



Air Quality Criteria for Ozone and Related Photochemical Oxidants

**Review
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Volume I of III

Notice

This document is a preliminary draft. It has not been formally released by EPA and should not at this stage be construed to represent Agency policy. It is being circulated for comment on its technical accuracy and policy implications.



TECHNICAL REPORT DATA (Please read instructions on the reverse before complete)		
1. REPORT NO. EPA/600/AP-93/004a	2.	3.
4. TITLE AND SUBTITLE Air Quality Criteria for Ozone and Related Photochemical Oxidants - Volume I of III	5. REPORT DATE December 1993	
7. AUTHOR(S)	6. PERFORMING ORGANIZATION CODE 600/23	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Criteria and Assessment Office (MD-52) Office of Health and Environmental Assessment, ORD U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	8. PERFORMING ORGANIZATION REPORT NO. ECAO-R-0746	
12. SPONSORING AGENCY NAME AND ADDRESS Office of Health and Environmental Assessment (RD-689) Office of Research and Development U.S. Environmental Protection Agency Washington, D.C. 20460	10. PROGRAM ELEMENT NO.	
	11. CONTRACT/GRANT NO.	
	13. TYPE OF REPORT AND PERIOD COVERED External Review Draft	
	14. SPONSORING AGENCY CODE 600/21	
15. SUPPLEMENTARY NOTES		
16. ABSTRACT The U.S. Environmental Protection Agency (EPA) promulgates the National Ambient Air Quality Standards (NAAQS) on the basis of scientific information contained in air quality criteria documents. The previous ozone (O ₃) criteria document, <i>Air Quality Criteria for Ozone and Other Photochemical Oxidants</i> , was released in August 1986 and a supplement, <i>Summary of Selected New Information on Effects of Ozone on Health and Vegetation</i> , was released in January 1992. These documents were used as the basis for a March 1993 decision by EPA that revision of the existing 1-h NAAQS for O ₃ 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 O ₃ 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 O ₃ 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 the end of 1993.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 457
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

RAFT-DO NOT QUOTE OR CITE

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**Environmental Criteria and Assessment Office
Office of Health and Environmental Assessment
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711**



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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 (O_3). This document, therefore, focuses primarily on the scientific air quality criteria for O_3 and, to a lesser extent, for other photochemical oxidants like hydrogen peroxide and the peroxyacyl nitrates.

The EPA promulgates the NAAQS on the basis of scientific information contained in air quality criteria documents. The previous O_3 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 used as the basis for a March 1993 decision by EPA that revision of the existing 1-h NAAQS for O_3 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 O_3 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 O_3 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 the end of 1993.

This document was prepared and peer reviewed by experts from various state and Federal governmental offices, academia, and private industry for use by EPA to support decision making regarding potential risks to public health and welfare. The Environmental Criteria and Assessment Office of EPA's Office of Health and Environmental Assessment 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 Other Photochemical Oxidants

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LIST OF ABBREVIATIONS AND ACRONYMS

ADOM	Acid Deposition and Oxidant Model
AGL	Above ground level
AQCD	Air Quality Criteria Document
AUSPEX	Atmospheric Utility Signatures, Predictions, and Experiments
CAA	Clean Air Act
CAL-RAMS	Coast and Lake Regional Atmospheric Modeling System
CASAC	Clean Air Scientific Advisory Committee
CBM	Carbon Bond Mechanism (has several versions)
CCM	Community Climate Model
CFC(s)	Chlorofluorocarbon(s)
CFR	Code of Federal Regulations
CI	Chemical ionization
CIT	California Institute of Technology/Carnegie Institute of Technology Model
CL	Chemiluminescence
CTWM	Complex Terrain Wind Model
3-D	Three-dimensional
DIAL	Differential absorption lidar
DOAS	Differential optical absorption spectrometry
DWM	Diagnostic Wind Model
EKMA	Empirical Kinetic Modeling Approach (has several versions)
EMS	Emissions Modeling System
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
EPS	Emissions Preprocessor System
FDDA	Four-dimensional data assimilation
GMEP	Geocoded Model of Emissions and Projections
GRIDS	Topography database operated by U.S. EPA
GTP	Gas-phase titration
HCFC(s)	Hydrochlorofluorocarbon(s)
IR	Infrared radiation; in Section 3.2., "incremental reactivity"
K	Degrees Kelvin
LMOS	Lake Michigan Oxidant Study
LT	Local time

LIST OF ABBREVIATIONS AND ACRONYMS (cont'd)

M	Third body in atmospheric chemical reactions; absorbs energy
MASS	Dynamic wind model used in STEM-II
MIDROXA	Midwest domain of the ROM
MM4/MM5	Mesoscale Model, versions 4 and 5
MOBILE5	U.S. EPA emissions model for mobile sources (version 5)
MODELS 3	Modeling framework that consolidates all of U.S. EPA's 3-D photochemical air quality models
NAAQS	National Ambient Air Quality Standard(s)
NAPAP	National Acid Precipitation Assessment Program
NBS	National Bureau of Standards; has been renamed NIST
NCAR	National Center for Atmospheric Research
NECRMP	Northeast Corridor Regional Modeling Project
NEROS1	Northeast Regional Oxidant Study; a northeast domain of the ROM
NEROXA	A northeast domain of the ROM
NIST	National Institute of Standards and Technology
NMHC(s)	Nonmethane hydrocarbon(s)
NMOC(s)	Nonmethane organic compound(s)
NO ₂	Nitrogen dioxide
O ₃	Ozone
OAQPS	Office of Air Quality Planning and Standards
PAMS	Photochemical Aerometric Monitoring System
PAN	Peroxyacetyl nitrate
PANs	Peroxyacyl nitrates
PBL	Planetary boundary layer
PLANR	Practice for Low-cost Application in Nonattainment Regions
PF/TPLIF	Photofragmentation TPLIF
PSD(s)	Passive sampling device(s)
PVOC(s)	Polar volatile organic compound(s)
RADM	Regional Acid Deposition Model (has several versions)
RAPS	Regional Air Pollution Study (Illinois and Missouri)
RMSD	Root-mean-square difference
ROG	Reactive organic gas(es)
ROM	Regional Oxidant Model (has several versions)

LIST OF ABBREVIATIONS AND ACRONYMS (cont'd)

ROMNET	A northeast domain of the ROM; also, Regional Ozone Modeling for Northeast Transport program
SAB	Science Advisory Board
SAPRC	Statewide Air Pollution Research Center, University of California, Riverside
SARMAP	SJVAQS/AUSPEX Regional Model Adaptation Project
SCAQS	South Coast Air Quality Study (California)
SCCCAMP	South Central Coast Cooperative Aerometric Monitoring Program (California)
SEROS1	A southeast domain of the ROM
SEROXA	A southeast domain of the ROM
SIP(s)	State Implementation Plan(s)
SJVAQS	San Joaquin Valley Air Quality Study
SOS	Southern Oxidant Study
SRM(s)	Standard Reference Material(s)
STEM-II	Sulfur Transport Eulerian Model (version II)
SUPROXA	Super domain of the ROM
TDLAS	Tunable-diode laser absorption spectroscopy
TEA	Triethanolamine
TEXROXA	Southern domain of the ROM
TPLIF	Two-photon laser-induced fluorescence
TTFMS	Two-tone frequency-modulated spectroscopy
UAM	Urban Airshed Model (has several versions)
UV	Ultraviolet radiation
UV-B	Ultraviolet radiation of wavelengths 280 to 320 nanometers
VMT	Vehicle miles traveled
VOC(s)	Volatile organic compound(s)

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2. INTRODUCTION

The photochemical oxidants found in ambient air in the highest concentrations are ozone (O₃) and nitrogen dioxide (NO₂). Other oxidants, such as hydrogen peroxide and the peroxyacyl nitrates, have also been observed, but in lower and less certain concentrations. 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 O₃. This document, therefore, focuses primarily on the scientific air quality criteria for O₃ and, to a lesser extent, for hydrogen peroxide and the peroxyacyl nitrates, particularly peroxyacetyl nitrate. The scientific air quality criteria for NO₂ are discussed in a separate document (U.S. Environmental Protection Agency, 1993).

The previous O₃ criteria document, *Air Quality Criteria for Ozone and Other Photochemical Oxidants* (U.S. Environmental Protection Agency, 1986) was released by EPA in August 1986 and a supplement, *Summary of Selected New Information on Effects of Ozone on Health and Vegetation* (U.S. Environmental Protection Agency, 1992), was released in January 1992. These documents were used as 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 did not take into account newer scientific data that became available after completion of the 1986 criteria document. The purpose of this document is to summarize the air quality criteria for O₃ available in the published literature through the end of 1993. This review was performed in accordance with provisions of the Clean Air Act (CAA) to provide the scientific basis for periodic reevaluation of the O₃ NAAQS.

This chapter provides a general introduction to the legislative and regulatory background for decisions on the O₃ NAAQS, as well as a general summary of the organization, content, and major scientific topics presented in this document.

2.1 LEGISLATIVE BACKGROUND

Two sections of the CAA govern the establishment, review, and revision of the NAAQS. Section 108 (U.S. Code, 1991) directs the Administrator of EPA to identify ubiquitous pollutants that may reasonably be anticipated to endanger public health or welfare and to issue air quality criteria for them. These air quality criteria are to reflect the latest scientific information useful in indicating the kind and extent of all identifiable effects on public health or welfare that may be expected from the presence of the pollutant in ambient air.

Section 109(a) of the CAA (U.S. Code, 1991) directs the Administrator of EPA to propose and promulgate primary and secondary NAAQS for pollutants identified under Section 108. Section 109(b)(1) defines a primary standard as one the attainment and maintenance of which, in the judgment of the Administrator and based on the criteria and allowing for an adequate margin of safety, is requisite to protect the public health. The secondary standard, as defined in Section 109(b)(2), must specify a level of air quality the attainment and maintenance of which, in the judgment of the Administrator and based on the criteria, is requisite to protect the public welfare from any known or anticipated adverse effects associated with the presence of the pollutant in ambient air.

Section 109(d) of the CAA (U.S. Code, 1991) requires periodic review and, if appropriate, revision of existing criteria and standards. If, in the Administrator's judgment, the EPA's review and revision of criteria make appropriate the proposal of new or revised standards, such standards are to be revised and promulgated in accordance with Section 109(b). Alternatively, the Administrator may find that revision of the standards is inappropriate and conclude the review by leaving the existing standards unchanged.

2.2 REGULATORY BACKGROUND*

On April 30, 1971, the EPA promulgated primary and secondary NAAQS for photochemical oxidants under Section 109 of the CAA (Federal Register, 1971). These were

*This text is excerpted and adapted from the *Proposed Decision on the National Ambient Air Quality Standards for Ozone* (Federal Register, 1992).

set at an hourly average of 0.08 ppm total photochemical oxidants not to be exceeded more than 1 h per year. On April 20, 1977, the EPA announced (Federal Register, 1977) the first review and updating of the 1970 Air Quality Criteria Document (AQCD) for Photochemical Oxidants in accordance with Section 109(d) of the CAA. In preparing the AQCD, the EPA made two external review drafts of the document available for public comment, and these drafts were peer reviewed by the Subcommittee on Scientific Criteria for Photochemical Oxidants of EPA's Science Advisory Board (SAB). A final revised AQCD for O₃ and other photochemical oxidants was published on June 22, 1978.

Based on the 1978 revised AQCD and taking into account the advice and recommendations of the Subcommittee, and the comments received from the public, the EPA announced (Federal Register, 1979) a final decision to revise the NAAQS for photochemical oxidants on February 8, 1979. The final ruling revised the level of the primary standard from 0.08 ppm to 0.12 ppm, set the secondary standard identical to the primary standard, changed the chemical designation of the standards from photochemical oxidants to O₃, and revised the definition of the point at which the standard is attained to "when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is equal to or less than one" (see Table 2-1).

TABLE 2-1. NATIONAL AMBIENT AIR QUALITY STANDARDS FOR OZONE

Date of Promulgation	Primary and Secondary NAAQS	Averaging Time
February 8, 1979	0.12 ppm ^a (235 µg/m ³)	1 h ^b

^a1 ppm = 1962 µg/m³, 1 µg/m³ = 5.097 × 10⁻⁴ ppm @ 25 °C, 760 mm Hg.

^bThe standard is attained when the expected number of days per calendar year with a maximum hourly average concentration above 235 µg/m³ (0.12 ppm) is equal to or less than one.

On March 17, 1982, in response to requirements of Section 109(d) of the CAA, the EPA announced (Federal Register, 1982) that it was undertaking plans to revise the existing 1978 AQCD for O₃ and other photochemical oxidants, and on August 22, 1983, it announced (Federal Register, 1983) that review of the primary and secondary NAAQS for O₃ had been initiated. Public peer-review workshops on draft chapters of the revised AQCD were held on December 15-17, 1982, and on November 16-18, 1983. The EPA considered comments

1 made at both workshops in preparing the first external review draft that was made available
2 (Federal Register, 1984) on July 24, 1984, for public review.

3 On February 13, 1985 (Federal Register, 1985), and on April 2, 1986 (Federal
4 Register, 1986), the EPA announced two public meetings of the Clean Air Scientific
5 Advisory Committee (CASAC) of EPA's SAB to be held on March 4-6, 1985, and on April
6 21-22, 1986, respectively. At these meetings, the CASAC reviewed external review drafts
7 of the revised AQCD for O₃ and other photochemical oxidants. After completion of this
8 review, the CASAC sent the Administrator of EPA a closure letter, dated October 22, 1986,
9 indicating that the document "represents a scientifically balanced and defensible summary of
10 the extensive scientific literature." The EPA released the final draft document in August
11 1986.

12 The first draft of the Staff Paper "Review of the National Ambient Air Quality
13 Standards for Ozone: Assessment of Scientific and Technical Information" was reviewed by
14 CASAC at the public meeting on April 21-22, 1986. At that meeting, the CASAC
15 recommended that new information on prolonged exposure effects of O₃ be considered in a
16 second draft of the Staff Paper prior to closure. The CASAC reviewed this second draft and
17 also a presentation of new and emerging information on the health and welfare effects of
18 O₃ at a public review meeting held on December 14-15, 1987. The CASAC concluded that
19 sufficient new information existed to recommend incorporation of relevant new data into a
20 supplement to the 1986 AQCD (O₃ Supplement) and in a third draft of the Staff Paper.

21 A draft O₃ Supplement, "Summary of Selected New Information on Effects of Ozone
22 on Health and Vegetation: Draft Supplement to Air Quality Criteria for Ozone and Other
23 Photochemical Oxidants," and the revised Staff Paper were made available to CASAC and to
24 the public for review in November 1988. The O₃ Supplement reviewed and evaluated
25 selected literature concerning exposure- and concentration-response relationships observed for
26 health effects in humans and experimental animals and for vegetation effects. This literature
27 appeared as peer-reviewed journal publications or as proceedings papers from 1986 through
28 late 1988.

29 On December 14-15, 1988, CASAC held a public meeting to review these documents.
30 The CASAC sent the Administrator a closure letter dated May 1, 1989, indicating that the
31 draft O₃ Supplement, along with the 1986 AQCD, and the draft Staff Paper "provide an

adequate scientific basis for the EPA to retain or revise the primary and secondary standards of ozone." The CASAC concluded that it would be some time before enough new information on the health effects of multihour and chronic exposure to O₃ would be published in scientific journals to receive full peer review and, thus, be suitable for inclusion in a criteria document. The CASAC further concluded that such information could better be considered in the next review of the O₃ NAAQS. A final version of the O₃ Supplement has been published (U.S. Environmental Protection Agency, 1992).

