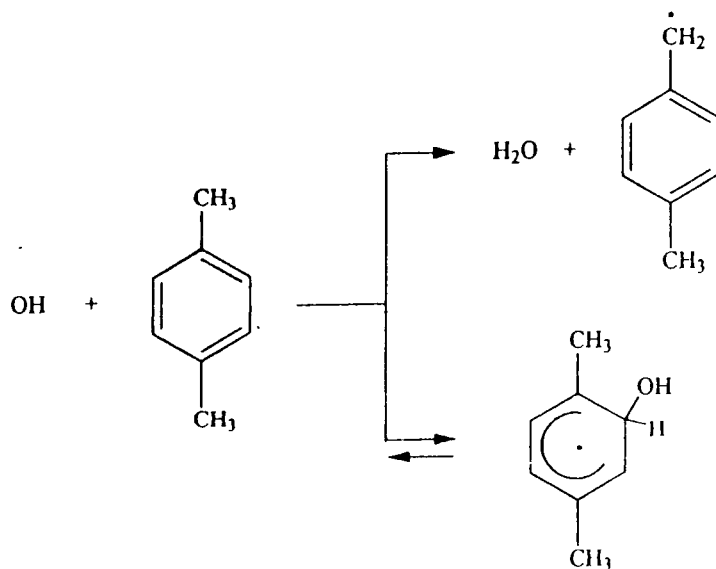
- Reactions of the thermalized biradicals.
 - Appear to be with water vapor under atmospheric conditions.
 - The $\dot{\text{C}}\text{H}_2\text{O}\dot{\text{O}}$ biradical reacts with H_2O to form HOCH_2OOH which (heterogeneously?) decomposes to $\text{HC(O)OH} + \text{H}_2\text{O}$.
 - Certain more complex biradicals appear to react with water vapor to form the carbonyl (plus H_2O_2).



- Reactions of the organic radical co-product to OH; *e.g.*, $\text{CH}_3\text{C(O)}\dot{\text{C}}\text{H}_2$ radical from the $[(\text{CH}_3)_2\dot{\text{C}}\text{OO}]^*$ biradical.

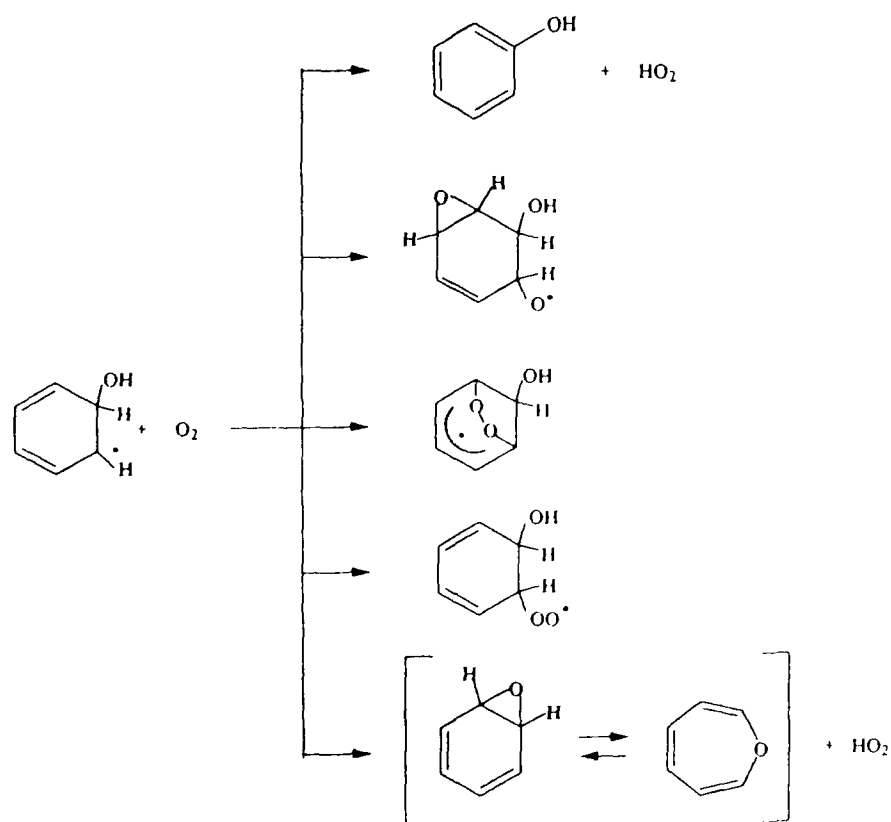
AROMATIC HYDROCARBONS

- For benzene and the alkyl-substituted benzenes, the major atmospheric reactions are with OH radicals (major) and NO_3 radicals (minor).
- NO_3 radical reactions proceed by overall H-atom abstraction from the alkyl substituent groups.
- OH radical reactions proceed by overall H-atom abstraction from the alkyl substituent groups ($\leq 10\%$) and by OH radical addition to the aromatic ring to form a hydroxycyclohexadienyl radical ($\geq 90\%$).

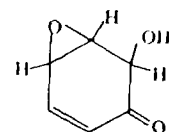


- Under tropospheric conditions, the hydroxycyclohexadienyl radicals (OH-aromatic adducts) react with O_2 ; at elevated NO_2 concentrations encountered in some laboratory studies the OH-aromatic adduct reactions with NO_2 may be important.
- The products and mechanisms of the reactions of the OH-aromatic adducts with O_2 and NO_2 are not presently understood in any detail, although product data (sometimes contradictory) are available from a number of laboratory product studies.
- Formation of ring-opened unsaturated dicarbonyls $[-\text{C}(\text{O})\text{C}=\text{CC}(\text{O})-]$ and di-unsaturated dicarbonyls $[-\text{C}(\text{O})\text{C}=\text{CC}=\text{CC}(\text{O})-]$ have been observed and may be very important.

S-9



These radicals formed after O_2 addition to the OH-benzene adduct react further to (potentially) form:



Additionally benzene oxide/oxepin reacts to form



Tropospheric Chemistry of Oxygen-Containing Compounds

- Aliphatic aldehydes, ketones and α -dicarbonyls.
- Alcohols.
- Ethers and glycol ethers.
- α,β -Unsaturated carbonyl compounds.
- Unsaturated dicarbonyls.
- Esters.
- Hydroperoxides.
- Other oxygenated compounds.

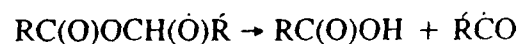
Aliphatic aldehydes, ketones and α -dicarbonyls

- These react with OH radicals and (to a lesser extent) with NO_3 radicals, and also photolyze.
- Need absorption cross-sections and photolysis quantum yields as a function of wavelength [apparently reliable cross-section and quantum yield data are available only for HCHO, CH_3CHO and $(\text{CHO})_2$].
- The OH radical and NO_3 radical reactions with $\geq \text{C}_2$ aldehydes lead to peroxyacyl nitrate (PAN) formation.

NITROGEN-CONTAINING ORGANICS

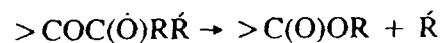
Esters

- Reaction of $\text{RC(O)OCH}(\dot{\text{O}})\dot{\text{R}}$ radicals:



Ethers and Glycol Ethers

- Decomposition of $>\text{COC}(\dot{\text{O}})\text{RR}$ radicals appears to be a factor of $\sim 10^3$ faster than expected by analogy with the alkoxy radicals formed from alkanes and alkenes.



- Organic nitrates (RONO_2) and peroxyacyl nitrates (RC(O)OONO_2) appear to be the most important N-containing compounds.
- Rate constants for the OH radical reactions are available for alkyl nitrates; product data are needed.
- For RC(O)OONO_2 compounds (apart from PAN), data are needed for photolysis and thermal decomposition.

CONCLUSIONS

- Much progress has been made over the past 2 decades:
 - Importance of NO_3 radical reactions.
 - Kinetics of OH and NO_3 radical and O_3 reactions with VOCs.
 - Studies of RO_2 radical reactions.
 - Alkoxy radical reactions (isomerization)
 - Fate of hydroxycyclohexadienyl radicals, including formation of ring-opened unsaturated dicarbonyls from aromatic hydrocarbons
 - Product and mechanism studies of O_3 + alkenes; formation of OH radicals from these reactions.
- Still many details to deal with!

Needed Research

- Quantitative knowledge of the rate constants and mechanisms of the reactions of organic peroxy (RO_2) radicals with NO, HO_2 radicals, NO_3 radicals and other RO_2 radicals (the latter mainly to allow accurate modeling of irradiated NO_x - VOC - air mixtures).
- Additional data concerning the organic nitrates yields from the reactions of organic peroxy radicals with NO, preferably as a function of temperature and pressure.
- The reaction rates of alkoxy radicals for decomposition, isomerization and reaction with O_2 , especially of alkoxy radicals other than those formed from alkanes and alkenes (for example, from hydroxy-compounds, ethers, glycol ethers and esters).

- Detailed mechanisms of the reactions of O_3 with alkenes and VOCs containing $>C=C<$ bonds. This involves understanding the reactions of the initially energy-rich biradicals, and thermalized biradicals, formed in these reactions.
- Mechanisms and products of the reactions of OH-aromatic adducts with O_2 and NO_2 .
- Tropospheric chemistry of many oxygenated VOCs formed as first-generation products of VOC photooxidations, including (but not limited to) carbonyls (including unsaturated dicarbonyls, di-unsaturated dicarbonyls, and unsaturated epoxy-carbonyls), hydroperoxides, and esters.

Atmospheric Chemistry of Oxygenated Organic Compounds

Ray Wells

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Uncharacterized volatile organic compound (VOC) emissions from complex formulations (coatings, coating strippers, cleaners) are involved in the production of tropospheric ozone (O_3), a regulated pollutant. Since the detailed atmospheric chemistry of several of these chemicals has never been investigated, experimental atmospheric research coupled with incremental reactivity calculations is useful to more accurately assess the atmospheric impact of coatings emissions. The atmospheric impact of the coating systems was determined, using individual VOC incremental reactivity calculations, coupled with a detailed description of coating system emissions. The concentrations and identification of VOCs in the coating emissions were determined by combining gas chromatography, mass spectroscopy and Fourier transform infrared spectroscopy (GC/MS/FTIR) techniques. The OH rate constant for ethyl 3-ethoxypropionate was determined using the relative rate technique. The products of the OH + ethyl 3-ethoxypropionate reaction were determined and an atmospheric reaction mechanism for ethyl 3-ethoxypropionate was proposed.



AIR FORCE RESEARCH LABORATORY



ATMOSPHERIC CHEMISTRY OF OXYGENATED ORGANIC COMPOUNDS

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AIR TEAM



Lt. Leon Perkowski
Dr. Ray Wells
Darrell Winner
Stewart Markgraf
Steve Baxley
Sheryl Wyatt
Bill Bradley

We determine impact on air quality.



URGENCY

- 1990 Clean Air Act -

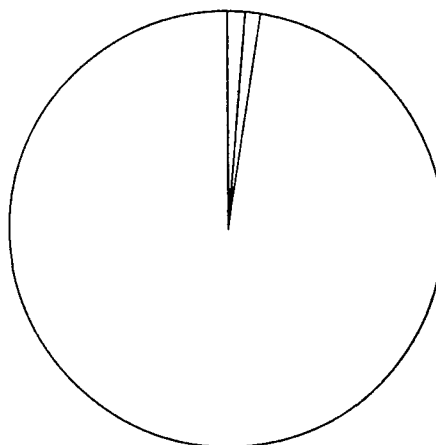
200 new regulations
and guidance documents

They impact our missions!



DoD Releases by Media, 1994

Land	Water
1.31%	1.25%

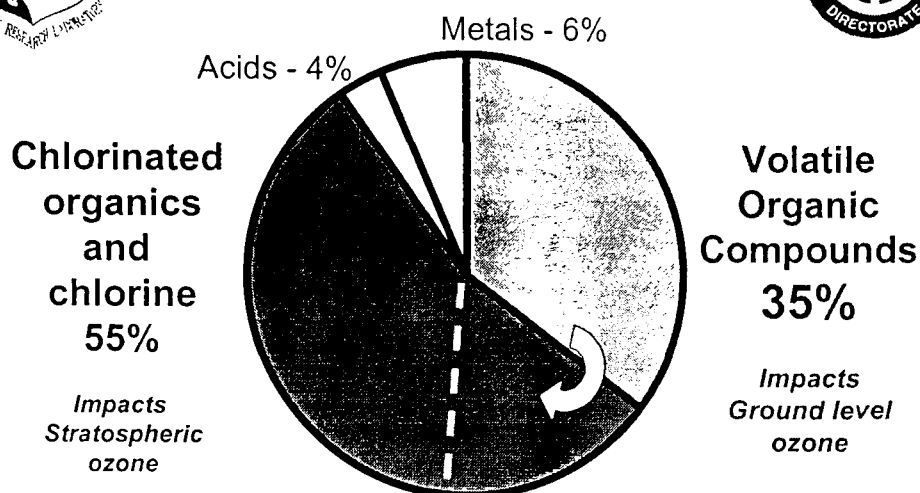


Air
97.44%

From: 1994 Toxics Release Inventory for the DoD Public Data Report, March 7, 1996



Of That 97%...



