

Disclaimer

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Preface

In 1971, the U.S. Environmental Protection Agency (EPA) promulgated National Ambient Air Quality Standards (NAAQS) to protect the public health and welfare from adverse effects of photochemical oxidants. In 1979, the chemical designation of the standards was changed from photochemical oxidants to ozone (O₃). This document focuses primarily on the scientific air quality criteria for O₃ and, to a lesser extent, on those for other photochemical oxidants such as hydrogen peroxide and the peroxyacyl nitrates.

The EPA promulgates the NAAQS on the basis of scientific information contained in air quality criteria issued under Section 108 of the Clean Air Act. The previous O₃ criteria document, *Air Quality Criteria for Ozone and Other Photochemical Oxidants*, was released in August 1986 and a supplement, *Summary of Selected New Information on Effects of Ozone on Health and Vegetation*, was released in January 1992. These documents were the basis for a March 1993 decision by EPA that revision of the existing 1-h NAAQS for O₃ was not appropriate at that time. That decision, however, did not take into account some of the newer scientific data that became available after completion of the 1986 criteria document. The purpose of this revised air quality criteria document for O₃ and related photochemical oxidants is to critically evaluate and assess the latest scientific data associated with exposure to the concentrations of these pollutants found in ambient air. Emphasis is placed on the presentation of health and environmental effects data; however, other scientific data are presented and evaluated in order to provide a better understanding of the nature, sources, distribution, measurement, and concentrations of O₃ and related photochemical oxidants and their precursors in the environment. Although the document is not intended to be an exhaustive literature review, it is intended to cover all pertinent literature available through 1995.

This document was prepared and peer reviewed by experts from various state and Federal governmental offices, academia, and private industry and reviewed in several public meetings by the Clean Air Scientific Advisory Committee. The National Center for Environmental Assessment (formerly the Environmental Criteria and Assessment Office) of EPA's Office of Research and Development acknowledges with appreciation the contributions provided by these authors and reviewers as well as the diligence of its staff and contractors in the preparation of this document at the request of the Office of Air Quality Planning and Standards.

***Air Quality Criteria for Ozone
and Related Photochemical Oxidants***

Table of Contents

Volume I

1. Executive Summary	1-1
2. Introduction	2-1
3. Tropospheric Ozone and Its Precursors	3-1
4. Environmental Concentrations, Patterns, and Exposure Estimates	4-1
Appendix A: Abbreviations and Acronyms	A-1

Volume II

5. Environmental Effects of Ozone and Related Photochemical Oxidants	5-1
Appendix A: Abbreviations and Acronyms	A-1
Appendix B: Colloquial and Latin Names	B-1

Volume III

6. Toxicological Effects of Ozone and Related Photochemical Oxidants ...	6-1
7. Human Health Effects of Ozone and Related Photochemical Oxidants ...	7-1
8. Extrapolation of Animal Toxicological Data to Humans	8-1
9. Integrative Summary of Ozone Health Effects	9-1
Appendix A: Abbreviations and Acronyms	A-1

Table of Contents

	<u>Page</u>
List of Tables	I-xiii
List of Figures	I-xviii
Authors, Contributors, and Reviewers	I-xxv
U.S. Environmental Protection Agency Science Advisory Board, Clean Air Scientific Advisory Committee	I-xxxix
U.S. Environmental Protection Agency Project Team for Development of Air Quality Criteria for Ozone and Related Photochemical Oxidants	I-xxxiii
1. EXECUTIVE SUMMARY	1-1
1.1 INTRODUCTION	1-1
1.2 LEGISLATIVE AND REGULATORY BACKGROUND	1-1
1.3 TROPOSPHERIC OZONE AND ITS PRECURSORS	1-2
1.4 ENVIRONMENTAL CONCENTRATIONS, PATTERNS, AND EXPOSURE ESTIMATES	1-9
1.5 ENVIRONMENTAL EFFECTS OF OZONE AND RELATED PHOTOCHEMICAL OXIDANTS	1-12
1.6 TOXICOLOGICAL EFFECTS OF OZONE AND RELATED PHOTOCHEMICAL OXIDANTS	1-18
1.7 HUMAN HEALTH EFFECTS OF OZONE AND RELATED PHOTOCHEMICAL OXIDANTS	1-22
1.8 EXTRAPOLATION OF ANIMAL TOXICOLOGICAL DATA TO HUMANS	1-27
1.9 INTEGRATIVE SUMMARY OF OZONE HEALTH EFFECTS	1-28
2. INTRODUCTION	2-1
2.1 LEGISLATIVE BACKGROUND	2-2
2.2 REGULATORY BACKGROUND	2-2
2.3 SUMMARY OF MAJOR SCIENTIFIC TOPICS PRESENTED	2-5
2.3.1 Air Chemistry	2-5
2.3.2 Air Quality	2-5
2.3.3 Environmental Effects	2-5
2.3.4 Health Effects	2-6
2.4 ORGANIZATION AND CONTENT OF THE DOCUMENT	2-6
REFERENCES	2-8
3. TROPOSPHERIC OZONE AND ITS PRECURSORS	3-1
3.1 INTRODUCTION	3-1

Table of Contents (cont'd)

