



Proceedings Fourth US/FRG/EC Workshop on Photochemical Ozone Problem and Its Control

PROPERTY OF
DIVISION
OF
METEOROLOGY

Urban, Regional, and Global Scale

Issues and Studies in the 1990s

Marriott Hotel, Charleston, SC, USA
June 13-17, 1994

**Proceedings
Fourth US/FRG/EC
Workshop on Photochemical Ozone
Problem and Its Control:**

**Urban, Regional, and
Global Scale**

Issues and Studies in the 1990s

Marriott Hotel, Charleston, SC, USA

June 13-17, 1994

**Atmospheric Research and Exposure Assessment Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park NC 27711 USA**



Printed on Recycled Paper

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DISCLAIMER

This Workshop Proceedings report was developed by assembling summary statements prepared subsequent to the Workshop by the Steering Committee with the help of assigned Workshop participants. Although the statements reflect the Workshop discussions in general, they have not been subjected to review, and, therefore, do not necessarily reflect a consensus of viewpoint among the participants.

Although the research described in this report has been funded wholly or in part by the United States Environmental Protection Agency, it has not been subjected to Agency review and, therefore, does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

ACKNOWLEDGMENTS

The Workshop was organized at the instigation of Drs. Basil Dimitriadis (USA) and Erich Weber (Germany). The Workshop program and agenda were developed by Drs. Dimitriadis and Becker (Germany). Workshop arrangements were made by Research & Evaluation Associates on contract with USEPA. The Workshop proceedings report was prepared based on presentations and follow-up discussions. Summary statements were prepared by the Steering Committee with the help of assigned participants. The contribution of these individuals and of all Workshop participants are acknowledged with gratitude by the Workshop organizers. Last, but not least, the financial support by the USEPA, Bundesministerium fur Umwelt und Reaktorsicherheit (BMU), German Ministry for Science and Technology (BMFT), and European Commission (EC), is gratefully acknowledged.

PREFACE

This Workshop was held within the framework of cooperation under the US-German Environmental Agreement (Agreement Number: 011, Project Number: 002). It contributes to high priority activities identified by Minister Toepfer and Administrator Thomas during their December 1987 meeting. As of to date, such Workshops have been held as follows:

- | | |
|------------------|--|
| First Workshop: | Cologne, Germany, May 4-6, 1988 |
| Second Workshop: | Chapel Hill, NC, USA, June 5-8, 1990
(Held in coordination with the EC) |
| Third Workshop: | Lindau/Lake Constance, Germany,
June 30-July 3, 1992 (Held in coordination
with BMFT and EC) |
| Fourth Workshop: | Charleston, SC, USA, June 13-17, 1994
(Held in coordination with BMFT and EC) |

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WORKSHOP ANNOUNCEMENT

FOURTH US/FRG WORKSHOP ON THE PHOTOCHEMICAL OZONE PROBLEM AND ITS CONTROL: IN URBAN, REGIONAL, AND GLOBAL SCALE

Issues & Studies in the 1990s

[To be held within the framework of cooperation under the United States-German Environment Agreement. It contributes to high priority activities identified by Minister Toepfer and Administrator Thomas during their December 1987 meeting. It is supported by the USEPA, the German Government (BMU and BMFT), and the European Commission (EC).]

Charleston, SC
United States of America

June 13-17, 1994

This is to announce the organization of the Fourth US/FRG Workshop on the photochemical ozone pollution problem, scheduled for June 13 - 17, 1994, in Charleston, SC, USA. Dr. Basil Dimitriadis, USEPA, Research Triangle Park, NC, USA, and Dr. Dieter Jost, UBA, Berlin, Germany, are the Workshop Co-Chairmen. As with the last two Workshops, the scope of this Fourth Workshop also has been expanded to include participation of other countries within the European Union (EU).

The purpose and scope of the Fourth Workshop relate to common concerns of the United States and Europe about the pervasiveness and effects of photochemical air pollution and also about the relatively low confidence with which past and on-going ozone control efforts in the US have been received. Consistent with the recommendations from the Third Workshop, the Fourth Workshop seeks to focus on specific issues that are expected to dominate the research scene in the decade of 1990s, in the areas of atmospheric photochemistry, emission inventories, instrumental analysis of pollutants, and ozone air quality modeling. Some currently thought to be key issues to be discussed are the status of Process-Based Modeling (PBM) science and prospects for future advances, questions of how to deal with the PBM uncertainty problem and how promising are the observational approaches to studying the photochemical ozone problem. Furthermore, because of the strong current interest in the regulatory policy-science inter-connection, discussions are also to be included on policy developments and their influence on research in the various countries, and on experiences from regulatory applications of air quality models. An outline of the program planned, in terms of Workshop Session titles, is attached. Specifics on intended Workshop topics and on the input to be solicited from the Workshop participants are explained next.

In the atmospheric photochemistry area, the dominant issues continue to be those related to disagreements between model predictions and smog chamber data and/or field data on ozone yield, on NO_x inhibition of ozone, and on composition of NO_x -oxidation products. A major cause of such disagreement is thought to be errors in the chemical mechanism of aromatic and biogenic Volatile Organic Compounds (VOCs) and in the mechanism of ozone formation under low concentration and VOC/ NO_x conditions. Testing of such mechanisms against data from special smog chamber tests provides a powerful tool for researching the problem, but such smog chamber data are not currently in existence, or are not comprehensive enough for that purpose, and, also, are not easy to obtain. These and other issues in the VOC photochemistry, ozone-olefin reactions, and radical reactions areas are Workshop topics for which presentations and discussions are invited.

The Workshop agenda includes for the first time, the closely related subject of interactions of the ozone problem with other photochemical air pollution problems. Studies of such interactions are essential to understanding the effects of ozone related controls on other photochemical pollutants (e.g., aerosol particles, acid pollutants, etc.), and vice versa. Furthermore, expanding the scope of photochemical ozone models to treat formation and transport of other photochemical pollutants will greatly enhance the value and credibility of models. First, attention will be given to the coupling of photochemistry and fine particles. It is frequently observed that high ozone concentrations are associated with high fine particle concentrations. Aside from their health and visibility effects, particles by virtue of their large surface area also act as sinks of free radicals thereby slowing the photochemical process. Such issues also are Workshop topics for which presentations and discussions are solicited.

In the emissions inventory area, the bulk of on-going research effort continues to be on studies seeking to improve measurement of sources and emissions with emphasis on mobile sources, area sources, and natural VOC emissions, where the largest uncertainties are thought to exist. A new development is an increased appreciation of the importance of natural NO_x emissions and of the large uncertainties associated with mobile source NO_x emissions. However, the crucially important issue of inconsistency between emission inventory and ambient concentration data has attracted only sporadic research efforts, mainly for development of methods for assessing degree of consistency, and very little for remedying the problem (e.g., direct measurement of pollutant fluxes in urban plumes). Discussions of these issues and suggestions for encouraging both new and needed research are invited.

Numerous field studies in the US and other countries have been completed since the Third Workshop in 1992, and results are being reported and interpreted both in terms of evidence pertaining to local problems, and in terms of evidence advancing the science in

the areas of ozone-to-precursors dependencies, ozone and precursors measurement and distribution within the boundary layer, and model testing methodology. The need has been stressed for a concentrated and coordinated effort to analyze all such evidence, define areas of agreement and disagreement, and ultimately identify issues of national and international scope to be the subjects of recommended future research. Special attention also needs to be directed (a) to instrumental analysis methods for hydrocarbons, carbonyls, NO_x , NO_y , H_2O_2 , HNO_3 , HNO_2 , organic peroxides, and OH, for use in field studies, (b) to the utility of such and other observational data alone or in conjunction with grid models as an approach to studying the photochemical ozone problem, and (c) to the significance of the BNL-free troposphere exchange process in accumulation and transport of ambient ozone. An effort is made by the Workshop organizers to solicit presentations and discussions on recent field studies and especially on the utility of observational data as a complement to grid models, and to derive conclusions with respect to lessons learned and implications in terms of new study approaches and specific research needed.

In the model evaluation area, the dominant issues are those related to disagreements between Eulerian (regional/urban) model predictions and field data on levels of NO_x in the atmosphere, on NO_x oxidation and oxidation products, and on the efficiency of oxidant production. Also at issue is how much of the disagreement is due to chemical mechanism errors and how much is due to failure of the model to resolve scales of chemical and meteorological interactions in the Eulerian framework. Process-level testing of the models at rural concentration levels is an important complement to smog chamber testing, but requires special, difficult to make, chemical measurements. Another broader scope new issue is the question of how close the PBM modeling science is to the point at which further development efforts will likely have diminishing returns. The Workshop organizers solicit presentations and discussions on new measurements to probe the model chemistry in situ on diagnostic analyses of model behavior, to illuminate its chemical workings or the dependency of the chemistry on scale, and on viewpoints regarding potential for further improvement of process-based models.

A significant part of the Workshop effort will be dedicated to discussing topics relevant to the application of science to regulatory programs and to the interdependence of regulatory and research programs. Workshop participants are invited to report on recent regulatory policy developments, experiences from regulatory applications of models, and the influence that regulatory programs are having on future research in the US, EU and the other countries represented in the Workshop. Of particular interest are topics specifically related to the issue of VOC vs. NO_x control for ambient ozone reduction, to the use of ambient monitoring data in assessing and/or diagnosing ozone episode problems and most importantly to the treatment of the uncertainty factor in development of model-derived ozone strategies. Presentations and

discussions are invited that would help compare experiences and viewpoints from different countries and identify issues of common concern.

**FOURTH US/FRG/EC WORKSHOP
ON
THE PHOTOCHEMICAL OZONE PROBLEM AND ITS CONTROL:
In Urban, Regional, and Global Scale
Issues & Studies in the 1990s**

**Marriott Hotel
Charleston, S.C.**

June 13 - 17, 1994

Sunday, June 12

6:00 PM - 9:00 PM Registration
Hotel Lobby

Monday, June 13

7:00 AM - 8:00 AM Registration
Hotel Lobby

A G E N D A

Monday, June 13

8:00 AM	Welcome	B.Dimitriades, USA Envir. Protection Agency
		E.Weber, Germany Department of Environment
		H. Ott, Belgium EC--Envir. Research Programme
		W. Schoett, Germany German Embassy, Wash. D.C.
8:15 AM	Keynote Address	G.Foley, USA Acting AA/ORD, EPA

SESSION I. Regulatory & Research Developments

**Co- Chairs: B.Dimitriades, USA
K.Becker, Germany**

8:45 AM	Review of the EU Regulatory Work in the Field of Photochemical Pollution	<u>P. Hecq</u>, Belgium
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9:00 AM	Results from Monitoring and Modeling Studies of Ozone Reduction Strategies for Germany	<u>J. Pankrath</u> , Germany
9:15 AM	AM Photooxidant Research within the CEC Environmental Programme	<u>G. Angeletti</u> , Belgium
9:30 AM	EUROTRAC: A Coordinated Project for Tropospheric Research	<u>P. Borrell</u> , Germany
9:45 AM	The North American Research Strategy for Tropospheric Ozone (NARSTO): An Update	<u>K. Schere</u> , USA
10:00 AM	BREAK	