On October 22, 1991, the American Lung Association and other plaintiffs filed suit to compel the EPA to complete the review of the criteria and standards for O₃ in accordance with the CAA. The U.S. District Court for the Eastern District of New York subsequently issued an order requiring the EPA to announce its proposed decision on whether to revise the standards for O₃ by August 1, 1992, and to announce its final decision by March 1, 1993.

The proposed decision on O₃ appearing in the Federal Register on August 10, 1992 (Federal Register, 1992), indicated that revision of the existing 1-h NAAQS was not appropriate at that time. A public hearing on this proposal took place on September 1, 1992, at the EPA Education Center in Washington, DC, and public comments were received through October 9, 1992. The final decision was published in the Federal Register on March 9, 1993 (Federal Register, 1993). This decision does not take into consideration a number of recent studies on the health and welfare effects of O₃ that have been published since the last literature review in early 1989. The EPA estimates that approximately 3 years will be necessary to (1) incorporate the new studies into a revised criteria document, (2) complete mandated CASAC review, (3) evaluate the significance of the key information for regulatory decision-making purposes, and (4) publish a proposed decision on the O₃ NAAQS in the Federal Register.

As stated in the 1993 final decision, the EPA's Environmental Criteria and Assessment Office in Research Triangle Park, NC, is proceeding as rapidly as possible with the next periodic review of the air quality criteria for O₃. Under the processes established in Sections 108 and 109 of the CAA and refined by the EPA and CASAC, the EPA began by announcing the commencement of the review in the Federal Register. After assessing and evaluating the pertinent new studies, the EPA has prepared a preliminary draft of a revised criteria document and subjected it successively to review at expert peer-review workshops.

Comments received at the workshops were used to revise the preliminary draft for external review. Once the public and CASAC have reviewed the external review draft of the revised criteria document, thus providing a preliminary basis for review of the existing standards, EPA's Office of Air Quality Planning and Standards (OAQPS) will complete their preparation of a draft Staff Paper assessing the most significant information contained in the draft criteria document and will develop recommendations for revisions, if appropriate, to the NAAQS for O₃. Subsequent reviews by the public and by CASAC will occur, as warranted.

2.3 SUMMARY OF MAJOR SCIENTIFIC TOPICS PRESENTED

A number of separate topics and issues are addressed in this revised O₃ criteria document. Some of the key topics and issues addressed are highlighted below by document section.

2.3.1 Air Chemistry

- What concerns still exist regarding precision and accuracy of measurements of O₃ and its precursors?
- What is the order of magnitude of current estimates of natural emissions of O₃ precursors and emissions from anthropogenic sources and their relevance to tropospheric O₃ photochemistry?
- What new scientific information exists on the roles of meteorologic and climatologic factors in O₃ formation and transport?
- Are the reaction pathways of all major precursors to O₃ understood? Have all major reaction products been identified? How are the reactions and products represented in air quality models?
- What is the status of development, application, evaluation, and verification of air quality models?

2.3.2 Air Quality

- What are the trends and geographic differences in O₃ concentrations across the United States?

- What are diurnal and seasonal patterns of 1-h average O₃ concentrations for urban and nonurban sites, for attainment versus nonattainment areas?
- What is known about patterns of co-occurrence of O₃ with other pollutants in the atmosphere?
- What O₃ exposure assessment data are available for agricultural crops and for forests?
- To what level and to what extent are humans typically exposed to O₃ in the course of normal everyday activities?

2.3.3 Environmental Effects

- What are the effects of ambient O₃ concentrations on vegetation (i.e., agricultural and horticultural crops; urban landscape trees, shrubs, and flowers; forest tree species)?
- What characteristics of air quality (e.g., summary statistics) are relevant to these effects on vegetation?
- What are the long-term effects of O₃ exposures on natural ecosystems?
- Is there important new information on the effects of O₃ on nonbiological materials?

2.3.4 Health Effects

- What O₃ concentration and exposure duration relationships exist for effects on lung structure, function, and host defense mechanisms and what are the important modifiers of these effects?
- What are the mechanisms of O₃-induced lung injury?
- Can dosimetry models predict human population responses to O₃ on the basis of laboratory animal data?
- Does long-term exposure to O₃ lead to the development of chronic lung disease or to an increased frequency or exacerbation of other chronic respiratory outcomes?
- What segment(s) of the population are most susceptible to effects from exposure to O₃?

2.4 ORGANIZATION AND CONTENT OF THE DOCUMENT

This document critically evaluates and assesses scientific information on the health and welfare effects associated with exposure to the concentrations of O₃ and related photochemical oxidants in ambient air. Although the document is not intended to be an exhaustive literature review, it is intended to cover all pertinent literature through 1993. The references cited in the document should be reflective of the state of knowledge on those issues most relevant to review of the NAAQS for O₃, now set at 0.12 ppm for 1 h. Although emphasis is placed on the presentation of health and welfare effects data, other scientific data will be presented and evaluated in order to provide a better understanding of the nature, sources, distribution, measurement, and concentrations of O₃ and related photochemical oxidants in ambient air, as well as the characterization of population exposure to these pollutants.

To aid in the development of this document, summary tables of the relevant published literature have been provided to supplement a selective discussion of the literature. Most of the scientific information selected for review and comment in the text comes from the more recent literature published since completion of the previous O₃ criteria document (U.S. Environmental Protection Agency, 1986). Some of these newer studies were briefly reviewed in the supplement to that document (U.S. Environmental Protection Agency, 1992) but more intense evaluation of these studies has been included. Emphasis is placed on studies conducted at or near O₃ concentrations found in ambient air. Other studies, however, are included if they contain unique data, such as the documentation of a previously unreported effect or of a mechanism of an effect; or if they were multiple-concentration studies designed to provide exposure-response relationships. Generally, O₃ concentration is not an issue for human clinical or epidemiology studies; however, for animal toxicology studies, typically only those studies conducted at less than 1 ppm O₃ are considered. Studies that are presented in the previous criteria document and whose data were judged to be significant because of their usefulness in deriving the current NAAQS are briefly discussed in the text. The reader should, however, consult the more extensive discussion of these "key" studies in the previous document. Other, older studies are also discussed in the text if they were judged to be (1) open to reinterpretation because of newer data, or (2) potentially useful in deriving revised standards for O₃. Generally, only published information that has undergone

1 scientific peer review is included in the criteria document. Some newer studies not published
2 in the open literature but meeting high standards of scientific reporting and review have been
3 included.

4 Certain issues of direct relevance to standard setting are not explicitly addressed in this
5 document, but are instead analyzed in documentation prepared by OAQPS as part of its
6 regulatory analyses. Such analyses include (1) a discussion of what constitutes an "adverse
7 effect" and delineation of particular adverse effects that the primary and secondary NAAQS
8 are intended to protect against, (2) exposure analyses and assessment of consequent risk, and
9 (3) a discussion of factors to be considered in determining an adequate margin of safety.
10 Key points and conclusions from such analyses are summarized in the Staff Paper prepared
11 by OAQPS and reviewed by CASAC. Although scientific data contribute significantly to
12 decisions regarding the above issues, their resolution cannot be achieved solely on the basis
13 of experimentally acquired information. Final decisions on items (1) and (3) are made by the
14 Administrator, as mandated by the CAA.

15 A fourth issue directly pertinent to standard setting is identification of populations at
16 risk, which is basically a determination by EPA of the subpopulation(s) to be protected by
17 the promulgation of a given standard. This issue is addressed only partially in this
18 document. For example, information is presented on factors, such as preexisting disease,
19 that may biologically predispose individuals and subpopulations to adverse effects from
20 exposures to O₃. The identification of a population at risk, however, requires information
21 above and beyond data on biological predisposition, such as information on levels of
22 exposure, activity patterns, and personal habits. Such information is included in the Staff
23 Paper developed by OAQPS.

24 The structure of this document includes, first, an Executive Summary and Conclusions
25 (Chapter 1) providing a concise presentation of key information and conclusions from all
26 subsequent chapters. This is followed by this brief Introduction (Chapter 2) containing
27 information on the legislative and regulatory background for review of the O₃ NAAQS, as
28 well as an overview of the organization of this document. Chapter 3 provides information on
29 the chemistry, sources, emissions, measurement, and transport of O₃ and related
30 photochemical oxidants and their precursors, whereas Chapter 4 covers environmental
31 concentrations, patterns, and exposure estimates of O₃ and oxidant air quality. This is

1 followed by Chapter 5, dealing with environmental effects of O₃ and related photochemical
2 oxidants. Chapters 6, 7, and 8 discuss, respectively, animal toxicological studies, human
3 health effects, and extrapolation of animal toxicological data to humans. The last chapter,
4 Chapter 9, provides an integrative, interpretive evaluation of health risks associated with
5 exposure to O₃.

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3. TROPOSPHERIC OZONE AND ITS PRECURSORS

3.1 INTRODUCTION

Ozone and other oxidants found in ambient air, such as the peroxyacyl nitrates and hydrogen peroxide, are formed as the result of atmospheric physical and chemical processes involving two classes of precursor pollutants, volatile organic compounds (VOCs) and nitrogen oxides (NO_x). The formation of ozone and other oxidants from these precursors is a complex, nonlinear function of many factors, including the intensity and spectral distribution of sunlight; atmospheric mixing and related meteorological conditions; the concentrations of the precursors in ambient air and, within reasonable concentration ranges, the ratio between VOC and NO_x (VOC/NO_x); and the reactivity of the organic precursors.

An understanding of the atmospheric chemistry and meteorological parameters and processes responsible for the formation and occurrence of elevated concentrations of ozone in ambient air is basic to the formulation of strategies and techniques for its abatement. Such an understanding is required for representing those parameters and processes adequately in predictive models used to determine the emission reductions needed for complying with the NAAQS for ozone. In addition, the identification and quantification of ozone precursors in ambient air is essential, along with emission inventories or emission models, or both, for the development, verification, and refinement of photochemical air quality models and for comparisons of ambient concentrations with emission inventories as a check on the accuracy of measurements and of inventories.

Product identification and quantification of yields, in chambers and in ambient air, are helpful in the verification of photochemical air quality models and in testing theoretical chemical mechanisms. Likewise, product identification and quantification are useful in determining the need for research on the potential effects of the simultaneous or sequential co-occurrence with ozone and related oxidants of multiple air pollutants.

The ability to measure ozone and its precursors, its reaction products, and the products of the atmospheric reactions of its respective precursors is essential for (1) understanding atmospheric chemistry of ozone formation, (2) for verifying chemical mechanisms, (3) for

1 verifying models, (4) for quantifying emission rates, and (5) for adequately characterizing
2 exposure-response factors for both biological and nonbiological receptors.

3 For these reasons, this chapter presents information on a broad range of topics. The
4 chapter describes the chemical processes by which ozone and other photochemical oxidants
5 are formed in ambient air (Section 3.2). It also characterizes the nature of the precursors in
6 terms of their sources and emissions into the atmosphere and their concentrations in ambient
7 air (Section 3.4), and methods by which their concentrations in ambient air are measured
8 (Section 3.5).

9 In addition to information on the chemistry of oxidants and their precursors, the chapter
10 includes a discussion of meteorological processes (Section 3.3) that contribute to the
11 formation of ozone and other oxidants and that govern their transport and dispersion once
12 formed. Finally, an overview is given (Section 3.6) of models of the relationships between
13 precursor emissions and ozone formation in the atmosphere.

14 Readers are referred to other sources (e.g., Finlayson-Pitts and Pitts, 1986; Seinfeld,
15 1986; U.S. Environmental Protection Agency, 1986; National Research Council, 1991) for
16 additional information on the chemical and physical aspects of photochemical air pollution.

19 **3.2 TROPOSPHERIC OZONE CHEMISTRY**

20 **3.2.1 Background Information**

21 Ozone is formed photochemically in the stratosphere and transported downward,
22 leading to the presence of O₃ at low concentrations in the natural, or "clean", troposphere.
23 The presence of O₃ at low concentrations in the "clean" troposphere, in the absence of
24 perturbations caused by human activities, is highly important since O₃ is a precursor to the
25 hydroxyl (OH) radical, the key intermediate species in the tropospheric degradation of VOCs
26 emitted into the atmosphere. Although O₃ at low concentrations is an integral part of the
27 "clean" troposphere, its presence at higher concentrations is detrimental.

28 The chemical processes occurring in the atmosphere that lead to the formation of ozone
29 and other photochemical air pollutants are complex. Tropospheric ozone is formed as a
30 result of (1) emissions of NO_x and VOCs into the atmosphere from anthropogenic and
31 biogenic sources; (2) transport of these emissions and their reaction products; and

(3) chemical reactions occurring in the atmosphere concurrent with transport and dispersion of the emissions, leading to the formation of O₃ and other photochemical oxidants such as peroxyacetyl nitrate (PAN), nitric and sulfuric acids, and to other compounds such as formaldehyde (HCHO) and other carbonyl compounds, and particulate matter. Additionally, deposition of gases and particles along the trajectory occurs to reduce the concentrations of precursors and products in the atmosphere, but may lead to adverse impacts on the earth's environment.

The chemical process leading to the chemical formation of O₃ in the troposphere involves the photolysis of NO₂ to yield nitric oxide (NO) and a ground-state oxygen atom,



which then reacts with molecular oxygen to form O₃:



The NO and O₃ react to reform NO₂:



The presence of reactive VOCs leads to the conversion of NO to NO₂ without the intermediary of O₃ (Reaction 3-3), and the photolysis of NO₂ then leads to the formation of elevated levels of O₃:



The photochemical cycles leading to O₃ production are best understood through a knowledge of the chemistry of the atmospheric oxidation of methane, which can be viewed as being the chemistry of the clean, or unpolluted, troposphere (although this is also a

1 simplification, since vegetation releases large quantities of complex VOCs into the
2 atmosphere). Although the chemistry of the VOCs emitted from anthropogenic and biogenic
3 sources in polluted urban and rural areas is more complex, a knowledge of the methane
4 oxidation reactions aids in understanding the chemical processes occurring in the polluted
5 atmosphere because the underlying chemical principles are the same.

6 This section first describes the structure of the atmosphere, and then discusses the
7 formation of the OH radical, the key intermediate species in the chemistry of the
8 troposphere; and tropospheric NO_x chemistry. The photochemical formation of tropospheric
9 O₃ from the oxidation of methane is then discussed in some detail since, as noted above, the
10 methane oxidation cycle serves as a model for the photochemical formation of O₃ from the
11 more complex nonmethane VOCs emitted into the atmosphere from anthropogenic and
12 biogenic sources. In Section 3.2.4, the chemistry of the major classes of nonmethane VOCs
13 and the formation of O₃ from these VOCs are discussed. Finally, in Section 3.2.5, the
14 photochemical formation of aerosols is briefly discussed, since the same processes that lead
15 to the formation of elevated levels of O₃ (over those present in the "clean" troposphere)
16 result in the formation of particulate matter, leading to visibility degradation, and in the
17 formation of atmospheric acidity.

18 19 3.2.2 Structure of the Atmosphere

20 The earth's atmosphere is composed of a number of layers (McIlveen, 1992). For the
21 purposes of this chapter, those of importance are the troposphere and the stratosphere, and
22 the boundary between them, which is the tropopause.