Compromise ozone formation and depletion



Sources of Pollution

Paints

Thinners

Solvents

Combustion

Exhausts

Emissions

New replacements affect these sources



Purpose

GOAL: Prevent pollution intelligently while maintaining performance

Achieved by addressing:

1. What is being emitted?
2. What happens to emitted chemicals?

Tech Need: 1940 - Replacement of chlorinated cleaners for engines (High)

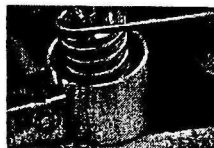


Experimental Apparatus

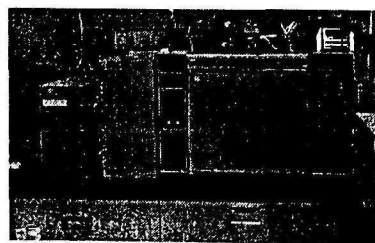
Reaction Chamber



Sample Loop



Analysis System

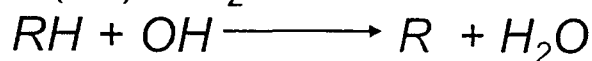




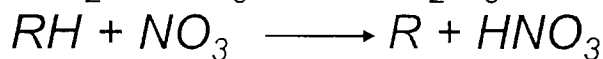
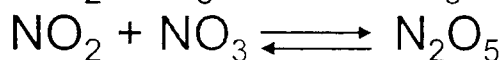
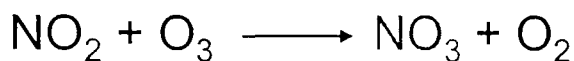
Pertinent Radical Formation Reactions



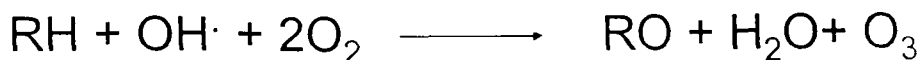
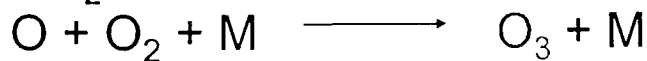
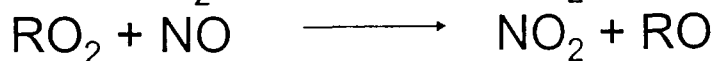
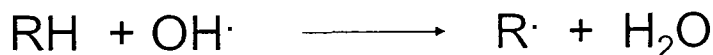
OH Radical



NO₃ Radical



Atmospheric Transformation Processes





Experimental Methods



I. Relative Rate Technique:

Compare unknown hydroxyl reaction rate to one that is known:

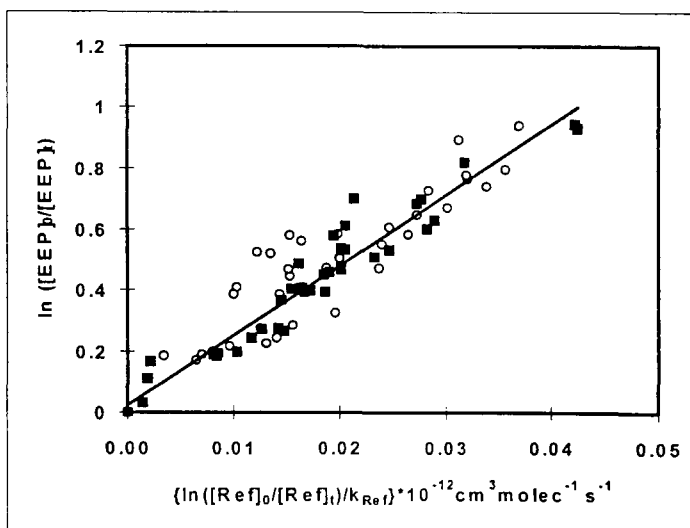
- 1) Reference + OH \longrightarrow Products
- 2) Unknown + OH \longrightarrow Products

Dividing differential equations to remove OH concentration and time and integrating yields:

$$\ln \left[\frac{[\text{Unknown}]_0}{[\text{Unknown}]_t} \right] = \frac{k_{\text{Unknown}}}{k_{\text{Reference}}} \ln \left[\frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right]$$



Hydroxyl Radical Rate Constant for EEP CH3CH2OCH2CH2C(=O)OCH2CH3





Hydroxyl Radical Rate Constants



Rate constants and chemical structures are variable

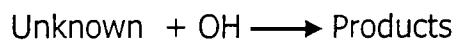
Compound/Structure	$k_{OH}(10^{-12}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1})/\text{lifetime (hr)}$
Ethyl 3-ethoxypropionate $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_2\text{CH}_3$	23/12
Hexyl Acetate $\text{CH}_3(\text{CH}_2)_5\text{OC}(=\text{O})\text{CH}_3$	9.3/30
Isobutyl Acetate $(\text{CH}_3)_2\text{CHCH}_2\text{OC}(=\text{O})\text{CH}_3$	6.5/43
2-Butoxyethanol $\text{CH}_3(\text{CH}_2)_3\text{OCH}_2\text{CH}_2(\text{OH})$	22.5/12
2-Butanol $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	8.1/34



Experimental Methods

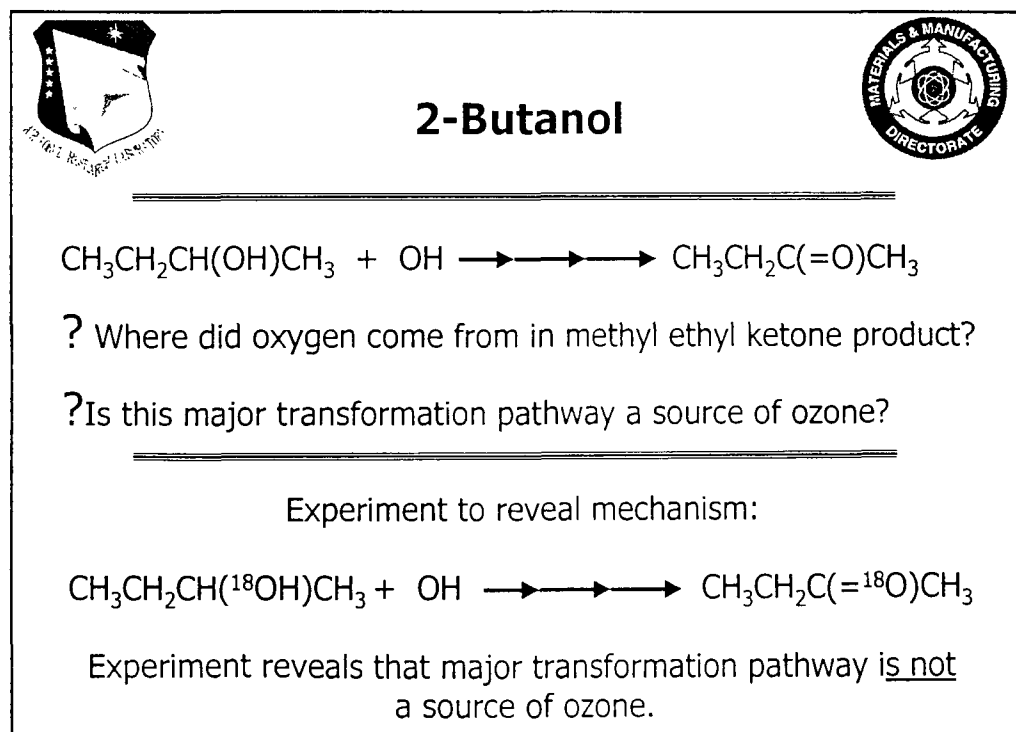
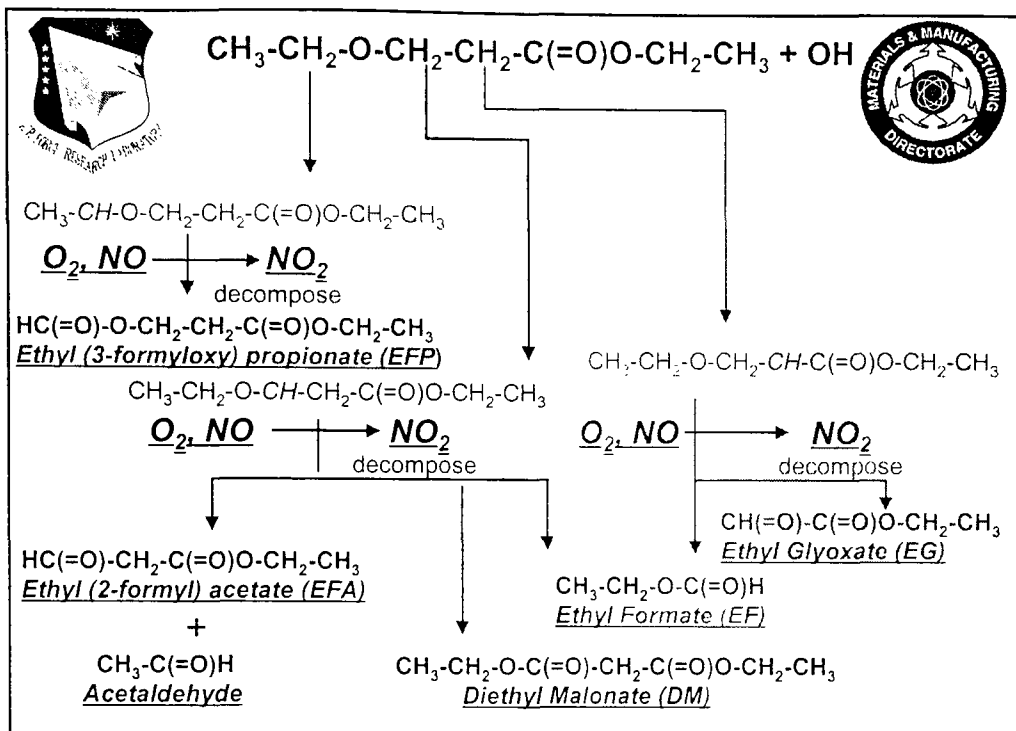


II. Product Identification and Yields:



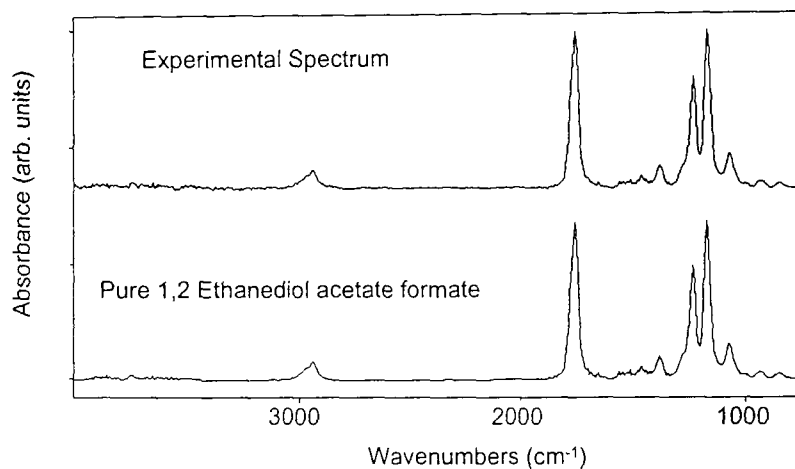
Must correct for transformation product/OH reaction to determine yield:

$$F = \frac{k_{\text{unknown}} - k_{\text{product}}}{k_{\text{unknown}}} \times \frac{1 - \frac{[\text{Unknown}]_t}{[\text{Unknown}]_0}}{\left(\frac{[\text{Unknown}]_t}{[\text{Unknown}]_0} \right)^{\frac{k_{\text{product}}}{k_{\text{unknown}}}} - \frac{[\text{Unknown}]_t}{[\text{Unknown}]_0}}$$

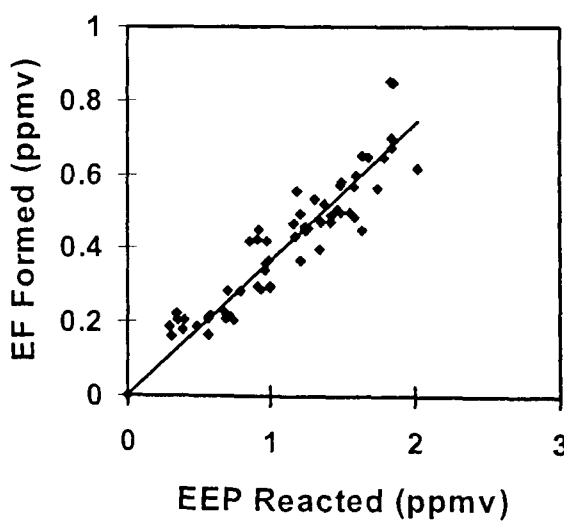




Reaction Product Identification



Corrected Ethyl Formate Product Yield





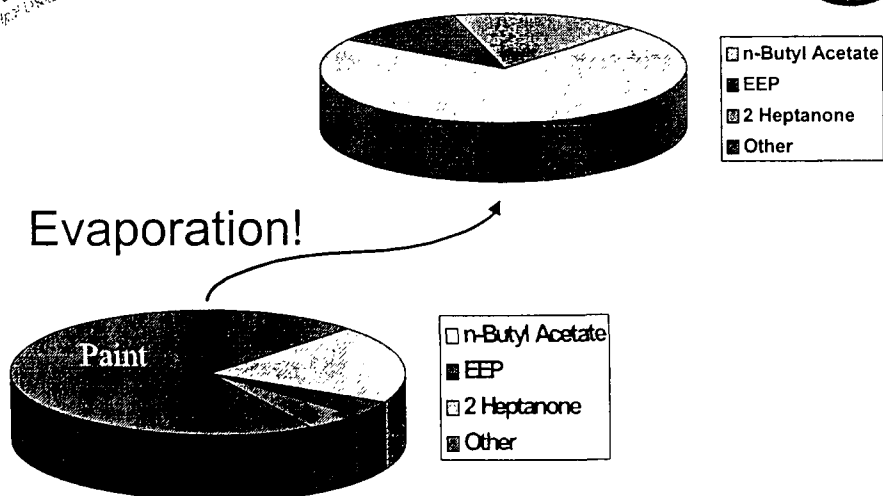
Reactivity of Emissions



- Reactivity (ozone forming potential) of individual chemicals requires knowledge of atmospheric kinetics and mechanisms.
- Reactivity of emissions is based on summation of reactivity of individual chemicals.
- Reactivity values for each formulation are used to assess impact on air quality and minimize regulatory impact.



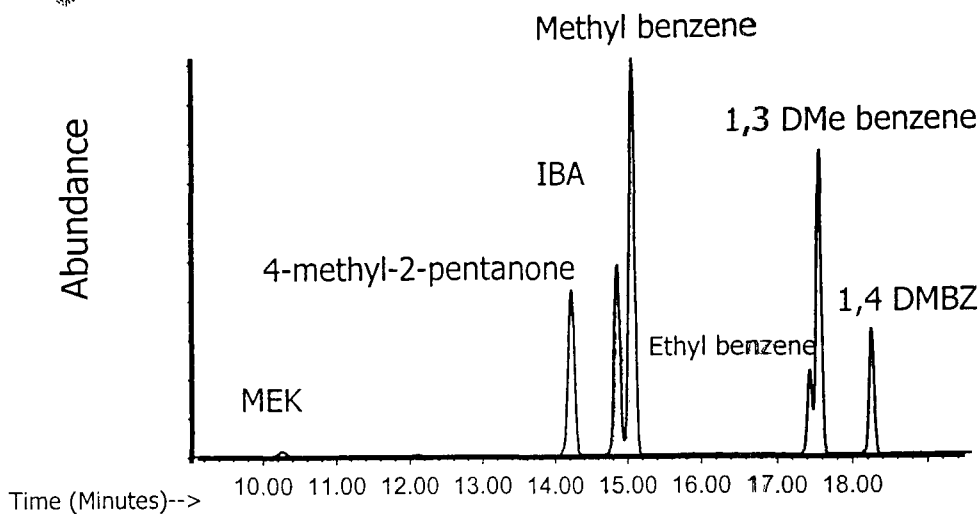
EMISSIONS - The Real Problem



Emissions NOT content !