		<u>Page</u>
3.2	TROPOSPHERIC OZONE CHEMISTRY	3-2
	3.2.1 Background Information	3-2
	3.2.2 Structure of the Atmosphere	3-3
	3.2.2.1 Vertical and Horizontal Mixing in the Atmosphere	3-4
	3.2.2.2 Formation of Stratospheric Ozone	3-4
	3.2.3 Background Ozone in the Troposphere	3-6
	3.2.3.1 Tropospheric Hydroxyl Radicals	3-7
	3.2.3.2 Tropospheric Nitrogen Oxides Chemistry	3-8
	3.2.3.3 The Methane Oxidation Cycle	3-10
	3.2.3.4 Cloud Processes in the Methane-Dominated Troposphere	3-15
	3.2.4 Photochemistry of the Polluted Atmosphere	3-16
	3.2.4.1 Tropospheric Loss Processes of Volatile Organic Compounds	3-17
	3.2.4.2 Chemical Formation of Ozone in Polluted Air	3-30
	3.2.4.3 Hydrocarbon Reactivity with Respect to Ozone Formation	3-34
	3.2.5 Photochemical Production of Aerosols	3-38
	3.2.5.1 Phase Distributions of Organic Compounds ...	3-38
	3.2.5.2 Acid Deposition	3-40
3.3	METEOROLOGICAL PROCESSES INFLUENCING OZONE FORMATION AND TRANSPORT	3-42
	3.3.1 Meteorological Processes	3-42
	3.3.1.1 Surface Energy Budgets	3-42
	3.3.1.2 Planetary Boundary Layer	3-43
	3.3.1.3 Cloud Venting	3-46
	3.3.1.4 Stratospheric-Tropospheric Ozone Exchange	3-47
	3.3.2 Meteorological Parameters	3-48
	3.3.2.1 Sunlight	3-48
	3.3.2.2 Temperature	3-49
	3.3.2.3 Wind Speed	3-54
	3.3.2.4 Air Mass Characteristics	3-56
	3.3.3 Normalization of Trends	3-58
3.4	PRECURSORS OF OZONE AND OTHER OXIDANTS	3-59
	3.4.1 Sources and Emissions of Precursors	3-59
	3.4.1.1 Introduction	3-59
	3.4.1.2 Nitrogen Oxides	3-60
	3.4.1.3 Volatile Organic Compounds	3-70

Table of Contents (cont'd)

		<u>Page</u>
	3.4.1.4 Relationship of Summertime Precursor Emissions and Ozone Production	3-79
3.4.2	Concentrations of Precursor Substances in Ambient Air	3-80
	3.4.2.1 Nonmethane Organic Compounds	3-81
	3.4.2.2 Nitrogen Oxides	3-84
	3.4.2.3 Ratios of Concentrations of Nonmethane Organic Compounds and Nitrogen Oxides	3-85
3.4.3	Source Apportionment and Reconciliation	3-86
	3.4.3.1 Source Apportionment	3-86
	3.4.3.2 Source Reconciliation	3-89
3.5	ANALYTICAL METHODS FOR OXIDANTS AND THEIR PRECURSORS	3-90
3.5.1	Sampling and Analysis of Ozone and Other Oxidants	3-90
	3.5.1.1 Ozone	3-90
	3.5.1.2 Peroxyacetyl Nitrate and Its Homologues	3-101
	3.5.1.3 Gaseous Hydrogen Peroxide	3-105
3.5.2	Sampling and Analysis of Volatile Organic Compounds	3-107
	3.5.2.1 Introduction	3-107
	3.5.2.2 Nonmethane Hydrocarbons	3-108
	3.5.2.3 Carbonyl Species	3-114
	3.5.2.4 Polar Volatile Organic Compounds	3-116
3.5.3	Sampling and Analysis of Nitrogen Oxides	3-117
	3.5.3.1 Introduction	3-117
	3.5.3.2 Measurement of Nitric Oxide	3-118
	3.5.3.3 Measurements for Nitrogen Dioxide	3-120
	3.5.3.4 Calibration Methods	3-126
3.6	OZONE AIR QUALITY MODELS	3-127
3.6.1	Definitions, Description, and Uses	3-128
	3.6.1.1 Grid-Based Models	3-129
	3.6.1.2 Trajectory Models	3-131
3.6.2	Model Components	3-133
	3.6.2.1 Emissions Inventory	3-133
	3.6.2.2 Meteorological Input to Air Quality Models	3-135
	3.6.2.3 Chemical Mechanisms	3-139
	3.6.2.4 Deposition Processes	3-140
	3.6.2.5 Boundary and Initial Conditions	3-143
	3.6.2.6 Numerical Methods	3-143

Table of Contents (cont'd)

		<u>Page</u>
3.6.3	Urban and Regional Ozone Air Quality Models	3-144
	3.6.3.1 The Urban Airshed Model	3-148
	3.6.3.2 The Regional Oxidant Model	3-151
	3.6.3.3 The Regional Acid Deposition Model	3-154
3.6.4	Evaluation of Model Performance	3-156
	3.6.4.1 Model Performance Evaluation Procedures	3-157
	3.6.4.2 Performance Evaluation of Ozone Air Quality Models	3-159
	3.6.4.3 Database Limitations	3-160
3.6.5	Use of Ozone Air Quality Models for Evaluating Control Strategies	3-162
3.6.6	Conclusions	3-163
3.7	SUMMARY AND CONCLUSIONS	3-165
3.7.1	Tropospheric Ozone Chemistry	3-165
	3.7.1.1 Ozone in the Unpolluted Atmosphere	3-165
	3.7.1.2 Ozone Formation in the Polluted Troposphere	3-166
3.7.2	Meteorological Processes Influencing Ozone Formation and Transport	3-168
	3.7.2.1 Meteorological Processes	3-168
	3.7.2.2 Meteorological Parameters	3-168
	3.7.2.3 Normalization of Trends	3-169
3.7.3	Precursors	3-169
	3.7.3.1 Volatile Organic Compound Emissions	3-169
	3.7.3.2 Nitrogen Oxides Emissions	3-169
	3.7.3.3 Concentrations of Volatile Organic Compounds in Ambient Air	3-170
	3.7.3.4 Concentrations of Nitrogen Oxides in Ambient Air	3-170
	3.7.3.5 Ratios of Concentrations of Nonmethane Organic Compounds to Nitrogen Oxides	3-171
	3.7.3.6 Source Apportionment and Reconciliation	3-171
3.7.4	Analytical Methods for Oxidants and Their Precursors	3-172
	3.7.4.1 Oxidants	3-172
	3.7.4.2 Volatile Organic Compounds	3-173
	3.7.4.3 Oxides of Nitrogen	3-174
3.7.5	Ozone Air Quality Models	3-174
	3.7.5.1 Definitions, Descriptions, and Uses	3-174
	3.7.5.2 Model Components	3-175
	3.7.5.3 Evaluation of Model Performance	3-176