23 The troposphere extends from the earth's surface to the tropopause, which is at ≈ 10 to
24 18 km altitude, depending on the latitude and season. The altitude of the tropopause is
25 greatest in the tropics and lowest in the wintertime polar regions, with an average altitude of
26 ≈ 14 km. The temperature in the troposphere decreases with increasing altitude from an
27 average of 290 K at the earth's surface to ≈ 210 to 220 K at the tropopause, and the pressure
28 decreases from ≈ 760 torr at the earth's surface to ≈ 100 torr at the tropopause.

29 The stratosphere extends from the tropopause to an altitude of ≈ 50 km. In the
30 stratosphere, the temperature increases with increasing altitude from ≈ 210 to 220 K at the
31 tropopause to ≈ 270 K at the top of the stratosphere. The pressure in the stratosphere

1 decreases with increasing altitude from ≈ 100 torr at the tropopause to ≈ 1 torr at the top of
2 the stratosphere.

3 4 **3.2.2.1 Vertical and Horizontal Mixing in the Atmosphere**

5 In the troposphere, temperature generally decreases with increasing altitude.
6 As discussed in Section 3.3., the lowest 1 to 2 km of the troposphere is influenced by the
7 planetary boundary layer and, in certain locales, by inversion layers. These boundary and
8 inversion layers inhibit the vertical movement of pollutants into the free troposphere. Above
9 inversion and boundary layers, vertical mixing in the "free" troposphere has a time scale of
10 ≈ 10 to 30 days (Langner et al., 1990; World Meteorological Organization, 1990a).

11 Because temperature increases with increasing altitude in the stratosphere, vertical
12 mixing in the stratosphere is slow, with a time scale of the order of months to a few years.

13 Horizontal mixing in the troposphere occurs both within and between the hemispheres.
14 The time scale for mixing between the northern and southern hemispheres is ≈ 1 year
15 (Cicerone, 1989; Singh and Kanakidou, 1993). Transport within a hemisphere is more rapid
16 (Graedel et al., 1986a), and local, regional, and global transport distances of < 100 km,
17 100 to 1,000 km, and $> 1,000$ km, respectively, are observed. For a wind speed of
18 15 km h^{-1} ($\approx 4 \text{ m s}^{-1}$), transport times over these local, regional, and global distances are
19 a few hours, a few hours to a few days, and ≥ 10 days, respectively.

20 21 **3.2.2.2 Formation of Stratospheric Ozone**

22 At altitudes between approximately 20 and 35 km, the stratosphere has a layer of air
23 containing O_3 at mixing ratios up to approximately 10 ppm. The sun emits radiation
24 $> 170 \text{ nm}$, and this radiation impacts the upper levels of the atmosphere. The bulk
25 composition of the atmosphere (78.1% N_2 , 21.0% O_2 , 0.9% Ar, 0.03% CO_2 , with variable
26 trace gas concentrations) is invariant up to $> 50 \text{ km}$ (McIlveen, 1992), and the shorter
27 wavelength radiation (175 to 240 nm) is absorbed by molecular oxygen (O_2) in the
28 stratosphere, leading to dissociation into two ground-state oxygen atoms, $\text{O}(^3\text{P})$,
29



1 followed by the reaction of $O(^3P)$ atoms with O_2 in the presence of a third-body, M , to form
2 ozone.



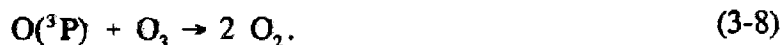
4
5 Ozone also photolyzes, at wavelengths < 360 nm (DeMore et al., 1992),
6



7
8 where the oxygen atom produced can be in the ground state, $O(^3P)$, or electronically excited
9 state, $O(^1D)$. The $O(^1D)$ atoms produced are deactivated to the ground state $O(^3P)$ atom by
10 N_2 , O_2 , CO_2 , and Ar:
11



12
13 The reaction of $O(^3P)$ atoms with O_3 is the termination step of this reaction sequence,
14



15
16 These reactions, called the Chapman reactions (Chapman, 1930), are responsible for the
17 layer of ozone found in the stratosphere. Because the stratospheric ozone layer absorbs the
18 sun's radiation below ≈ 290 nm, only radiation of wavelengths ≥ 290 nm can penetrate into
19 the troposphere and impact the earth's surface. Any depletion of the stratospheric ozone
20 layer allows shorter wavelength ultraviolet radiation to be transmitted through the
21 stratosphere and into the troposphere.

22 In addition to the biological effects expected from increased UV-B radiation (280 to
23 320 nm), increased penetration of UV-B into the troposphere can lead to changes in
24 tropospheric ozone. Model calculations indicate that O_3 in the troposphere could increase
25 with increasing UV-B in urban and rural areas impacted by anthropogenic NO_x emissions
26 (Gery et al., 1988; Liu and Trainer, 1988; Thompson et al., 1989; Thompson, 1992), but

could decrease with increasing UV-B in remote tropospheric areas characterized by low NO_x levels (Liu and Trainer, 1988; Thompson et al., 1989). Besides the implications of long-term trends in stratospheric O₃ concentrations leading to corresponding changes in the intensity of UV-B radiation impacting the troposphere, short-term changes, including daily changes, in stratospheric ozone levels lead to short-term changes in the rates of photolysis of several important species, including the photolysis of formaldehyde to produce radicals and of O₃ to form the OH radical. These changes in photolysis rates affect the formation rates and ambient concentrations of key radical intermediates, specifically of the OH radical, in the troposphere. Information concerning such short-term changes in stratospheric O₃ concentrations is needed as input to urban and regional airshed computer models of photochemical air pollution formation.

In the clean atmosphere, stratospheric ozone is also influenced by the emission of N₂O from soils and oceans (World Meteorological Organization, 1992). Because N₂O is chemically inert in the troposphere and does not photolyze (Prinn et al., 1990), it is therefore transported into the stratosphere, where it undergoes photolysis and also reacts with O(¹D) atoms (DeMore et al., 1992; Atkinson et al., 1992a). The reaction of N₂O with the O(¹D) atom is the major source of stratospheric NO, which then participates in a series of reactions known as the NO_x catalytic cycle (Crutzen, 1970; Johnston, 1971).



The Chapman reactions and the NO_x catalytic cycle reactions control the ozone concentrations in the lower "clean" stratosphere.

Additional reaction sequences leading to the removal of stratospheric ozone arise from the ClO_x and BrO_x catalytic cycles, which result when chlorine- and bromine-containing organic compounds are emitted into the atmosphere. These O₃-depleting compounds include

1 the chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), carbon tetrachloride
2 (CCl_4), methyl chloroform, halons, and methyl bromide (Anderson et al., 1991; Rowland,
3 1990, 1991; World Meteorological Organization, 1992). Analogous to N_2O , the CFCs,
4 CCl_4 , and certain halons (CF_3Br and CF_2ClBr) are inert in the troposphere and are
5 transported into the stratosphere, where they photolyze to generate Cl or Br atoms (World
6 Meteorological Organization, 1992). Methyl bromide and the HCFCs react to a large extent
7 in the troposphere, so that only a fraction of these Cl- and Br-containing species that are
8 emitted into the troposphere are transported into the stratosphere (World Meteorological
9 Organization, 1990b, 1992).

11 3.2.3 Tropospheric Ozone in the Unpolluted Atmosphere

12 As noted in Section 3.2.1, ozone is present in the troposphere, even in the absence of
13 human activities. The presence of ozone in the clean, unpolluted, troposphere is the result of
14 downward transport from the stratosphere and in situ production from the oxidation of
15 methane (National Research Council, 1991), emitted from swamps and wetlands, in the
16 presence of natural sources of NO_x (emissions from soils, lightning, and downward transport
17 from the stratosphere). It is believed that on a global basis the photochemical formation of
18 ozone in the "clean" troposphere would be approximately balanced by its destruction (Logan,
19 1985; World Meteorological Organization, 1992; Ayers et al., 1992). In the clean,
20 unpolluted lower troposphere, the ozone mixing ratios are in the range 10 to 40 ppb
21 (Oltmans, 1981; Logan, 1985), with higher mixing ratios of ≈ 100 ppb in the upper
22 troposphere (Logan, 1985). A reasonable estimate for background O_3 mixing ratios near
23 sea-level in the United States is 20 to 35 ppb (U.S. Environmental Protection Agency, 1989)
24 (see Chapter 4). Because of the decrease of total pressure with increasing altitude, the ozone
25 concentration in the "clean" troposphere may be taken to be reasonably independent of
26 altitude at $\approx 7 \times 10^{11}$ molecule cm^{-3} . Transport of O_3 from polluted urban areas (see
27 Section 3.3) impacts the "clean" troposphere and leads to O_3 concentrations in the
28 troposphere that have been increasing with time over the past few decades (Logan, 1985).

3.2.3.1 Tropospheric Hydroxyl Radicals

It is now recognized that the key reactive species in the troposphere is the hydroxyl (OH) radical, which is responsible for initiating the degradation reactions of almost all VOCs. In the presence of NO, these OH radical reactions with VOCs lead to the formation of O₃ and hence to O₃ concentrations above those encountered in the "clean" troposphere. The OH radical is produced from the ultraviolet photolysis of O₃. Ozone photolyzes in the ultraviolet at wavelengths < 320 nm to generate the electronically excited O(¹D) atom (DeMore et al., 1992; Atkinson et al., 1992a),



The O(¹D) atoms are either deactivated to the ground state O(³P) atom by Reaction 3-7 or they react with water vapor to form the OH radical:



The O(³P) atoms formed directly in the photolysis of O₃ or formed from deactivation of O(¹D) atoms (Reaction 3-7) reform O₃ through Reaction 3-2. At room temperature and 50% relative humidity, 0.2 OH radicals are formed per O(¹D) atom generated from the photolysis of ozone. Hydroxyl radical production from reactions (3-6a) and (3-10) is balanced by reaction of the OH radical with CO and methane. Because the water vapor mixing ratio decreases with increasing altitude in the troposphere (Logan et al., 1981; World Meteorological Organization, 1992), whereas the ozone mixing ratio generally increases with increasing altitude, the OH radical concentration is expected to be reasonably independent of altitude (Dentener and Crutzen, 1993).

A knowledge of ambient tropospheric OH radical concentrations is needed to test our understanding of tropospheric chemistry and allow the lifetimes of chemical compounds to be reliably calculated. Since, as shown below in Section 3.2.3.3, OH and HO₂ radicals are interrelated through a series of reactions, concurrent measurements of OH and HO₂ radical concentrations are a further test of our knowledge of tropospheric chemistry. Only in the past few years have measurements been made of lower tropospheric OH radical

concentrations (see, for example, Felton et al., 1990; Hofzumahaus et al., 1991; Eisele and Tanner, 1991; Mount and Eisele, 1992; Comes et al., 1992; Hard et al., 1992). The limited data available show that, as expected, the OH radical concentrations exhibit a diurnal profile, with daytime maximum concentrations of several $\times 10^6$ molecule cm^{-3} . A global, annually, seasonally, and diurnally averaged tropospheric OH radical concentration can also be derived from the estimated emissions and measured atmospheric concentrations of methylchloroform (CH_3CCl_3) and the rate constant for the reaction of the OH radical with methylchloroform (its major tropospheric loss process). Using this method, Prinn et al. (1992) have derived a 24-h average OH radical concentration of 8×10^5 molecule cm^{-3} (equivalent to a 12-h daytime average of 1.6×10^6 molecule cm^{-3}). Ambient air measurements of the decays of nonmethane hydrocarbons in urban plumes (Blake et al., 1993) give OH radical concentrations of a similar magnitude as direct tropospheric measurements and globally averaged estimates.

3.2.3.2 Tropospheric Nitrogen Oxides Chemistry

The presence of oxides of nitrogen is necessary for the formation of O_3 from the oxidation of methane and other VOCs. Sources of tropospheric NO_x include downward transport from the stratosphere, in situ formation from lightning (National Research Council, 1991; World Meteorological Organization, 1992) (Section 3.4.1.2), and emission from soils (National Research Council, 1991; World Meteorological Organization, 1992). Recent measurements show that the NO_x concentrations over maritime areas increase slightly with increasing altitude, from ≈ 15 ppt in the marine boundary layer (Carroll et al., 1990) to ≈ 30 to 40 ppt at 3 to 7 km altitude (Ridley et al., 1989; Carroll et al., 1990). Significantly higher NO_x concentrations (≈ 100 ppt) have been observed in the boundary layer over relatively unpolluted continental areas (Carroll et al., 1990), with the NO_x concentrations decreasing with increasing altitude to ≈ 50 ppt at 3 to 7 km (Ridley et al., 1989; Carroll et al., 1990).

In the troposphere, NO, NO_2 , and O_3 are interrelated by the following reactions:





Because Reaction 3-2 is fast (the lifetime of an $\text{O}(^3\text{P})$ atom at 298 K and 760 torr of air is $\approx 10^{-5}$ s), the ozone concentration at photoequilibrium is given by,

$$[\text{O}_3] = J_1[\text{NO}_2]/k_3[\text{NO}] \quad (3-11)$$

where J_1 and k_3 are the photolysis rate of NO_2 ($\approx 0.5 \text{ min}^{-1}$ for an overhead sun) and the rate constant for the reaction of NO with O_3 , respectively.

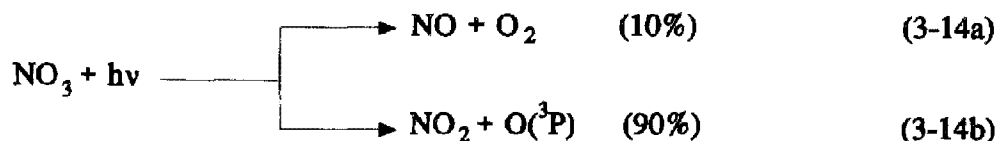
There are other important reactions involving NO_x . The reaction of NO_2 with O_3 leads to the formation of the nitrate (NO_3) radical,



which in the lower troposphere is nearly in equilibrium with dinitrogen pentoxide (N_2O_5):



However, because the NO_3 radical photolyzes rapidly [with a lifetime of ≈ 5 s for an overhead sun (Atkinson et al., 1992a)],



its concentration remains low during daylight hours, but can increase after sunset to nighttime concentrations of $<5 \times 10^7$ to 1×10^{10} molecule cm^{-3} (<2 to 430 ppt) over continental areas influenced by anthropogenic emissions of NO_x (Atkinson et al., 1986). Nitrate radical concentrations over marine areas are low because NO_x concentrations are low over lower tropospheric marine areas (Noxon, 1983), and an NO_3 radical mixing ratio of 0.25 ppt has been measured at 3 km altitude in Hawaii (Noxon, 1983). Atkinson (1991) has suggested the use of a 12-h nighttime average NO_3 radical concentration of 5×10^8 molecule cm^{-3} in the lower troposphere over continental areas, with an uncertainty of a factor of ≈ 10 .