TIC for MIL-P-23377F



Air Quality Impact



Coating A = 0.27 g O₃/g paint

Coating B = 0.27 g O₃/g paint

MIL-P-23377F = 0.75 g O₃/g paint

$$\text{gram O}_3/\text{gram paint} = \sum (\text{gram emitted VOC/gram paint}) * \text{Factor}_{\text{VOC}}$$



Materials Benefits

- Meet pollution prevention goals.
- Formulation flexibility.

Multicomponent Aerosol Generation System (MAGS) for the Study of Fine Particulates on Photochemical Reactivity of Organics

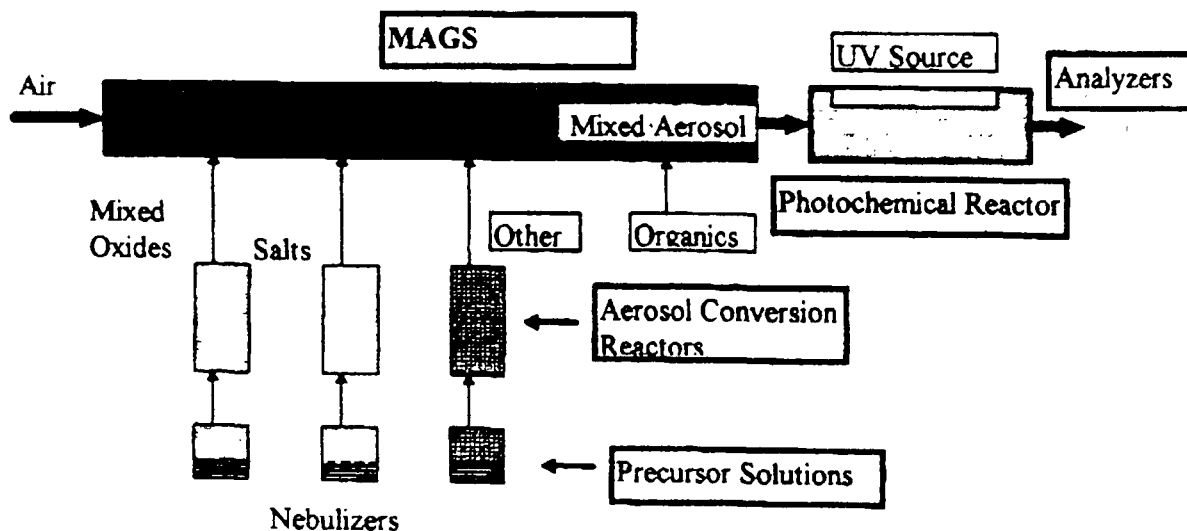
*S. V. Kulkarni, KulTech Incorporated
Research Triangle Park, North Carolina*

*M. B. Ranade, Particle Technology Inc.
Beltsville, Maryland*

Considering the relative merits of using individual VOC species reactivities versus VOC-group ratings (S Question/Issue 4) may address the effects of synergism within the VOCs present in an organics emission source, but it does not consider the chemical reactions that may affect photochemically active VOC species. Mixed oxides and salts such as $\text{SiO}_2/\text{TiO}_2$ are known photocatalysts in oxidation of ethylene. In the study of binary metal oxides as photocatalysts, it has been noted that there is a strong correlation between surface acidity and reactivity. Other reactions between gaseous species and VOCs are also likely to be affected. The fine particles in industrial emissions may contain metal oxides and sulfates and nitrates and may enhance or reduce the photochemical reactivity depending upon the organics present in the emissions. We propose to study the role of atmospheric fine particulates on the photochemistry of volatile organic compounds (VOCs).

We have developed a compact and portable multicomponent aerosol generation system (MAGS) which produces a particulate composition closely mimicking the ambient and stack particulates. The system has the ability to produce representative aerosols containing inorganic oxides (and Ca, Al silicates), sulfates, ammonium nitrate, organics - hygroscopic, solid and liquid, volatile components in appropriate size ranges.

MAGS, shown in the Figure below, can combine several types of particulates such as mixed oxides, mixed salts and other species such as carbonaceous compounds. Each type may be produced by nebulization and chemical conversion of precursor solution droplets. Particle size distribution of each component may be varied from submicrometer to 10 micrometers.



Numerical Study of the Development of an Ozone Episode in Germany: Relation of Anthropogenic and Biogenic Hydrocarbons

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Abstract

A mesoscale numerical model is used to study the development of ozone concentrations within the atmospheric boundary layer for different emission scenarios of anthropogenic and biogenic emissions. The major results are:

- In the reference case the maximum ozone concentrations are in the order of 100 ppb.
- When all anthropogenic emissions are switched off the maximum ozone concentrations are in the order of 60 ppb.
- When the anthropogenic emissions of the four most reactive hydrocarbons within the RADM2 gas phase mechanism are switched off the ozone concentrations are reduced up to 15 ppb.
- When all anthropogenic hydrocarbon emissions are switched off the ozone concentrations are reduced up to 50 ppb.

1 The problem

The atmosphere is a huge deposit for gaseous waste from a large variety of anthropogenic and biogenic sources. Due to the complex interaction of the chemical and physical processes in the atmosphere a clear determination of the importance of individual substances for the development e.g. of photooxidants like ozone is very difficult.

In this paper a comprehensive model system including the most relevant atmospheric and chemical processes is used to estimate the influence of man made nitrogen oxides and hydrocarbons on the development of maximum ozone concentrations during an ozone episode. Especially four cases will be studied:

- The reference case where both the anthropogenic and the biogenic emissions are included.

- The background case where all anthropogenic sources are switched off and only natural emissions of nitrogen from soil and of hydrocarbons from biogenic sources are considered.
- The case where all anthropogenic emissions of hydrocarbons are switched off.
- The case where the anthropogenic emissions of the four most reactive hydrocarbons within the RADM2 chemical mechanism are switched off.

2 The model system and the data base

For this study the non-hydrostatic mesoscale model system KAMM (KAMM = Karlsruhe Atmospheric Mesoscale Model) together with the gas phase mechanism RADM2 (Stockwell et al., 1990) is used. The model system is driven by a basic state which is derived from the larger scale observations. It is documented in more detail in Adrian and Fiedler (1991), Vogel et al., (1995) and Fiedler (1993). As a result the model provides all important meteorological variables and the concentrations of chemical species for episodes of several days.

Emission data of the most important anthropogenic emissions have been compiled in hourly time steps and for an area of 177 km x 177 km with a horizontal resolution of 3 km. Additional data like terrain height, land use and soil data have also been provided as close to reality as possible. Those data are especially important for the parameterization of the turbulent fluxes of momentum, energy, water vapour but also for the parameterization of the emission and the dry deposition of chemical species at the surface. In addition with the temperature and the photosynthetic active radiation calculated by KAMM the natural emissions of nitrogen oxides from soil surfaces and of hydrocarbons from vegetation are determined online by the model system.

3 Results

A situation for south-west Germany is selected, where high ozone concentrations have been observed. It was accompanied by high air temperatures (~34 °C) and therefore enhanced biogenic emissions. For the simulations with the model system a day at the beginning of August 1990 has been chosen. On that day ozone concentrations have been observed up to about 100 ppb in the early afternoon. Winds were rather weak and showed a dominant easterly component in most of the of the area.

The dominant emission area for the anthropogenic emissions is within and in the surroundings of the city of Stuttgart (Fig.1) which is located in the centre of the model domain. Fig. 2 shows the simulated ozone (O₃) concentration for the reference case at about 18 m above

ground. Areas of maximum ozone concentration appear in the west and south-west of the city and approximately 30 to 40 km downstream. The highest concentrations reached are at about 100 ppb. They are comparable to the observations.

An extreme situation is a case where no anthropogenic emissions would be available. Therefore only natural emission from soil and from biogenic source have been included. In this case the maximum ozone concentration is around 60 ppb. This value gives the lowest level which can be achieved by abatement strategies. The reductions in ozone at the same time as for the reference case (Fig. 2) are given in Fig. 3. Maximum reduction areas are in the range of 50 km downstream of the city complex.

The more realistic procedure would be the reduction of the most reactive species. In order to estimate the level of reduction by eliminating the four most reactive groups of the hydrocarbons, a scenario has been used, where emissions of propene, butene, toluene, and xylene were switched off. Compared to the total anthropogenic emissions for the whole model domain, about 20 to 25 percent of the hydrocarbons have been extracted by this procedure. The ozone reduction in this case is shown in Fig. 4, where again the difference in ozone concentration compared to the reference case (Fig. 2) is presented. Significant reductions in ozone concentration are confined to rather small areas in the west of the city of Stuttgart and to the south-west of Heilbronn. Therefore Fig. 4 gives also those areas where the ozone production is limited by the availability of hydrocarbons.

5 Conclusions

Numerical models are capable to study the effects of emission reductions but only according to the state of the art of the understanding physical and chemical processes in the atmosphere. However they provide the possibility to study quite realistic cases comparable to observations. It is therefore possible to quantify the effects of different abatement strategies.

For the episode and the area of interest we focused on the ozone level is decreased by 30 to 50 % when all anthropogenic emissions are switched off.

When the emissions of the four most reactive groups of hydrocarbons are switched off the ozone reduction reaches only about 15 % and the reduction is also confined to rather small areas compared to the case with total reduction of anthropogenic emissions.

5 References

- Adrian, G., F. Fiedler (1991): Simulation of unstationary wind and temperature fields over complex terrain and comparison with observations - *Contr. Phys. Atmos.*, 64, 27-48.
Fiedler, F. (1993): Development of meteorological computer models
Interdisciplinary Science Reviews, 18, 192-198.
Stockwell B.W., P. Middleton, J.S. Chang, X. Tang (1990): The second generation regional acid deposition model chemical mechanism for regional air quality modeling, *J. Geophys. Res.*, 95, 16343-16368.

Vogel, B., F. Fiedler, H. Vogel (1995): Influence of topography and biogenic volatile organic compounds emission in the state of Baden-Wuerttemberg on ozone concentrations during episodes of high air temperatures, J. Geophys. Res., 100, 22907-22928.

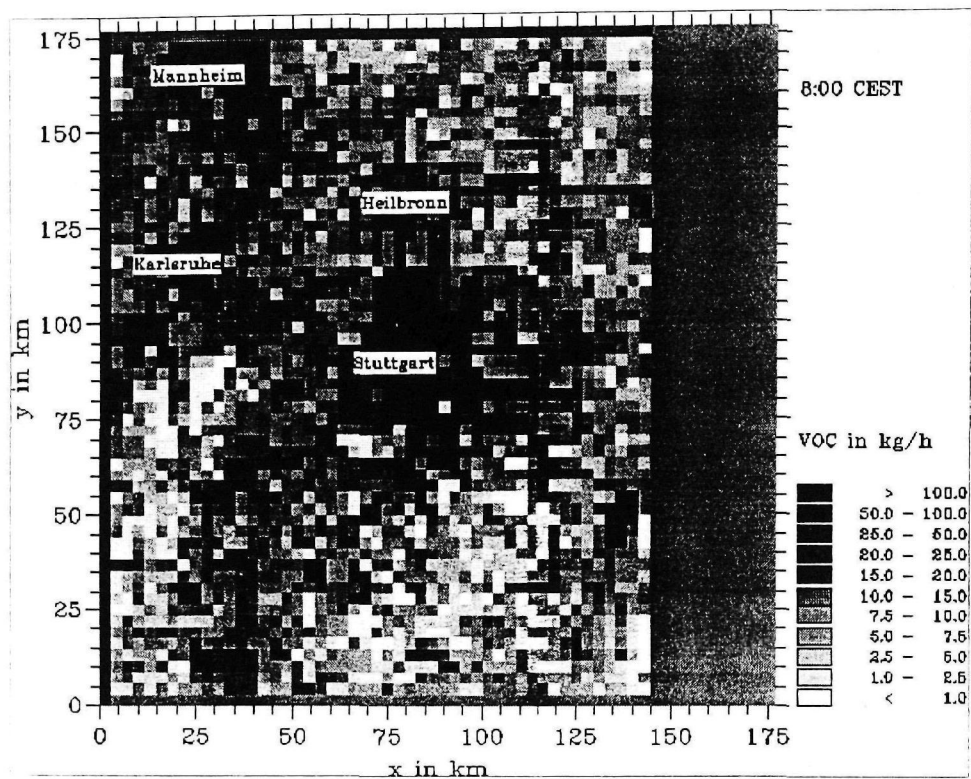


Figure 1: Horizontal distribution of the anthropogenic VOC emissions at 0800 CEST.