SESSION II. Atmospheric Photochemistry

Chair: H. Jeffries, USA

10:15 AM	Evaluation of Chemical Mechanism for Ozone Formation in Europe	<u>D. Derwent</u> , UK
10:40 AM	Critical Mechanisms of the Photooxidant Chemistry and Their Evaluation in European Simulation Facilities	<u>K.H. Becker</u> , FRG
11:05 AM	Aromatic VOC Chemistry Uncertainties and Their Impacts Upon Model-Derived Ozone Control Strategies	<u>R. Atkinson</u> , USA
11:30 AM	Chemical Mechanism of the Oxidation of Aromatic Hydrocarbons	<u>I. Barnes</u> , FRG
12:55 PM	LUNCH	
1:30 PM	Uncertainties in Chemical Mechanisms for Urban and Regional Scale Air Quality Modeling	<u>J. Milford</u> , D. Gao, and Y-J Yang, USA
1:50 PM	Simulation of Tropospheric Chemistry for a New Generation of Atmospheric Models.	<u>M. Gery</u> , USA; H. Jeffries,
2:15 PM	Development and Evaluation of Advanced Chemical Reaction Solvers for Use in Photochemical Models	<u>G. Gipson</u> , USA
2:35 PM	Tests of some Reduction Hypothesis in Photochemical Mechanism for Air Quality Modeling	<u>B. Aumont</u> , France
3:00 PM	BREAK	

- 3:15 PM Recent Development of the Gas-Phase Chemical Mechanism for the Reg. Acid Dep. Model W. Stockwell, FRG
- 3:40 PM Recent Laboratory Kinetic Studies Related to VOC Oxidation ($\text{NO}_3 + \text{RO}_2$, $\text{OH} + \text{Oxygenated VOCs}$) G. Le Bras, France
- 4:05 PM Peroxy Radical Chemistry: Recent Studies on Reactivity Patterns G. D. Hayman, UK
T. P. Murrells, UK
- 4:25 PM Impact of Heterogeneous Reactions Involving HO_2 and N_2O_5 on Mesoscale Photochemistry-- A Modeling Study J. Pleim, USA
F. Binkowski
- 4:45 PM Indoor Smog Chamber Measurements of Incremental Reactivity Factors N. Kelly, USA

5:05 PM **BREAK FOR DINNER**

7:30 PM **Panel Discussion on Ozone Mechanism Issues**

Moderator: H. Jeffries, USA

Panel Members: R. Derwent, UK
G. Le Bras, France
K. Becker, Germany
R. Atkinson, USA

- What are current major scientific issues (e.g., chemistry of aromatics/of biogenics, ozone chemistry under certain precursor concentration conditions, carbonyl photochemistry, etc.)?
- What are their relative importance?
- What are current major research needs and what are their relative priorities (e.g., chemical mechanism issues, mechanism evaluation methods against smog chamber data/against field data, chemical solvers, computer methodology, etc.)?
- What plans are there for such research in the US, Europe, elsewhere?

9:00 PM **ADJOURN**

Tuesday, June 14

SESSION III. Emission Studies

Chair: J. Pankrath, Germany

- 8:00 AM Emission Inventory Verification Studies: D. Lawson, USA
The California Experience
- 8:20 AM Comparison of Observed and Predicted Vehicle R. Zweidinger,
Emission Factors for the Fort McHenry and K. Knapp, W. Ray,
Tuscarora Mountain Tunnels and N. Robinson, USA
- 8:35 AM Rationale, Experimental Design and J. Ching, USA
Methodology for Determining the Overall
Accuracy of Whole City VOC and NO_x Inventories
- 8:55 AM Hydrocarbon Emission Estimates Based M. Roemer,
on Aircraft and Ground Level Data The Netherlands
- 9:15 AM Advances in Biogenic Emissions Research P. Zimmerman, USA
- 9:35 AM **BREAK**
- 9:45 AM Regional Natural Volatile Organic Compound A. Guenther and
Emission Modeling and Measurements P. Zimmerman, USA
- 10:05 AM A Second-Generation Biogenic Emissions T. Pierce, USA
Inventory System for Ozone Modeling C. Geron
- 10:20 AM C14 Estimates of Ambient Biogenic VOC Ratios C. Lewis
-- Methodology & Preliminary Results W. Lonneman, USA

10:35 AM Panel Discussion on Emission Inventory Issues

Moderator: K. Becker, Germany
Panel Members: R. Friedrich, Germany
D. Lawson, USA
P. Zimmerman, USA
M. Rogers, USA

- What are current estimates of Emission Inventory (EI) data uncertainties for mobile source VOC and NO_x, area source anthropogenic VOC, isoprene and non-isoprene biogenic emissions, and biogenic NO_x emissions?
- How promising/useful are observational data for improving EI data accuracy?

- What are current emissions-modeling and EI research needs? What are their relative priorities?
- What plans are there for such research in the United States, Europe, and elsewhere?

11:45 AM

Break for Lunch

12:15 PM

LUNCHEON IN HONOR OF RETIRING ERICH WEBER
(French Quarter Restaurant)

SESSION IV. Photochemical Grid Model Development & Evaluation

Chair: K. Becker, Germany

- | | | |
|---------|--|-------------------------------------|
| 2:45 PM | The Air Quality Management Approach in the US: Modeling Expectations and Application USA Realities. Part I | <u>K. Demerjian</u> , USA
P.Roth |
| 3:10 PM | The Air Quality Management Approach in the US: Modeling Expectations and Application Realities. Part II | <u>P.Roth</u> , USA
K. Demerjian |
| 3:35 PM | Estimating Model Uncertainty through Alternative Base Case Analyses | <u>A. Hansen</u> , USA |
| 4:00 PM | BREAK | |
| 4:15 PM | Effect of Eulerian Model's Vertical and Horizontal Resolutions on the Prediction of Ozone Concentration over the Rural and Urban Areas | <u>D. Byun</u> , USA |
| 4:35 PM | On the Coupled Use of Photochemical Grid Models and Observations-Based Approaches | <u>R. Dennis</u> , USA |
| 5:00 PM | Intercomparison Results of Urban Airshed Model Versions with Different Meteorological Drivers | <u>J. Godowitch</u> , USA |
| 5:20 PM | BREAK FOR DINNER | |

8:00 PM Panel Discussion on Photochemical Grid Modeling Issues

Moderator: K. Schere, USA
Panel Members: R. Derwent, UK
R. Dennis, USA
K. Dermerjian, USA
F. Fiedler, Germany
D. Simpson, Norway
P. Roth, USA

- Where in the modeling method (used for development of ozone strategies) lie the major sources of uncertainty [e.g., dispersion module (spatial resolution), chemistry, EI-, wind field-, and boundary conditions-inputs, etc.]? What are their relative importance?
- What are current major research/development needs?
- What are their relative priorities?
- What plans are there for such research (in the US, Europe, elsewhere)?

9:30 PM

ADJOURN

Wednesday, June 15

SESSION V. Model Application and Field Studies -- Europe

Chair: G. Le Bras, France

- | | | |
|----------------|---|-----------------------------------|
| 8:00 AM | Photochemical Pollution in Southern Europe
Experimental Results from EC Research
Projects | <u>M. Millan</u>, Spain |
| 8:30 AM | Nitrous Acid Occurrence in Urban Areas and
Its Role in Atmospheric Oxidation Processes | <u>I. Allegrini</u>, Italy |
| 9:00 AM | Trend Analysis of Ozone Concentration
between 1975-93 in the Cologne Area | <u>W. Dulson</u>, Germany |
| 9:30 AM | The Influence of Automobile Speed on the
Oxidant Concentration in Cities During
Smog Episodes | <u>D. Kley</u>, Germany |

10:00 AM

BREAK

- 10:10 AM Emission Reduction Scenarios for VOC and NO_x and their Effect on Tropospheric Ozone -- a Case Study for the State of Baden-Wurttemberg R. Friedrich, Germany
- 10:40 AM Summer Smog Development in South-Western Germany: Observation and Numerical Simulations F. Fiedler, Germany
- 11:10 AM Relations between Ambient Ozone Concentrations in Germany and Precursor Emissions in Central Europe W. Fricke, Germany
- 11:40 AM Modeling the Role of Isoprene Emissions in Europe: Impact on Control Strategies D. Simpson, Norway
- 12:10 PM LUNCH
- 2:00 PM The Impact of Different European Emission Inventories on Air Quality Modeling with the EURAD Model H. Hass, Germany

SESSION VI. MODEL APPLICATION & FIELD STUDIES -- USA

Chair: J. Ching, USA

- 2:30 PM Intercomparison of Scientific Findings from 20 Regional Air Quality Studies in Europe and N. America E. Cowling, USA
P. Solomon,
- 3:00 PM The United States Photochemical Assessment Monitoring Stations (PAMS) Program for Ozone Non-attainment Areas N. Gerald, USA
W. Hunt, Jr.
- 3:30 PM BREAK
- 3:40 PM Photochemical Ozone in Atlanta, Georgia: Influence of Mobile Source Emissions M. Rodgers, USA
R. Dubose, M. Fogelson,
M. Meyer, C. Ross,
M. Saunders, A. Gilliland,
G. Grodzinski, S. Rhudy,
D. Jager, M. Cannon,
T. Barker, X. Gong,
and H. Honnecutt,
- 4:05 PM Ozone Reactivities of Real-World Emissions of Organic Species from Motor Vehicles Determined in the Ft. McHenry and Tuscarora Mountain Tunnels J. Sagebiel, USA
A. Gertler, W. Pierson
B. Zielinska
- 4:30 PM ADJOURN

DINNER ABOARD THE "SPIRIT OF CHARLESTON"
(Need to congregate at the dock at 6:00 PM)

Thursday, June 16

SESSION VI (cont'd): Field & Model Application Studies -- USA

- 8:00 AM Assessing the Importance of Polar VOCs as Ozone Precursors: Observations from the SCION Sites P. Milne, USA
A. Bernado-Bricker
D. Riemer, R. Zika
- 8:25 AM Production of Ozone in Rural Georgia During the 1992 SOS Campaign L. Kleinman, USA
Y-N Lee, S. Springston,
J. Lee, J. Weinstein-Lloyd
L. Nunnermacker,
X. Zhou, and L. Newman
- 8:50 AM Ozone, Hydrocarbons, NO_x and Oxygenated Organics at a Rural Southeastern U.S. Site Y-N Lee, USA
S. Springston, L. Kleinman,
X. Zhou, L. Nunnermacker,
J. Lee, J. Weinstein-Lloyd,
L. Newman, M. Rodgers,
C. Stoneking, J. Pearson,
S. Smith
- 9:15 AM Reflections on a Regional Oxidant Model Study -- Predicted Response of Regional Ozone to Across-the-Board Reductions in Anthropogenic VOC and NO_x Emissions S. Roselle, USA
K. Schere
- 9:40 AM **BREAK**
- 9:55 AM Ozone Strategies for the Northeast U.S.: Effectiveness of NO_x Controls E. Meyers, USA
N. Possiel, R. Wayland
- 10:25 AM Ozone Strategies for the Northeast U.S.: Effectiveness of VOC Controls G. Wolff, USA
- 11:00 AM **LUNCHEON**
(Trawler Seafood Restaurant)
-

SESSION VII. Observational Models/Methods

Chair: P. Roth, USA

2:15 PM The Use of Observation-Based-Models for Studying Ozone Precursor Relationships W. Chameides, USA

2:40 PM Observation-based Approaches to Determining the Sensitivity of Ozone to VOC and NO_x: The "Indicator Species" Approach S. Sillman, USA

3:05 PM Spatial Mapping of NO_x-Limiting Conditions Adaptation of the Integrated Empirical Rate Approach C. Blanchard, USA
P.Roth. H.Jeffries

3:30 PM **BREAK**

3:40 PM An Experimental Evaluation of the Integrated Empirical Rate Model N. Kelly, USA

4:05 PM Atmospheric Reactivity of VOCs: AIRTRAK and the IER Model M. Hurley, USA
T.Wallington,
S.M. Japar

4:30 PM **Panel Discussion on Observational Model/Method Issues**

Moderator: P. Roth, USA
Panel Members: W. Chameides, USA
S. Sillman, USA
C. Blanchard, USA
N. Kelly, USA
S. Japar, USA

- What applications are there for which use of observational data/methods is or could be recommended?
- What are current major scientific issues in the observational methods development area? What are their relative importance?
- What are highest priority research/development needs in the observational data/methodology area?
- What plans are there for such research/development in the United States, Europe, elsewhere?