Table of Contents (cont'd)

	<u>Page</u>
3.7.5.4 Use of Ozone Air Quality Model for Evaluating Control Strategies	3-176
3.7.5.5 Conclusions	3-176
REFERENCES	3-177
4. ENVIRONMENTAL CONCENTRATIONS, PATTERNS, AND EXPOSURE ESTIMATES	4-1
4.1 INTRODUCTION	4-1
4.1.1 Characterizing Ambient Ozone Concentrations	4-2
4.1.2 The Identification and Use of Existing Ambient Ozone Data	4-4
4.2 TRENDS IN AMBIENT OZONE CONCENTRATIONS	4-6
4.3 SURFACE OZONE CONCENTRATIONS	4-14
4.3.1 Introduction	4-14
4.3.2 Urban Area Concentrations	4-15
4.3.3 Nonurban Area Concentrations	4-27
4.3.3.1 Sites That Experience Low Maximum Hourly Average Concentrations	4-27
4.3.3.2 Urban-Influenced Nonurban Areas	4-36
4.4 DIURNAL VARIATIONS IN OZONE CONCENTRATIONS	4-46
4.4.1 Introduction	4-46
4.4.2 Urban Area Diurnal Patterns	4-47
4.4.3 Nonurban Area Diurnal Patterns	4-51
4.5 SEASONAL PATTERNS IN OZONE CONCENTRATIONS	4-55
4.5.1 Urban Area Seasonal Patterns	4-55
4.5.2 Nonurban Area Seasonal Patterns	4-57
4.5.3 Seasonal Pattern Comparisons with Sites Experiencing Low Exposures	4-61
4.6 SPATIAL VARIATIONS IN OZONE CONCENTRATIONS	4-62
4.6.1 Urban-Nonurban Area Concentration Differences	4-62
4.6.2 Concentrations Experienced at High-Elevation Sites	4-62
4.6.3 Other Spatial Variations in Ozone Concentrations	4-65
4.7 INDOOR OZONE CONCENTRATIONS	4-72
4.8 ESTIMATING EXPOSURE TO OZONE	4-73
4.8.1 Introduction	4-73
4.8.2 Fixed-Site Monitoring Information Used To Estimate Population and Vegetation Exposure	4-76
4.8.3 Personal Monitors	4-77
4.8.4 Population Exposure Models	4-78
4.8.5 Concentration and Exposures Used in Research Experiments	4-80

Table of Contents (cont'd)

	<u>Page</u>
4.9 CONCENTRATIONS OF PEROXYACETYL NITRATES IN AMBIENT ATMOSPHERES	4-81
4.9.1 Introduction	4-81
4.9.2 Urban Area Peroxyacetyl Nitrate Concentrations	4-82
4.9.3 Concentration of Peroxyacetyl Nitrate and Peroxypropionyl Nitrate in Rural Areas	4-83
4.10 CONCENTRATION AND PATTERNS OF HYDROGEN PEROXIDE IN THE AMBIENT ATMOSPHERE	4-86
4.11 CO-OCCURRENCE OF OZONE	4-88
4.11.1 Introduction	4-88
4.11.2 Nitrogen Oxides	4-89
4.11.3 Sulfur Dioxide	4-89
4.11.4 Acidic Sulfate Aerosols	4-90
4.11.5 Acid Precipitation	4-91
4.11.6 Acid Cloudwater	4-93
4.12 SUMMARY	4-94
REFERENCES	4-102
APPENDIX A: ABBREVIATIONS AND ACRONYMS	A-1

List of Tables

<u>Number</u>		<u>Page</u>
2-1	National Ambient Air Quality Standards for Ozone	2-3
3-1	Estimated Emissions of Methane, Nonmethane Organic Compounds, Nitrous Oxide, and Nitrogen Oxides into the Earth's Atmosphere from Biogenic and Anthropogenic Sources	3-16
3-2	Calculated Tropospheric Lifetimes of Selected Volatile Nonmethane Organic Compounds Due to Photolysis and Reaction with Hydroxyl and Nitrate Radicals and with Ozone	3-19
3-3	Calculated Incremental Reactivities of Selected Volatile Organic Compounds as a Function of the Volatile Organic Compound/Nitrogen Oxide Ratio for an Eight-Component Volatile Organic Compound Mixture and Low-Dilution Conditions	3-37
3-4	Rates of Increase of Peak Ozone with Diurnal Maximum Temperature for Temperature Less Than 300 K and Temperature Greater Than 300 K, Based on Measurements for April 1 to September 30, 1988	3-52
3-5	Recent Studies Examining Trends in Ozone Data After Removal of Variability Associated with Meteorological Factors	3-60
3-6	Source Categories Used To Inventory Nitrogen Oxides Emissions	3-62
3-7	1991 Emission Estimates for Manmade Sources of Nitrogen Oxides in the United States	3-63
3-8	Recent Trends in Nitrogen Oxides Emissions for Major Manmade Source Categories	3-66
3-9	Comparison of Estimates of Nitrogen Oxides Emissions from Manmade Sources in the United States	3-68
3-10	Annual Nitrogen Oxides Emissions from Soils by U.S. Environmental Protection Agency Region	3-69