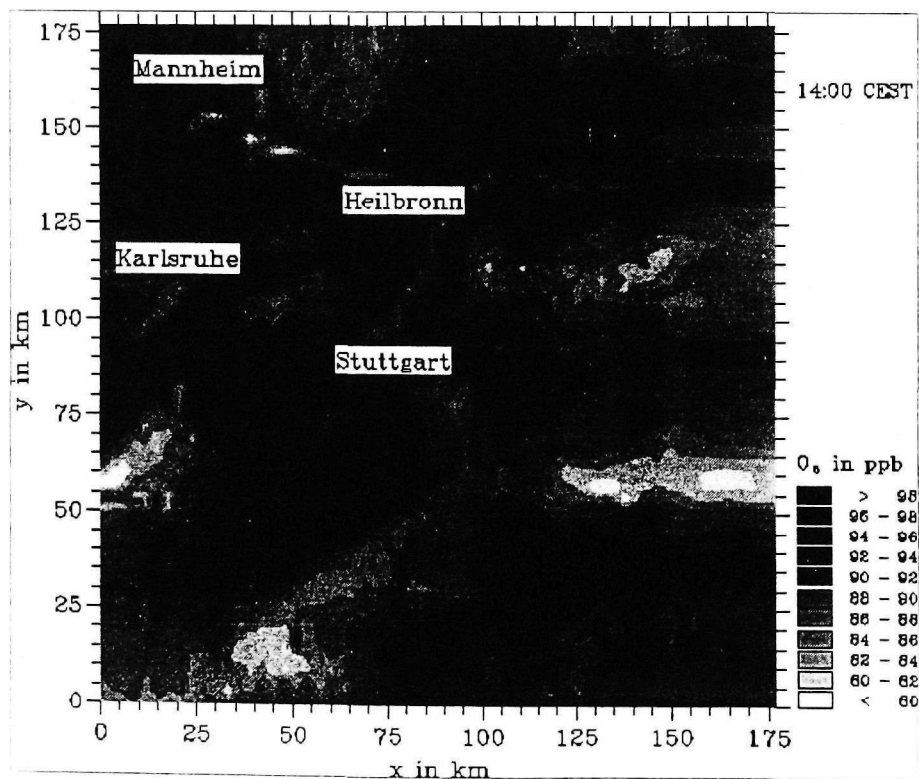


Figure 2: Horizontal distribution of ozone at 1400 CEST (18 m above ground).

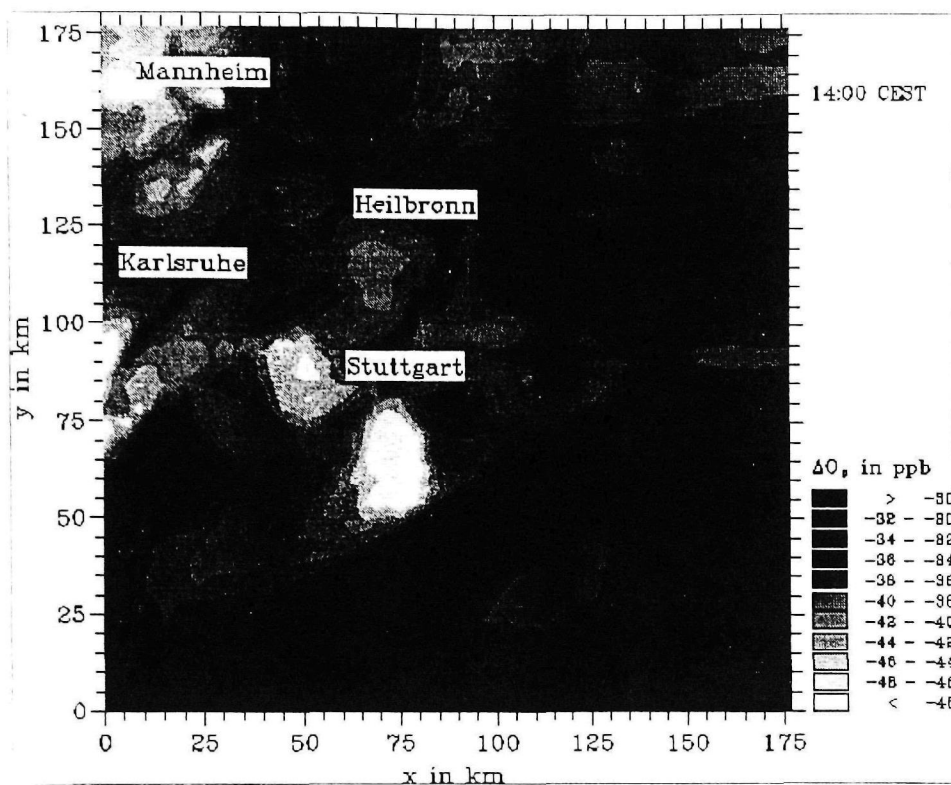


Figure 3: Simulated ozone concentrations without anthropogenic emissions, minus simulated ozone concentration with all emissions at 1400 CEST (18 m above ground).

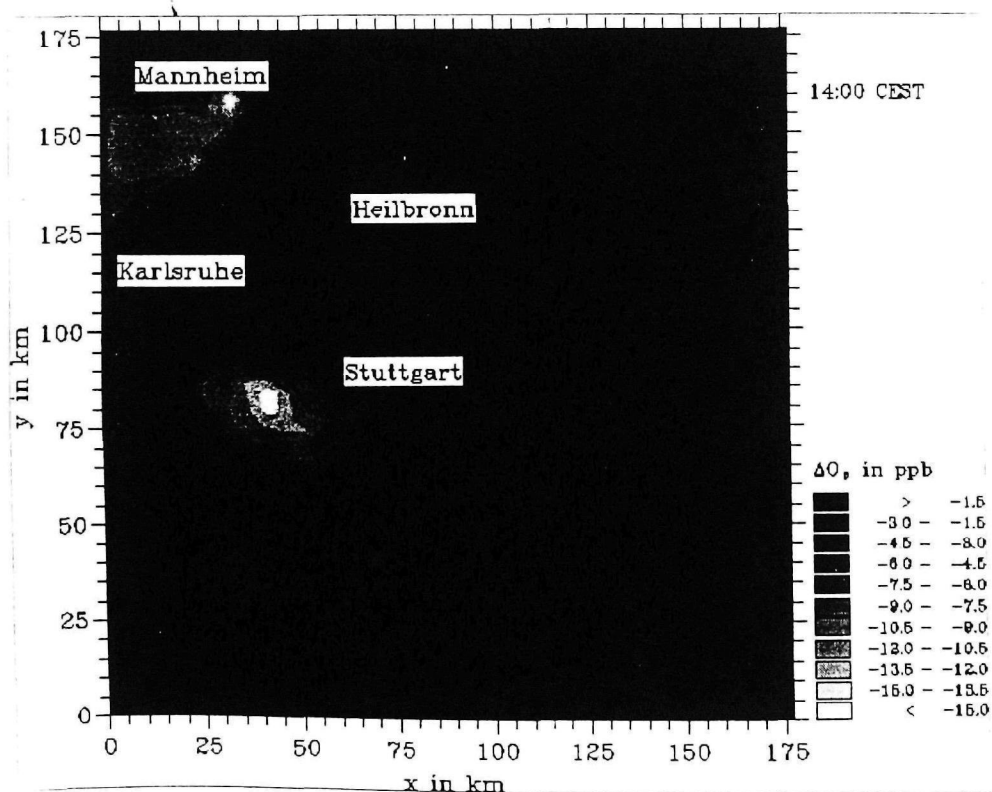


Figure 4: Simulated ozone concentrations without anthropogenic emissions of propene, butene, toluene, and xylene, minus simulated ozone concentration with all emissions at 1400 CEST (18 m above ground).

European Studies on the Photooxidation Mechanisms of Aromatic Hydrocarbons and Oxygenates: Reactivity Implications

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Physikalische Chemie/FB 9, Bergische Universität - Gesamthochschulke Wuppertal.
Gaußstraße 20, D-42097 Wuppertal, Germany

Within the framework of the German Tropospheric Research Programme (TFS) in Germany and the Chemical Mechanisms Development (CMD) subproject of EUROTRAC 2 research is currently in progress in Europe to elucidate the photooxidation mechanisms of VOCs, in particular aromatic hydrocarbons and oxygenates (e.g. dicarbonyls, ethers and acetals). The aim of these efforts is the development of chemical mechanisms for inclusion in CT models to better predict photooxidation formation.

Since model calculations indicate that aromatic hydrocarbons mainly BTX (benzene, toluene and the xylene isomers) can contribute up to as much as 40% to the formation of O₃ and other photooxidants in urban areas over Europe (Derwent *et al.*, 1996, 1998) substantial efforts have been expended on investigating aromatic hydrocarbon oxidation mechanisms. However, the accuracy of these predictions depends on the mechanism incorporated into the model and thus model validation is required. The types of work performed embrace:

- investigations on the atmospheric chemistry of benzene oxide and toluene oxide, possible primary oxidation products for benzene and toluene, respectively (Klotz *et al.* 1997, 1998).
- detailed product and kinetic studies including verification/identification of carbonyl products by GC/MS detection by their O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) derivatives (Yu *et al.*, 1997; Kwok *et al.*, 1997).
- measurement of photolysis frequencies of glyoxal, methylglyoxal, biacetyl, butenedial and 3-hexene-2,5-dione.

In the area of ethers and acetals (diethers) detailed chemical mechanisms are being developed. Particular attention has been given to diethers and cyclic ethers, which in Europe are under discussion for the use as fuel additives or alternative solvents. The developed chemical mechanisms are tested against experimental data obtained in the outdoor EUPHORE photoreactor in Valencia, Spain as well as in several indoor photoreactors. In collaboration with the Fraunhofer Institute, Garmisch-Partenkirchen, FRG, the influence of these oxygenates on tropospheric ozone formation is estimated by integration of the obtained chemical degradation schemes into the ozone prognosis model RACM (Stockwell *et al.* 1997) and application of the model to well defined scenarios.

The efforts in the area of aromatic hydrocarbon and oxygenates research within Europe will be briefly summarised and the results discussed in terms of ranking these VOC classes with regard to their reactivity.

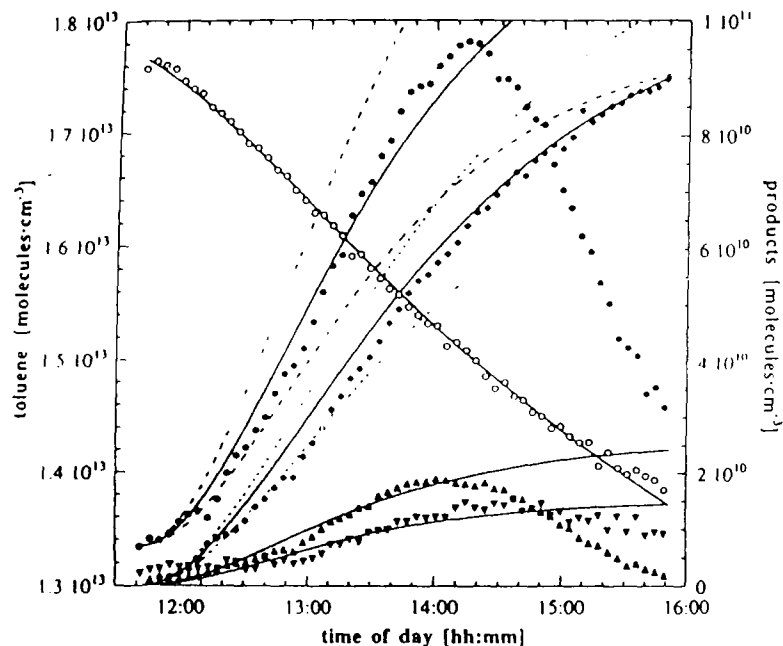
References

- Derwent, R.G., M.E. Jenkin, S.M. Saunders, *Atmos. Environ.* **30** (1996) 181-199.
Derwent, R.G., M.E. Jenkin, S.M. Saunders and M.J. Pilling *Atmos. Environ.* **32** (1998) in press.
Klotz, B., I. Barnes, K.H. Becker, B.T. Golding, *J. Chem. Soc. Faraday Trans.*, **93** (1997) 1507-1516.
Klotz, B., I. Barnes, K.H. Becker, accepted *Chem. Phys.*, (1998).
Kwok, E.S.C., S.M. Aschmann, R. Atkinson and J. Arey, *J. Chem. Soc., Faraday Trans.* **93** (1997) 2847-
Stockwell, W.R., F. Kirchner, M. Kuhn and S. Seefeld, *J. Geophys. Res.* **102** (1997) 25847-25879.
Yu, J., H.E. Jeffries, K.G. Sexton, *Atmos. Environ.* **31** (1997) 2261-2280; Yu, J., H.E. Jeffries, *Atmos. Environ.* **31** (1997) 2281-2287.

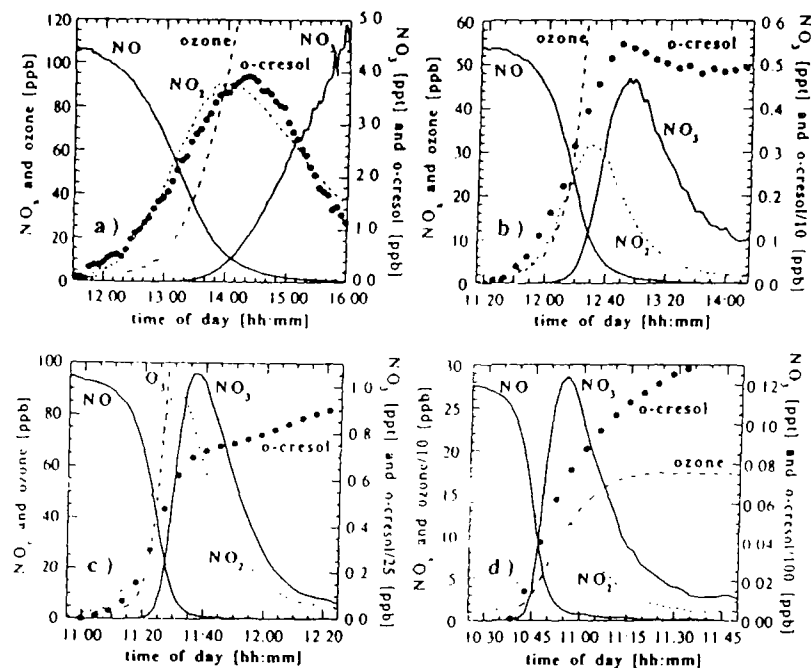
Experimental (symbols) and simulated (lines) concentration-time profile
in a toluene/NO photooxidation experiment

(730 ppb toluene / 115 ppb NO).

○): toluene, left scale; (◆): benzaldehyde; (●): o-cresol; (▼): m-cresol;
(▲): p-cresol, right scale.