The tropospheric chemical removal processes for NO_x involve the daytime reaction of NO_2 with the OH radical and the nighttime wet and dry deposition of N_2O_5 to produce nitric acid (HNO_3),



Gaseous nitric acid formed from Reaction 3-15 undergoes wet and dry deposition, including combination with gaseous ammonia to form particulate phase ammonium nitrate. The tropospheric lifetime of NO_x due to chemical reaction (mainly Reaction 3-15) is ≈ 1 to 2 days. The tropospheric NO_x reactions are shown schematically in Figure 3-1 below: It should be noted that OH radicals can also react with NO to produce nitrous acid (HONO):



In urban areas, HONO can also be formed during nighttime hours (Harris et al., 1982; Pitts et al., 1984a; Rodgers and Davis, 1989), apparently from the heterogeneous hydrolysis of NO_2 or NO_x , or both (Sakamaki et al., 1983; Pitts et al., 1984b; Svensson et al., 1987;

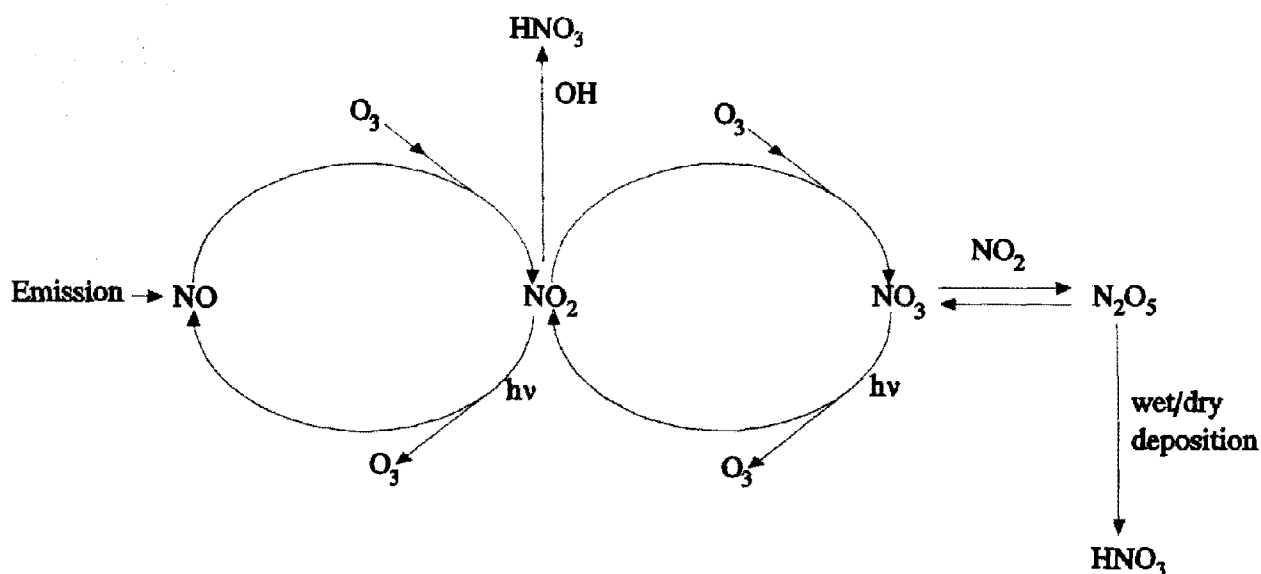


Figure 3-1. The cyclic reactions of tropospheric nitrogen oxides.

Jenkin et al., 1988; Lammel and Perner, 1988; Notholt et al., 1992a,b). The photolysis of HONO during the early morning hours,



can thus become an important source of OH radicals, leading to the rapid initiation of photochemical activity (Harris et al., 1982).

3.2.3.3 The Methane Oxidation Cycle

Methane is emitted into the atmosphere from swamps and wetlands, as well as from ruminants (Fung et al., 1991a; World Meteorological Organization, 1992). The major tropospheric removal process for methane is by reaction with the OH radical, with methane lifetime equal to

$$(k_{21} [\text{OH}])^{-1} \quad (3-19)$$

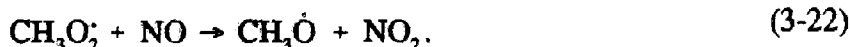
1 where k_{21} is the rate constant for Reaction 3-21 and $[\text{OH}]$ is the (variable) atmospheric
2 OH radical concentration. The calculated lifetime of methane in the troposphere is ≈ 10 to
3 12 years. As for other saturated organic compounds, the OH radical reaction with methane
4 proceeds by H-atom abstraction from the C-H bonds to form the methyl radical:
5



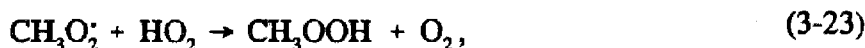
6
7 In the troposphere, the methyl radical reacts solely with O_2 to yield the methyl peroxy
8 (CH_3O_2) radical (Atkinson et al., 1992a):
9



10 In the troposphere, the methyl peroxy radical can react with NO, NO_2 , HO_2 radicals,
11 and other organic peroxy (RO_2) radicals, with the reactions with NO and HO_2 radicals being
12 the most important (see, for example, World Meteorological Organization, 1990b). The
13 reaction with NO leads to the formation of the methoxy ($\text{CH}_3\dot{\text{O}}$) radical,
14

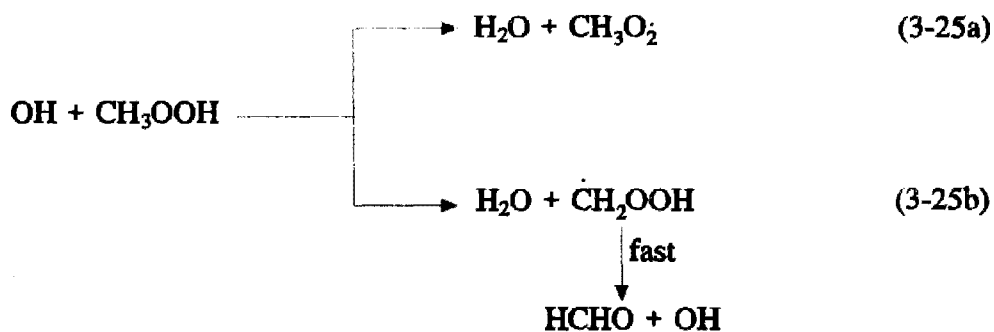


15
16 The reaction with the HO_2 radical leads to the formation of methyl hydroperoxide,
17



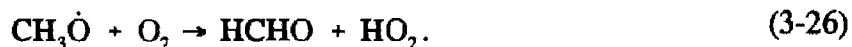
18
19 which can photolyze or react with the OH radical (Atkinson et al., 1992a):
20



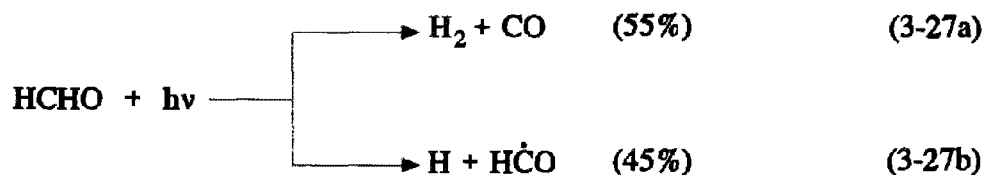


Methyl hydroperoxide also undergoes wet and dry deposition or incorporation into cloud water, or both. The lifetime of methyl hydroperoxide in the troposphere due to photolysis and reaction with the OH radical is calculated to be ≈ 2 days. Methyl hydroperoxide is then a temporary sink of radicals, with its wet or dry deposition being a tropospheric loss process for radicals.

The only important reaction for the methoxy radical in the troposphere is with O_2 to form formaldehyde (HCHO) and the HO_2 radical,



Formaldehyde is a "first-generation" product that reacts further, by photolysis:



where the percentages are for overhead sun conditions (Rogers, 1990); and also by reaction with the OH radical,



1 In the troposphere, the H atom and $\dot{\text{H}}\text{CO}$ (formyl) radical produced in these processes react
2 solely with O_2 to form the HO_2 radical:



5
6 The lifetimes of HCHO due to photolysis and OH radical reaction are ≈ 4 h and 1.5 days,
7 respectively, leading to an overall lifetime of ≈ 3 h for overhead sun conditions.

8 The final step in the oxidation of methane in the earth's atmosphere involves the
9 oxidation of carbon monoxide by reaction with the OH radical (the only tropospheric reaction
10 of CO) to form CO_2 :



13
14 The lifetime of CO in the lower troposphere is ≈ 2 mo.

15 The overall reaction sequence leading to CO_2 formation, through the HCHO and CO
16 intermediate products, is shown in Figure 3-2.

17 There is competition between NO and the HO_2 radical for reaction with the CH_3O_2
18 radical, and the reaction route depends on the rate constants for these two reactions and the
19 tropospheric concentrations of HO_2 radicals and NO. The rate constants for the reaction of
20 the CH_3O_2 radicals with NO (Reaction 3-22) and HO_2 radicals (Reaction 3-23) are of
21 comparable magnitude (Atkinson et al., 1992a). Based on the expected HO_2 radical
22 concentration in the troposphere, Logan et al. (1981) calculated that the reaction of the
23 CH_3O_2 radical with NO dominates for NO mixing ratios of > 30 ppt (equivalent to an NO
24 concentration of $> 7 \times 10^8$ molecule cm^{-3} in the lower troposphere). For NO mixing ratios
25 < 30 ppt, the reaction of the CH_3O_2 radical with HO_2 dominates.

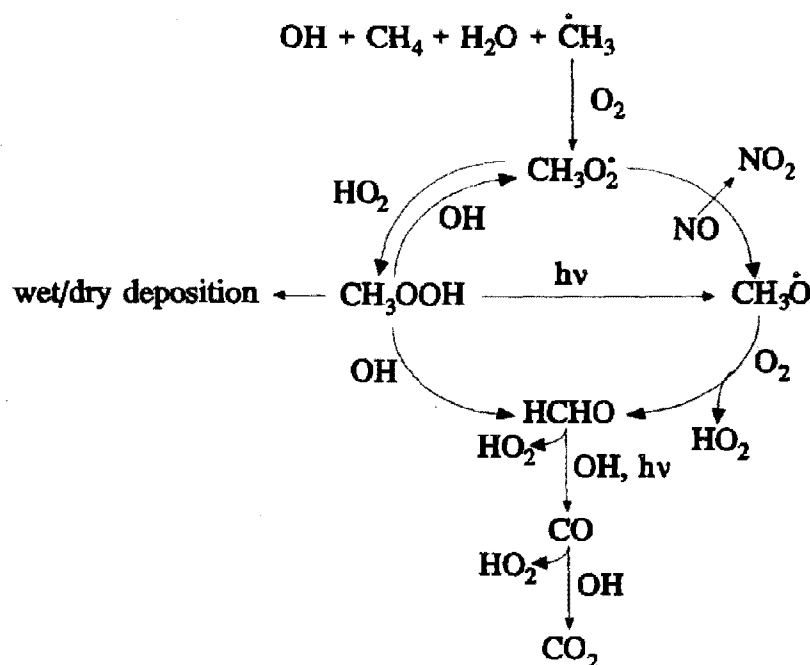


Figure 3-2. Atmospheric reactions in the complete oxidation of methane.

Hydroperoxy radicals formed from, for example, Reactions 3-26, 3-29, and 3-30 can react with NO, O₃, or themselves, depending mainly on the concentration of NO. The reaction with NO leads to regeneration of the OH radical,



whereas the reactions with O₃ and HO₂ radicals lead to a net destruction of tropospheric O₃:

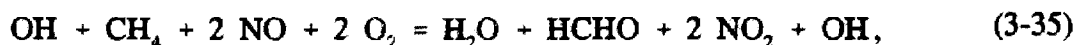


This net loss of tropospheric O₃ occurs because the photolytic production of the OH radical from O₃, via the intermediary of the O(¹D) atom, represents a loss process for tropospheric

ozone. Hence the absence of any O₃ formation from the methane oxidation cycle is equivalent to a net ozone loss. Using the rate constants reported for Reactions 3-32 and 3-34 (Atkinson et al., 1992a) and the tropospheric ozone mixing ratios given above, it is calculated that the HO₂ radical reaction with NO dominates over reaction with O₃ for NO mixing ratios > 10 ppt. The rate constant for Reaction 3-33 is such that an NO mixing ratio of this magnitude also means that the HO₂ radical reaction with NO dominates over the self-reaction of HO₂ radicals.

There are therefore two regimes, depending on the fate of HO₂ and CH₃O₂ radicals: (1) a high-NO regime in which HO₂ and CH₃O₂ radicals react with NO to convert NO to NO₂, regenerate the OH radical and, through the photolysis of NO₂, produce O₃; and (2) a low-NO regime in which HO₂ and CH₃O₂ radicals combine (Reaction 3-23) and HO₂ radicals undergo self-reaction and react with O₃ (Reactions 3-33 and 3-34), leading to a net destruction of O₃ and inefficient OH radical regeneration (see also Ehhalt et al., 1991; Ayers et al., 1992).

Under high-NO conditions, the oxidation of methane leading to the formation of HCHO can be written as the net reaction,



showing the conversion of two molecules of NO to NO₂ and regeneration of the OH radical. Because NO₂ photolyzes to form O₃ in the presence of O₂,



the oxidation of methane to HCHO under high-NO conditions can be written as,



showing the formation of ozone from methane oxidation in the troposphere. The reaction cycles oxidizing methane to formaldehyde, converting NO to NO₂, and forming ozone are shown schematically in Figure 3-3.

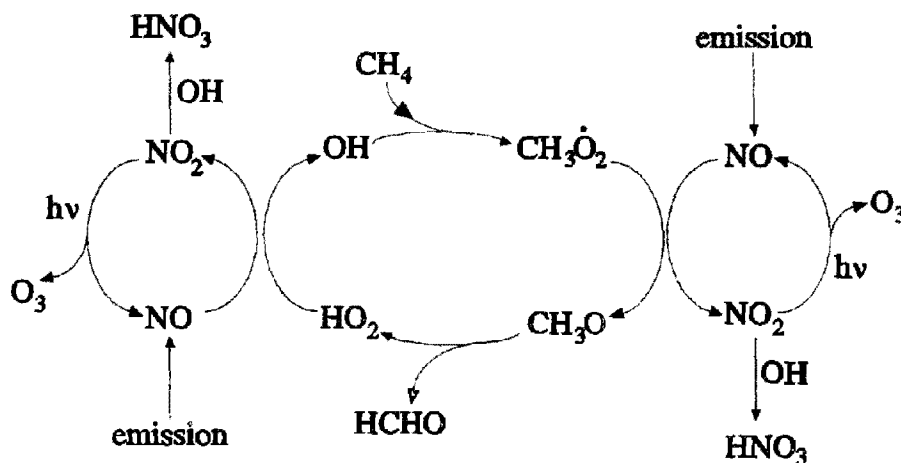
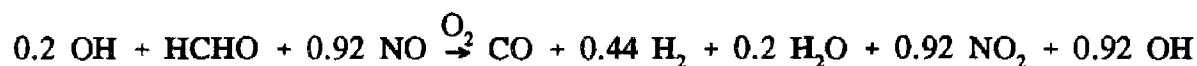


Figure 3-3. Cyclic reactions of methane oxidation to formaldehyde, conversion of nitric oxide to nitrogen dioxide, and concomitant formation of ozone in the atmosphere.

In a similar manner, under high-NO conditions, the photolysis of HCHO and its reaction with the OH radical is given approximately by:



(3-37)

Formaldehyde photooxidation is thus a source of HO₂ radicals (and of OH radicals in high-NO conditions) (Ehhalt et al., 1991), especially in urban areas where its concentration is elevated because it is produced during the oxidation of anthropogenic nonmethane VOCs (Finlayson-Pitts and Pitts, 1986).