5:45 PM **ADJOURN**

Friday, June 17

SESSION VIII. Wrap-up/Conclusions

Chair: P. Roth, USA

**8:15 AM Preparation of Proceedings statements by Steering Committee
and assigned participants**

Steering Committee

Chair: P. Roth, USA

Members: K. Becker, Germany

H. Jeffries, USA

R. Derwent, UK

D. Kley, Germany

12:00

ADJOURN

**FOURTH US/GERMAN/EC WORKSHOP
ON
PHOTOCHEMICAL OZONE PROBLEM AND ITS CONTROL**

**Charleston, S.C.
June 13 - 17, 1994**

PROCEEDINGS REPORT

SESSION I. RESEARCH AND REGULATORY DEVELOPMENTS

1.1 REGULATORY DEVELOPMENTS IN EUROPE

The work of the European Commission (EC) in general and particularly in the environment is mainly oriented towards the harmonization of policies among the twelve Member states and the integration of needs for protection of the environment in other policies (transport, tourism, industry, etc.). Photochemical air pollution is recognized as being amongst the problems against which action has to be taken. In that field, the regulations adopted or in preparation cover both the emission reductions and the assessment of ambient air quality.

On the emissions side, four main sectors are covered: exhaust/evaporation from cars, evaporation from the refuelling systems, solvent usage, and combustion installations. The "Directives" are driven by the principles of prevention and correction at the source, and by the need to fulfill the obligations resulting from the international protocols on NO_x and VOC reductions. They are based on the use of the best available technology with no excessive costs. However, increase concerns for health protection and ambient air quality are included.

With regard to ambient air quality, one standard has been fixed for the maximum concentration of NO₂ on the basis of health protection criteria. In the framework of the photochemical problem in Europe: a "Directive" on O₃ pollution has been adopted, which fixes thresholds for health and vegetation protection and population information or warning. This regulation is to improve monitoring of O₃ (and as far as possible its precursors) and to coordinate the actions against photochemical pollution.

New measures for reducing the emissions of precursors will be necessary in Europe, but they will have to be justified on the needs to meet ambient air quality objectives. In the future, the assessment of air quality in general, and of O₃ and its precursors in particular, will be a crucial element of the European policy towards cleaner air.

1.2 REGULATORY DEVELOPMENTS IN GERMANY

- In Germany, several regulations for controlling NO_x and VOC emissions have been initiated for compliance with:
 - United Nations Economic Commission for Europe (UNECE) protocols on NO_x and VOC reductions,
 - EU directives on ozone and its precursors, and
 - Amendment to the Federal Immission Control Act.
- Emission control potentials according to this "trendscenario" have been estimated to be 36% NO_x reduction and 47% VOC reduction for the year 2005 compared to 1987. The trendscenario meets the reduction goal of the UNECE protocols (30% NO_x, 30% VOC reduction).
- For further CO₂ reduction, Germany needs additional technically feasible measures which would result in a 50% NO_x and 72% VOC reduction. Further reductions cannot be achieved by technical measures alone; economic and fiscal measures, etc. are then required.
- For assessing compliance of these national emission reduction potentials with air quality levels of ozone [e.g., EC health protection level of 110 µg O₃/m³/8 hours average, UNECE accumulated exposure threshold of 40 ppb O₃ for protection of forests (AOT40)] that guide subsequent pollution control efforts, an Action Programme and a Measure Plan for ozone reduction have been launched. Modeling-based emission control scenarios on the European/Federal States-hierarchy levels are supposed to support the decision finding for the Measure Plan.

1.3 RESEARCH DEVELOPMENTS IN EUROPE

1.3.1. PHOTOOXIDANT RESEARCH WITHIN THE EC ENVIRONMENT PROGRAMME

The research activities in the field of photooxidants, promoted by the European Commission (EC), are presently treated within the Environment Research Programme 1991-1994, which is the continuation of past programmes started initially about 20 years ago.

European Commission R&D programs on environmental protection give particular importance to atmospheric chemistry, which is part of the Global Change Area. The other areas included in the Environment Programme are: Technology and Engineering for the Environment, Research on Socio-economic Aspects, and Technological and Natural Risks.

About 15 research projects related to photooxidants formation are presently supported by the EC. The contribution outlined some selected projects with a brief description of the main results obtained, e.g., the determination of rate constants and mechanism for reactions which are relevant to ozone formation, the elucidation of the role of natural VOCs, and the development of sampling and analytical techniques for the detection of hydrocarbons.

The importance of the subject is evident from the increase of financial resources allocated from the previous programmes up to now. There is need to mention that this part of the programme is implemented also by concerted actions, i.e., by coordination of national research in the Member States with the assistance of a specific Science Panel.

It is foreseen to maintain the efforts in this area at a high level within the 4th Framework R&D Programme 1994-1998, where research in the field of photochemical oxidants as described in the strategic document, "Chemistry in the Atmosphere", prepared by the adhoc EC Science Panel, is included through topics as the oxidizing capacity of the atmosphere and the role of biogenic emissions in photooxidant formation. These items are the basis to design and implement a work programme starting in 1995, part of the next Specific Environment Programme for which an overall allocation of 1080 MECU has been provided, including Climatology, Marine Sciences, and Technologies Programmes.

1.3.2 EUROTRAC

EUROPEan Experiment on TRANsport and Transformation of Environmentally Relevant Trace Constituents in the Troposphere Over Europe (EUROTRAC), the European coordinated research project within the EUREKA initiative, addresses three major scientific problems in tropospheric research:

- the formation of photo-oxidants,
- acid precipitation, and
- biosphere-atmosphere exchange of trace substances.

The project has achieved a remarkable success since its start in 1989 in bringing together international groups of scientists to work on problems directly related to the transport and chemical transformation of trace substances in the troposphere.

The contribution briefly outlined the organization of the project, which involves some 250 research groups in 23 European countries and focused on two particular aspects: the newly formed application project and the current discussions on a project to follow EUROTRAC when it finishes at the end of 1995.

The Application Project (AP) is intended to assimilate the results from EUROTRAC and present them in a condensed form so that they are suitable for use by those responsible for environmental planning and management in Europe. Its principal themes are:

- Formation, distribution and trends of photooxidants in Europe,
- Acidification of soil and water and the atmospheric contribution to nutrients, and
- Contribution of EUROTRAC to the development of tools for the study of atmospheric pollution, in particular, tropospheric modelling, new or improved instrumentation, and the provision of laboratory data.

The first draft of the AP report will be ready at the end of 1994, and the report will be published in 1995.

Following surveys of opinion among principal investigators and other interested parties, prospects for formation of a proposed project to follow EUROTRAC in 1996 are presently under discussion within the project. It is likely that the main goal will be to understand and quantify the source/receptor relationships for photo-oxidants and acidifying substances on a regional scale over Europe. While the future project will probably be organized similarly to the present one, there will be substantially greater emphasis on the work applications to current environmental issues. The project will probably be formally introduced towards the end of this year (1994).

1.4 RESEARCH DEVELOPMENTS IN THE US -- NARSTO

The US has undertaken in 1993-94, a major international research initiative entitled, "North American Research Strategy for Tropospheric Ozone (NARSTO)," to deal with formation and inter-country transport of ozone at problem levels. The initiative was instigated by recent efforts of the scientific and regulatory communities in the United States (US) to rethink the ozone problem and its controls, in the face of the disturbing failure of past controls to achieve significant improvement of ozone air quality. It is intended to serve policy-related interests of all segments of government and private sectors, and its scientific scope is limited to addressing outstanding issues within the areas of understanding the processes and factors associated with problematic accumulation of ozone in ambient air, and development of effective strategies for managing the ozone problem. A significant novelty of NARSTO is the joint support of the effort by governmental agencies, private industry, and university communities in the form of public-private partnerships. Clearly, this is a major initiative dedicated as much to supporting the regulatory programs mandated by law or governmental agencies as to advancing the science underlying the photochemical smog formation phenomenon.

Regulatory or policy-related concerns dealt with by NARSTO are associated with the role and responsibility of the anthropogenic sources in ozone problems in distinction from the natural sources, trans-boundary transport of ozone and its precursors, approaches to managing ozone problems, and the use of scientific evidence and uncertainties by the air quality management and policy communities. Key science questions to be addressed range from general ones pertaining to further understanding atmospheric processes responsible for ozone accumulation and transport to specific ones pertaining to effects of emissions and their controls and of meteorological factors.

SESSION II. ATMOSPHERIC CHEMISTRY

This session had the largest number of contributed papers in the conference. Topics included detailed kinetics studies conducted in the laboratory, advances in the oxidation reaction mechanisms of biogenic and aromatic hydrocarbons, results of smog chamber studies, new formulation

principles for reaction mechanisms for use in air quality models, new fast chemistry solvers, inter-comparison of model mechanisms produced by different researchers, sensitivity studies of mechanisms parameters, and studies of reactivity. The session also included a panel discussion that dealt with the questions of what are the major issues currently, what are their relative importance, what major research needs do they raise, what are their priorities, and finally what plans are there for such research in the US, Europe, and elsewhere.

2.1 LABORATORY STUDIES

2.1.1 BIOGENIC HYDROCARBONS

The degradation of natural hydrocarbon is initiated by reaction, not only by OH, but also by O_3 and NO_3 . The database on the reactions is reasonably well established at room temperature. The mechanisms of subsequent degradations are poorly characterized with carbon balances of less than 60% for even the most widely studied system -- the OH initiated degradation of isoprene in the presence of NO_x . The O_3 initiated degradation of natural compounds is of particular interest because of the uncertain fate these processes play in the production of OH, organic acids, and hydroperoxides.

Current studies have observed features (nitro-oxy carbonyls and hydroxy-aldehydes) that have not been quantified. New techniques need to be developed for poly-functional compounds to improve the carbon balance and our understanding of these reaction systems.

2.1.2 PEROXYRADICAL CHEMISTRY

Peroxy radicals play an important role in photochemical production of oxidants on both the regional and global scales. The reactions of peroxy radicals with NO perturbs the photochemical stationary state leading to the production of O_3 . In low NO_x regions, other peroxy radical reactions ($RO_2 + HO_2$, $RO_2 + RO_2$, and $RO_2 + R'O_2$) become important resulting in the formation of hydroperoxides, organic acids, and other products.

The self-reaction of peroxy radicals have been more widely studied than the reactions of peroxy radicals with HO_2 , NO, NO_2 , or other peroxy radicals. The database on the reactions of $RO_2 + RO_2$ show a tremendous variation in reactivity over six orders of magnitude, with primary RO_2 s showing greater reactivity than secondary RO_2 s which in turn are more reactive than tertiary RO_2 s. Activation of the RO_2 is shown on substitution by different functional groups. Although the databases on the reactivity of peroxy radicals with HO_2 and NO are less extensive, the variation of reactivity is less than an order of magnitude. Tentative structure-reactivity trends can be identified, but further data are needed to both confirm and extend the patterns.