Bergische Universität Wuppertal
Universität Heidelberg
LT3 - Projekt D.1 / D.2



Bergische Universität Wuppertal
LT3 - Projekt D.1

Untersuchung an ungesättigten 1,4-Dicarbonylen
im Europäischen Photoreaktor

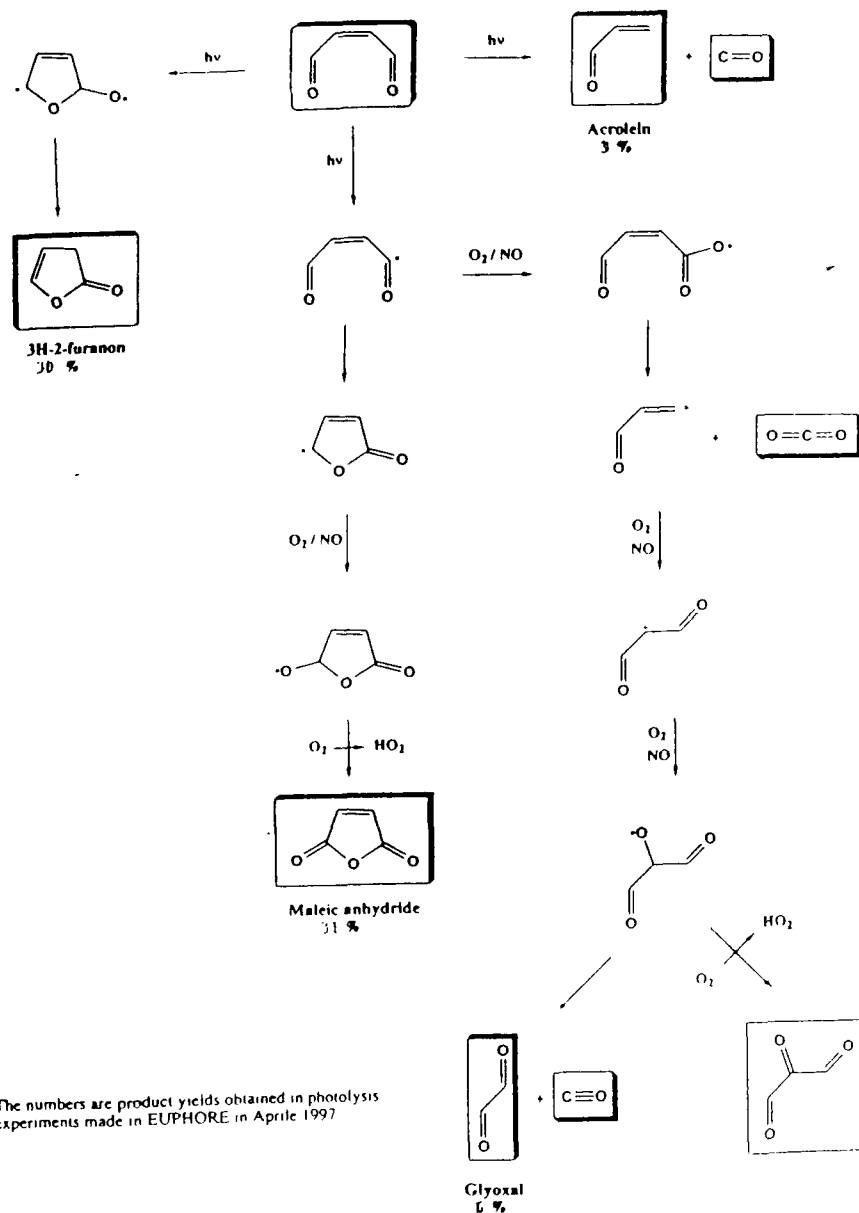
	Z-Butendial	Z-4-Oxo-2-pentenal
J(Dicarbonyl)	$1,62 \times 10^{-3} \text{ s}^{-1}$	$1,98 \times 10^{-3} \text{ s}^{-1}$
J(NO ₂) (40°N, Mittag, 1 Juli)	$9 \times 10^{-3} \text{ s}^{-1}$	$9 \times 10^{-3} \text{ s}^{-1}$
Lebensdauer τ_{phot}	10 Minuten	8,4 Minuten
Hauptprodukte:		
3H-2-Furanon	30,1 %	-
5-Methyl-3H-2-furanon	-	31,9 %
Maleinsäureanhydrid	31,0 %	13,6 %
k(OH) (Bierbach et al. 1994)	$5,2 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$	$5,6 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
Lebensdauer τ_{OH}		
[OH] = $1,6 \cdot 10^6 \text{ cm}^{-3}$	200 min	186 min
[OH] = $3,5 \cdot 10^7 \text{ cm}^{-3}$	9 min	8 min

cis-butenedial: product yields

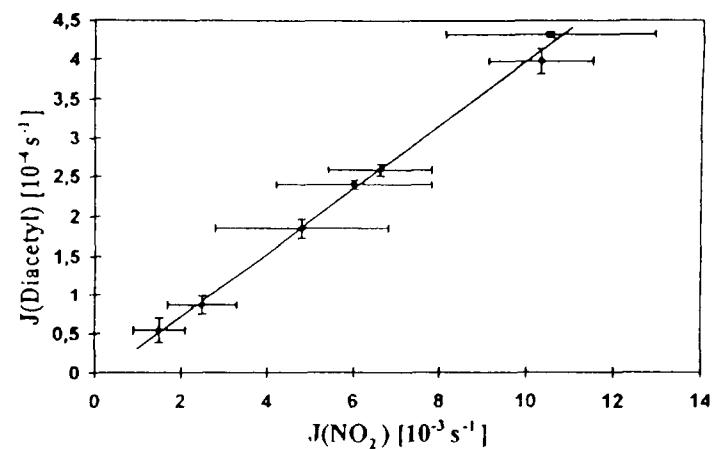
	Photolysis (Valencia)	OH radicals (CH ₃ ONO/NO)	OH radicals (H ₂ O ₂)
2-3H-furanone	30 %	< 2 %	not observed
maleic anhydride	31 %	40-50 %	6-12 %
glyoxal	6 %	15-20 %	20-45 %
acrolein	3 %	observed	not observed
carbon monoxide (% per C)	< 3 %	< 13 %	(<27 %)
sum of products	70-73 %	55-85 %	26-60 %



cis-butenedial



The numbers are product yields obtained in photolysis experiments made in EUPHORE in April 1997

Abhängigkeit der Diacetyl-Photolysefrequenz von $J(NO_2)$ 

Bergische Universität Wuppertal
LT3 - Projekt D.1

QUESTION/DISCUSSION SUMMARIES

PRESENTATION SUMMARIES

Session I Summary of Questions and Discussions

Current EPA Regulatory Viewpoint on Reactivity

Bill Johnson, Ozone Policy and Strategies Group, EPA

Mr. Johnson was asked how to get a copy of Rule 66 and vapor pressure cutoffs. He responded that inquiries on this rule, now referred to as Rule 442, can be made through Los Angeles County (i.e., South Coast Air Quality Management District). Mr. Johnson was also asked about obtaining a list of the 14 pending petitions. Mr. Johnson said that he will make this list available.

William Carter (University of California) commented that this workshop group should look at other scales in addition to the maximum incremental reactivity (MIR) scale. He added that for compounds with low vapor pressure, the equilibrium vapor pressure should be considered.

Robert Hamilton (Amway Corporation) asked about the mole versus mass based reactivity and what the advantage would be if the standards are weight based. Mr. Johnson commented that reactivity comparisons made on the mole basis would be more scientifically sound. The regulation of emissions is still done on a weight-basis. A question was asked concerning the basis for exempting compounds and what goal was trying to be accomplished. Mr. Johnson responded that the goal is ozone reduction, but that other collateral effects are being considered as well.

Brian Keen (Union Carbide) commented about the wide range of compound concentrations and reactivities, and about the pit falls of using bright line cutoffs. Mr. Johnson responded by stating that this is one of the issues he hopes will be discussed at this workshop. At the present time, bright line cutoffs work well from a regulatory perspective. Dr. Keen also commented on the problem of the uncertainty of the information.

Current EPA Research Viewpoint on Reactivity

Basil Dimitriadis, National Exposure Research Laboratory, EPA

Alan Hansen (EPRI) asked about the difference between relative versus absolute reactivity. He stated that the question of gram-based versus mole-based reactivity shouldn't be important since the two are related by a proportionality constant. Dr. Dimitriadis responded by stating that the problem depends on how the data are used. The differences between cases depends on the applications or how the material is used. For example, comparing paint solvents with ethane on a per-gram basis is affected by the problem; but intercomparing solvents on a per-gallon basis is not. John Festa (American Forest and Paper Association) asked if Dr. Dimitriadis had stated that there was no basis for excluding any VOC. Dr. Dimitriadis responded that he was referring to an exclusion from the inventory requirements. Another question was asked about the distinction made between VOCs and non-VOCs. Dr. Dimitriadis and William Carter

(University of California) clarified this issue. The distinction is a legal or regulatory one; EPA has defined compounds as being VOCs or non-VOCs and this information is provided by means of a table.

Dr. Carter also commented that there are several issues that will drive the science. The first issue is what type of policy is going to be used. If the policy continues to be the exemption policy, then the question is whether ethane is the appropriate dividing line and, if not, what substance should be used. One area of research is to determine what is the best dividing line or bright line. The second issue, once the bright line has been determined, is to determine where other compounds fall relative to the bright line. Dr. Carter commented that the most appropriate comparison is on a mass basis, because this is how the VOCs are emitted. Dr. Dimitriadis responded by stating that the question of which basis to use is one that needs further discussion.

Dave Morgott (Eastman Kodak Company) asked if MOIR has been considered over MIR as the basis for a reactivity scale. Dr. Carter commented that exemption decisions were based on a number of reactivity scales (e.g. EBIR or MOIR) and not on just the MIR scale. Dr. Dimitriadis commented that the discussion on the reactivity scales is still an open one. Jake Hales (ENVAIR) suggested that this workshop group try to develop a good definition for the term reactivity.

California's Hydrocarbon Reactivity Program

Randy Pasek, California Air Resources Board

Cari Roque (Naval Aviation Depot) asked if California was integrating their research with those from other states. She continued by asking if there would be a shift from air pollution to water pollution when changing over to material using water-based chemistry. Dr. Pasek responded by stating that they are seeking opportunities to share studies. He also stated that California doesn't plan to shift from air to water pollution. An addition, a comment was made concerning the need to recognize instances where multimedia consideration must be made.

Bernie Zysman (Occidental Chemical Corporation) asked about other research facilities doing work on MIR. William Carter (University of California) stated that he was not aware of others doing reactivity research, except Harvey Jeffries's group (University of North Carolina). Mr. Zysman add that he would like to see more research and development to clarify Dr. Carter's work.

Bob Kozak (Atlantic Biomass Conversions, Inc.) asked if CARB was considering in-use vehicle speciation testing for possible upgrading of smog check equipment. Dr. Pasek stated that these types of measurements are not being done on a routine basis, but there is a need for this type of information. Mr. Kozak also asked if tropospheric ozone production work might interfere with any stratospheric ozone depletion work being done by CARB. Dr. Pasek stated that they have taken this into account by considering the effects compounds might have on stratospheric ozone and global warming, as well as its toxicity.

VOC Reactivity - Beyond Ozone
Alan Hansen, EPRI

Dave Golden (SRI/Stanford) stated that no one knows the chemical mechanism of the SO₂ to sulfuric acid reaction. There is a lot of the chemistry in the models that may not be correct, but care must be taken when jumping to the complexity of the model. Mr. Hansen agreed with these comments.

Jake Hales (ENVAIR) asked about the counter-intuitive findings that result when you increase NO_x, the nitrate aerosol decreases. He asked if there was a mechanistic explanation for this occurrence. Mr. Hansen responded that he didn't know the mechanistic reason why this occurred. Ted Russell (Georgia Institute of Technology) commented that since you're decreasing NO₂, you're increasing the OH radical pool. This allows for faster oxidation of VOCs, the ozone concentration increases, and, with more ozone, there is more OH. The presence of more ozone also causes faster nighttime conversion of NO₂ to nitric acid.

Session II Summary of Questions and Discussions

Comparison of POCP and MIR Scales

Richard Derwent, Meteorological Office, United Kingdom

Eduardo Olaguer (The Dow Chemical Company) asked if by moving from the MIR scale to a regional reactivity scale, there would be as much of an advantage in moving from highly reactive to moderately reactive compounds. Dr. Derwent responded by stating that the best benefit is from changing from a high reactive compound to a low reactive compound. He stated that the MIR scale underestimates the impact of controlling the middle reactive compounds. Dr. Olaguer also asked if there would be any significant impact on reactivity values if fast vertical motions associated with convective activity, such as precedes thunderstorms, were accounted for in models used to derive reactivity scales. Dr. Derwent stated that this has not been considered, because ozone is not produced in thunderstorms.

Donna Carvalho (Pennzoil) asked if Dr. Derwent had made any assumptions about the reactivity of C-13 or greater compounds. Dr. Derwent responded that he had not. These compound were not included in his calculations, because they are not included in the emission inventory.

Dr. Derwent was asked about why formaldehyde was not photolyzed. He responded that it was, but whether or not to photolyze formaldehyde is not a user's choice, but is determined by the hydroxyl radical concentration. In Dr. Carter's MIR scale, because of the high NO_x levels used, much of the formaldehyde is photolysed and so it appears to be highly reactive. In the regional POCP scale, because NO_x levels are lower, much of the formaldehyde reacts with hydroxyl radicals and its reactivity appears lower.

Session III Summary of Questions and Discussions

Dunn-Edwards Proposed NARSTO Research on Ozone Formation Potential of VOC Emissions from Architectural Coatings

Edward Edwards, Dunn-Edwards Corporation

Jeff Gaffney (Argonne National Laboratory) commented that by investigating low NO_x chemistry, a great deal can be learned about regional scale reactivity. He also commented that on a regional scale, consideration must be given to the formation of species other than ozone, such as organic peroxides and the conversion of SO_2 to sulfate. These species have impacts on other environmental concerns such as regional haze.

Harvey Jeffries (University of North Carolina) commented on the importance of reactivity in low NO_x conditions. In low NO_x environments, the VOCs determine the fate of the NO_x ; the loss of NO_x limits the formation of ozone. These effects can cause increases in ozone downwind of urban areas. As illustrated by an SAI study, changes in solvent content from a more reactive solvent based on toluene to a less reactive solvent based on paraffins can cause increases in ozone concentrations in a downwind NO_x -limited environment. Dr. Jeffries concluded by stating that some of Dr. Edwards' concerns are legitimate and the issues of nitrate yields and nitrate formation in these mechanisms are important pieces of information.

William Carter (University of California) commented about his chamber study that was used to evaluate the isoprene mechanism. The changes made to the model were based on better fundamental chemistry, but the predictive capability of the model was not evaluated. Dr. Carter continued by stating that the current regional models are not designed to handle organic reactions under low NO_x conditions, with the exception of the RADM mechanism. He stated that the data have not been adequate to evaluate these models and to gather the necessary data would require the use of advanced analytical equipment to analyze for other species.