Nitric oxide mixing ratios are sufficiently low in the lower troposphere over marine areas that oxidation of methane will lead to a net destruction of O₃ (low-NO conditions), as discussed by Carroll et al. (1990) and Ayers et al. (1992). However, in the upper troposphere and over continental areas impacted by NO_x emissions from combustion sources,

1 NO mixing ratios are high enough (high NO-conditions) for methane oxidation to lead to net
2 ozone formation (Carroll et al., 1990; World Meteorological Organization, 1992).

3 4 **3.2.3.4 Cloud Processes in the Methane-Dominated Troposphere**

5 In addition to the dry and wet deposition of certain products of the NO_x -methane-air
6 photooxidation (for example, wet and dry deposition of nitric acid and methylhydroperoxide
7 [Atkinson, 1988 and references therein; Hellpointner and G  b, 1989]), cloud processes can
8 have significant effects on the gas-phase chemistry of the "clean" troposphere (Lelieveld and
9 Crutzen, 1990, 1991; Warneck, 1991, 1992). Lelieveld and Crutzen (1990, 1991) have
10 postulated from modeling studies that the uptake of HCHO, HO_2 radicals, and N_2O_5 into
11 clouds can markedly decrease the production of O_3 . The incorporation of HCHO into
12 cloudwater removes HCHO from the gas-phase and hence reduces the gas-phase formation of
13 HO_2 ; uptake of HO_2 radicals into cloudwater has the same effect. Moreover, the aqueous-
14 phase reactions of $\text{CH}_2(\text{OH})_2$ (the hydrated form of HCHO) lead to the formation of O_2^- ,
15 which reacts with dissolved O_3 to act as a sink for O_3 during cloudy periods. During
16 nighttime, N_2O_5 formed in the gas-phase from Reactions 3-3, 3-12, and 3-13 can be readily
17 incorporated into cloudwater with hydrolysis to nitric acid, precluding the reformation of
18 NO_x during the following day from Reactions 3-13 and 3-14. Dentener and Crutzen (1993)
19 have also concluded from a computer modeling study that the heterogeneous reactions of
20 NO_3 radicals and N_2O_5 on aerosols can have significant effects on global O_3 mixing ratios
21 and on OH concentrations by reducing NO_x levels.

22 The net effect of these cloud processes is to reduce the gas-phase concentrations of
23 HCHO, NO_x , HO_x , and O_3 . Additional, but related, processes can occur in the polluted
24 troposphere (see, for example, Jacob et al., 1989; Dentener and Crutzen, 1993;
25 Section 3.2.5).

26 27 **3.2.4 Photochemistry of the Polluted Atmosphere**

28 Human activities lead to the emissions of NO_x ($\text{NO} + \text{NO}_2$) and both methane- and
29 nonmethane organic compounds into the atmosphere (Table 3-1). Methane emissions are
30 important on a global scale (World Meteorological Organization, 1992), whereas nonmethane
31 VOC emissions are most important in urban and regional areas. In addition to the emissions

TABLE 3-1. ESTIMATED EMISSIONS OF METHANE, NONMETHANE ORGANIC COMPOUNDS, NITROUS OXIDE, AND OXIDES OF NITROGEN (NO + NO₂) INTO THE EARTH'S ATMOSPHERE FROM BIOGENIC AND ANTHROPOGENIC SOURCES

Chemical	Emissions (Tg/year ^a)	
	Biogenic Sources	Anthropogenic Sources
CH ₄ ^b	≈ 150	≈ 350
NMOC ^c	≈ 1,000	≈ 100
N ₂ O (as N) ^d	≈ 7	≈ 6
NO _x (as N) ^e	≈ 10	≈ 40

^aTeragram = 10¹² g; or ≈ 10⁶ metric tons.

^bFung et al. (1991a); World Meteorological Organization (1992). Emissions from ruminants, rice paddies, and biomass burning are considered as anthropogenic emissions.

^cLogan et al. (1981); World Meteorological Organization (1992), with biogenic emissions being assumed to be 50% isoprene and 50% monoterpenes.

^dPrinn et al. (1990).

^eNational Research Council (1991); World Meteorological Organization (1992); biogenic sources ≈ 50% from soils; ≈ 50% from lightning.

of nonmethane VOCs from anthropogenic sources, large quantities of biogenic nonmethane VOCs (mainly of isoprene and monoterpenes) are emitted, both in polluted and nonpolluted areas, into the atmosphere from vegetation (see, for example, Isidorov et al., 1985; Lamb et al., 1987; Winer et al., 1991a,b).

Analogous to the photooxidation of methane, the interaction of NO_x with nonmethane VOCs from anthropogenic and biogenic sources under the influence of sunlight leads to the formation of photochemical air pollution (National Research Council, 1991). In urban areas, emissions of NO_x and VOCs from human activities (combustion sources, including transportation; industrial sources; solvent usage; landfills; etc.) dominate over biogenic sources (National Research Council, 1991; Chameides et al., 1992). However, the emissions of VOCs from vegetation have been implicated in the formation of photochemical air pollution in urban (Chameides et al., 1988; 1992) as well as rural (Trainer et al., 1987; Roselle et al., 1991; Chameides et al., 1992) areas.

In essence, the chemistry of the polluted urban and regional atmosphere is an extension of that of the clean, methane-dominated troposphere, with a number of additional

complexities because of the number and types of VOCs emitted from anthropogenic and biogenic sources. At least in certain urban areas, the NMOC content of ambient air is similar to the composition of typical gasolines (Mayrsohn and Crabtree, 1976; Mayrsohn et al., 1977; Harley et al., 1992; see Section 3.4.3). For example, gasolines typically consist of ≈ 55 to 65 % alkanes, ≈ 5 to 10 % alkenes, and ≈ 25 to 35 % aromatic hydrocarbons (Lonneman et al., 1986; Sigsby et al., 1987), whereas in Los Angeles the ambient urban air composition is ≈ 50 to 55 % alkanes, ≈ 5 to 15 % alkenes, ≈ 25 to 30 % aromatic hydrocarbons, and ≈ 5 to 15 % carbonyls (Grosjean and Fung, 1984; California Air Resources Board, 1992). Emissions of NO_x and VOCs are dealt with in detail in Section 3.4.1.

3.2.4.1 Tropospheric Loss Processes of Volatile Organic Compounds

The chemical loss processes of gas-phase VOCs include photolysis and chemical reaction with the OH radical during daylight hours, reaction with the NO_3 radical during nighttime hours, and reaction with O_3 , which is often present throughout the 24-h period (Atkinson, 1988).

As discussed earlier, photolysis of chemical compounds in the troposphere is restricted to the wavelength region above ≈ 290 nm. Because of the strength of chemical bonds, the tropospheric wavelength region in which photolysis can occur extends from ≈ 290 to ≈ 800 nm, and this wavelength region is often referred to as the "actinic" region. For photolysis to occur, a chemical compound must be able to absorb radiation in the actinic region (and hence have a non-zero absorption cross-section, σ_λ , in this wavelength region) and, having absorbed radiation, must then undergo chemical change (i.e., have a non-zero quantum yield, ϕ_λ , for photodissociation or photoisomerization). The quantum yield, ϕ_λ , is defined as (number of molecules of the chemical undergoing change)/(number of photons of light absorbed). The photolysis rate, $k_{\text{photolysis}}$, for the process,



is given by,

$$k_{\text{photolysis}} = \int J_{\lambda} \sigma_{\lambda} \phi_{\lambda} d\lambda, \quad (3-39)$$

where J_{λ} is the radiation flux at wavelength λ , and σ_{λ} and ϕ_{λ} are the absorption cross-section and photolysis quantum yield, respectively, at wavelength λ . Photolysis is therefore a pseudo-first-order process (depending on the radiation flux and spectral distribution) and the lifetime of a chemical with respect to photolysis is given by:

$$\tau_{\text{photolysis}} = k_{\text{photolysis}}^{-1} \quad (3-40)$$

For the reaction of a VOC with a reactive species, X (for tropospheric purposes, X = OH, NO₃, and O₃), the lifetime for the reaction process, C + X → products, is given by:

$$\tau_X = (k_X[X])^{-1} \quad (3-41)$$

and depends on the concentration of the reactive species X and the rate constant (k_X) for reaction of the VOC with X. In general, the ambient atmospheric concentrations of OH radicals, NO₃ radicals, and O₃ are variable, depending on time of day, season, latitude, altitude, etc. For the purpose of comparing lifetime calculations for various classes of VOCs, average ambient tropospheric concentrations of these three species are often used. The concentrations used here have been presented in the sections above and are: OH radicals, a 12-h average daytime concentration of 1.6×10^6 molecule cm⁻³ (equivalent to a 24-h average concentration of 8×10^5 molecule cm⁻³) (Prinn et al., 1992); NO₃ radicals, a 12-h nighttime average concentration of 5×10^8 molecule cm⁻³ (Atkinson, 1991); and O₃, a 24-h average of 7×10^{11} molecule cm⁻³ (30 ppb) (Logan, 1985).

The major classes of VOCs are the alkanes, alkenes (including alkenes from biogenic sources), aromatic hydrocarbons, carbonyl compounds, alcohols, and ethers (see California Air Resources Board, 1992). The calculated lifetimes with respect to the individual atmospheric loss processes of compounds representing a range of reactivities in each class are given in Table 3-2. Note that the lifetimes given are dependent on the reaction rate

TABLE 3-2. CALCULATED TROPOSPHERIC LIFETIMES OF SELECTED VOLATILE NONMETHANE ORGANIC COMPOUNDS DUE TO PHOTOLYSIS AND REACTION WITH HYDROXYL AND NO₃ RADICALS AND WITH OZONE

Organic	Lifetime Due to Reaction with			
	OH	NO ₃	O ₃	hν
n-Butane	5.7 days	2.8 years	> 4,500 years	
2-Methylbutane	3.7 days	290 days	> 4,500 years	
n-Octane	1.7 days	250 days	> 4,500 years	
Ethane	1.7 days	230 days	10 days	
Propene	6.6 h	4.9 days	1.6 days	
Isoprene	1.7 h	0.8 h	1.3 days	
Limonene	1.0 h	3 min	2.0 h	
Benzene	12 days	> 4 years	> 4.5 years	
Toluene	2.4 days	1.9 years	> 4.5 years	
m-Xylene	7.4 h	200 days	> 4.5 years	
Formaldehyde	1.5 days	80 days	> 4.5 years	4 h
Acetaldehyde	11 h	17 days	> 4.5 years	6 days
Acetone	66 days	—	> 4.5 years	60 days
2-Butanone	13 days	—	> 4.5 years	
Methanol	15 days	> 77 days	—	
Ethanol	4.4 days	> 50 days	—	
Methyl <i>t</i> -butyl ether	4.9 days	—	—	
Ethyl <i>t</i> -butyl ether	1.6 days	—	—	
Methylglyoxal	10 h	—	> 4.5 years	2 h

Sources: Lifetimes resulting from reaction with OH, NO₃, and O₃ were calculated using rate constants given in Atkinson and Carter (1984) and Atkinson (1989, 1991, 1993); data for photolysis lifetimes are from Horowitz and Calvert (1982), Meyrahn et al. (1982; 1986), Plum et al. (1983), and Rogers (1990). The OH radical NO₃ radical, and O₃ concentrations used (molecule cm⁻³) were: OH, 12-h average of 1.6×10^6 ; NO₃, 12-h average of 5×10^8 ; O₃, 24-h average of 7×10^{11} .

- 1 constants and the assumed ambient concentrations of OH radicals, NO₃ radicals, and O₃.
- 2 Uncertainties in the ambient concentrations of the reactive species translate directly into
- 3 corresponding uncertainties in the lifetimes.

1 The following brief discussions of the tropospheric chemistry of the important classes
2 of VOCs are based on the recent review and evaluation article of Atkinson (1993), and that
3 article should be consulted for further details of the tropospheric reactions of VOCs.
4

5 3.2.4.1.1 Alkanes

6 Since gasoline and diesel fuels contain alkanes of carbon number C_4 to $\geq C_{15}$, a large
7 number of alkanes are present in ambient air (see, for example, Grosjean and Fung, 1984;
8 California Air Resources Board, 1992; Section 3.4). Table 3-2 shows that the only
9 important tropospheric loss process for the alkanes is by reaction with the OH radical, with
10 calculated lifetimes of the C_3 to C_{10} alkanes ranging from ≈ 1 to 15 days. As for methane,
11 the OH radical reaction proceeds by H-atom abstraction from the various C-H bonds. The
12 nighttime reactions of the NO_3 radical with alkanes (calculated to be generally of minor
13 importance, but see Penkett et al. [1993]) also proceed by initial H-atom abstraction. For an
14 alkane (RH) the initially formed radical is an alkyl radical (R):
15

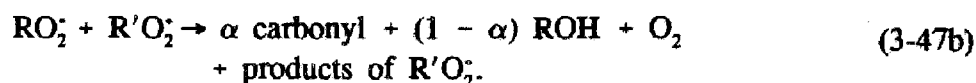
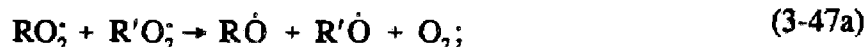
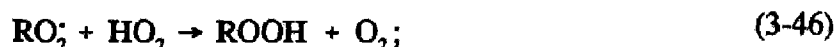


16 which rapidly adds O_2 to form an alkyl peroxy (RO_2) radical,
17



18 with the simplest of the RO_2 radicals being the methylperoxy radical, described in
19 Section 3.2.3.3 dealing with methane oxidation. Alkyl peroxy radicals (RO_2) can react with
20 NO , NO_2 , HO_2 radicals, and other organic peroxy radicals ($R'O_2$),
21





The reactions with organic peroxy radicals are expected to be of less importance in the troposphere than the other reactions listed. Since low NO conditions occur even in air masses in urban areas, the HO₂ radical reactions with RO₂ radicals and the subsequent chemistry must be considered. However, because of space constraints and a general lack of knowledge concerning the tropospheric chemistry of RO₂ radicals under low-NO conditions, only the reactions occurring under high-HO conditions are presented and discussed here. For the ≥C₃ alkyl peroxy radicals, in addition to the reaction pathway leading to NO-to-NO₂ conversion (Reaction 3-44a), a second reaction pathway leading to formation of an alkyl nitrate becomes important:

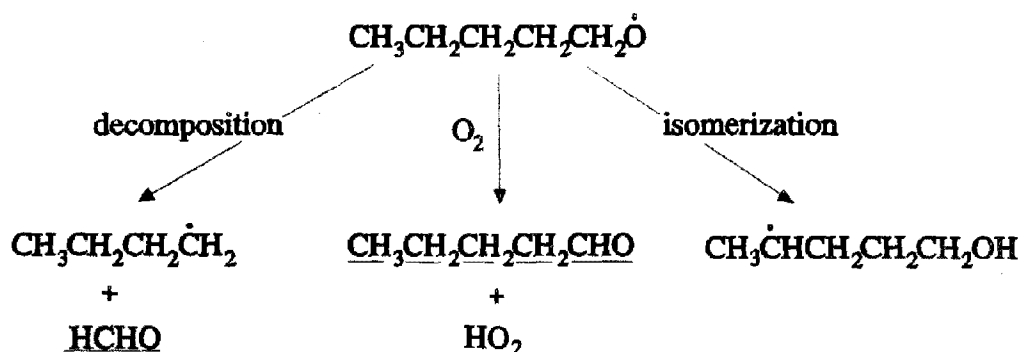


For a given alkyl peroxy radical, the alkyl nitrate yield increases with increasing pressure and with decreasing temperature (Carter and Atkinson, 1989a).