List of Tables (cont'd)

<u>Number</u>		<u>Page</u>
3-11	Estimated 1991 Emissions of Volatile Organic Compounds from Manmade Sources in the United States	3-71
3-12	Recent Trends in Emissions of Volatile Organic Compounds from Major Categories of Manmade Sources	3-73
3-13	Annual Biogenic Hydrocarbon Emission Inventory for the United States	3-77
3-14	Annual Biogenic Hydrocarbon Emission Inventory by Month and by U.S. Environmental Protection Agency Region for United States Emissions	3-78
3-15	Performance Specifications for Automated Methods of Ozone Analysis	3-92
3-16	Reference and Equivalent Methods for Ozone Designated by the U.S. Environmental Protection Agency	3-93
3-17	List of Designated Reference and Equivalent Methods for Ozone	3-94
3-18	Performance Specifications for Nitrogen Dioxide Automated Methods	3-121
3-19	Comparability Test Specifications for Nitrogen Dioxide	3-121
3-20	Reference and Equivalent Methods for Nitrogen Dioxide Designated by the U.S. Environmental Protection Agency	3-122
3-21	Grid-Based Urban and Regional Air Pollution Models: Overview of Three-Dimensional Air Quality Models	3-145
3-22	Grid-Based Urban and Regional Air Pollution Models: Treatment of Emissions and Spatial Resolution	3-146
3-23	Grid-Based Urban and Regional Air Pollution Models: Treatment of Meteorological Fields, Transport, and Dispersion	3-147
3-24	Grid-Based Urban and Regional Air Pollution Models: Treatment of Chemical Processes	3-149

List of Tables (cont'd)

<u>Number</u>		<u>Page</u>
3-25	Grid-Based Urban and Regional Air Pollution Models: Treatment of Cloud and Deposition Processes	3-150
3-26	Regional Oxidant Model Geographical Domains	3-152
3-27	Applications of Photochemical Air Quality Models to Evaluating Ozone	3-164
4-1	Ozone Monitoring Season by State	4-5
4-2	Summary by Forestry and Agricultural Regions for Ozone Trends Using the W126 Exposure Parameter Accumulated on a Seasonal Basis	4-13
4-3	The Highest Second Daily Maximum One-Hour Ozone Concentration by Metropolitan Statistical Area for the Years 1989 to 1991	4-17
4-4	Summary of Percentiles of Hourly Average Concentrations for the April-to-October Period	4-20
4-5	The Highest Second Daily Maximum Eight-Hour Average Ozone Concentration by Metropolitan Statistical Area for the Years 1989 to 1991	4-22
4-6	Seasonal (April to October) Percentile Distribution of Hourly Ozone Concentrations, Number of Hourly Mean Ozone Occurrences Greater Than or Equal to 0.08 and Greater Than or Equal to 0.10, Seasonal Seven-Hour Average Concentrations, W126, and SUM06 Values for Sites Experiencing Low Hourly Average Concentrations with Data Capture Greater Than or Equal to 75%	4-30
4-7	Seasonal (April to October) Percentile Distribution of Hourly Ozone Concentrations, Number of Hourly Mean Ozone Occurrences Greater Than or Equal to 0.08 and Greater Than or Equal to 0.10, Seasonal Seven-Hour Average Concentrations, and W126 Values for Three "Clean" National Forest Sites with Data Capture Greater Than or Equal to 75%	4-33

List of Tables (cont'd)

<u>Number</u>		<u>Page</u>
4-8	The Value of the W126 Sigmoidal Exposure Parameter Calculated Over the Annual Period	4-34
4-9	The Value of the Ozone Season (Seven-Month) Average of the Daily Seven-Hour (0900 to 1559 Hours) Concentration	4-35
4-10	Summary of Percentiles, Number of Hourly Occurrences Greater Than or Equal to 0.10 ppm, and Three-Month SUM06 Values for Selected Rural Ozone Monitoring Sites in 1989 (April to October)	4-37
4-11	Summary of Percentiles of Hourly Average Concentrations for Electric Power Research Institute Sulfate Regional Experiment Program Sites/Eastern Regional Air Quality Study Ozone Monitoring Sites	4-38
4-12	Seven-Hour Growing Season Mean, W126 Values, and Number of Hourly Ozone Concentrations Greater Than or Equal to 80 ppb for Selected Eastern National Dry Deposition Network Sites	4-40
4-13	Summary of Percentiles for National Dry Deposition Network Monitoring Sites	4-41
4-14	Description of Mountain Cloud Chemistry Program Sites	4-63
4-15	Seasonal (April to October) Percentiles, SUM06, SUM08, and W126 Values for the Mountain Cloud Chemistry Program Sites	4-64
4-16	Summary Statistics for 11 Integrated Forest Study Sites	4-67
4-17	Quarterly Maximum One-Hour Ozone Values at Sites in and Around New Haven, Connecticut, 1976	4-69
4-18	Summary of Reported Indoor-Outdoor Ozone Ratios	4-74
4-19	Summary of Measurements of Peroxyacetyl Nitrate and Peroxypropionyl Nitrate in Urban Areas	4-84

List of Tables (cont'd)