Edward Edwards (Dunn-Edwards Corporation) added a comment about the need to do full circle analysis: model, chamber, and ambient air.

CMA Research Initiatives

Jonathan Kurland, Union Carbide Corporation

Following Dr. Kurland's presentation, William Carter (University of California) discussed the different factors that affect reactivity and the ways to evaluate whether a model can adequately predict them all. In systems with VOC reacting in the presence of excess nitrous acid and where the nitrous acid is forming all of the OH radicals, the amount of ozone or NO formed is very sensitive to how fast the VOC reacts and the NO is converted to NO_2 . There is almost no sensitivity to radical initiation or inhibition effects. This provides a way of testing that aspect of the model independent of the other uncertainties. This method could potentially be used for very low volatility compounds that cannot be done practically in environmental chambers. Dr. Carter commented on his new program with the California Air Resources Board to develop more generally applicable methods of measuring reactivity to replace the more expensive chamber experiments.

CSMA Position on the Importance of Relative Reactivity

Doug Fratz, Chemical Specialties Manufacturers Association

Harvey Jeffries (University of North Carolina) commented that the ozone formation in an urban area cannot be determined by multiplying an inventory by the MIR; a whole airshed model has to be used. He reiterated that nearly half of the ozone is produced by low reactivity chemicals. Mr. Fratz responded by stating that they found very good agreement between the MIR-weighted inventory approach and the urban airshed model approach. Both approaches predicted very small amounts of ozone formed considering the VOC controls targeted. Both the MIR-weighted approach and the modeling approach were being used to assess the effects of marginal changes in VOC emissions on marginal ozone formation. William Carter (University of California) commented that he agreed with the way Mr. Fratz had used the MIR to look at how to prioritize controls and not to look at what caused ozone formation.

Reactivity Concerns

Phil Ostrowski, Occidental Chemical Corporation

John Festa (American Forest and Paper Association) commented that the branch of EPA administering TRI requires the air program to declare a chemical as a negligibly reactive VOC before it can be removed from TRI. Mr. Ostrowski responded that maybe there would be a rethinking of the TRI exemption in the new policy.

Bob Avery (Eastman Chemical Company) commented that the cutoff for exemptions should be raised in the short term, rather than lowered, in order to get more useful chemicals in the 'tool box.' Mr. Ostrowski expressed his concern that this approach may end up impacting air quality in a negative way. Mr. Avery continued by stating that there may be some local adverse impacts, but overall, the substitution of low reactivity compounds would be directionally correct, and, overall, an improvement.

Categorization of Low Reactivity Compounds

John Owens, 3M Company

William Carter (University of California) commented that there are procedures to estimate upper limits of reactivity that could be used to establish the cutoff.

Harvey Jeffries (University of North Carolina) stated that, although compounds with a low kOH must be looked at closely, he is not calling for compounds with lifetimes on the order of months or years being studied in the smog chamber.

Richard Derwent (Meteorological Office, United Kingdom) stated that this is not so simple for theoretical studies. When working on CFC replacements, they looked at long-lived VOCs. It is important to have information about the degradation products and to consider the by-products from the production of these low reactive VOCs. This will require more than just a theoretical study, because there are a whole range of other problems. Mr. Owens responded by stating that 3M does sponsor these studies of degradation products and does a life cycle analysis of byproducts and products.

*Impact of a Molar Ethane Standard on the Number and Type of VOC-Exemptible Compounds:
Practical and Environmental Implications*

Daniel Pourreau, ARCO Chemical Company

Harvey Jeffries (University of North Carolina) proposed a deferred control system of five years with possible renewal based on further analysis. Dr. Pourreau responded by stating that industry would be reluctant to use an alternative that might not be available in the future. He proposed that the new reactivity-based policy revisit the exemptions, but he thinks the exemptions granted now for the low-reactivity materials would still benefit under a reactivity based policy. Dr. Jeffries continued by commenting that it would be necessary to inventory the exempt products. He stated that it is necessary to know where and when and in what quantities the VOCs are emitted to know the impact on the environment. Dr. Pourreau stated that, although they are trying to replace highly reactive compounds to reduce ozone, there are practical limitations on how they can do this.

Jim Berry (Berry Environmental) commented on a specific slide referring to 37% solids from water-based solvents. He stated that for the comparison to be appropriate, the water must be removed. Dr. Pourreau stated that the information was in pounds/ VOC and pounds/solids and, therefore, water was not an issue. The weight percent solids was included as an illustration to show that the non-water coating applies more solids per application.

Session IV Summary of Questions and Discussions

Computing Volatile Organic Compound Reactivities with a 3-D AQM

Zion Wang, University of North Carolina at Chapel Hill

Jake Hales (ENVAIR) commented that there are many choices: use KOH, use sensitivity coefficient, use MIR or MOIR, etc or use 3-D models over EKMA. It needs to be remembered that MIR isn't all that simple; even with the one-dimensional EKMA model, many parameters need to be specified such as the different ways to titrate the NO_x, how peak ozone is used in the numerator of the equation, and what domain is used. Dr. Hales concluded by soliciting comments from the 3-D modelers.

Ted Russell (Georgia Institute of Technology) commented that many of these are policy questions. It needs to be asked: what is the metric for the policy makers. Once that decision is made, then the modelers can react. There is a need to get away from boundary conditions and initial conditions and to look at how these emissions are added. When looking at the impact of change in fuel composition, the emissions change needs to be linked to the fuel. For a solvent, the solvent emission distribution used would be different. It is necessary to normalize the results to a mixture of compounds and different people might have different ideas on this normalization process. It will also be necessary to compare the 3-D models results to the box model results.

Gary Whitten (Systems Applications International, Inc.) agreed with Dr. Russell's comments about policy. A policy decision is needed. Currently, xylene and ethane are treated equally, but clearly they are not. He commented that there needs to be a methodology for trading

solvents with lower reactivities. He proposed a 4-tier reactivity scheme in place of the 1-tier scheme currently in place. Compounds in the highest tier (e.g. xylene) would be counted twice as much; lower reactive compounds would be counted half as much. This would encourage switching from solvents like xylene to paraffins and would be beneficial even if the alternative was still somewhat reactive. In this way, industry can be a big credit for making the switch and for making improvements in the reactivity in the atmosphere. Dr. Russell responded to this proposal by stating that more bright lines don't help, especially there aren't huge gaps in the reactivity spectrum where these different classes would divide. Dr. Russell believes that this is defeating the purpose of reactivity and he would prefer the policy to be driven by the best science.

William Carter (University of California) agreed that the policy will drive the approach. He continued by stating that there are two main ways of looking at policy: (1) reactivity scale which is generalized and (2) assessment or specific substitution scenario where replacement should be handled in detail with a detailed model. There is also a need for a generalized scale to be used for prioritizing, but the reactivity scale poses different modeling problems in trying to answer the question: what is the optimum scale to use. The scale would need to be representative of the criteria and to represent a distribution of conditions (set of scenarios). Lastly, Dr. Carter is not convinced that an EKMA model is not adequate for the purposes of developing a scale.

Chris Walcek (State University of NY at Albany) commented that, because the scale can't be made to be a simple one, this doesn't mean that it is impossible to have a scale. The scale won't be simple and there will be a great deal of controversy about its development. Dr. Carter added that it is important to have a standardized protocol for the scale; it is important not to vary the metrics.

Barbara Francis (CMA) commented that CMA has not yet developed positions on the issues raised in yesterday's or today's discussions and noted that the positions expressed here by CMA member companies are company specific and not necessarily industry consensus positions. She continued by saying that CMA is conducting research on specific chemicals and that CMA believes that research programs should, wherever possible, be policy relevant.

Temperature Dependence of Ozone Chemiluminescent Reactions with Organics: Potential Screening Method for VOC Reactivities

Jeffrey Gaffney, Argonne National Laboratory

Chris Walcek (State University of NY at Albany) asked about the cost of the chemiluminescence system. Dr. Gaffney stated that the system costs between \$6,000 and \$7,000 which is cheaper than the NO_x system and it could also be used to look at reduced sulfur gases.

VOC Receptor Modeling as an Aid to Evaluating the Effect of Reactivity Changes on Ozone Formation

Donna Kenski, US Environmental Protection Agency

Alan Hansen (EPRI) asked about the reconstruction of the emissions mix at the monitoring stations and the complicating factor of emissions in between the monitoring sites.

Ms. Kenski responded by stating that the model a very simple, screening-level model and does not include any reinforcement or deposition. Mr. Hansen continued by asking about the lack of impact from refineries being an artifact of the location of intermediate sources. Ms. Kenski answered that they tried to account for this issue with the trajectory, and by comparing the upwind trajectories.

Computational Studies of Oxidant Reactions of Volatile Organic Compounds Relevant to the Formation of Tropospheric Ozone

David Dixon, Pacific NW National Laboratory

Eduardo Olaguer (The Dow Chemical Company) asked all the presenters if neural network techniques had been applied. Dr. Dixon responded that he was not sure if neural nets are being used in the field of VOC reactivity. Neural nets are a data analysis tool and could probably be used effectively to correlate a range of experimental measurements. Dr. Dixon was not aware of any reasons why neural nets can not be used in this area and research on their use and applicability would be appropriate.

It was asked if Dr. Dixon was going to look at the reaction between the hydroxyl radical and NO_2 and he answered affirmatively. Dave Golden (SRI) commented that the potential energy surfaces for the hydroxyl radical and NO_2 reaction are inaccurate. There are two groups that have estimated this, the IUPAC estimate is wrong and the JPL estimate is correct. It has been measured to 5%, but could it be calculated better. Dr. Dixon responded by stating that temperature and pressure corrections could be included in the calculations. A question was also asked concerning the impact of water on this reaction. Dr. Dixon responded by stating that there would be no effect from water, unless the reaction was taking place in a droplet, but because these reactions are fundamental gas-phase processes, this would not be expected.

Session V Summary of Questions and Discussions

Oxygenates: Reactivity Implications

Ian Barnes, Bergische University at Wuppertal, Germany

Eduardo Olaguer (The Dow Chemical Company) commented that the ideal approach would be to learn all that could be learned about reactivity options, then decide how to design the reactivity strategy. It seems that currently, all the money goes into designing a policy index, and the science is done to make that convenient. Dr. Olaguer would prefer to do the science first.

FREE FORUM SUMMARY

Howard Feldman (Moderator) described this portion of the workshop as the opportunity for any attendee to express their 'two cents worth.' There were many experts in the audience, not all of whom made a presentation, and many others with opinions or points of view. The free forum was their opportunity to make whatever presentation they wished to make.

S. Kent Hoekman (Chevron Products Company) began his comments by observing that there had been talk about how desirable it was to separate policy and science issues. He expressed his opinion that, in the case of reactivity, this is impossible, and that policy is actually required to define reactivity. He continued by stating that science has been stymied by the lack of policy or, at least, a broad policy outline. In California, there is a policy definition of reactivity, but it's limited to the certification of new vehicles with respect to exhaust emissions. It was not designed to result in an ozone benefit, but only to achieve an equivalent ozone impact. Therefore, the absence of the automobile industry from this meeting is conspicuous, with the exception of Honda. This is perhaps because the California system is complex and burdensome and it does not achieve an air quality benefit. Therefore, automobile companies haven't taken advantage of the opportunity to develop their own reactivity factors, but have relied on the default values developed by CARB. Establishing the default values is a very expensive process; CARB has spent hundreds of thousands of dollars to establish and maintain their ability to determine reactivity adjustment factors.

When reactivity is applied to stationary sources and consumer products, there are some simplifications and some additional complexities. The first simplification is the absence of simultaneous emissions of VOC and NO_x from stationary sources or consumer products. This is very important when dealing with automobile exhaust. Another simplification is that, for automobiles, the VOC's are changed during the combustion processes within the car. Therefore, the fuel put into the car is not what is emitted in the exhaust. Thirdly, there is a great variability between the vehicles, between operating conditions, and between technology classes whereas this complication is not present for the stationary sources.

The first complication for stationary sources and consumer products over the mobile sources is the great diversity of chemical structures and classes of solvents. In addition, the atmospheric chemistry is not understood well. Secondly, it will be much more difficult to trade, and trade fairly, for consumer products, because the materials being traded are very dissimilar. For mobile sources, we are trading one gasoline emission mixture for another and these mixtures are very much like one another. For consumer products and stationary sources, this will require greater quantification and certainty in the reactivity of materials.

Dr. Hoekman continued by discussing two associated issues for which reactivity arguments are being used, but that he believes must remain separate: (1) to reduce the ambient ozone levels and (2) the exemption of specific VOCs. For the issue of exempting VOCs, the focus is on establishing a bright line by looking at the least reactive VOCs. For the issue of reducing the ambient ozone levels, the focus is on what materials should be controlled (VOCs, which VOCs, or NO_x) by looking at the most reactive VOCs. The attainment of the standard is a broader, more urgent issue, but a VOC reactivity policy must be developed to encompass the full spectrum of issues. It can also be asked whether or not there is any real justification for exempting anything if it contributes to ozone.

Dr. Hoekman summarized his remarks by stating that there are two main concerns for industry. The first concern deals with all of the different decisions which must be made on defining conditions, setting the scale, and measuring reactivity. There is a great deal of arbitrariness in any policy, and although this is not good, instability is worse. It is very difficult for industry to deal with changes in the rules. The second concern of industry is that reactivity may become an attractive control measure, that appeals to different states (and districts) to different extents. Dr. Hoekman encouraged EPA to be sure, when developing its policy, that it can be applied generally and fairly to the whole country and not as a patchwork of different requirements.