There are no data (kinetic or mechanistic) on the reactions of peroxy radicals with more than one substituent. Such peroxy radicals will be formed in the degradation of biogenic hydrocarbons. In the absence of

direct measurements, reliance on structure-reactivity relationships will be needed to estimate kinetic or mechanistic data for these reactions. Methods to develop peroxy radicals with specific structures are needed along with instrumentation to detect peroxy radicals both sensitively and selectively.

2.1.3 NIGHTTIME CHEMISTRY

Based on CH_3O_2 and $\text{C}_2\text{H}_5\text{O}_2$ data, the $\text{NO}_3 + \text{RO}_2$ reaction can be significant in the conversion of RO_2 to RO . In the case of peroxy nitrates, the extension of the database confirms that the acyl peroxy nitrates are thermally much more stable than the alkyl peroxy nitrates. The new absorption cross section data of PAN gives a photolysis rate three times higher than the currently accepted rate.

Additional data are still needed: (1) extension of the $\text{NO}_3 + \text{RO}_2$ studies to include larger RO_2 s; (2) mechanism studies of $\text{NO}_3 + \text{VOCs}$ (especially alkenes) to identify and quantify the products formed (nitroxy- and carbonyl compounds); (3) work on the formation and fate of organic nitrates ($\text{RO}_2 + \text{NO}$, $\text{NO}_3 + \text{VOC}$), particularly in relation to long range transport of NO_x ; and (4) the heterogeneous formation of HONO needs study.

In the area of ozonolysis of alkenes, rate constants of alkene + O_3 measured as a function of temperature, and mechanistic studies are needed. The latter needs to be especially focused on the fate of the Criegee biradical or other intermediates besides the Criegee biradical.

Photolysis rates and mechanisms for carbonyl compounds have been improved by a new determination of the quantum yields of methyl glyoxal, but many more compounds need to be studied.

2.2 AROMATIC HYDROCARBON CHEMISTRY

All urban areas in the US, as well as in Europe, show a significant contribution of aromatics (benzene, toluene, xylene isomers, and other alkylated benzenes) to the emission of anthropogenic hydrocarbons. Smog chamber experiments indicate that their contribution to photooxidant formation is also significant. Modeling of ozone formation, therefore, requires a proper description of the impact of aromatics on the photooxidant chemistry within the chemical module.

K.H. Becker noted in his presentation that one of the areas of uncertainty in current chemical mechanisms for atmospheric chemistry involves the atmospheric degradation reactions of aromatic hydrocarbons. As discussed by R. Atkinson, I. Barnes, and K.H. Becker, the aromatic hydrocarbons react in the atmosphere primarily with the OH radical by two pathways: H-atom abstraction from the substituent alkyl groups and OH radical addition to the aromatic ring to form a hydroxy-cyclo-hexadienyl-type radical (OH-aromatic adduct).

The subsequent reactions under atmospheric conditions of the benzyl radicals formed from the H-atom abstraction channel -- the minor reaction pathway -- are now understood. However, the reactions of the OH-aromatic adduct are not well understood. As discussed by R. Atkinson, the kinetic data of Zetzsch and coworkers, and product data of Atkinson and coworkers dealing with the formation of biacetyl from o-xylene as a function of the NO_2 and NO_x concentrations, show that the OH-aromatic adducts react with O_2 and NO_2 , with the O_2 reaction dominating in the troposphere. The products of these reactions are not known with any degree of certainty, as discussed by Dr. Barnes, and data are required in the presence and absence of NO_x . Dr. Barnes discussed the atmospheric loss processes and products formed from a series of oxygenated compounds observed and/or expected as products formed from the atmospheric photooxidation of aromatic hydrocarbons, including 1,4- and 1,6- unsaturated dicarbonyls.

The data presented by I. Barnes indicates that cresols are not formed in any significant yield from toluene and p-xylene in the absence of NO_x , but that carbonyl-containing compounds (multi-functional compounds including poly-ketones and their hydrates) account for a large fraction of the products.

The processes which scavenge NO_x , in smog chamber studies of the oxidation of aromatics have not been identified -- these processes slow down the formation of O_3 in the chambers. No indications have been found in the aromatic oxidation studies for typical peroxy-type reactions of the OH-aromatic adduct, i.e., reactions of the hydroxy-cyclo-hexadienyl-peroxy radicals with NO to form oxy radicals, with NO_2 to form peroxy nitrates, and with HO_2 to form characteristic hydroperoxides.

It was pointed out that the photooxidation of aromatics leads to products with mutagenic properties. The identity of the products causing the mutagenicity is not clear, but possible candidates are nitro-aromatics and unsaturated carbonyl compounds.

Maleic anhydride appears to be unique to the oxidation of aromatics and may serve as a "marker" of the extent of transformation of aromatic hydrocarbons.

Remaining Problems for Research:

- a direct analysis of the ring-cleavage step is required and could be done with the use of a suitable precursor; work in this direction is ongoing in Europe,
- detailed chemical characterization is needed of the identified ring-cleavage products, in particular, the photolysis and OH reactions of the unsaturated carbonyl products,
- the toxic compounds formed in the aromatic oxidation need to be pinpointed,

- a comparison between the oxidation mechanisms of benzene and the alkylated benzenes is necessary -- benzene may be different,
- NO_x loss pathways in the aromatic oxidation need to be identified:
 - artifacts in smog chamber studies, and
 - important processes in the atmosphere,
- without an understanding of the NO_x loss, no reliable definition of the "Ozone Formation Potential (OFP)" is possible, and
- formulation of a representative chemical mechanism is required for models, and also OFP values.

2.3 SMOG CHAMBER DATA NEEDS

Smog chambers are the only way to test our understanding of the chemistry of complex atmospheric reaction systems, such as the dark and photochemical oxidation of biogenic, aromatic, and real world urban hydrocarbon mixtures. Smog chambers provide macroscopic data to aid in the formulation of reaction mechanisms based mainly on more microscopic data from the kinetics laboratory. That is, chamber data show the combined effects of all chemical processes acting together, including ones that may not have been studied in the laboratory and for which there are no kinetics rate or reaction pathway data.

Previous studies conducted in the United States, Japan, and Australia have provided a large, yet still insufficient, smog chamber database. The United States data set, mainly from the University of North Carolina (UNC) and the University of California, Riverside (UCR), has been assembled by the United States Environmental Protection Agency (EPA) into a "Standard Chamber Data Base" for use in reaction mechanism testing. Under the EPA sponsorship, the Commonwealth Scientific and Industrial Research Organization (CSIRO) chamber data from Sydney, Australia, is currently being prepared for inclusion into this database. Also under EPA sponsorship, additional low level NO_x/VOC experiments are being performed by the Tennessee Valley Authority (TVA) in their indoor smog chamber. At present, the standard database contains over 300 dual experiments from UNC and over 400 experiments from UCR. In spite of this large number of experiments, there are many shortcomings in this data set: e.g., multiple chamber data exist for only about 20 VOC compounds, only one chamber has run a variety of alternative fuel mixtures, and additional chamber characterization experiments are needed in all chambers.

Participants at this meeting suggested that new studies are needed for:

- lower NO_x conditions more typical of urban and regional levels,

- more VOC-mix experiments, including biogenics at realistic levels,
- for VOC compositions likely in the year 2005,
- more mixtures typical of alternative fuel emissions in urban background VOC mixtures,
- a large number of chamber experiments on newly discovered reaction intermediates (e.g., hydroxy carbonyls) for which no kinetics data exist and for which organic synthesis will be needed to produce the reactant materials, and
- many more experiments on heterogeneous reactions on surfaces (especially chamber surfaces) and on particles.

There is a need for more standard and advanced equipment that is used with chambers. The sensitivity of many standard monitoring instruments has been improved and would allow work closer to ambient conditions in chamber experiments. Further, spectral radiometers are now available allowing detailed characterization of the light flux in chambers and these should be used routinely. Major advances in gas chromatography and mass spectrometry (MS) have occurred recently and new ion trap MS detectors show very high sensitivity as well as ability to produce molecular ion information. New continuous instruments are also available for continuous measurement of HONO, an important radical source in smog chambers that probably is formed by heterogeneous processes different in different chambers. Finally, measurements of radicals (HO₂ and OH) in chambers are needed to confirm our understanding of the internal radical sources in the mechanisms.

These new smog chamber experiments need to be conducted in both indoor and outdoor chambers. This is because indoor chambers offer consistent and controlled conditions useful for verifying or testing portions of the reaction mechanism, but ultimately the mechanism must function under outdoor conditions. Indoor chambers also have a difficult time creating the intensity and spectral distribution of sunlight and, therefore, outdoor chambers must be used to assure that the mechanisms do function properly under atmospheric conditions of radiation and temperature.

Participants also agreed that a need exists for multiple chambers in multiple locations. By showing that a principle mechanism, in combination with a chamber-specific auxiliary reaction mechanism, is capable of making correct predictions in at least four chambers (two indoors and two outdoors), we can develop faith that the mechanism is free of compensating errors between the chamber-dependent chemistry necessary to simulate a particular chamber and the chamber-independent chemistry necessary to simulate all chambers and the ambient air. Further, in some outdoor locations, climatological conditions differ from those in other outdoor locations, and stress reaction mechanism models in unique ways. For example, the cooler temperatures and lower radiation intensities in

Europe will provide a different test than the typically hot and humid summer conditions of North Carolina that are common in the UNC outdoor chamber data set.

Finally, it was agreed that all smog chamber groups must cooperate. The amount of work that must be accomplished in smog chambers exceeds the production capacity of all current chambers combined. Further, each chamber has unique attributes that can be exploited in testing mechanisms. All chambers should have the same characterization of radiation intensity and spectral conditions. All chambers should be tested with both simple (e.g., methane) and complex synthetic urban VOC mixtures under identical conditions to provide a direct comparison of chamber results. Chamber groups should also share in quality assurance activities and inter-comparison tests.

2.4 MECHANISMS AND THEIR UNCERTAINTIES

The applicability of chemical mechanisms for atmospheric prediction can be tested, and their ozone production mechanisms diagnosed, using pathway analysis and the relative and integrated rates of radical-initiated odd oxygen production (i.e., NO to NO₂ oxidation), and the partitioning of odd oxygen into ozone and other species. In such analyses, current mechanisms generate consistent downwind ozone concentrations through markedly different reaction pathways, generating sometimes divergent PeroxyAcetylNitrate (PAN) and hydrogen peroxide concentrations.

Explicit chemical mechanisms addressing a large number of hydrocarbons can be generated using structure-reactivity relationships for the peroxy, oxy, carbonyl, and multi-functional carbonyls generated by OH oxidation of the hydrocarbons.

Individual hydrocarbons make markedly different contributions to episodic ozone formation depending on their OH+hydrocarbon rate coefficients, mass emission rates, and the typical number of peroxy radicals produced per hydrocarbon+OH reaction.

Chemical mechanisms in use have known errors because the state of hydrocarbon reaction kinetics knowledge is incomplete, especially for aromatic and biogenic compounds, and some elements of the mechanisms for higher alkanes and aromatics. Even for the well-studied inorganic reaction set there are still uncertainties, and better characterization of these rate parameters by National Aeronautics and Space Administration (NASA), International Union of Pure and Applied Chemistry (IUPAC), and other evaluation panels are needed. A new evaluation currently underway is a study of the effects of RO₂ reactions on the nitrogen balance. In this study, the most important reactions are CH₃O₂ and CH₃(CO)O₂ with HO₂, CH₃O₂, and with CH₃(CO)O₂ radicals.