<u>Number</u>		<u>Page</u>
4-20	Summary of Measurements of Peroxyacetyl Nitrate and Peroxypropionyl Nitrate in Rural Areas	4-87

List of Figures

<u>Number</u>		<u>Page</u>
3-1	The cyclic reactions of tropospheric nitrogen oxides	3-10
3-2	Atmospheric reactions in the complete oxidation of methane	3-13
3-3	Cyclic reactions of methane oxidation to formaldehyde, conversion of nitric oxide to nitrogen dioxide, and concomitant formation of ozone in the atmosphere	3-15
3-4	Major steps in production of ozone in ambient air	3-31
3-5	Time-concentration profiles for selected species during irradiations of a nitrogen oxide-propene-air mixture in an indoor chamber with constant light intensity	3-32
3-6	Time-concentration profiles for selected species during irradiations of a nitrogen oxide-propene-air mixture in an outdoor chamber with diurnally varying light intensity	3-32
3-7	Surface radiation budget for short- and long-wave radiation	3-43
3-8	The number of reports of ozone concentrations greater than or equal to 120 ppb at the 17 cities studied in Samson and Shi (1988)	3-50
3-9	A scatter plot of maximum daily ozone concentration in Atlanta, Georgia, and New York, New York, versus maximum daily temperature	3-51
3-10	A scatter plot of maximum daily ozone concentration in Detroit, Michigan, and Phoenix, Arizona, versus maximum daily temperature	3-51
3-11	A scatter plot of maximum ozone concentration versus maximum daily temperature for four nonurban sites	3-52

List of Figures (cont'd)

<u>Number</u>		<u>Page</u>
3-12	The frequency of 24-hour trajectory transport distance en route to city when ozone was greater than or equal to 120 ppb in four Southern U.S. cities, compared with the percent frequency distribution for all 17 cities of a nationwide study, 1983 to 1985	3-55
3-13	The frequency of 24-hour trajectory transport distance en route to city when ozone was greater than or equal to 120 ppb in four New England cities, compared with the percent frequency distribution for all 17 cities of a nationwide study, 1983 to 1985	3-55
3-14	The root-mean-square-difference between CLASS observations and profiler observations as a function of height above ground level	3-56
3-15	The root-mean-square-difference between CLASS observations and lidar observations as a function of height above ground level	3-57
3-16	Model of ozone levels using regression techniques	3-58
3-17	Simulated versus observed ozone levels using regression techniques on an independent data set obtained in the summer of 1992 in Atlanta, Georgia	3-59
3-18	The 50 largest sources of nitrogen oxides (power plants) in the United States	3-63
3-19	Nitrogen oxides emissions from manmade sources in the 10 U.S. Environmental Protection Agency regions of the United States, 1991	3-64
3-20	Changes in nitrogen oxides emissions from manmade sources in the United States, 10-year intervals, 1940 through 1990	3-65
3-21	Changes in nitrogen oxides emissions from stationary source fuel combustion and transportation from 1940 through 1990	3-66

List of Figures (cont'd)

<u>Number</u>		<u>Page</u>
3-22	Changes in emissions of volatile organic compounds from major manmade sources in the United States, 10-year intervals, 1940 through 1990	3-72
3-23	Changes in emissions of volatile organic compounds from major manmade sources, 1940 through 1990	3-73
3-24	Estimated biogenic emissions of volatile organic compounds in the United States as a function of season	3-80
3-25	Example of Empirical Kinetic Modeling Approach diagram for high-oxidant urban area	3-132
3-26	Regional oxidant model superdomain with modeling domains	3-153
4-1	National trend in the composite average of the second highest maximum one-hour ozone concentration at both National Air Monitoring Stations and all sites with 95% confidence intervals, 1983 to 1992	4-7
4-2	The annually averaged composite diurnal curves for the following sites that changed from nonattainment to attainment status: Montgomery County, Alabama; Concord, California; Louisville, Kentucky; and Dade County, Florida; for the period 1987 to 1990	4-10
4-3	A summary of the seasonal (January to December) averaged composite ozone diurnal curve and integrated exposure W126 index for the Los Angeles, California, site for the period 1980 to 1991	4-11
4-4	United States map of the highest second daily maximum one-hour average ozone concentration by Metropolitan Statistical Area, 1991	4-16
4-5	The relationship between the second highest daily maximum hourly average ozone concentration and the maximum three-month SUM06 value and the second highest daily maximum eight-hour average ozone concentration and the maximum three-month SUM06 value for specific site years at rural agricultural sites for the 1980-to-1991 period	4-24

List of Figures (cont'd)

<u>Number</u>		<u>Page</u>
4-6	The relationship between the second highest daily maximum hourly average ozone concentration and the maximum three-month SUM06 value and the second highest daily maximum eight-hour average ozone concentration and the maximum three-month SUM06 value for specific site years at rural forested sites for the 1980-to-1991 period	4-25
4-7	The location of National Dry Deposition Network monitoring sites as of December 1990	4-39
4-8	The kriged 1985 to 1986 maximum seven-hour and 12-hour average concentrations of ozone across the United States	4-44
4-9	The kriged estimates of the W126 integrated ozone exposure index for the eastern United States for 1988 and 1989	4-45
4-10	The comparison of the seasonal diurnal patterns using 1988 data for Jefferson County, Kentucky, and Oliver County, North Dakota	4-48
4-11	Diurnal behavior of ozone at rural sites in the United States in July	4-49
4-12	Percent of time hourly average concentrations greater than or equal to 0.1 ppm occurred between 0900 and 1559 hours in comparison to 24-hour period for all rural agricultural and forested sites with three-month SUM06 greater than or equal to 26.4 ppm per hour	4-50
4-13	Percent of time hourly average concentrations greater than or equal to 0.1 ppm occurred between 0900 and 1559 hours in comparison to 24-hour period for all non-California rural agricultural and forested sites with three-month SUM06 greater than or equal to 26.4 ppm per hour	4-50
4-14	Diurnal pattern of one-hour ozone concentrations on July 13, 1979, Philadelphia, Pennsylvania	4-51
4-15	Diurnal and one-month composite diurnal variations in ozone concentrations, Washington, District of Columbia, July 1981	4-52