Analogous to the case for the methoxy radical, those alkoxy radicals (RO₂) formed from the higher alkanes that have an abstractable H atom can react with O₂ to form the HO₂ radical and a carbonyl; for example,



In addition, unimolecular decomposition by C-C bond scission and unimolecular isomerization via a six-member transition state (Atkinson and Carter, 1991; Atkinson, 1993) can be important for the larger alkoxy radicals. For example, the following chemistry can occur for the 1-pentoxo radical:



with the alkyl radicals $\text{C}_4\text{H}_9\cdot$ and $\text{HOCH}_2\text{CH}_2\text{CH}_2\dot{\text{C}}\text{HCH}_3$ undergoing further reaction.

The majority of the reaction rate constants and reaction pathways in the alkane degradation schemes are assumed by analogy with the chemistry of C_1 - C_3 alkyl, alkyl peroxy, and alkoxy radicals (Atkinson, 1990, 1993; Carter, 1990; Atkinson et al., 1992a). A number of areas of uncertainty still exist for the tropospheric chemistry of the alkanes (Atkinson, 1993). These include (a) the relative importance of alkoxy radical reaction with O_2 , decomposition and isomerization, and the reactions occurring subsequent to the isomerization reaction; (b) the formation of alkyl nitrates from the reactions of the peroxy radicals with NO ; and (c) reactions of the alkyl peroxy radicals with HO_2 and other peroxy radicals, reactions that can be important in the nonurban troposphere.

3.2.4.1.2 Alkenes (Anthropogenic and Biogenic)

The alkenes emitted from anthropogenic sources are mainly ethene, propene, and the butenes, with lesser amounts of the $\geq \text{C}_5$ alkenes. The major biogenic alkenes emitted from vegetation are isoprene (2-methyl-1,3-butadiene) and $\text{C}_{10}\text{H}_{16}$ monoterpenes (Isidorov et al., 1985; Winer et al., 1992), and their tropospheric chemistry is currently the focus of much attention (see, for example, Hatakeyama et al., 1989, 1991; Arey et al., 1990; Tuazon and Atkinson, 1990a; Pandis et al., 1991; Paulson et al., 1992a,b; Paulson and Seinfeld, 1992a; Zhang et al., 1992; Hakola et al., 1993a,b).

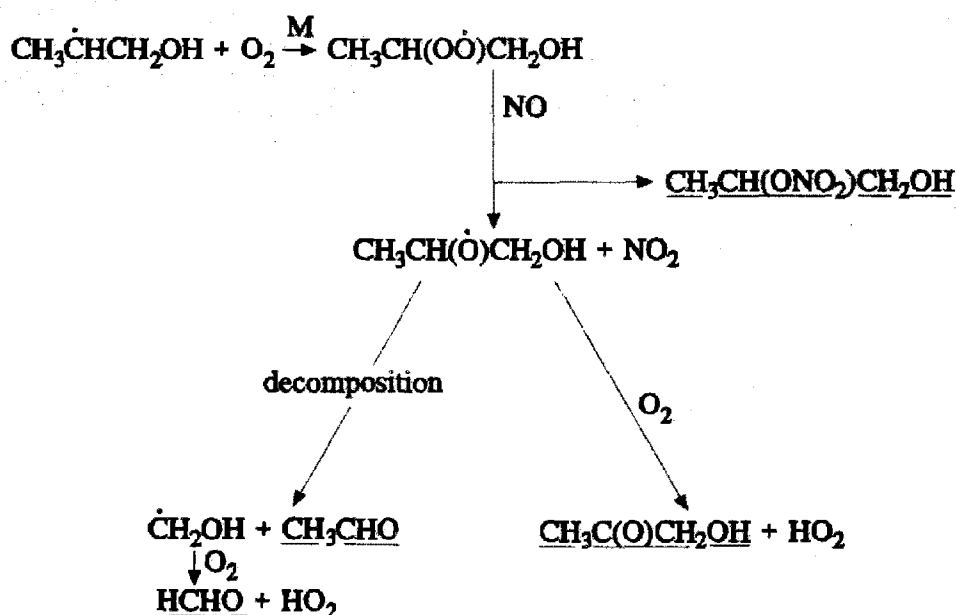
As evident from Table 3-2, the alkenes react with OH and NO_3 radicals and O_3 . All three processes are important atmospheric transformation processes, and all three reactions proceed by initial addition to the $>\text{C}=\text{C}<$ bond(s). These reactions are briefly discussed below.

Hydroxyl Radical Reactions

As noted above, the OH radical reactions with the alkenes proceed mainly by OH radical addition to the $>C=C<$ bond(s). For example, the OH radical reaction with propene leads to the formation of the two OH-containing radicals,



The subsequent reactions of these radicals are similar to those of the alkyl radicals formed by H-atom abstraction from the alkanes. Taking the $CH_3\dot{C}HCH_2OH$ radical as an example, under high-NO conditions, the following chemistry occurs:



The underlined species represent products that, although stable, can undergo further reaction; and hence they can lead to "second-generation" products. For the simple $\leq C_4$ alkenes, the intermediate OH-containing radicals appear to undergo mainly decomposition at room temperature and atmospheric pressure of air. Hence for propene, the "first-generation" products of the OH radical reaction in the presence of NO are HCHO and CH_3CHO , irrespective of which OH-containing radical is formed.

1 However, this is not the case for the more complex alkenes of biogenic origin. The
2 product studies of Tuazon and Atkinson (1990a) and Paulson et al. (1992a) for the OH
3 radical reaction with isoprene in the presence of NO_x show that the products expected from
4 reaction schemes analogous to that shown above for propene (i.e., HCHO + methyl vinyl
5 ketone [$\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CH}_2$] and HCHO + methacrolein [$\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO}$], arising from
6 initial OH radical addition to the $\text{CH}_2=\text{CH}-$ and $\text{CH}_2=\text{C}<$ bond, respectively) do not
7 account for the entire reaction pathways. The product yields obtained from the studies of
8 Tuazon and Atkinson (1990a) and Paulson et al. (1992a) are (Atkinson, 1993): methyl vinyl
9 ketone, 34%; methacrolein, 24%; 3-methylfuran, 5%; organic nitrates, $\approx 12\%$; and
10 unidentified carbonyl compounds, $\approx 25\%$. The HCHO yield was consistent with being a
11 co-product formed with methyl vinyl ketone and methacrolein (Tuazon and Atkinson, 1990a).
12 Aerosol formation for isoprene photooxidation has been shown to be of negligible importance
13 under atmospheric conditions (Pandis et al., 1991; Zhang et al., 1992).

14 To date, few quantitative product studies have been carried out for the monoterpenes
15 (Arey et al., 1990; Hatakeyama et al., 1991; Hakola et al., 1993a,b). Arey et al. (1990) and
16 Hakola et al. (1993a,b) have observed the C_7 - C_{10} carbonyl compounds expected by analogy
17 with the reaction scheme shown above for propene, but with total carbonyl formation yields
18 of $\leq 50\%$. These data (Arey et al., 1990; Hakola et al., 1993a,b) indicate the formation of
19 other products in significant, and often dominant, yields. Hatakeyama et al. (1991) used
20 Fourier transform infrared (FTIR) absorption spectroscopy and reported carbonyl compounds
21 to be formed in high yield from α -pinene and β -pinene, in apparent disagreement with the
22 data of Arey et al. (1990) and Hakola et al. (1993b). While Hatakeyama et al. (1991)
23 ascribed these carbonyl products to those expected from oxidative cleavage of the $>\text{C}=\text{C}<$
24 bonds, it is possible that the yields reported for these carbonyls included contributions by
25 other, as yet unidentified, carbonyl-containing products.

27 *Nitrate Radical Reactions*

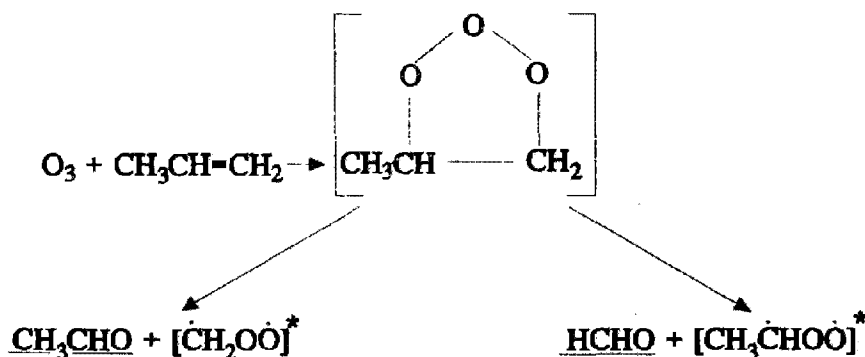
28 The NO_3 radical reactions proceed by reaction schemes generally similar to the OH
29 radical reactions, except that when NO_3 radicals are present, NO concentrations are low (see
30 above) and $\text{RO}_2 + \text{RO}_2$ and $\text{RO}_2 + \text{HO}_2$ radical reactions are expected to dominate over
31 $\text{RO}_2 + \text{NO}$ reactions. For propene the initial reaction is (Atkinson, 1991),



followed by a series of reactions that are expected (Atkinson, 1991) to lead to the formation of, among others, carbonyls and nitrato-carbonyls (for example, HCHO, CH₃CHO, CH₃CH(ONO₂)CHO, and CH₃C(O)CH₂ONO₂ from propene). Few data are presently available concerning the products and detailed mechanisms of NO₃-alkene reactions (Atkinson, 1991, 1993 and references therein). In particular, the reaction products and mechanisms for the NO₃ radical reactions with isoprene and the monoterpenes are still not quantitatively understood (Kotzias et al., 1989; Barnes et al., 1990; Hjorth et al., 1990; Skov et al., 1992).

Ozone Reactions

The O₃ reactions also proceed by addition of O₃ to the alkene, to form an energy-rich ozonide that rapidly decomposes to form carbonyls and energy-rich biradicals []^{*},



The energy-rich biradicals, [CH₂OÖ]^{*} and [CH₃CHOÖ]^{*}, undergo collisional stabilization or decomposition:



1 There are still significant uncertainties concerning the reactions of the energy-rich biradicals
2 (see, for example, Horie and Moortgat, 1991; Atkinson, 1990, 1993), with recent studies
3 showing the production of OH radicals in high yields for several alkenes (Niki et al., 1987;
4 Paulson et al., 1992a; Atkinson et al., 1992b; Paulson and Seinfeld, 1992b; Atkinson and
5 Aschmann, 1993).

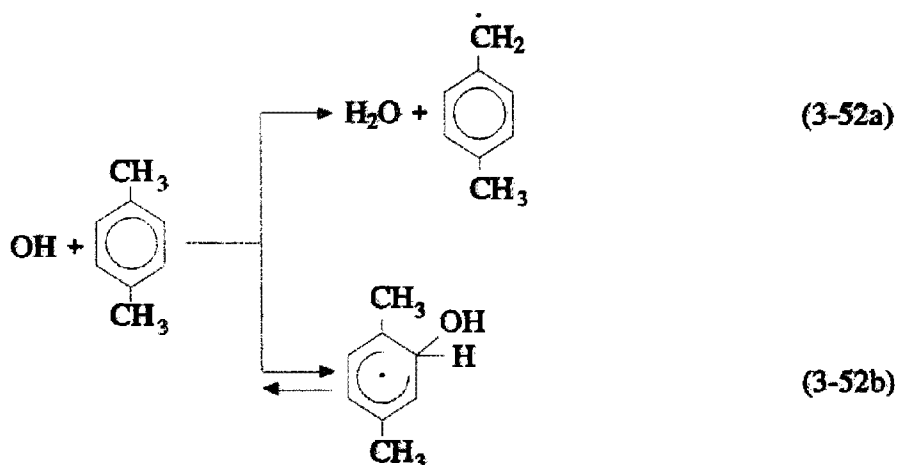
6 For isoprene, the major products are methacrolein and methyl vinyl ketone (Kamens
7 et al., 1982; Niki et al., 1983; Paulson et al., 1992b). Paulson et al. (1992b) derived
8 OH radical and O(³P) atom formation yields of 0.68 ± 0.15 and 0.45 ± 0.2 , respectively,
9 from the O₃ reaction with isoprene, indicating the dominance of secondary reactions.
10 However, Atkinson et al. (1992b) derived a significantly lower OH radical formation yield of
11 0.27 (uncertain to a factor of ≈ 1.5). Clearly, further studies of this important reaction are
12 needed.

13 The only quantitative studies of the gas-phase O₃ reactions with the monoterpenes are
14 those of Hatakeyama et al. (1989) for α - and β -pinene and Hakola et al. (1993a,b) for a
15 series of monoterpenes. Additionally, Atkinson et al. (1992b) derived OH radical formation
16 yields from these reactions under atmospheric conditions.

17 Several groups (Gäb et al., 1985; Becker et al., 1990, 1993; Simonaitis et al., 1991;
18 Hewitt and Kok, 1991) have reported the formation of H₂O₂ and organic peroxides from
19 O₃ reactions with alkenes. However, there are significant disagreements in the quantitative
20 results reported by Becker et al. (1990, 1993) and Simonaitis et al. (1991).

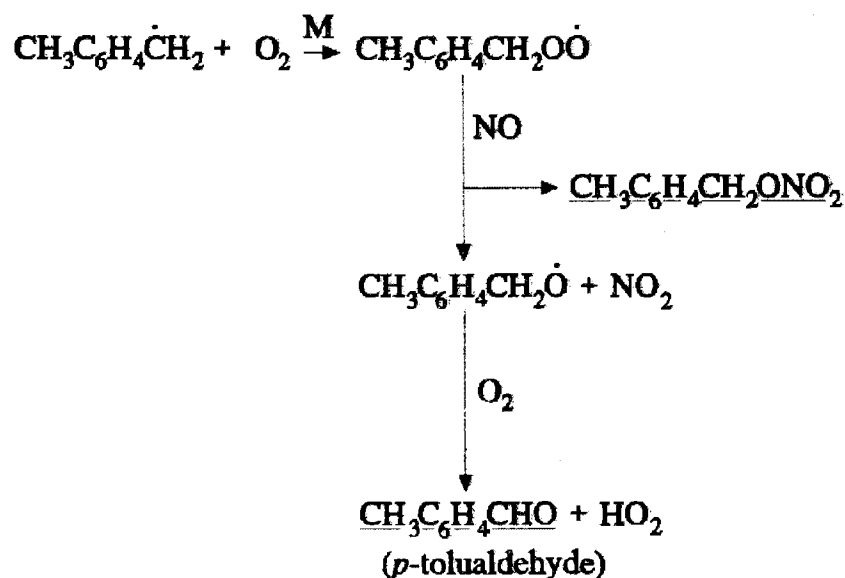
21 22 **3.2.4.1.3 Aromatic Hydrocarbons**

23 The most abundant aromatic hydrocarbons in urban atmospheres are benzene, toluene,
24 the xylenes, and the trimethylbenzenes (Grosjean and Fung, 1984; California Air Resources
25 Board, 1992). As shown in Table 3-2, the only tropospherically important loss process for
26 benzene and the alkyl-substituted benzenes is by reaction with the OH radical. For the alkyl-
27 substituted benzenes, the OH radical reactions proceed by two pathways: H-atom abstraction
28 from the C-H bonds of the alkyl substituent group(s) and OH radical addition to the aromatic
29 ring, as shown here, for *p*-xylene,
30



with the OH radical addition pathway being reversible above ≈ 325 K (Atkinson, 1989).