Anne Giesecke (American Bakers Association) discussed the concerns of the baking industry. Yeast fermentation releases ethanol, which is released to the air. In addition, they operate the third largest trucking fleet in the nation. Dr. Giesecke stated that this industry is encouraged by these discussions. This industry has spent about \$30,000,000 turning ethanol into CO₂ and increasing the NO_x emissions through catalytic oxidation. The modeling discussions were interesting and this work needs to move forward. Although access to the models is important, Dr. Giesecke believes that not every state and industry needs to operate the model. The resources of many states are strained as are many industries and she suggested that modeling work could be out-sourced. Dr. Giesecke is encouraged by the work on relative or incremental reactivity or the potential for ozone formation and the shifting of the emphasis away from the 'yes or no' system currently in place for evaluating VOC emissions. She expressed the need for more sophisticated tools such as the baking industry's interest in the holistic or life cycle approach. The baking industry also recommends looking at emissions trading and how to change from the current system where all VOCs are considered equal to one where a more reactive VOC can be replaced by a less reactive VOC. This industry would like to see more effort put into the study of more reactive chemicals and those that have other complications. They would also like to see more of their money going into fleet conversion instead of ethanol control. The baking industry operates at a 2% profit margin and, therefore, they don't have a surplus of money to do both.

Leslie Ritts (Hogan & Hartson), who represents a large number of stationary source categories, commented that for 20 years billions of dollars have been spent on control strategies and on decisions that have led to moving business offshore. She expressed her concern about how the discussions held at this workshop will feed into regulations and whether or not there is a time line for such regulations.

Barbara Francis (CMA) commented that the consensus among the solvents producers is that the models are not really ready for the regulatory community to use. They believe that there is enough information available now, especially on the incremental reactivity, to implement reactivity-based regulations.

Neil Wheeler (MCNC-NC Supercomputing Center) began his comments by reminding the audience that establishing a reactivity policy was not going to be easy and that the issue of reactivity can not be simplified. It will take a great deal of work to apply the policy fairly and effectively.

Mr. Wheeler stressed the need for this to be a community effort and that people need to participate and to share information. He commented that there is a wide range of possibilities of how to use reactivity in the regulatory process: from setting exemptions with a bright-line (or not) to reactivity-weighted emissions. He also commented that models do not make decisions. There will be external information (scientific or policy) that will affect the decision making process and consideration must be given to other environmental issues as well.

He expressed the need for multiple metrics to help the policy makers and the need for the scientific community to clearly describe the meaning of these metrics. Consideration should be given to the range of conditions from the current time out into the future. It is important to monitor an exempt VOC both in the inventory and in the ambient environment into the future to be certain that a poor decision has not been made. He agrees that stability is important in a regulatory process but noted that we cannot have absolute stability, especially in light of possibly making a bad decision. There needs to be a systematic process for dealing with necessary change based on new information.

Mr. Wheeler discussed the range of metrics needed such as metrics to assess exposure, various meteorological conditions, multiple locations, multiple pollutants, and total risk. He emphasized the need to develop metrics using photochemical models with the best science available. He feels that it may be possible to use simpler models, such as EKMA, for developing a reactivity scale but they must first be evaluated against state-of-the-science models.

Roger Tanner (TVA) commented that the data shows clearly that ozone formation is NO_x -limited in some areas and is VOC-limited in others and that these conditions vary greatly by location and by season, depending on the sources of VOCs and NO_x . He believes that a metric is needed that scales with the actual conditions within an airshed. In order to predict ozone reduction in particular locations and at the times necessary get below the standard, a sliding airshed-specific metric is needed. Dr. Tanner believes that this type of metric can be devised with our current scientific knowledge.

Ken Schere (EPA/ORD) discussed the differences between developing assessment tools and procedures and screening tools for implementation. Between these two ends of the spectrum, there are many possibilities. The scientific tools are available to do a full scale assessment to describe reactivity as a function of various environmental variables. Dr. Schere commented that Dr. Russell showed that a sophisticated tool can be reduced down to a simple screening tool. In order to decide where on the spectrum we need to be, it is necessary to know what the policy makers need.

Randy Pasek (CARB) expressed his agreement with comments made previously about California's reactivity regulation. The regulation is limited and complex. But California has been moving ahead since the regulation was developed. From a regulatory perspective, Dr. Pasek believes that the policy must be based on good science and that the complexity should be understood. And it is very important that the policy be constant. He echoed Dr. Wheeler's suggestion to build into the policy a process for change in order to make the policy more stable. CARB has a policy based on the MIR scale, because it is a good complement to the NO_x controls. Lastly, Dr. Pasek expressed his agreement with the comment of Ms. Francis that the science is adequate to develop regulations, as has been done in California.

Dave Golden (SRI and Stanford University) believes that good models are needed to understand any complex process. He continued by commenting that although the science has advanced very far and the models are reasonable, there are a lot of things we don't know. He warned that we shouldn't think that because we can model something that the models are necessarily correct. He expressed his inability to believe in a model that predicts PM_{2.5}. He concluded by urging that the scientific work and the funding be continued.

George Brown (National Aerosol Association) discussed the problems caused by the huge variability in VOCs and the fact that the current regulations treat them as being equal. This situation severely inhibits the use of certain substances and outlaws the use of others. As an example, on January 1, 1999, CARB will implement a rule that allows zero VOCs in one product. Mr. Brown believed this is ludicrous. The National Aerosol Association (NAA) has supported several reactivity studies over the last ten years and, based in these studies, they are committed to the regulatory use of relative reactivity. The NAA realizes that some substances or products will have difficulty operating under that system and they don't, as yet, have the solutions to these problems. At the present time in California, the NAA believes that relative reactivity ought to be used on an optional basis by sources having trouble meeting a mass-based standard. Lastly, Mr. Brown believes we should stop thinking in terms of cutting down the mass of precursors of ozone and begin thinking in terms of ozone limitation itself.

Phil Ostrowski (Occidental Chemical Corporation) commented about the economic benefits of reactivity regulations. Properly designed reactivity regulations should provide a tool whereby small solvent users can avoid installing costly control equipment. This will provide good environmental benefit at a low cost.

Jeff Gaffney (Argonne National Laboratory) echoed some of Dr. Golden's preceding comments. He urged the group not to forget about VOC chemistry and not limit the discussion to only the ozone-driven aspects. It should be remembered that VOCs form fine aerosols and other products such as nitro-phenols that are very toxic and water soluble. Wet deposition, cloud condensation, climate effect, and radiative properties (UV and IR absorption) of VOCs should also be considered. He made a plea for the science and the sum-level support of the science. He believes that by understanding the science better, the scientific community will be able to provide a knowledge base to allow the policy makers and the modelers to do a better job.

Tim Lawrence (Georgia Pacific and American Paper and Forestry Association) commented that, although the science has been fascinating, we must recognize the need for pragmatic regulatory tool development in parallel with the existing scientific research. At this time, EPA is moving forward with implementation plans for a national ambient air quality standard for fine particulates, ozone, and regional haze; VOC and NO_x are all listed for controls under these programs. By November 2000, 170 different industrial categories will receive MACT standards. For organic HAPs, many of the MACT floors are being set based on existing VOC controls. There is also implementation of the Kyoto Treaty that needs to be considered. Mr. Lawrence feels that there need to be two parallel tracks: (1) one track moving forward very quickly because of pending regulatory decision that have to be made and (2) the other track continuing to understand the details of the science. Regulatory tools such as those described by

Donna Kenski (EPA, Region 5) are important in the near term to assess the effectiveness of proposed regulatory action.

Praveen Amar (NESCAUM) stressed the need to look at aerosol forming potential of VOCs which might be exempted, in addition to the ozone forming potential. As an example, between 33% and 40% of the fine particles in the Northeast are organics. Consideration should also be given to wet deposition, dry deposition, and toxicity.

Doug Fratz (Chemical Specialties Manufacturers Association) made comments comparing the use of regional or local reactivity scales versus the use of a linear national scale. There are a number of control types that could be controlled locally. For other sources, such as consumer products, it would not be practical to have a different product for every local region. Therefore, to use reactivity, there must be a single national scale based on a single metric. Mr. Fratz also commented on the funding of research as compared to the cost of controls. He feels that research is still under-funded and that the ratio of money spent on controls to money spent on research is far too high.

Jeffrey Holmstead (Latham & Watkins) stated that in the regulatory arena, we operate in a legal framework that doesn't offer much flexibility. He hopes that in the long term, the framework can be changed to allow flexibility. But in the near term, there are things that can be done. Mr. Holmstead reminded that group that they already have a reactivity scale where everything is either a 0 or a 1, and he believed that it would be hard for this group to do worse than that. In the near term, he believes that the current knowledge can be used to help people move from using highly reactive compounds to using lower reactive compounds. In the long term, the scientific research needs to continue. Mr. Holmstead urged the group not to let the perfect be the enemy of the good in the short term.

William Carter (University of California) wanted to echo what Mr. Holmstead said about the near term problems. There are three approaches to using reactivity: the two currently used reactivity scales (the binary national scale and the California MIR scale) and airshed/scenario specific assessment. The scientific basis of the ethane exemption standard is not good. This is why the EPA has frozen the exemption petitions, but these can't stay frozen for long. Dr. Carter suggested that in the near term the EPA do a modeling assessment to recertify the ethane standard or identify another standard. This would then allow the present method to continue while alternative methods are being developed. In California, the regulations they are developing require a scale which, if nothing else is put forward, is going to be the MIR scale. With the demand for stability, if the MIR scale is implemented (later in the year), it will be difficult to change. Therefore, this is the time to provide an alternative. Dr. Carter strongly emphasized the urgency of this problem.

Bob Avery (Eastman Chemical Company) recommended two tracks be followed in the future. Although the modelers are improving our understanding, the necessary results will not be available for three to five years, optimistically. A more realistic time frame is between five and ten years. The current system is bad and, therefore, a better interim system is needed for the next two to five years. Mr. Avery suggested that a few dozen individuals should be able to sit down in a room and improve on the current binary policy.

Cyril Durrenburger (Texas Natural Resource Conservation Commission) discussed the Control Measure Catalog developed for the last SIP submitted by Texas. It is a metric that ranks the VOC controls based on the tons reduced, toxicity, and the reactivity using Dr. Carter's MIR scale.

Robert Wendoll (Dunn- Edwards Corporation) discussed two approaches to the policy/science issue first raised by Mr. Hokeman. The scaling approach is used to rank VOCs by some reactivity metric for regulatory purposes. There are policy decisions that have to be made and some of these will be arbitrary, by necessity. Other decisions would be arbitrary only because of the lack of scientific information. The complementary approach is the systemic approach which is the study of actual emissions into ambient air to determine their potential to contribute to high ozone levels across the full range of environmental conditions. Mr. Wendoll believes that the systemic approach is important because it is the area of research that will develop the policy-relative science or the science that links actions with outcomes. This allows the policy makers to choose action intelligently. Mr. Wendoll believes that both the scaling approach and the systemic approach should be pursued simultaneously. The policy makers must realize that both of these approaches together are embedded in the total ecological impacts. There will be other factors that affect the regulatory decisions being made, such as the impact of the regulations, including material resource and energy consumption, waste disposal, and water quality. Mr. Wendoll echoed the comment made by Mr. Fratz about the ratio of research spending to compliance spending. He believed that the amount of money that needs to be spent on the research necessary to provide a better basis for sound regulations is minuscule compared to the cost of compliance. Lastly, Mr. Wendoll reminded the group that control costs also have indirect health impacts by reducing available income.

Dave Morgott (Eastman Kodak Company) commented that in order to assess the intrinsic impact of VOCs on the environment, the more appropriate scale is the MOIR scale and not the MIR scale. The MOIR scale provides information about the peak amount of ozone that can be formed when a quantity of VOC is introduced into the environment.

POLICY AND SCIENCE QUESTIONS SUMMARIES

Howard Feldman (Moderator) introduced this segment of the workshop by asking the group to consider what needs to be done next. A review of these policy and science questions will be a form of guidance. This is a genesis workshop and a group will be formed as a result of this workshop and will continue these discussions. Mr. Feldman reviewed the policy questions listed below and asked the group if these are the right policy questions. He also asked the group if there are other questions that should be added to this list.

POLICY QUESTIONS

1. How should reactivity policy account for interaction with other air-pollution problems?
2. How should the reactivity concept be used to both maximize environmental benefit and encourage environmentally superior product development? "Exemption" vs. "substitution"?
3. What is the maximum uncertainty level that can be tolerated for reactivity-related decision making?
4. Exemption policies:
 - Bright line vs. bright band?
 - Environmental cofactors?
 - Where, ethane?
 - Molar or mass basis?
5. Exemption protocols:
 - Cookbook?
 - Maintenance and tracking?
 - Automatic testing criteria?
6. Procedures for modifying exemption criteria? Grandfathering? Grace periods?
7. Substitution protocols and guidelines?
8. How should vapor pressure be incorporated into the decision process?

Bob Avery (Eastman Chemical Company) raised the issue of national standards versus regional standards, and he believes that this question needs to be added to the list.

Edward Edwards (Dunn-Edwards Corporation) was concerned about availability and whether availability will be considered when making policy decisions. Availability is the issue of the difference between what's in the can and what's in the air. He was also concerned about looking at the time domain used to assess the ozone impact. For example, a paint may last from between two to fifteen years, depending on how it is formulated. The question is will the ozone impact be assessed only for the one-time application or for the full life cycle of the product. These are both very critical policy decisions in analyzing how to- determine whether the VOC life cycle is important for ozone forming potential.

Jonathan Kurland (Union Carbide) made comments on question 8 that deals with vapor pressure. He stated that the issue of volatility is a subset of the general issue on how much of the

content becomes emissions. There are other environmental non-evaporative fates (e.g. down the drain). Dr. Kurland believes that this question should be expanded to include consideration of whether the policy can properly determine the actual emissions released into the atmosphere as opposed to other estimates such as gross sales.

John Durkee (Creative Enterprizes) commented that an additional policy question is needed that deals with the issue of communication of the policy to the affected community. Policy which can't be communicated may not be good policy. As the policy is developed, consideration should be given to how the policy will be communicated, because, regardless of the quality of the science, the end-user won't buy it if they don't understand it.

Howard Feldman (Moderator) reviewed the science questions listed below and asked the group if these are the right science questions. He also asked the group if there are other questions that should be added to this list or if any of these questions should be taken off the list.

SCIENCE QUESTIONS

1. Is a reactivity-based policy practical, feasible, and beneficial?
2. How do we best factor long-range transport into a reactivity-based strategy? How about co-dependencies with PM?
3. What are the uncertainties of the various possible reactivity scales?
4. What are the advantages/disadvantages of using MODELS3 for estimating reactivity?
5. What are the merits of using speciated VOC reactivities, as opposed to lumped VOC reactivities?