List of Figures (cont'd)

<u>Number</u>		<u>Page</u>
4-16	Diurnal and one-month composite diurnal variations in ozone concentrations, St. Louis County, Missouri, September 1981	4-53
4-17	Diurnal and one-month composite diurnal variations in ozone concentrations, Alton, Illinois, October 1981 (fourth quarter)	4-54
4-18	Composite diurnal patterns of ozone concentrations by quarter, Alton, Illinois, 1981	4-55
4-19	Quarterly composite diurnal patterns of ozone concentrations at selected sites representing potential for exposure of major crops, 1981	4-56
4-20	Composite diurnal ozone pattern at a rural National Crop Loss Assessment Network site in Argonne, Illinois, August 6 through September 30, 1980	4-57
4-21	Composite diurnal ozone pattern at selected National Dry Deposition Network sites	4-58
4-22	Composite diurnal pattern at Whiteface Mountain, New York, and the Mountain Cloud Chemistry Program Shenandoah National Park site for May to September 1987	4-59
4-23	Seasonal variations in ozone concentrations as indicated by monthly averages and the one-hour maximum in each month at selected sites, 1981	4-60
4-24	Seven- and 12-hour means at Whiteface Mountain and Shenandoah National Park for May to September 1987 and integrated exposures at Whiteface Mountain and Shenandoah National Park for May to September 1987	4-65
4-25	Integrated exposures for three non-Mountain Cloud Chemistry Program Shenandoah National Park sites, 1983 to 1987	4-66
4-26	Number of days in 1991 for which the maximum hourly average ozone concentration was greater than 0.1 ppm at Chicago, Illinois	4-70

List of Figures (cont'd)

<u>Number</u>		<u>Page</u>
4-27	Maximum one-hour ozone concentrations and average 0800 to 2000 hours strong acid concentrations for each day that pulmonary function data were collected at Fairview Lake camp in 1988	4-78
4-28	Maximal one-hour ozone concentrations at Fairview Lake during the study period	4-79
4-29	The number of occurrences for each of the seven categories described in text	4-82
4-30	The co-occurrence pattern of ozone and sulfuric acid for July 25, 1986, at a summer camp on the north shore of Lake Erie, Ontario, Canada	4-91
4-31	Sulfate, hydrogen ion, and ozone measured at Breadalbane Street (Site 3) in Toronto during July and August, 1986, 1987, and 1988	4-92

Authors, Contributors, and Reviewers

Chapter 1. Executive Summary

Principal Authors

Mr. James A. Raub—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. William G. Ewald—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. J.H.B. Garner—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Judith A. Graham—National Exposure Research Laboratory (MD-75), U.S. Environmental
Protection Agency, Research Triangle Park, NC 27711

Ms. Beverly E. Tilton—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Chapter 2. Introduction

Principal Author

Mr. James A. Raub—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Chapter 3. Tropospheric Ozone and Its Precursors

Principal Authors

Dr. A. Paul Altshuller—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Roger Atkinson—Statewide Air Pollution Research Center, University of California,
900 Watkins Avenue, Riverside, CA 92521

Mr. Michael W. Holdren—Battelle, 505 King Avenue, Columbus, OH 43201

Dr. Thomas J. Kelly—Battelle, 505 King Avenue, Columbus, OH 43201-2693

Authors, Contributors, and Reviewers (cont'd)

Dr. Charles W. Lewis—National Exposure Research Laboratory (MD-47) U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Perry J. Samson—Department of Atmospheric, Oceanic, and Space Sciences, University of Michigan, 2455 Hayward Street, Ann Arbor, MI 48109

Dr. John H. Seinfeld—Division of Engineering and Applied Science, California Institute of Technology, 391 South Holliston Avenue, Pasadena, CA 91125

Dr. Joseph Sickles II—National Exposure Research Laboratory (MD-75), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Ms. Beverly E. Tilton—National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Halvor (Hal) Westberg—Department of Civil and Environmental Engineering, Washington State University, Pullman, WA 99164

Reviewers

Dr. A. Paul Altshuller—National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Robert R. Arnts—National Exposure Research Laboratory (MD-84) U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Frank M. Black—National Exposure Research Laboratory (MD-46), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Joseph J. Bufalini—National Exposure Research Laboratory (MD-84), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Daewon Byun—National Exposure Research Laboratory (MD-80), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Jason K. S. Ching—National Exposure Research Laboratory (MD-80), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Kenneth L. Demerjian—Atmospheric Sciences Research Center (SUNY-Albany), 100 Fuller Road, Albany NY 12205

Authors, Contributors, and Reviewers (cont'd)

Dr. Robin L. Dennis—National Exposure Research Laboratory (MD-80), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Basil Dimitriadis—National Exposure Research Laboratory (MD-75), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Marcia C. Dodge—National Exposure Research Laboratory (MD-84), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Chris D. Geron—National Risk Management Laboratory (MD-62), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Michael W. Gery—Atmospheric Research Associates, 160 North Washington Street, Boston, MA 02114