Estimated uncertainties in rate parameters and product yields in the Regional Acid Deposition Model 2 (RADM2) mechanism were produced by multiple simulations over distributions of the parameters. For surface

urban conditions, the calculated uncertainties in predicted ozone concentrations are about 20-30 % (one sigma) of mean predictions. Somewhat higher uncertainties are estimated for H₂O₂ and PAN.

Formal uncertainty apportionment results show the importance of improved characterization of photolysis conditions, updating the PAN chemistry in the RADM2 mechanism, and improved understanding of aromatics oxidation pathways and of carbonyl and radical yields in alkenes chemistry.

An expanded version of the Regional Acid Deposition Model (RADM) mechanism has been produced that includes more explicit input hydrocarbons (the reaction products remain "lumped" in this version). The mechanism is currently being updated according to the most recent evaluated kinetics data.

2.5 NEW MECHANISM REPRESENTATIONS AND MODEL SOLVERS

Ongoing improvements in both computer capabilities and numerical algorithms are leading to new methods that are directly applicable to the simulation of atmospheric chemistry. In particular, research into improved chemistry solution modules and expanded representation of "real" chemistry in the models show promise of significant advances.

Computationally efficient solvers are essential for large photochemical air quality simulation models (PAQSMs) because of the relatively large number of grid cells and the complexity of the chemical mechanisms (i.e., in terms of the number of species and reactions). Historically, heuristic solvers, which attempt to exploit special features in the set of ordinary differential equations (ODEs) that arise from the chemical reaction mechanism rather than perusing a general and mathematically rigorous solution, have been employed in PAQSMs. This is because these heuristic solvers were faster than the more rigorous solvers by factors of 10 to 100. In some instances, however, these less rigorous solvers can introduce undesirable numerical inaccuracies. Advances in computer technology and commensurate re-structuring of numerical algorithms now make possible the use of the mathematically sound and more generalized solvers. For example, a re-casting of the Gear method, which is especially designed to solve stiff ODE systems, and to operate on a large block of model cells rather than solving one cell at a time, is now considered to be a viable solver option for PAQSMs, particularly on vector machines, such as CRAYS. On a CRAY C90, for example, 10,000 cells of a 40 species reaction mechanism can be simulated in less than 4 minutes of Central Processing Unit (CPU) time.

The incorporation of generalized solvers, such as the Gear method, can also increase the ease with which different chemical reaction mechanisms can be incorporated in the model. Nevertheless, the ever-increasing desire to enhance spatial resolution and expanded chemical mechanisms in PAQSMs will almost surely spur the need for even faster solvers. More research in this area is clearly warranted.

At the same time the solvers are being improved, research is underway to expand the chemical detail represented in the reaction mechanism (particularly, for the intermediates and final products) without increasing the number of ODEs that must be solved. The first public description of an "allomorphic" chemical reaction mechanism was given at this workshop. These mechanisms have both molecules and morphecules. A morphecule is a type of dynamic shape-shifting molecule and its allomorphs are the variants on the morphecule. For example, an N-ALKANE morphecule has only normal alkanes as allomorphs. Allomorphs have not only mass, they have additional traits, such as OH rate coefficients and other properties. Thus, transport, deposit, and emission of VOCs are done using allomorphs (non-ODE species), but the ODE solver is only operated with the molecules and morphecules of the mechanisms. This seemingly contradictory operation is achieved by a type of "identity splitting" over time. At the beginning of a chemical timestep, the concentrations and other traits of the allomorphic species are used to compute the concentrations and weighted properties of the morphecule. After a reaction step, the change in the morphecules are "back propagated" to the individual allomorphs of the reacting morphecule and "forward propagated" to the allomorphs of the reaction products. When emissions and transport of allomorphs are computed, the changes of each allomorphs are updated. Thus, the RO₂s and carbonyl products have time-varying character.

This approach has a number of advantages, most notably:

- even though chemical detail is vastly expanded, the chemical solver can more quickly deal with a small number of reacting entities,
- the method eliminates surrogate representations of VOC's and reaction products instead of tracking the chemical characteristics through the radical oxidation reactions so that the "real" product distributions can be followed and subsequently reacted, and
- such detailed chemical representations allows for dynamic chemical linkages between models or model cells of different chemical scales (e.g., using mechanisms devised for urban, troposphere, and global scales).

2.6 REACTIVITY ISSUES

Assigning reactivity values to individual hydrocarbons is not straightforward because they are unlikely to be geophysical quantities and are likely to be dependent on both chemical mechanism and environmental conditions. Thus, the Maximum Incremental Reactivity/Maximum Ozone Incremental Reactivity (MIR/MOIR) reactivity values depend on hydrocarbon/NO_x ratios and care must be taken to use values appropriate to each application. More experimental testing is needed of the basic assumptions to the various "reactivity models" and empirical models [e.g., G. Johnson's Integrated Empirical Rate (IER) model] based on limited smog chamber studies. For example, some reactivity models suggest that

reactivities are additive. Many attendees have suggested that careful testing of hydrocarbon mixtures in other smog chambers needs to be conducted to confirm the various assertions about reactivities characteristics.

In addition, strong temperature effects have been observed in captive air outdoor smog chamber studies, and model calculated reactivities do not include these effects. The omission of this effect leads to some uncertainty in understanding the value of reactivities.

In Europe, the VOC Protocol to the UNECE International Convention on Long Range Transboundary Air Pollution encourages member states to use reactivity in the development of hydrocarbon control strategies to address those sources which contribute to ozone formation in Europe. This work needs to be extended in its coverage of hydrocarbon species, source categories, and to different areas of Europe.

2.7 HETEROGENEOUS REACTIONS

J. Pleim showed results of a preliminary modeling study using RADM, including heterogeneous reactions involving N_2O_5 and HO_2 . Aerosols were represented by a bi-modal method and their surface area was computed as a function of sulfate concentration, relative humidity (RH), and NH_4/SO_4 . The heterogeneous reaction rates were computed for the diffusion limited assumption. However, for the HO_2 reaction, Cu(II) is thought to be the key catalyst. Therefore, the reaction cuts off above some critical RH when Cu(II) concentration gets too low. Probably this is an underestimate of reality since the reaction probably continues even when it is no longer diffusion limited. The model results show potential impact on O_3 (downward) and H_2O_2 (upward) concentrations. Clearly, these reactions need more study, both in the laboratory and the field.

2.8 CONCLUSIONS

- The degradation pathways of alkylated benzenes have to be studied in greater detail to obtain a reliable mechanism which describes the impact of the aromatics on the photooxidant chemistry at high, as well as, low NO_x concentrations.
- The ozonolysis of biogenic alkenes is of great importance for the O_3 budget. A reliable mechanism needed for modeling requires:
 - a better understanding of reaction intermediates in both the gas phase and the aqueous phase, and
 - a quantitative analysis of the formation yields of different alkyl-hydroperoxides, hydroxy-alkyl-hydroperoxides, and the OH radical.

- The HONO formation before sunrise observed in urban areas has a significant impact on the OH radical budget in the troposphere. The formation mechanism needs studying because models must include the processes in their chemical module.
- Different types of laboratory facilities are now available in Europe. There is an urgent need to operate a larger simulation chamber where complex chemical mechanisms can be evaluated and tested under appropriate troposphere conditions.

SESSION III. EMISSIONS STUDIES

3.1 EMISSION INVENTORY ISSUES

This session dealt entirely with emission inventory issues. A summary of presentations and panel discussions on those issues follow. Panel discussions dealt with questions on current estimates of emission inventory data uncertainties, the potential of observational data and methods for reducing such uncertainties, specific research needs in the emissions modeling and emission inventorying areas, and plans for such research in the US, Europe, and elsewhere.

The emission inventory is a key component of any air pollution control program. It includes many types of emission sources, quantities of emissions, the temporal and spatial characteristics of emissions, and the process and emission control devices used at sources. Air pollution control agencies use emission inventories to identify potential control measures and sources that would be subject to controls, to determine control program effectiveness, and to predict future air quality through air quality simulation models. Therefore, accurate emission inventories are critically essential to provide the least costly basis and most effective pollution control strategies.

3.1.1 INACCURACY PROBLEMS IN EXISTING EMISSION INVENTORY DATA

Ambient Reactive Organic Gases ROG/NO_x measurements from more than twenty US cities differ considerably from the corresponding ratios derived from those cities' emissions inventories. Although this discrepancy has existed for years, until 1987 the difference was explained by photochemical reactions and deposition of NO_x. Ambient CO/NO_x ratios also differed considerably from corresponding emission inventory ratios. No independent means to reconcile these gross differences for aggregate whole-city inventories have been attempted to date. The magnitude of these inaccuracies in emission inventories, if left unresolved, leads to air pollution control strategies that are flawed, costly, and misdirected.

A series of independent studies resulting from the 1987 Southern California Air Quality Study (SCAQS) have documented serious underestimations of mobile source emissions in current US emission

inventories. This has been demonstrated through the use of urban tunnel studies, "top-down" comparison of ambient data with emission inventories, and air quality simulation modeling efforts. Since the 1987 Study, similar efforts from San Joaquin Valley, Lake Michigan, and Southern Oxidant Studies (SOS) have shown similar results, although these results have not yet been published in peer-reviewed literature. The current inventory appears to underestimate mobile source hydrocarbons and carbon monoxide by factors of 2-2.5 and 1.5, respectively. It is uncertain whether NO_x emissions from mobile sources are underestimated, but the most recent mobile source emissions estimates have shown significant NO_x increases, as large as 60% in California. Although it is not certain how long this discrepancy has existed in the United States, it may have existed for up to twenty years. A major reason for this underestimation is the presence of high emitters, whose emissions are not being reduced by motor vehicle inspection and maintenance programs.

Findings from two additional studies suggest mobile sources are the overwhelming source of hydrocarbon emissions in Los Angeles, even though official inventories suggest that mobile sources are responsible for only 50% of the ROG emissions. Detailed hydrocarbon speciation suggests a common source/source type, and receptor modeling also suggests mobile source/whole gasoline sources account for nearly 90% of the measured hydrocarbons.

In Europe, the quality and accuracy of emissions data vary considerably from region to region. Only a few studies for emission inventory verification have been carried out. However, these indicate for the most complex emissions models, e.g., in Germany, United Kingdom (U.K.), and the Netherlands, discrepancies similar to those observed in the United States may not be present. Other workshop members, including Europeans, disagreed. Differences between US and European inventory estimates are expected due to the following possible reasons:

- The mobile source emission control program in Europe is less mature than in the US, and modeled emission reductions in the European fleet have not yet taken place,
- Methods for measuring or estimating emission factors from in-use vehicles from real-world samples differ for the US and Europe,
- Different vehicle fleet is present -- only recently have vehicles with three-way catalysts been sold in a few countries, and
- Unleaded gasoline is less expensive than leaded gasoline (because the taxes on gasoline are higher for leaded than for unleaded fuels), therefore, fuel switching should be less frequent.

In the United States, several studies regarding mobile source emission verification have been carried out, but little effort has been directed toward understanding real-world emissions from point and area sources in the US and Europe. In Europe, a tunnel study was recently conducted in Switzerland, but results are not available yet. There was no

substantial information presented in the Workshop on ambient European measurements to verify such inventories, so the accuracies of the European inventories remain largely indeterminate.