William Carter (University of California) commented that several of these questions are actually policy questions. The questions on the practicality and feasibility of a reactivity-based policy are policy issues. Although the question on the benefits of a reactivity policy is a scientific issue, it would require a policy on how to measure the benefit. Also, the question on using MODELS3 (question 4) has both a policy and a science component. Whether or not photochemical grid models can be trusted is a science question, but the advantage or disadvantage to using one is a policy question.

Anne Giesecke (American Bakers Association) commented that it is difficult to divide science and policy issues. From an industry perspective, they are looking for regulatory baselines: predictability, long-term planning, and basic functionality. Baking companies currently work with a very high level of uncertainty on their emissions (+/- 30%). This is acceptable, because it provides a regulatory baseline that tells them if they are in or out of an EPA threshold for clear air requirements. For this reactivity-based policy, the same level of science and policy would be acceptable, if it establishes a regulatory baseline.

Jason Ching (EPA) pointed out that a powerful system framework such as Models-3, together with its Community Multiscale Air Quality (CMAQ) model provides a modeling capability for estimating model reactivity. The Models-3/CMAQ system ability to provide a plug and play capability allows the substitution or replacement of various science process options including the means to modify (edit) existing chemical mechanisms or by exchanging and

studying alternative chemical mechanisms. This capability and the other unique suite of modeling capabilities and features in this system provide a powerful means to perform the various model experiments and sensitivity tests needed to evaluate model response to changes in reactivities. Further, because this is a publicly available system, it provides a means for the entire community of interested parties to become involved and to contribute to the research, development and assessment of reactivity models, and ultimately, to improved air quality models.

Jake Hales (ENVAIR) commented that Question 4 was intended to be more generic than just MODELS3. He suggested that MODELS3 be replaced with 3-D or Eulerian models. Howard Feldman (API) suggested that a Question 4a be added: how do you use one of these models to determine a relative or incremental reactivity for substitution purposes. Other related questions are: how many simulations are needed, how good do the databases need to be for a given urban area to do these calculations on a national level, or, if a scale is used, was the modeling used to develop the scale adequate.

Jim Vickery (EPA/ORD) would like to add a question about timing. He asked the scientists what could they produce in the next two to three years that could help guide the policy. This would allow the policy maker to decide if they should develop an interim policy or if they should wait for a permanent answer.

William Carter (University of California) wanted to add to Question 4: What is the distribution of conditions where ozone is a problem and where VOC control is relevant.

Howard Feldman (API) commented about the time period of a scale: 1-hour or 8-hour or some other time period.

Ed Edwards (Dunn-Edwards Corporation) was concerned about the sensitivity of the models and their ability to measure small changes in product formulations and how these small changes are expanded into an airshed which contains only a fractional percentage of VOCs.

Jim Berry (Berry Environmental) made several comments concerning the change in 1976 from Rule 66 to the beginning of the federal program. Rule 66 was based on reactivity measurement for one solar day. Subsequent work based on multi-day exposures, recognized that many of the compounds that Rule 66 exempted actually reacted over the longer term. In earlier discussions, Dr. Jeffries stated that half of the ozone formation was the result of slower reacting materials. Mr. Berry continued by discussing the impact that Rule 66 and, subsequently the change to the federal program, had on various industries. He commented on the resources spent on reformation to comply with Rule 66 and then again to comply with the federal program. He urged that the lessons learned in 1976 not be forgotten, and that changes be made to the federal program only after there is a longer term vision.

Paul Makar (Atmospheric Environment Service) asked if it would be possible to create a hierarchy of methods for measuring reactivity that agree with one another. Many methods of dealing with reactivity had been presented; his concern was that the use of more than one method for regulatory purposes may necessitate intercomparison to ensure that the methods do not give

conflicting results. For example, before using 3D models for regulatory purposes, their results should be compared to the current ethane standard and/or MIR indices. Any differences should be fully understood in advance of implementation of regulations, to avoid undermining their scientific credibility.

Jeffrey Gaffney (Argonne National Laboratory) suggested that a question be added about the reactivity of secondary products of the primary emitted VOCs. The chemistry of these secondary products needs to be understood, because they will play a role in the long-range transport issue.

PUBLIC/PRIVATE PARTNERSHIP DISCUSSION SUMMARY

Jake Hales (Moderator) began this portion of the workshop by describing NARSTO. Dr. Hales then asked the group if it is appropriate to go into a public/private partnership to pursue the reactivity issue, either within NARSTO or separate from NARSTO. Dr. Hales described his views on the function of this committee as follows: (1) to establish the forum for communication among interested participants, including the policy community and (2) to design a plan for the future strategy for reactivity research and to provide a time table for the research. He asked the group if there were any strong feeling against forming a public/private partnership. He took the lack of response from the group as consent.

AD HOC OPERATIONS TASK FORCE DISCUSSION SUMMARY

Jake Hales (Moderator) began by describing his thoughts about generally how this ad hoc task force would operate. Anyone would be welcome to participate. At a minimum, there would be several meetings per year. There would be communications on a regular basis. Travel expenses would be the responsibility of the individuals participating.

A question was asked about whether the ad hoc task force would necessarily function under NARSTO. Dr. Hales responded by stating that the task force could be either independent or it could work as a functionary group under NARSTO. It could blend into all of the NARSTO task activities: modeling, chemistry, observations, assessment, etc. If the group was to work under NARSTO, it would have to adhere to the quality assurance and data management guidelines. It would also have to adhere to the basic NARSTO principles which are to do good research for the benefit of policy.

Dr. Hales continued by asking for volunteers to serve on the ad hoc task force. There was a show of hands. Dr. Hales suggested that a sign-up list be circulated, and that the group caucus immediately after lunch.

Dr. Hales began the discussion by asking the group if this ad hoc group should function under the NARSTO umbrella. Robert Wendoll (Dunn-Edwards Corporation) asked if NARSTO doesn't also have to agree to this association. Jake Hales described the standard procedures for NARSTO to accept a field program under its umbrella. The Science and Resource Planning group makes these decisions, but he expects no problem with this. William Carter (University of California) suggested that the group encourage European participation, who have made important contributions to this work. Dr. Hales responded by saying that NARSTO has in the past worked with the Europeans. EuroTrac is an affiliate member of NARSTO and other European efforts could be in the future.

Bob Avery (Eastman Chemical Company) asked about alternatives to NARSTO. He didn't feel that the workshop group had the information available to make the decision on whether to associate with NARSTO. Mr. Avery was particularly interested in more information about the costs associated with association with NARSTO. He asked if the EPA could provide the leadership as an alternative. Jim Vickery (EPA/ORD) responded by stating that the EPA is committed to conducting and organizing all of their ozone related research through NARSTO for two primary reasons. This has helped to coordinate all of the different aspects of the research and to effectively allocate the scarce resources of people and money. Dr. Vickery strongly recommended that the ad hoc task force operate under NARSTO.

Jeffrey Holmstead (Latham & Watkins) asked how this effort would feed into the EPA's policy decisions. He asked about the EPA's level of interest in pursuing these issues and whether the EPA is in a position to accommodate the changes in the policy that this group would recommend. Jake Hales expressed his observation that a simple liaison with a policy team is not effective. There needs to be a strong presence of EPA policy people in the partnership. Bill Johnson (EPA/OAQPS) responded to Mr. Holmstead's question by stating that this question is one that EPA's management would need to answer. Joe Paisie (EPA/OAQPS) added that as

Sally Shaver (EPA/OAQPS) said in her introductory comments to this workshop, the EPA is here to listen, and has been listening, but they are not prepared to say what the results will be yet.

It was asked if this activity could enjoy equivalent status with the recent FACA process. That is, could there be direct EPA/OAQPS participation in the process.

Jeffrey Gaffney (Argonne National Laboratory) asked about extending invitations for participation in the task force to people who had left or who didn't attend the workshop, such as automobile makers. Ron Patterson (EPA/ and NARSTO) commented that several people who are no longer here did complete the commitment forms made available at the beginning of the workshop. He added that many of the automakers are members of NARSTO.

Tim Lawrence (Georgia Pacific and American Paper and Forestry Association) commented, based on his experience with several FACA processes, that the level of interest, participation, and commitment of resources, particularly by the regulating community, is directly related to their sense of just how serious EPA is about moving the process forward to a useful endpoint. He concluded that it will be very important at the beginning to see some real finite indication of EPA's level of interest.

Howard Feldman (API) commented that the next step is to develop a plan with a specified time horizon. It will be important to know what time horizon EPA would be receptive to on the policy side. On the other hand, it is important to continue to work towards the good science, because the policy makers will use it if it is there.

Jim Vickery (EPA/ORD) agrees with Mr. Feldman's comment about the importance of good science and the fact that it will feed into the policy process. He described the difference between the FACA processes and NARSTO. For the FACA process, there was a statutory driver that required an output by a certain date. There is no such a driver for the reactivity policy. Reactivity research is very much like the other ozone research organized under NARSTO. Under NARSTO, the researchers and the policy makers are brought together to organize the research in such a way as to use the resources efficiently and solve the most important questions for the policy maker as quickly as possible. The EPA policy office is committed to using good science as soon as it is produced.

Jake Hales (Moderator) summarized this discussion by stating that there is consensus to form a public/private partnership on reactivity research and there are people interested in participating in an ad hoc task force to develop the forum, the research plan and the time table. Whether this task force operates under NARSTO is a question that will be deferred to the task force itself. Everyone interested in serving on the task force was asked to meet after the conclusion of the workshop.

APPENDICES

APPENDIX A
Photochemical Reactivity Workshop
May 12-14, 1998
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During the discussion period on the last day of the Photochemical Reactivity Workshop, moderator Jake Hales explained the NARSTO organization and asked if there was interest in forming a group under NARSTO to explore research needs concerning reactivity. There was tentative interest among attendees. Interested persons were asked to remain in the room after the Workshop itself was adjourned to discuss possible formation of such a group. At this time, participants did not identify specific research tasks to sponsor. Here are the minutes of that meeting.

**Ad Hoc Task Force on VOC Reactivity
Minutes of Initial Meeting
May 14, 1998**

The meeting was called to order at around 1:00 pm by Robert Wendoll, who stated that the first order of business was to establish the initial steps for Task-Force action.

John Dege noted that we need to establish EPA's position on this topic, and then we need to formulate a concept paper to establish the basis for our downstream operations. It was emphasized that we need to set forth a list of the relevant research needs. Cyril Durrenburger suggested that we might want to develop one or more "issue papers" that define the primary considerations at hand. He also suggested that we consider commissioning several "critical review" papers, similar to those for the NARSTO Ozone Assessment, as a means of codifying salient scientific aspects. Gary Foley stated that we need to start thinking about focusing our scientific efforts, e.g., chamber studies, modeling efforts . . . , in order to maximize relevance to the policy community; we need to reach closure on how to produce the most definitive information. He also recommended parallel, evolving, and communicative efforts between the scientific and policy communities.

There was a general discussion of how the science/policy interface should be handled. This arose at several points during the ensuing conversation. In particular it was asked whether NARSTO had any direct chain-of-command linkage to EPA's Office of Air and Radiation. Jake Hales said definitely no. Although OAQPS is a NARSTO signatory, NARSTO tries to be scrupulous in observing the line between policy-making, and performing policy relevant research. In observing this line, NARSTO - in Jake's estimation - has been less effective than desirable to date in getting our research products conveyed to the policy community. Currently NARSTO is designed to make this linkage through a Liaison Team for Policy, a standing box on the NARSTO organization chart. This has been relatively ineffective, however, and because of this, NARSTO's Executive Steering Committee feels that in the future such liaisons need to be hard-wired into active, functioning groups. In view of this, Jake stressed the importance of having OAQPS staff take a strong and active role directly in this Reactivity Task Force.

Bob Avery stated that we need to plan a meeting to formulate a mission statement. Robert Wendoll agreed, saying that we need to establish a list of meaningful scientific objectives to go along with such a statement.

Howard Feldman stated that it is desirable to develop an assessment of the current state of the science associated with the reactivity issue. Is the scientific underpinning sufficiently "ripe" for policy application? If not, when will it be?

It was asked if this Task Force is to be considered a science group, a funding group, or both. If it's a funding group, what are the money sources? Basil Dimitriades responded that we need some time after this meeting to think this over; then we should reconvene to write a research plan.

Referring to the question of whether this effort should be incorporated as a part of NARSTO, Ed Edwards recommend that everyone here review NARSTO's structure and operational process. Jake Hales commented that the best way to do this is to visit the NARSTO Web site on <<<http://narsto.owt.com/Narsto/>>. Robert asked for a show of hands for those favoring incorporation into NARSTO. The response was ambivalent, mainly because of unfamiliarity of many of the attendees with NARSTO. There was a consensus that everyone should visit the Web site in the near future.

There were some questions regarding alternatives to NARSTO, such as a possible FACA [Federal Advisory Committee Act] committee or a dedicated EPA-coordinated arrangement. Jim Vickery responded that EPA definitely prefers the NARSTO route to a dedicated EPA option, for several reasons. First, NARSTO was established to promote public/private communications and offers an established resource base for operations of this sort. Secondly, EPA desires to operate on a multiorganizational, pooled resource basis with operations of this type, in order to encourage all interested parties to enter in the discussion process. FACA arrangements, on the other hand, are more suitable to short-term issues such as evaluating proposed standards and similar concerns.

Robert Wendoll then asked for a list of action items for this initial meeting. These items and their resolutions appear below:

1. Set date and place for our follow-on meeting. It was agreed that this meeting should be during the first week in September at RTP, NC, at EPA's conference facilities. A pilot team will convene by conference call in early June to draft a mission strategy and design this meeting. This team will consist of Barbara Frances, Ed Edwards/Robert Wendoll, John Dege, John Schwind, Cyril Durrenburger, Basil Dimitriades, and Ron Patterson (or Jake Hales).
2. Draft a Mission Strategy. This will be performed by the pilot team, as noted above.
3. Draft an agenda for the September meeting. Basil Dimitriades will do this.
4. Determine methods for communication. Jake Hales suggested that, for the time-being, at least, the group use the NARSTO home page as a primary communication medium. He will set up a reactivity sub-page there for that purpose. There was also some question of how we

communicate activities of this group to individuals not present at this meeting. Jake suggested that, as a first measure, we put an article describing our activities to-date in the NARSTO newsletter, the 1998 summer/fall issue of which will go into press in early June. Robert Wendoll agreed to write this article and send it to Jake for inclusion in this issue.

The meeting concluded at 1:40 pm.