Dr. James M. Godowitch—National Exposure Research Laboratory (MD-80), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Jimmie W. Hodgeson—National Exposure Research Laboratory (MD-84), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Harvey E. Jeffries—Department of Environmental Sciences and Engineering, School of Public Health, CB #7400, University of North Carolina, Chapel Hill, North Carolina 27599-7400

Dr. Douglas R. Lawson—Energy and Environmental Engineering Center, Desert Research Institute, Reno, NV 89506

Dr. Charles W. Lewis—National Exposure Research Laboratory (MD-47), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. William A. Lonneman—National Exposure Research Laboratory (MD-84), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. William A. McClenny—National Exposure Research Laboratory (MD-44), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Frank F. McElroy—National Exposure Research Laboratory (MD-77), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Thomas B. McMullen—Office of Air Quality Planning and Standards (MD-14), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Authors, Contributors, and Reviewers (cont'd)

Dr. Edwin L. Meyer—Office of Air Quality Planning and Standards (MD-14),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. David C. Misenheimer—Office of Air Quality Planning and Standards (MD-14),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. J. David Mobley—Office of Air Quality Planning and Standards (MD-14),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Will Ollison—American Petroleum Institute, 1220 L Street NW, Washington, DC 20005

Dr. Kenneth Olszyna—Tennessee Valley Authority, CEB 2A, Muscle Shoals, AL 35660

Mr. Thomas E. Pierce—National Exposure Research Laboratory (MD-80), U.S. Environmental
Protection Agency, Research Triangle Park, NC 27711

Mr. Larry J. Purdue—National Exposure Research Laboratory (MD-56), U.S. Environmental
Protection Agency, Research Triangle Park, NC 27711

Mr. Kenneth A. Rehme—National Exposure Research Laboratory (MD-77),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Harold G. Richter—Private consultant, 8601 Little Creek Farm Road, Chapel Hill, NC
27516

Mr. Shawn J. Roselle—National Exposure Research Laboratory (MD-80), U.S. Environmental
Protection Agency, Research Triangle Park, NC 27711

Mr. Kenneth L. Schere—National Exposure Research Laboratory (MD-80),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Jack H. Shreffler—National Exposure Research Laboratory (MD-75), U.S. Environmental
Protection Agency, Research Triangle Park, NC 27711

Dr. Joseph Sickles II—National Exposure Research Laboratory (MD-75), U.S. Environmental
Protection Agency, Research Triangle Park, NC 27711

Mr. Robert L. Seila—National Exposure Research Laboratory (MD-84), U.S. Environmental
Protection Agency, Research Triangle Park, NC 27711

Ms. Beverly E. Tilton—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Authors, Contributors, and Reviewers (cont'd)

Dr. Fred Vukovich—Private consultant, 7820 Harps Mill Road, Raleigh, NC 27615

Mr. Richard A. Wayland—Office of Air Quality Planning and Standards (MD-14),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Chapter 4. Environmental Concentrations, Patterns, and Exposure Estimates

Principal Authors

Dr. Allen S. Lefohn—A.S.L. & Associates, 111 Last Chance Gulch, Suite 4A,
Helena, MT 59601

Dr. A. Paul Altshuller—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Reviewers

Dr. Thomas C. Curran—Office of Air Quality Planning and Standards (MD-12),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Gary F. Evans—National Exposure Research Laboratory (MD-56), U.S. Environmental
Protection Agency, Research Triangle Park, NC 27711

Mr. William G. Ewald—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Warren P. Freas—Office of Air Quality Planning and Standards (MD-14),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Jon Heuss—General Motors Environmental and Energy Staff, 3044 West Grand Blvd.,
Detroit, MI 48202

Dr. Nelson Kelly—Environmental Sciences Department, General Motors Research and
Development Center, Warren, MI 48090

Dr. Paul J. Liroy—Department of Environmental and Community Medicine, UMDNJ-Robert
Wood Johnson Medical School, Piscataway, NY 08854

Mr. Thomas R. McCurdy—National Exposure Research Laboratory (MD-56),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Authors, Contributors, and Reviewers (cont'd)

Mr. Cornelius J. Nelson—National Exposure Research Laboratory (MD-56),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. William Parkhurst—Tennessee Valley Authority, CEB 2A, Muscle Shoals, AL 35660

Mr. Harvey M. Richmond—Office of Air Quality Planning and Standards (MD-12),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

**U.S. Environmental Protection Agency
Science Advisory Board
Clean Air Scientific Advisory Committee**

Ozone Review

Chairman

Dr. George T. Wolff—General Motors Corporation, Environmental and Energy Staff,
General Motors Bldg., 12th Floor, 3044 West Grand Blvd., Detroit, MI 48202

Members

Dr. Stephen Ayres—Office of International Health Programs, Virginia Commonwealth
University, Medical College of Virginia, Box 980565, Richmond, VA 23298

Dr. Jay S. Jacobson—Boyce Thompson Institute, Tower Road, Cornell University, Ithaca, NY
14853

Dr. Joseph Mauderly—Inhalation Toxicology Research Institute, Lovelace Biomedical and
Environmental Research Institute, P.O. Box 5890, Albuquerque, NM 87185

Dr. Paulette Middleton—Science & Policy Associates, Inc., Western Office, Suite 140,
3445 Penrose Place, Boulder, CO 80301

Dr. James H. Price, Jr.—Research and Technology Section, Texas Natural Resources
Conservation Commission, P.O. Box 13087, Austin, TX 78711

Invited Scientific Advisory Board Members

Dr. Morton Lippmann—Institute of Environmental Medicine, New York University Medical
Center, Long Meadow Road, Tuxedo, NY 10987