3.1.2 RESEARCH/DEVELOPMENT NEEDS

The serious underestimation of mobile source emissions, along with possible overestimation of point and area sources in the US inventories, suggests that a plan for addressing this issue is urgently needed. Independent approaches to evaluate the overall accuracy of whole-city emissions inventories are needed to determine the accuracy of the inventory and to provide critical information from which to diagnose source(s) of errors introduced in the bottom-up construction of inventories. In Europe, there may be a lack of detailed ambient hydrocarbon data along with data to calculate ROG/NO_x ratios, and a summary of existing data and their quality should be carried out. Verification of emissions inventories in Europe is especially challenging because there are several different countries with differing degrees of resources.

In the US, major changes recently have been made to the biogenic emissions inventory, suggesting that major efforts are needed in this area. European scientists report that serious deficiencies exist in their knowledge of biogenic emissions, and these needs are discussed later in this summary.

Emission estimates are produced by scaling a source emission factor by some appropriate set of activity factors to yield an overall estimate of emissions. Current and future modeling requirements are increasingly demanding that emission estimates be produced on spatial scales of at most a few kilometers and time scales on the order of an hour.

While significant progress has been made over the last decade in evaluating emission factors, especially in the area of biogenic hydrocarbon emissions, proportional improvement in methods of producing localized and hour-specific activity factors has not been achieved. In some European locations, however, remarkable progress in providing hourly emissions have been reported from the GENERation of European EMISSION (GENEMIS), TRANsport of Pollutants over Complex Terrain (TRACT), and "Sanierung der Atmosphaere ueber den Neuen Bundeslaendern" or Changes in the Atmosphere over the former Eastern Germany (SANA) Projects. Many current methods for determining annual emissions (e.g., annual sales of solvents in a city) provide little information to temporally and spatially allocate these emissions.

Improvements in emission estimates over the coming decade will require development, testing, and methods development to produce highly specific emission and activity factors, for all source types. A major problem with all inventories is the lack of scientific methods to evaluate accuracy of the different components of the inventory. These must be developed. Uncertainty analysis needs to become an integral component of

all inventories. These emission estimates need to be evaluated for their ability to reproduce the range of emissions inferred from ambient observations.

If possible, emission inventories in the different European countries and the US need to be made compatible. Speciation, temporal, and spatial resolution need to be improved. Quality assurance efforts on the inventories also need to be undertaken. The policy makers from respective regulatory agencies should define the degree of accuracy that is needed in the inventories according to specific needs. Emission inventories requiring independent validation, through the use of ambient measurements, tunnel studies, and model calculations whenever possible. "Top-down" emission verification results need to agree with bottom-up approaches.

Oxygenated organic emissions may be significant, and they will become more important in the US with the introduction of federally mandated alternative fuels in 1995 and Phase-2 fuels in California in 1996. Many of these compounds are not measured as part of the PAMS network, and must be measured in order to quantify the influence of alternative fuels upon air quality in regions where they are in use. Future research requires better analytical tools. Research needs to focus on one or two dominant oxygenated compounds to determine the factors which control emissions. Surveys need to be done to test for emissions of the most likely compounds. If possible, rapid, inexpensive analytical techniques are required to improve flux estimates. Virtually all hydrocarbon speciation studies are limited by the number of samples that can be analyzed.

The relative importance of biogenic vs. anthropogenic hydrocarbons in the inventory deserves additional work. Initial results from the Southern Oxidant Study (SOS) show that although different approaches (¹⁴C counting, individual species composition, chemical mass balance model, and emission inventory comparison) give somewhat different results, biogenics probably do not contribute to more than 15% of the total observed hydrocarbon composition in Atlanta. This work holds promise for future research.

3.1.3 BIOGENIC EMISSION INVENTORY NEEDS.

The following needs were identified:

- In Europe, a comprehensive survey is needed of the number and variety of biogenic sources. The emission rates for important species are needed. However, some work is in progress within the European sub-project BIATEX to produce biogenic emission maps for Europe.
- Testing needs to continue to determine if emission algorithms for isoprene are universal. Studies need to be done which include nutrient status and other variables which can be monitored by remote sensing. Work needs to continue to elucidate the biochemistry of isoprene so that taxonomic and ecological links can be developed.

- Terpene research needs to focus on the variables that affect carbon allocation in plants. Real-time measurement techniques for specific terpenes needs to be developed.

- Aerometric flux techniques are promising. They require further development to determine the size of the emission footprint they observe and to better define the range of conditions under which valid fluxes can be analyzed.

- Remote sensing can be a powerful tool to define vegetation variability and annual variability. The flux community needs to emphasize the measurement of variables which facilitate remote sensing connections.

- Emphasis needs to be made to conduct studies which integrate elements of atmospheric chemistry, remote sensing, ecology, plant physiology, and plant biochemistry. Progress in understanding biogenic fluxes requires interdisciplinary teams working together.

- Emissions of nitrogen oxides from soils may be important in rural areas; thus, it deserves further investigation.

3.1.4 ANTHROPOGENIC EMISSION INVENTORY NEEDS

The following needs were identified:

- It is recommended that real-world evaluations of emission inventories must continue in order to verify the accuracy of the inventories, as well as to check for trends in emissions, and overall effectiveness of pollution control strategies. Direct measurements at the source (of all source types) are a requirement as input for the inventories.

- In both Europe and the United States, a comprehensive survey is needed to summarize all emissions verification data collected to date and to assess the quality of those data. Then a test of the accuracy of total emissions in the inventories needs to be performed. This needs to be done through the use of "top-down" comparisons of both ambient and inventory data and examination of hydrocarbon speciation. In addition to detailed hydrocarbon speciation, total hydrocarbon measurements are needed. Due to concern that mobile source NO_x emissions may be underestimated, this requires investigation.

- In Europe, the influence of vehicle speed on emissions has been reported, and this needs to be investigated under real-world conditions in the United States. The reactivity of hydrocarbon emissions from light-duty diesels on air quality in Europe also needs to be investigated because a higher percentage of the European light-duty fleet is diesels than in North America. The real-world emissions of heavy-duty diesels on ozone formation needs to be studied because the most recent tunnel studies have shown rather high reactivity resulting from the diesel fleet; in addition, the

NO_x emissions from the heavy-duty fleet are about twenty times those from the light-duty spark ignition engines.

- Within-grid cell studies of hydrocarbon speciation, NO_y and CO needs to be carried out, in order to verify accuracy of emissions within grid cells. Detailed hydrocarbon speciation along with CO and NO_x measurements needs to be carried out at several points within a grid cell in order to test for representativeness of sampling site data as well as variability within the cell. Data needs to be collected at specific one-hour intervals and compared with the inventory from that cell for the corresponding hours. It is important to compare ambient data with emissions data on the microscale in order to understand whether emissions are accurate, and whether they are being allocated to the appropriate source regions as input to air quality simulation models.

- Whole-city emission inventory verification and diagnostic evaluation studies, if feasible, are needed to provide reference checks on overall city emission inventories and to provide information to identify error sources as a step towards improving inventories. A mass balance approach that includes observing the total mass flux and measures of flux by source categories may provide the only known independent technique for the whole-city evaluation.

- Methods development must continue in order to make measurement of oxygenated compounds in ambient conditions. Pollutant species that are important in point and area source inventories, such as, aldehydes, ketones, alcohols, and esters need to be measured in order to verify their presence in ambient conditions.

- Research needs to be conducted to understand the "weekend effect" that has been observed in Europe and the United States. In Los Angeles, ambient ozone precursor concentrations are about 10% lower on weekends than on weekdays, but ozone concentrations are about 10% higher on weekends than on weekdays. In Germany, the inventory reports 30% lower emissions during weekends, but no decrease in ozone concentrations is observed. Once emissions patterns are understood on weekends, data from this natural experiment should be used for sensitivity testing for air quality simulation models.

- Within Europe, it is critical to obtain accurate emissions inventories from all countries, especially those from eastern Europe. As mentioned earlier, it would be ideal to unify inventories and inventory procedures for both Europe and North America.

- Experiments must be carried out to verify accuracy of the mobile source emissions models. For example, changes in California's mobile source emission model Emission Factor Model (EMFAC) from version EMFAC7D to version EMFAC7G have resulted in 186%, 142%, and 32% increases of hydrocarbons, carbon monoxide, and nitrogen oxides, respectively. It is important to verify that these models are giving the correct values for the right reasons.

3.2 SUMMARY

The workshop has provided a discussion forum of current issues facing the emission inventory community, both from Europe and North America. It is clear that the state of affairs is different in both regions. For example, the mobile source emission reduction programs in Europe do not have the same maturity as those in the United States. Therefore, predicted decreases resulting from such programs for emission reductions have not been incorporated into European inventories. It is clear that an urgent need exists to provide an overall plan for increasing the accuracy and credibility of emission inventories, both in North America and Europe. The list presented herein provides suggestions for areas of future research focus. Most of all, we recommend that participants in this effort be directly involved with those who produce the inventories.

SESSION IV. PHOTOCHEMICAL GRID MODEL DEVELOPMENT & EVALUATION

4.1 PRESENTATION HIGHLIGHTS

K. Demerjian and P. Roth jointly argued that too great a reliance is being placed on photochemical air quality simulation models (PASQMs) in national planning, as a consequence of the Clean Air Act (CAA). In particular, they stated that:

- The State Implementation Plan (SIP) process does not adequately reflect the need for interim iterations and correction, given the United States history of falling short of SIP projections for improvements in air quality.

- Models are not sufficiently accurate to justify their use alone, without corroboration or feedback in time. As justification, they discussed eleven types of deficiencies and issues that now accompany model use, including high noise-to-signal ratio, limited data availability, lack of "hands off" testing, presence of compensating errors, need for continuing extension of models to accommodate new understanding, increasing spatial scales and thus changes in the nature of difficulties to be resolved, increasing model complexity, high resource demands, inexperience of modeling staff, sole dependency on approach, and a history of past failures in projection.

- Consideration needs to be given to adopting "a process for attainment demonstration" rather than confining demonstration to the submission of a SIP.

- The process might consist of de-emphasis of the use of PAQSMs, introduction of the use of observation-based analyses to facilitate corroboration of the results of PAQSMs, emissions- and receptor-oriented monitoring (with careful prescription of the attributes of networks and instrumentation), and assessment of the risk of incorrect estimation of

outcomes. [An example of the methodology was presented subsequently by A. Hansen.]

A. Hansen pointed out that a major issue now facing decisions-makers concerned with attainment of the National Ambient Air Quality Standard (NAAQS) for ozone in northeastern United States is determining the need for reducing NO_x emissions and, if necessary, specifying the extent of reductions warranted. In order to evaluate the merits of requiring reductions in NO_x emissions, Federal and state regulatory agencies have enlisted the use of PAQSMs. Questions have been raised about the validity of modeling efforts conducted to date. Dr. Hansen described an alternative approach to examining the usefulness of today's models in estimating emissions reduction requirements. The primary attributes of the approach are:

- Applying models of interest in a geographical area having a data base adequate to support model performance evaluation [such data also allows the choice of model inputs to be constrained to a narrower range than routinely allowed by available (sparse) data],

- Accepting the models for application only after adequate performance is demonstrated,

- Generating generic findings for the study area, and

- Developing inferences, based upon what has been learned, for areas relying primarily on routinely available data, such as, the Northeast.