The radical formed in Reaction 3-52a reacts analogously to an alkyl radical (Atkinson, 1993), leading in the presence of NO to aromatic aldehydes and organic nitrates:



The OH-containing radical formed in Reaction 3-52b can undergo reaction with both NO₂ and O₂. Knispel et al. (1990) reported rate constants for the reactions of NO₂ and O₂ with the OH-containing radicals formed from benzene and toluene. The magnitude of the rate constants they obtained implies that in the troposphere the major reactions of these radicals will be with O₂. However, laboratory studies conducted under a range of NO₂

1 concentrations such that the expected reactions varied from being mainly with O₂ to being
2 mainly with NO₂ showed no obvious change in the major ring-addition product yields
3 (Atkinson et al., 1989). The data of Atkinson et al. (1989), obtained from the OH radical-
4 initiated reactions of benzene and toluene, may indicate that the product yields from the
5 O₂ and NO₂ reactions with these radicals are fairly similar. The present uncertainties
6 concerning the fate of these radicals need to be resolved before a detailed mechanism of the
7 tropospheric degradation of aromatic hydrocarbons can be constructed.

8 Despite these uncertainties, however, products from the OH radical addition pathway
9 have been identified and their formation yields determined (Atkinson, 1993, and references
10 therein). The major products identified from the OH radical addition pathway are phenolic
11 compounds (for example, phenol from benzene and *o*-, *m*- and *p*-cresol from toluene) and
12 α-dicarbonyls (glyoxal, methylglyoxal, and 2,3-butanedione) arising from cleavage of the
13 aromatic ring (see, for example, Atkinson, 1990, 1993, and references therein). Significant
14 fractions (≥ 50% for benzene, toluene, and the xylenes) of the reaction products are,
15 however, still not accounted for.

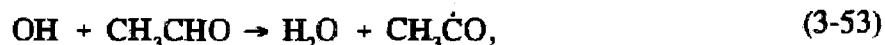
16 17 **3.2.4.1.4 Carbonyl Compounds**

18 As noted above, the OH radical reactions with the alkanes, alkenes, and aromatic
19 hydrocarbons lead, often in large yield, to the formation of carbonyl compounds. Likewise,
20 carbonyls are formed during the reactions of NO₃ radicals and O₃ with alkenes. As a first
21 approximation, the carbonyl compounds of tropospheric interest are: formaldehyde (see
22 Section 3.2.3.3), acetaldehyde, and the higher aliphatic aldehydes; benzaldehyde; acetone,
23 2-butanone, and the higher ketones; and simple dicarbonyls such as glyoxal, methylglyoxal,
24 and 2,3-butanedione.

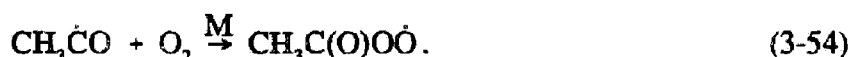
25 The tropospheric photooxidation of isoprene leads to the formation of methyl vinyl
26 ketone (CH₃C(O)CH=CH₂) and methacrolein (CH₃C(CHO)=CH₂). The OH radical-
27 initiated reactions of these two carbonyl compounds in the presence of NO_x have been
28 studied by Tuazon and Atkinson (1989, 1990b).

29 The tropospherically important loss processes of the carbonyls not containing >C=C<
30 bonds are photolysis and reaction with the OH radical. As shown in Tables 3-2, photolysis
31 is a major tropospheric loss process for the simplest aldehyde (HCHO) and the simplest

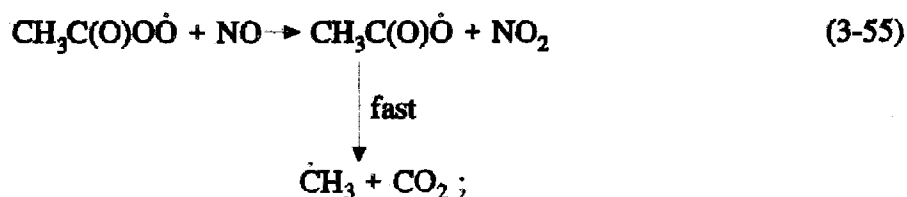
ketone ($\text{CH}_3\text{C}(\text{O})\text{CH}_3$), as well as for the dicarbonyls. For the higher aldehydes and ketones, the OH radical reactions are calculated to be the dominant gas-phase loss process (Table 3-2). For acetaldehyde, the reaction proceeds by H-atom abstraction from the -CHO group to form the acetyl ($\text{CH}_3\dot{\text{C}}\text{O}$) radical,



which rapidly adds O_2 to form the acetyl peroxy radical:



This O_2 addition pathway is in contrast to the reaction of O_2 with the formyl ($\text{H}\dot{\text{C}}\text{O}$) radical formed from HCHO, which reacts by an H-atom abstraction pathway (Reaction 3-30). The acetyl peroxy radical reacts with NO and NO_2 ,



with the NO_2 reaction forming the thermally unstable peroxyacetyl nitrate (PAN). The higher aldehydes also lead to PANs (Roberts, 1990); for example, propionaldehyde reactions lead to the formation of peroxypropionyl nitrate (PPN). While the rate constant at atmospheric pressure for the thermal decomposition of PAN (Atkinson et al., 1992a) is such that the lifetime of PAN with respect to thermal decomposition is ≈ 30 min at 298 K in the lower troposphere, the thermal lifetime of PAN is calculated to be several hundred years in the upper troposphere. Reaction with OH radicals or photolysis, or both, will therefore dominate as the PAN loss processes in the upper troposphere (Atkinson et al., 1992a).

1 The transport of PAN out of urban areas into colder air masses (for example, to higher
2 altitude) leads to PANs becoming a temporary reservoir of NO_x and allowing for the long-
3 range transport of NO_x to less polluted areas. Release of NO_2 in these less polluted areas
4 via reaction (-3-56), with subsequent photolysis of NO_2 , then leads to O_3 formation and the
5 pollution of remote areas.

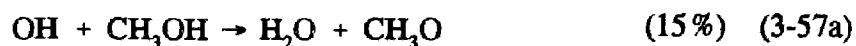
6 Since the $\dot{\text{C}}\text{H}_3$ radical formed from the NO reaction with the acetyl peroxy radical leads
7 to HCHO formation, the OH radical reaction with acetaldehyde forms formaldehyde. The
8 same process occurs for propionaldehyde, which reacts to form CH_3CHO and then HCHO.
9 Benzaldehyde appears to behave as a phenyl-substituted aldehyde with respect to its OH
10 radical reaction, and the analog to PAN is then peroxybenzoyl nitrate, PBzN
11 ($\text{C}_6\text{H}_5\text{C}(\text{O})\text{OONO}_2$).

12 The formation of formaldehyde from acetaldehyde, and of acetaldehyde and then
13 formaldehyde from propionaldehyde, are examples of "cascading", in which the
14 photochemical degradation of emitted VOCs leads to the formation of further VOCs,
15 typically containing fewer carbon atoms than the precursor VOC. This process continues
16 until the degradation products are removed by wet and dry deposition or until CO or CO_2 are
17 the degradation products. The reactions of each of these VOCs (i.e., the initially emitted
18 VOC and its first-, second-, and successive-generation products) in the presence of NO
19 (high-NO conditions) can lead to the formation of O_3 .

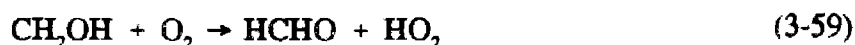
20 As discussed in Section 3.2.3.3 for formaldehyde, the photolysis of carbonyl
21 compounds can lead to the formation of new radicals that result in enhanced photochemical
22 activity. The OH radical reactions of the ketones are generally analogous to the reaction
23 schemes for the alkanes and aldehydes.

24 25 **3.2.4.1.5 Alcohols and Ethers**

26 A number of alcohols and ethers are used in present-day and reformulated gasolines and
27 in alternative fuels. The alcohols include methanol, ethanol, and *tert*-butyl alcohol, and the
28 ethers include methyl *tert*-butyl ether and ethyl *tert*-butyl ether. Table 3-2 shows that in the
29 troposphere these VOCs react only with the OH radical. These OH radical reactions proceed
30 by H-atom abstraction from the C-H bonds (and to a minor extent from the O-H bonds in the
31 alcohols). For example, for methanol



In the troposphere, both of the CH_3O and CH_2OH radicals react only with O_2 to form formaldehyde.



The overall reaction is then:



The reaction sequence for ethanol is similar (Atkinson, 1993). Product studies of the OH radical-initiated reactions of methyl *tert*-butyl ether and ethyl *tert*-butyl ether in the presence of NO_x have been carried out by Japer et al. (1990), Smith et al. (1991, 1992), Tuazon et al. (1991), and Wallington and Japar (1991). The major products from methyl *tert*-butyl ether are *tert* butyl formate, formaldehyde, and methyl acetate [$\text{CH}_3\text{C}(\text{O})\text{OCH}_3$]; and from ethyl *tert*-butyl ether, *tert*-butyl formate, *tert*-butyl acetate, formaldehyde, acetaldehyde, and ethyl acetate. The available product data and the reaction mechanisms have been reviewed by Atkinson (1993) and that reference should be consulted for further details.

In addition to the use of alcohols and ethers in gasolines and alternative fuels, unsaturated alcohols have been reported as emissions from vegetation (Arey et al., 1991a; Goldan et al., 1993), and kinetic and product studies have begun to be reported for these biogenic VOCs (Grosjean et al., 1993).

3.2.4.1.6 *Primary Products and Areas of Uncertainty for the Tropospheric Degradation Reactions of VOCs*

The tropospheric degradation reactions of the alkanes, alkenes (including those of biogenic origin), aromatic hydrocarbons, carbonyls (often formed as products of the degradation reactions of alkanes, alkenes, and aromatic hydrocarbons) and other oxygenates have been briefly discussed above. The "first-generation" products of the alkanes, alkenes, and aromatic hydrocarbons are as follows (unfortunately, complete product distributions have not been obtained for most of the VOCs studied):

Alkanes

- Carbonyl compounds (i.e., aldehydes and ketones) are formed as major products for the smaller ($\leq C_4$ alkanes).
- Alkyl nitrates are formed from the $\geq C_3$ alkanes studied to date. The yields increase with the size of the alkane from $\approx 4\%$ for propane to $\approx 30\%$ for *n*-octane.
- δ -Hydroxycarbonyls are expected to be formed after the alkoxy radical isomerization reaction. To date, no direct evidence for the formation of these compounds exists. For the larger alkanes, the formation yields of these compounds could be high.
- Alkl hydroperoxides are formed under low-NO conditions.
- Alkyl peroxy nitrates ($ROONO_2$) are formed but have short lifetimes (a few seconds at 298 K) due to thermal decomposition.
- Alcohols are formed from the combination reactions of the peroxy radicals under low-NO conditions. These compounds are expected to be formed in low overall yield in the troposphere.

The major uncertainties in the atmospheric chemistry of the alkanes concern the formation of alkyl nitrates from the reactions of the peroxy radicals with NO (Reaction 3-44b) and the reactions of the alkoxy radicals in the troposphere. These uncertainties affect the amount of NO to NO_2 conversion occurring and hence the amounts of O_3 which are formed during the NO_x -air photooxidations of the alkanes.

Alkenes

- Carbonyl compounds (aldehydes and ketones) are formed as major products of the OH radical, NO₃ radical, and O₃ reactions.
- Organic acids are formed from the O₃ reactions, but possibly in low yield.
- Hydroxynitrates and nitratocarbonyls are formed from the OH radical reactions and NO₃ radical reactions, respectively. The hydroxynitrates are formed in low yield from the OH radical reactions, while the nitratocarbonyls may be major products of the NO₃ radical reactions.
- Hydroxycarbonyls and carbonyl-acids are also expected to be formed, although few, if any, data exist to date.
- Decomposition products are produced from the initially energy-rich biradicals formed in the O₃ reactions; these include CO, CO₂, esters, hydroperoxides, and, in the presence of NO_x, peroxyacyl nitrates (RC(O)OONO₂; PANs).

The major areas of uncertainty concern the products and mechanisms of the O₃ reactions (in particular, the radical yields from these reactions that affect the O₃ formation yields from the NO_x-air photooxidations of the alkenes) and the reaction products and mechanisms of the OH radical reactions with the alkenes containing more than four carbon atoms.

Aromatic Hydrocarbons

- Phenolic compounds, such as phenol and cresols, have been observed as major products of the atmospheric reactions of the aromatic hydrocarbons under laboratory conditions.
- Aromatic aldehydes, such as benzaldehyde, are formed in ≤10% yield.
- α-Dicarbonyls, such as glyoxal, methylglyoxal, and biacetyl, are formed in fairly high (10 to 40%) yields. These dicarbonyls photolyze rapidly to form radicals and are therefore important products with respect to the photochemical activity of the aromatic hydrocarbons.
- Unsaturated carbonyl or hydroxycarbonyl compounds, or both, are formed, although there is little direct information concerning the formation of these products.

1 There is a lack of knowledge as to the detailed reaction mechanisms and reaction
2 products for the aromatic hydrocarbons under tropospheric conditions. (i.e., for the NO_x
3 concentration conditions encountered in urban and rural areas.). It is possible that the
4 products observed in laboratory studies, and their formation yields, are not representative of
5 the situation in the troposphere. This then leads to an inability to formulate detailed reaction
6 mechanisms for the atmospheric degradation reactions of the aromatic hydrocarbons, and the
7 chemical mechanisms used in urban airshed models must then rely heavily on environmental
8 (or "smog") chamber data.

10 *Oxygenated Compounds*

- 11 • The products observed from the atmospheric photooxidations of oxygenated
12 organics are carbonyls, organic acids (RC(O)OH), esters, alcohols, and, in
13 the presence of NO_x, PANs.

16 The major area of uncertainty concerns the importance of photolysis of carbonyl
17 compounds in the troposphere, and the products formed. In particular, there is a lack of
18 information concerning the absorption cross-sections and photodissociation quantum yields
19 for most of the aldehydes and ketones other than formaldehyde, acetaldehyde, and acetone.

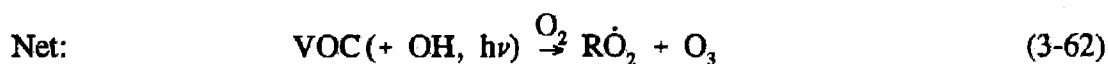
21 3.2.4.2 Chemical Formation of Ozone in Polluted Air

22 3.2.4.2.1 Major Steps in Ozone Formation

23 As discussed earlier, NO_x, and VOCs interact under the influence of sunlight to form
24 O₃ and other photochemical air pollutants. The major steps in this process are the
25 conversion of NO to NO₂ by peroxy radicals, with the photolysis of NO₂ leading to
26 O₃ production. In the absence of a VOC, Reactions 3-1 through 3-3,



lead to no net formation of O₃. The reaction of a VOC with the OH radical, or its photolysis, leads to the formation of HO₂ and organic peroxy (RO₂) radicals, which react with NO under high-NO conditions:



with the alkoxy (RO) radical producing further HO₂ or RO₂ radicals, or both, and, hence, further production of O₃. This process is shown schematically in Figure 3-4.