Dr. Roger O. McClellan—Chemical Industry Institute of Toxicology, P.O. Box 12137,
Research Triangle Park, NC 27711

Consultants

Dr. Stephen D. Colome—Integrated Environmental Services, University Tower, Suite 280,
4199 Campus Drive, Irvine, CA 92715

**U.S. Environmental Protection Agency
Science Advisory Board
Clean Air Scientific Advisory Committee
(cont'd)**

Dr. A. Myrick Freeman—Department of Economics, Bowdoin College, Brunswick, ME 04011

Dr. Allan Legge—Biosphere Solutions, 1601 11th Avenue, NW, Calgary, Alberta T2N 1H1,
CANADA

Dr. William Manning—Department of Plant Pathology, University of Massachusetts, Amherst,
MA 01003

Dr. D. Warner North—Decision Focus, Inc., 650 Castro Street, Suite 300, Mountain View,
CA 94041

Dr. Frank E. Speizer—Harvard Medical School, Channing Lab, 180 Longwood Avenue,
Boston, MA 02115

Dr. George E. Taylor—Department of Environmental and Resource Sciences, 130 Fleischmann
Agriculture Bldg. 199, University of Nevada, Reno, NV 89557

Dr. Mark J. Utell—Pulmonary Disease Unit, Box 692, University of Rochester Medical
Center, 601 Elmwood Avenue, Rochester, NY 14642

Designated Federal Official

Mr. Randall C. Bond—Science Advisory Board (1400), U.S. Environmental Protection
Agency, 401 M Street, SW, Washington, DC 20460

Staff Assistant

Ms. Lori Anne Gross—Science Advisory Board (1400), U.S. Environmental Protection
Agency, 401 M Street, SW, Washington, DC 20460

**U.S. Environmental Protection Agency
Project Team for Development of Air Quality Criteria
for Ozone and Related Photochemical Oxidants**

Scientific Staff

Mr. James A. Raub—Health Scientist, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. A. Paul Altshuller—Physical Scientist, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. William G. Ewald—Health Scientist, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. J.H.B. Garner—Ecologist, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Judith A. Graham—Associate Director, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Ms. Ellie R. Speh—Secretary, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Ms. Beverly E. Tilton—Physical Scientist, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Technical Support Staff

Mr. Douglas B. Fennell—Technical Information Specialist, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Allen G. Hoyt—Technical Editor and Graphic Artist, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Ms. Diane H. Ray—Technical Information Manager (Public Comments), National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

**U.S. Environmental Protection Agency
Project Team for Development of Air Quality Criteria
for Ozone and Related Photochemical Oxidants
(cont'd)**

Mr. Richard N. Wilson—Clerk, National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Document Production Staff

Ms. Marianne Barrier—Graphic Artist, ManTech Environmental Technology, Inc.,
P.O. Box 12313, Research Triangle Park, NC 27709

Mr. John R. Barton—Document Production Coordinator, ManTech Environmental Technology,
Inc., P.O. Box 12313, Research Triangle Park, NC 27709

Ms. Lynette D. Cradle—Word Processor, ManTech Environmental Technology, Inc., P.O. Box
12313, Research Triangle Park, NC 27709

Ms. Shelia H. Elliott—Word Processor, ManTech Environmental Technology, Inc.,
P.O. Box 12313, Research Triangle Park, NC 27709

Ms. Sandra K. Eltz—Word Processor, ManTech Environmental Technology, Inc.,
P.O. Box 12313, Research Triangle Park, NC 27709

Ms. Jorja R. Followill—Word Processor, ManTech Environmental Technology, Inc.,
P.O. Box 12313, Research Triangle Park, NC 27709

Ms. Sheila R. Lassiter—Word Processor, ManTech Environmental Technology, Inc.,
P.O. Box 12313, Research Triangle Park, NC 27709

Ms. Wendy B. Lloyd—Word Processor, ManTech Environmental Technology, Inc.,
P.O. Box 12313, Research Triangle Park, NC 27709

Ms. Carolyn T. Perry—Word Processor, ManTech Environmental Technology, Inc.,
P.O. Box 12313, Research Triangle Park, NC 27709

Ms. Cheryl B. Thomas—Word Processor, ManTech Environmental Technology, Inc.,
P.O. Box 12313, Research Triangle Park, NC 27709

Mr. Peter J. Winz—Technical Editor, ManTech Environmental Technology, Inc.,
P.O. Box 12313, Research Triangle Park, NC 27709

**U.S. Environmental Protection Agency
Project Team for Development of Air Quality Criteria
for Ozone and Related Photochemical Oxidants
(cont'd)**

Technical Reference Staff

Mr. John A. Bennett—Bibliographic Editor, ManTech Environmental Technology, Inc.,
P.O. Box 12313, Research Triangle Park, NC 27709

Ms. S. Blythe Hatcher—Bibliographic Editor, Information Organizers, Inc., P.O. Box 14391,
Research Triangle Park, NC 27709

Ms. Susan L. McDonald—Bibliographic Editor, Information Organizers, Inc., P.O. Box 14391,
Research Triangle Park, NC 27709

Ms. Carol J. Rankin—Bibliographic Editor, Information Organizers, Inc., P.O. Box 14391,
Research Triangle Park, NC 27709

Ms. Deborah L. Staves—Bibliographic Editor, Information Organizers, Inc., P.O. Box 14391,
Research Triangle Park, NC 27709

Ms. Patricia R. Tierney—Bibliographic Editor, ManTech Environmental Technology, Inc.,
P.O. Box 12313, Research Triangle Park, NC 27709