Key elements in the development and analysis of the proposed approach have been termed "risk-based" due to the desire to determine the risks of developing incorrect findings, and are:

- Evaluation of model performance under the constraints imposed by use of a sound and comprehensive data base through careful comparison of concentration estimates and observations, diagnostic analysis, and modification of inputs as needed, solely based on scientifically justifiable arguments. Demonstration of performance adequacy is requisite for further work as the degree of correctness of the results of sensitivity analyses depends on the soundness of the base case.

- Recognizing the likelihood of modeling representations evolving that contain compensating errors, an approach to develop an understanding of the uncertainties that arise in this situation are:

- to purposefully create alternative base cases that are essentially equivalent in ozone simulation performance to a reference base case, and

- to examine the response of each base case to changes in emissions that realistically mirror contemplated control strategies.

If responses are similar to the reference base case findings, which was developed using the comprehensive data base, the model is relatively insensitive to the presence of prevailing uncertainties and risk of developing incorrect strategies is relatively low for that case. On the other hand, if responses vary dramatically with the alternative base case, the risk of developing incorrect findings is high. In this case, depending on the model to "point the way" is indeed demonstrated to be risky. Alternative base cases constructed from less constraining sparse data in general will have a higher probability of responding differently to emissions changes than the reference (constrained) base case.

Demonstration of high risk over a sequence of alternative base cases is a generic finding. Yet an effort will be made to clearly delineate the implications of the Northeast findings. This will be pursued by:

- degrading the data base for the data-rich area and comparing findings both with the data-rich simulations and with those of the Northeast (for a similar data base), and
- comparing atmospheric process dynamics, physical characteristics, and attributes for the two areas in an attempt to draw comparisons and parallels, and if feasible to estimate "bounding levels" (e.g., a "ceiling" or "floor" on emissions reduction requirements) for uncertainties that attend control strategy findings.

Note: Examples of "degrading" the data base include:

- reducing the number of meteorological sounding sites available for Lake Michigan Ozone Study (LMOS) to a sparse data base and re-doing the meteorological modeling using only these data, and
- discarding all but one or two upwind monitoring sites and assuming that boundary concentrations derived from the retained data are spatially invariant.

In summary, the motivating elements of this approach relative to that being pursued in other current studies are:

- (a) properly evaluating model performance and reasonably assuring the acceptability of a reference base case,
- (b) developing alternative, approximately equivalent base cases that are consistent with available data, but contain "undetected" compensating errors, and
- (c) examining in depth the impact of these errors on findings of control strategy analyses.

In this way, modeling risk can be directly assessed.

4.2 PANEL DISCUSSION ON PHOTOCHEMICAL GRID MODELING ISSUES

A panel discussion was held on significant issues related to photochemical grid modeling. Six panelists were asked to respond to any or all of the following questions:

- Do the existing uncertainties in air quality modeling (chemical/transport/dispersion models, meteorological models, and emissions models) inhibit their utility for development of ozone control strategies?
- What are the most critical uncertainties to reduce, in order to gain confidence in ozone predictions and estimates of needed precursor controls?
- What are the principal modeling research directions in the next 5 years in the United States, and in Europe?
- What is the proper role of air quality modeling systems in research studies, and in air quality management/policy studies?
- How important is it to quantify errors/uncertainties in model results; can we do this? and
- What are the needed improvements in observational data to aid model evaluation, refinement, and/or application? What are the most critical data needed? Is grid scale incommensurability (point-to-grid comparisons) an insurmountable problem for evaluation?

The following principal points were made by the panel members:

P. Roth:

Emissions are crucial to proper simulations. Meteorology determines the mixing characteristics. Land/water interfaces play an important role in many serious ozone situations, and it is important to correctly model these. We must get the HC/NO_x ratios correct in the models to get credible results, and we must measure NO_x with sufficiently high resolution to capture low levels.

K. Demerjian:

There are not enough precision and accuracy in the routine measurements taken of ozone and precursors. The same issues in photochemical modeling that were important in 1976 are still important today. In order to avoid a backlash toward modeling, we need to turn the process around and use modeling and good observations together.

D. Simpson:

Control strategy assessment cannot be solely based upon one or a few case studies, as VOC and NO_x effects control vary from day to day. To be responsive to policy makers, we need to be modeling longer time periods -- preferably months or years -- and in larger areas. Simpler models are useful for these exercise type, and may provide as useful guidance as that from more complex models.

R. Derwent:

Existing uncertainties do not inhibit their use for strategy exercises. It is the scientists' duty to use the best science possible in the models at any given time. Meteorology is terribly important; we need to get the transport correct to have chances for the chemistry to work right. We need research on coupling the regional ozone models to global scale models. There is too long of a process to get current science into operational models; we must attempt to shorten it. Better capability for measuring OH is needed.

R. Dennis:

Adjusting, or "tuning", models does inhibit their utility for developing control strategies. Isoprene chemistry has some important errors which the regional models are sensitive to. Air quality models need to be used as numerical laboratories to test hypotheses. Prognostic meteorological models as drivers for air quality models need more work in terms of their accurate depiction of meteorology. We need measurement capabilities of OH, RO₂, and HO₂. Modeling a small number of episodes is problematic to gaining robust understanding of model response to emissions reductions.

F. Fiedler:

Better thermodynamics are needed in the meteorological models. Simple models are often incorrectly applied to complex situations. We need more specific studies targeted to discriminate between processes. Initialization and boundary condition problems continue to plague models. More sensitivity studies are required to bring out uncertainties and error bounds.

A lively discussion followed the opening panelists' statements sparked by questions from the audience. The initial discussion centered on specific weaknesses in the models' chemical, physical, and meteorological processes, as well as in the input data errors. The latter portion of the discussion tackled the question of the "adequacy" of current models for

development of control strategies. There was some disagreement among panel members on this issue -- some panelists indicated that the current science is the best we can do at present and we need to use the models in this vain, while other panelists indicated serious, possibly fatal, flaws exist in current modeling systems. Those holding the latter view indicated that current modeling capabilities may not be adequate for developing strategies. The conflicts between the United States' State Implementation Plan (SIP) process and its definitive modeling need, and the current unacceptably high error level and uncertainty in modeling systems was highlighted.

SESSION V. MODEL APPLICATIONS & FIELD STUDIES -- EUROPE

Session V brought researchers together from several European countries who reported on:

- the analysis of O₃-network results,
- pollution over the Iberian peninsula,
- observations of HONO in cities,
- box, Lagrangian, and Eulerian modeling studies on both the local and regional scale, and
- emission reduction scenarios.

W. Fricke used back trajectories to establish relationships between O₃ concentrations at a rural site and emission of O₃ precursors along the trajectories. Correlations among O₃ and NO_x and VOC, respectively, were the best for back trajectories 5 days back in time. The highest O₃ concentrations (approx. 150 ppb) were related at the high end of NO_x emissions and VOC emissions along the path from precursors source areas to receptor. The O₃/VOC relation was more linear than the O₃/NO_x relation which showed an O₃ leveling off for air parcels that had traveled over the highest NO_x source areas.

W. Dulson showed results from the operational O₃ monitoring at Cologne. Trend analysis gave a small (≈1 ppb/year) decrease of O₃, based on time since 1979. The significance was weak at the 10% level.

J. Allegrini reported interesting nitrous acid (HONO) measurements from the cities of Milan and Rome. He gave evidence for heterogeneous production of this unstable compound. Already early in the morning, the HONO values are quite large (up to 20 ppb in March) and represent a significant source for OH radicals.

M. Millan presented results from aircraft studies over Spain. Driven by inland heating and associated large-scale convergence over the Iberian peninsula, the pollutants move away from coastal source areas toward the interior, reaching high into the troposphere.

F. Fiedler reported on ozone concentrations in the state of Baden-Württemberg and Eulerian modeling for an August 1990 episode. Using a non-hydrostatic meteorology/chemistry model, he showed that local emission reductions have negligible effect on maximum O_3 concentrations in cities because cities in this state are surrounded by other cities and highly populated areas that lie within the transport-determined chemical lifetime of ozone and precursors.

D. Kley, using the EURORADMD model, showed the possible sensitivity of maximum O_3 concentration in cities to automobile speed. At higher speeds, the VOC/ NO_x ratios are low (VOC/ $NO_x \approx 2$ @ Velocity (v) = 30 km/hr) and vice versa (VOC/ $NO_x \approx 3$ @ v = 20 km/hr). This causes a dramatic increase of maximum O_3 concentration for a reduction speed from, say, 30 km/hr to 20 km/hr.

D. Simpson showed results from the European Monitoring and Evaluation Program (EMEP) Lagrangian model. Given the considerable uncertainty of possibly $\pm 500\%$ of isoprene emissions, he calculated the effects of 50% NO_x and 50% VOC reductions on summer-time ozone concentrations under a range of isoprene scenarios. Although maximum ozone events were found to be sensitive to isoprene assumptions, summer-time monthly average ozone values were quite insensitive. Thus, presently, it seems as if model predictions concerning summer-time ozone could give useful policy guidance, independent of the uncertainties in isoprene emissions.

H. Hass showed model results from European Acid Deposition Model (EURAD) for the joint EURAD/TOR case (etc) of summer 1990. The EURAD model is originally based on Mesoscale Meteorological Model-Version 4 (MM4) (now MM5) and RADM2. In this model application, Tropospheric Ozone Research (TOR) observations of critical parameters are compared with model results. The change of emissions, based on different EMEP emission inventories, was used to study the model sensitivity regarding emission changes. For a model sub-region consisting of Germany, Belgium, The Netherlands, and part of northern France, the influence of isoprene emissions was also studied. The important result was that the additional isoprene increase brought little increase of the O_3 maximum in these countries when compared to additional emission increases from anthropogenic sources.

R. Friederich considered a detailed emission inventory for the state of Baden-Wuerttemberg. Based on current emission trends in this state, he concluded that reductions of VOC of 61%, NO_x of 43%, and CO of 70% are expected in the year 2000 compared to 1990. He also predicted that VOC/ NO_x ratios will decrease. Such reductions considered for Baden-Württemberg are expected to reduce ozone by $\approx 10\%$ as compared to Fieldler's model run for the August 1990 base case.

SESSION VI. MODEL APPLICATION & FIELD STUDIES -- USA

This session began with an overview of salient points made in a 1991 National Academy of Science (NAS) report critiquing scientific

understanding underlying efforts in the United States to reduce a perceived widespread ozone problem. Conclusions reached at a November 1993 Air and Waste Management Association (AWMA) Specialty Conference on Measuring and Modeling Photochemical Pollutants were also highlighted. Points receiving particular emphasis were:

- need for ambient data to serve as means for assessing progress in implementing controls and reducing ozone,
- need to better recognize regional nature of ozone incidents in many parts of the United States,
- need to reassess effectiveness of VOC vs. NO_x controls, and
- need to define goals, plan carefully, and maintain good communications among intensive field studies participants.

Recently promulgated regulations to routinely obtain some of the ambient data identified as important were described. The Photochemical Assessment Monitoring Stations (PAMS) network resulting from these regulations will result in an estimated 94 monitoring stations being operated during June - August by the end of 1998, in and near 22 most severely polluted United States cities. Station deployment is ahead of schedule so that almost half are expected to be operational in 1994. Data will be archived and be accessible to the public through the Aerometric Information and Retrieval System (AIRS) system. Air quality measurements include ozone, NO, NO₂, approximately 60 organic species (including carbonyls), and surface meteorological measurements. Meteorological conditions aloft are to be measured at one site per city. Reaction to the PAMS regulations was generally favorable. However, several participants urged NO_y measurements be made and efforts be undertaken to deploy NO/NO₂ instruments capable of measuring concentrations as low as 5-10 ppb with confidence. These NO_y, NO, and NO_x measurements are needed to support the use of observational approaches as corroborative techniques. Many felt that ozone and NO_y measurements constitutes a more definitive means for evaluating photochemical models' performance than does ozone alone. Finally, the need for better measurements aloft was identified.

The session next focused on selected findings from the Southern Oxidants Study (SOS), an ongoing major program of field measurements and interpretive studies undertaken in the southeastern United States during the 1990's. The importance of mobile sources as contributors to measured VOC was first pointed out. Efforts toward developing means for characterizing mobile emission factors using more flexible models with the ability to characterize differing mixes of driving patterns were described. A defined goal is to have a tested approach available early next decade. Parallel efforts to define vehicle activity levels were also noted -- one surprising finding was many more extremely short "trips" occurred than anticipated. A second study to characterize vehicle emission factors in two tunnels (Ft. McHenry and Tuscarora) was described. In these studies, the current EPA MOBILE Emission Factor Model (MOBILE5) was found to perform better than an earlier California model did in characterizing Van Nuys

tunnel data. In fact modeled VOC emissions first appeared to agree reasonably well with observations, whereas NO_x emissions were overestimated. It was speculated that this finding probably reflects use of a driving cycle in the Federal Test Procedure (FTP) underlying the modeling which does not characterize the predominance of the high speed cruise operating mode observed in the tunnels. Need for greater flexibility in the United States emission model is, therefore, implied by these findings. Another significant finding was the importance of semi-volatile (>C10) organic species in diesel emissions. Given Europe's greater prominence of diesel emissions, it was felt to be particularly relevant for German studies. A discussion of the importance of characterizing reactivity of these emissions ensued, with one camp holding that use of concepts such as maximum incremental reactivity (MIR) provided a useful means for ranking importance of emissions, and a second camp maintaining that such results are misleading due to the preeminence of relatively "unreactive" emissions more than compensating for their low MIR ranking.

Results from analyzing VOC data from several rural SOS sites were discussed next. Complexity of resulting chromatographs and presence of overlapping peaks results in significant uncertainties in data interpretation. Oxygenated compounds (acetaldehyde, methanol, and acetone) were typically observed in the 30-60 ppbC range in the afternoon, and constituted about 10% of peak Non-Methane Organic Compound (NMOC) measurements. Other interpretative studies were undertaken to assess relative importance of ozone generation at the earth's surface in rural locations. Two assessment procedures were described: a "radical budget" approach, and the extent to which observations deviated from the photostationary state. The first approach provoked some controversy due to disagreement about the lack of consideration of chain length in its approach. However, both methods appeared to lead to similar conclusions that the near surface area in such locations is a net source for ozone in the mid-afternoon. The highest chemical formation rate for ozone at these sites typically occurred in mid-morning. A third presentation of rural SOS data noted the importance of several oxygenated organics (HCHO, acetone, and acetaldehyde) as important sources of radical production. In all, ozone itself appears to account for about two-thirds of the production with the 3 oxygenates accounting for the remaining third. This finding is encouraging on two counts:

- it appears consistent with reported European findings, and
- it is also consistent with the way in which current chemical models characterize radical production.

Another significant finding was methyl glyoxal (a product of isoprene oxidation) accounting for about half of peroxy radicals leading to PAN formation, with acetaldehyde constituting an important second source.

The presentations' focus, next, shifted to results of regional modeling studies and the trend data interpreting potential importance of VOC and NO_x controls in reducing ozone in the United States. A "matrix" of

Regional Oxidant Model (ROM) across-the-board simulations of VOC and/or NO_x reductions in the eastern half of the United States was summarized. For the Northeast and Midwest, VOC control appears effective in reducing the highest of the episode maximum ozone predictions. More moderate predictions appear increasingly more sensitive to NO_x reductions rather than VOC. In the Southeast, regional ozone generally appears more sensitive to NO_x reduction. PAN and peroxy radical predictions appear similar to the ozone response, while HNO₃ production is nearly proportional to NO_x. Other regional modeling studies focusing on the northeastern United States, were also presented. The regional modeling studies reported to date feature one severe episode which occurred during the first half of July 1988. They are consistent in their findings which suggest:

- NO_x control appears beneficial over a large area, but may be counterproductive in some locations with large NO_x emissions,
- VOC control is primarily effective in reducing the highest ozone concentrations near the largest sources of NO_x and in mitigating counterproductive effects of NO_x control,
- relative effectiveness of VOC and NO_x controls varies day-to-day with meteorological conditions,
- effectiveness of VOC controls appears more sensitive to uncertainties in biogenic emissions than do NO_x control strategies, and
- emissions within the Northeast Transport Region appear to be the primary cause of high ozone in the Northeast Corridor.

The presenters concluded that United States' strategies will most likely have to feature significant reductions in both NO_x and VOC.

The sessions' final presentation noted a downward trend in early morning measured VOC/NO_x ratios which corresponded with downward trends in ozone between the mid/late 1980's and early 1990's in many United States' cities. The trend in the ratio appears primarily due to reductions in VOC. This latter reduction was attributed to major reductions in mobile source emissions arising from fleet turnover and reduced Reid vapor pressure for automotive fuels. Discussion then ensued about whether the early morning VOC/NO_x ratio is a good indicator of effectiveness of VOC vs. NO_x controls. Other studies, such as one in the Lake Michigan area, were noted as supporting use of VOC controls to reduce ozone. Although there was no agreement about early morning VOC/NO_x ratios as a determinant of whether VOC or NO_x control is more effective, it follows that reducing this ratio should make ozone more responsive to additional VOC reductions, though not necessarily as effective as NO_x controls.

SESSION VII. OBSERVATIONAL MODELS/METHODS

Chameides and co-workers described the development of an observation-based approach for inferring ozone-precursor relationships.

This approach uses ozone and precursor concentrations rather than emission inventories to drive photochemical model calculations. The Observation-Based Model (OBM) which consists of a set of mechanistically complete, time-dependent box models, uses observed precursor and ozone concentrations as input, and determines the sensitivity of ozone concentrations at each location to the changes in precursor concentrations. The Observation-Based Application of the Urban Airshed Model (OBA-UAM) uses observed ozone and precursor concentrations to adjust the emissions inventories that drive an emission-based model. A series of OBM runs using data gathered from a 1990 United States EPA study yielded the following conclusions:

- an urban area similar to Atlanta may experience both VOC- and NO_x -limited ozone episodes during the same ozone season,
- high-sensitivity NO afternoon measurements are critical to characterizing urban ozone photochemistry,
- biogenic hydrocarbons play a key role in determining ozone sensitivities to anthropogenic VOC and NO_x emissions in Atlanta, and
- early-morning VOC-to- NO_x ratios are a poor indicator of ozone-precursor relationships in an urban area while the afternoon H_2O_2 -to- HNO_3 ratio shows promise.

Sillman used a photochemical model to identify "indicator species," which are species, or species ratios, that correlate consistently with VOC-sensitive versus NO_x -sensitive ozone in the model. The model was exercised using a range of assumptions to identify indicators that were insensitive to the assumptions. Three such indicators were identified:

- NO_y (or $\text{NO}_y - \text{NO}_x$),
- HCHO/NO_y , and
- $\text{H}_2\text{O}_2/\text{HNO}_3$.

$\Delta \text{O}_3/\Delta \text{NO}_y$ was also investigated as an indicator. The author recommended that these species (especially NO_y) be used as a basis for evaluating photochemical model predictions for VOC-vs- NO_x sensitivity.

Blanchard and co-workers described the Integrated Empirical Rate (IER) model, identified key assumptions and limitations, and developed a set of revisions to IER equations. Predictions from a chemical mechanism, Carbon Bond Mechanism-IV (CBM-IV), and smog-chamber data from chamber studies performed at the University of North Carolina and the University of California at Riverside, were used to demonstrate that the IER expression of maximum Smog Produced (SP_{max}) as a linear function of initial NO_x should be replaced with the function $\text{SP}_{\text{max}} = \beta [\text{NO}_x(0)]^\alpha$, where $\alpha < 1$. The authors also showed that Smog Produced (SP) could be expressed as $\text{SP} = \beta [\text{NO}_x(0) - \text{NO}_x(t)]^\alpha$, derived three equivalent expressions for extent of reaction, and identified the measurements required for calculating extent using each expression.

Kelly and Wang described a set of smog chamber experiments performed to test the Integrated Empirical Rate (IER) model and to evaluate the use of the IER for determining reactivity. Smog (NO oxidized plus O₃ formed) was used as the response variable. The authors varied initial NO at fixed VOC concentration, and added VOC or NO_x during the course of irradiations. For a constant radiation flux, NO(0) = 0.4 ppm, and VOC(0) varying from 2.0 to 2.42 ppm propene, smog formation was not linear with respect to irradiation time for the entire radiation. Delta smog was a linear function of irradiation for some compounds, but not for others. The rate of smog formation was independent of the initial NO concentration, which was varied from 0.4 to 0.58 ppm NO, for about the first half of the irradiation period. Addition of 0.4 ppm NO to a chamber in which VOC(0) = 2.0 ppm and NO(0) = 0.4 ppm halted smog formation, which was interpreted as an NO₂ inhibition effect.

For Hurley and co-workers, Japar reported:

- Application of the IER model (in the form of the AIRTRAK instrument) to the measurement of VOC reactivities shows promise;
- There appears to be significant sensitivity to initial conditions, perhaps indicating a poor representation of radical sources needed to initiate chemistry and thus sensitivity can have a serious impact on measurements' reproducibility; and
- Relationship between reactivities calculated from the IER model and airshed modeling is unclear.

7.1 PANEL DISCUSSION ON OBSERVATION-BASED MODELS AND METHODS

The panelists and audience were asked to discuss recommended applications of observational data/methods, existing major scientific issues in the observational methodology area, current research needs and their priorities, and plans for such research in the United States, Europe, and elsewhere.

The major portion of the ensued discussion -- repeated by several individuals -- was concern that observational-based approaches would be used in place of the full dynamical/photochemical simulations. There was wide spread support for the concept of using observations-based approaches in an attempt to corroborate (or refute) the accuracy of model applications or to constrain the standard models. It was pointed out that observations-based approaches in place of current dynamical/photochemical models (UAM, ROM, etc.) would be problematic. Among the concerns for overall accuracy of the observations-based approaches were:

- Concentrations of many species (especially, primary species) are spatially inhomogeneous and, especially, have height variance. Individual measurements (especially, surface measurements) may not represent the ozone-forming process as a whole.

- Some of the observations-based approaches seem too simplified and may omit the real atmosphere complexity.

- Uncertainties associated with observational-based approaches need to be identified and (if possible) quantified. For a useful model, the uncertainties must not overwhelm the information.

- Measurements do not represent "perfect information". In fact, measurements often have considerable uncertainty and concern was expressed that some approaches depend on measurements that are very difficult to make.

Despite these concerns, which point to future research directions, there was widespread support for observational-based approaches as a complement to standard models. It was pointed out that observational-based approaches represent a new and (hopefully) intelligent attempt to make use of atmospheric measurements and identify strengths and weaknesses in the current knowledge of the ozone-formation process.

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