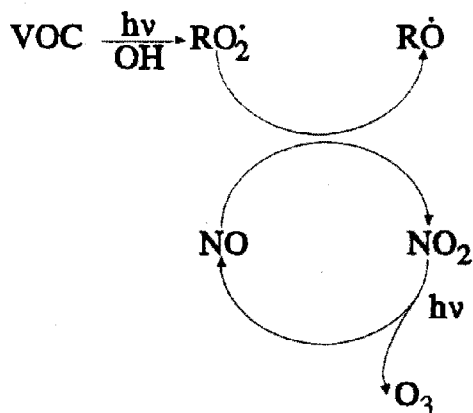


Figure 3-4. Major steps in production of ozone in ambient air (R = H, alkyl or substituted alkyl, or acyl).

The general time-concentration profiles for selected species during irradiation of an NO_x -VOC-air mixture are shown in Figure 3-5 for a constant light intensity and in Figure 3-6 for diurnally varying light intensity. These general features of an NMOC- NO_x -air irradiation are described by the following reactions:

(a) The conversion of NO to NO_2 occurs through the oxidation reactions,

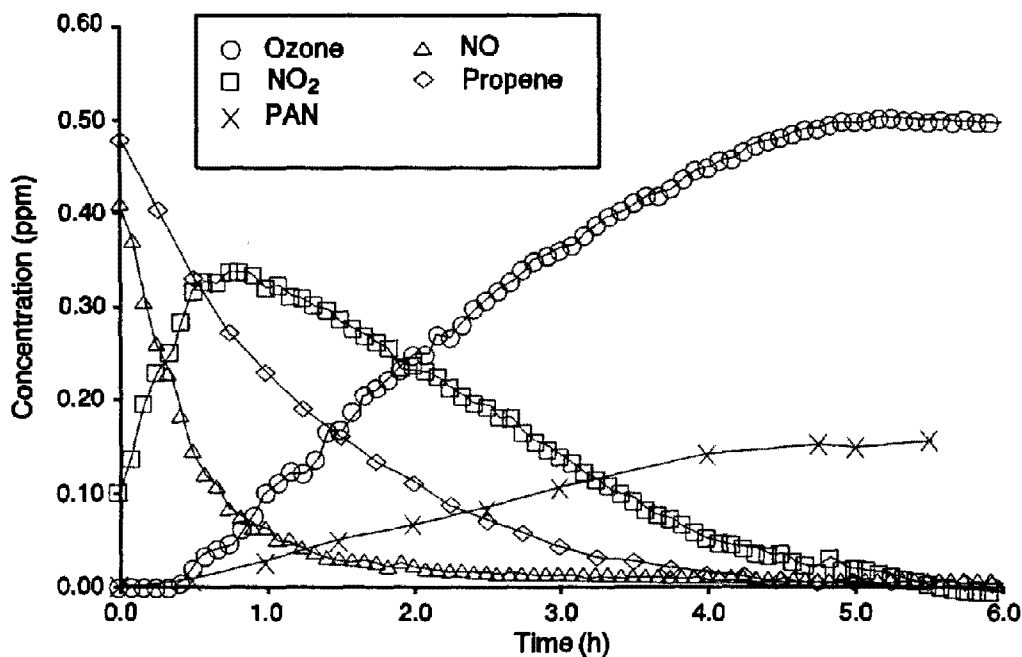
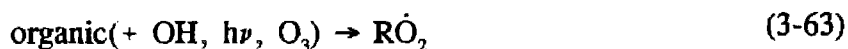


Figure 3-5. Time-concentration profiles for selected species during irradiations of an NO_x -propene-air mixture in an indoor chamber with constant light intensity.

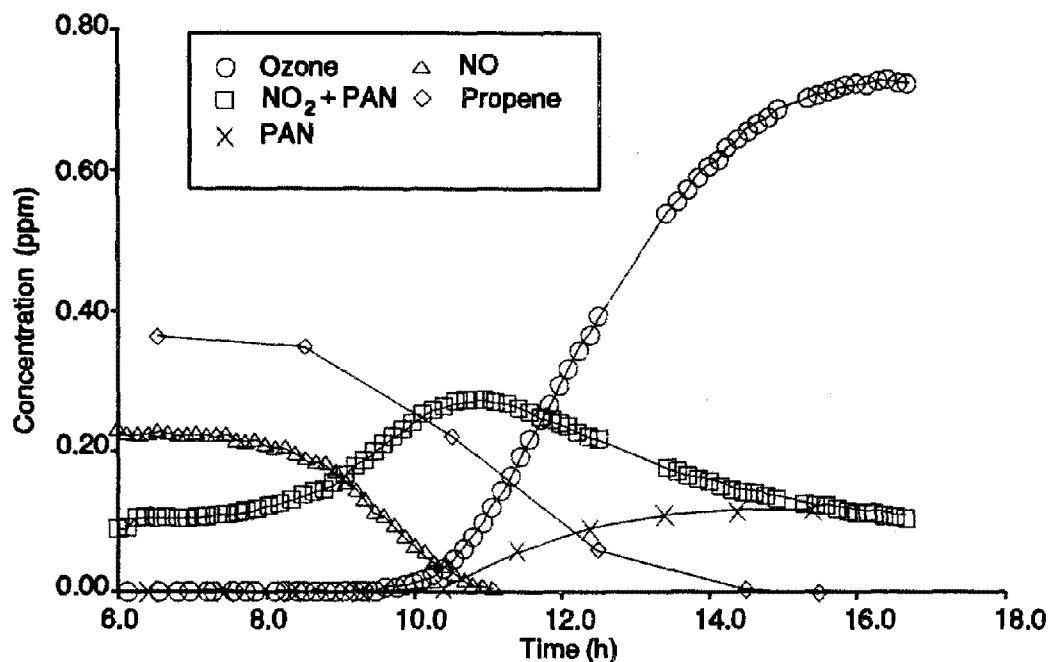


Figure 3-6. Time-concentration profiles for selected species during irradiations of an NO_x -propene-air mixture in an outdoor chamber with diurnally varying light intensity.



(b) The maximum concentration of NO_2 is less than the initial $\text{NO} + \text{NO}_2$ concentration because NO_2 is removed through the reaction,



(c) The O_3 concentration increases with the NO_2/NO concentration ratio, and O_3 formation ceases when NO_2 (and hence NO_x) has been removed by reaction.

(d) Formation of PAN occurs by Reaction 3-56. Because of Reactions 3-55 and 3-56, the PAN concentration also increases with the NO_2/NO concentration ratio, and PAN formation also ceases when NO_x has been depleted.

(e) The removal processes for NO_x are by reaction of NO_2 with the OH radical to form nitric acid (Reaction 3-16), the formation of organic nitrates from the $\text{ROO} \cdot + \text{NO}$ reaction pathway 3-42b, and the formation of PAN through Reaction 3-56. The initially present NO_x is converted to organic nitrates, nitric acid, and thermally unstable PAN(s). At ambient temperature, the PAN(s) will gradually thermally decompose to yield NO_2 and the acylperoxy radicals; hence the ultimate fate of NO_x will be to form nitric acid and organic nitrates.

3.2.4.2.2 *Effects of Varying Initial Nitrogen Oxide and Nonmethane VOC Concentrations*

As discussed above, NO_x and VOC interact in sunlight to form O_3 and other photochemical air pollutants. The formation of O_3 from the NO_x and VOC precursors is nonlinear with respect to the precursor emissions (or ambient concentrations) and, as discussed in detail in Section 3.6, computer models incorporating emissions, meteorology, and chemistry are necessary for a full understanding of the complexities of the NO_x -VOC- O_3 system. The effects of high versus low VOC/ NO_x ratios and of VOC versus NO_x emission reductions are also discussed in Section 3.6.

3.2.4.2.3 *Effects of Biogenic Nonmethane VOC Emissions*

Biogenic VOC emissions can be important in urban and rural areas (Trainer et al., 1987; Chameides et al., 1988, 1992; Roselle et al., 1991) and can contribute to O_3 formation in much the same way as anthropogenic VOCs. Modeling simulations in which urban biogenic VOC emissions are first included and then excluded from the calculations generally indicate little effect of the biogenic emissions on the predicted O_3 levels; this is not unexpected from the shape of the O_3 isopleths at high VOC/ NO_x ratios (see, for example, Chameides et al., 1988, and Section 3.6). However, results of modeling studies in which anthropogenic VOC emissions are removed from the simulations (but anthropogenic NO_x emissions are left unaltered) suggest that anthropogenic NO_x together with biogenic VOCs may form sufficient O_3 to exceed the National Ambient Air Quality Standards (NAAQS), at least in certain areas (Chameides et al., 1988). Thus, as discussed for the Atlanta, GA, region (Chameides et al., 1988), NO_x control may be more favorable than VOC control in urban areas with substantial biogenic NMOC emissions.

1 While it is known that isoprene is reactive with respect to the formation of
2 O₃ (Section 3.2.4.3) and that the monoterpenes react rapidly with OH radicals, NO₃ radicals,
3 and O₃, the ozone-forming potentials of the various monoterpenes emitted into the
4 atmosphere are not known.

6 3.2.4.3 Hydrocarbon Reactivity with Respect to Ozone Formation

7 As discussed in Section 3.2.4, VOCs are removed and transformed in the troposphere
8 by photolysis and by chemical reaction with OH radicals, NO₃ radicals, and O₃. In the
9 presence of sunlight, the degradation reactions of the VOCs lead to the conversion of NO to
10 NO₂ and the formation of O₃ and various organic products. However, different VOCs react
11 at differing rates in the troposphere because of their differing tropospheric lifetimes
12 (Table 3-2). The lifetimes of most VOCs with respect to reaction with OH radicals and
13 O₃ are in the range ≈ 1 h to ≈ 10 years. In large part because of these differing
14 tropospheric lifetimes and rates of reaction, VOCs exhibit a range of reactivities with respect
15 to the formation of O₃ (Altshuller and Bufalini, 1971, and references therein).

16 A number of "reactivity scales" have been developed over the years (see, for example,
17 Altshuller and Bufalini, 1971, and references therein; Darnall et al., 1976), including the rate
18 of VOC disappearance in NO_x-VOC-air irradiations, the rate of NO to NO₂ conversion in
19 NO_x-VOC-air irradiations, O₃ formation in NO_x-single VOC-air irradiations, eye irritation,
20 and the rate constant for reaction of the VOC with the OH radical. It appears, however, that
21 a useful definition of "reactivity" is that of "incremental reactivity" (IR), defined as the
22 amount of O₃ formed per unit of VOC added or subtracted from the VOC mixture in a given
23 air mass under high-NO conditions (Carter and Atkinson, 1987, 1989b):

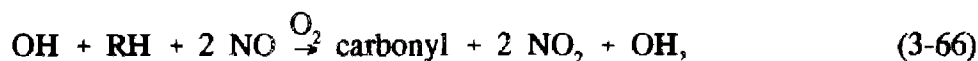
$$24 \quad \text{IR} = \Delta[\text{O}_3]/\Delta[\text{VOC}] \quad (3-65)$$

25
26 at the limit of $\Delta[\text{VOC}] \rightarrow 0$. The concept of incremental reactivity and some further details
27 of this approach are illustrated by the general reaction mechanism for the photooxidation of
28 an alkane, RH:



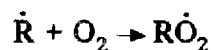
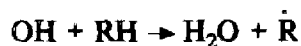


The net reaction,

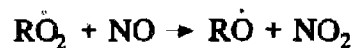


can be viewed as involving the two separate reaction sequences:

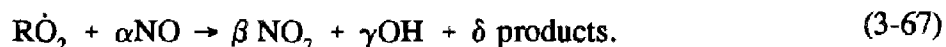
(1) Formation of organic peroxy (RO_2) radicals from the reactions,



and (2) Conversion of NO to NO_2 and the formation of O_3 and other products,



The photolysis of NO₂ then leads to O₃ formation (Reactions 3-1 and 3-2). The first reaction sequence determines how fast RO₂ radicals are generated from the VOC, and has been termed the "kinetic reactivity" (Carter and Atkinson, 1989b). For the case given above, where the only reaction of the VOC is with the OH radical, the kinetic reactivity depends solely on the OH radical reaction rate constant. The second reaction sequence, leading to NO to NO₂ conversion, regeneration of OH radicals, and the formation of product species determines the efficiency of formation of O₃ from the RO₂ radicals formed from the first reaction sequence, and has been termed the "mechanistic reactivity" (Carter and Atkinson, 1989b). The second reaction sequence can be represented as:



In general, the faster a VOC reacts in the atmosphere, the higher the incremental reactivity. However, the chemistry subsequent to the initial reaction does affect the ozone-forming potential of the VOC. Thus, the existence of NO_x sinks in the reaction mechanism (low values of β or values of $\alpha - \beta > 0$) lead to a decrease in the amount of O₃ formed. Examples of NO_x sinks are the formation of organic nitrates and PANs (which are also sinks for radicals). The generation or loss of radical species can lead to a net formation or net loss of OH radicals ($\gamma > 1$ or < 1 , respectively). This in turn leads to an enhancement or suppression of radical concentrations in the air parcel and to an enhancement or suppression of the overall reactivity of all VOCs in that air parcel by affecting the rate of formation of RO₂ radicals.

These effects vary in importance depending on the VOC/NO_x ratio. Nitrogen oxides sinks are most important at high VOC/NO_x ratios (NO_x-limited), affecting the maximum ozone formed; while the formation or loss of OH radicals is most important at low VOC/NO_x ratios, affecting the initial rate at which ozone is formed (Carter and Atkinson, 1989b). In addition to depending on the VOC/NO_x ratio (Table 3-3), incremental reactivity depends on the composition of the VOC mixture and on the physical conditions encountered by the air mass (including the dilution rate, light intensity, and spectral distribution (Carter and Atkinson, 1989b; Carter, 1991).

TABLE 3-3. CALCULATED INCREMENTAL REACTIVITIES OF SELECTED VOCs AS A FUNCTION OF THE VOC/NO_x RATIO FOR AN EIGHT-COMPONENT VOC MIXTURE^a AND LOW-DILUTION CONDITIONS

NMOC	VOC/NO _x Ratio (ppm C/ppm)			
	4	8	16	40
CO	0.011	0.022	0.016	0.005
Ethane	0.024	0.041	0.018	0.007
<i>n</i> -Butane	0.10	0.16	0.069	0.019
<i>n</i> -Octane	0.068	0.12	0.027	-0.031
Ethene	0.85	0.90	0.33	0.14
Propene	1.28	1.03	0.39	0.14
<i>trans</i> -2-Butene	1.42	0.97	0.31	0.054
Benzene	0.038	0.033	-0.002	-0.002
Toluene	0.26	0.16	-0.036	-0.051
<i>m</i> -Xylene	0.98	0.63	0.091	-0.025
Formaldehyde	2.42	1.20	0.32	0.051
Acetaldehyde	1.34	0.83	0.29	0.098
Methanol	0.12	0.17	0.066	0.029
Ethanol	0.18	0.22	0.065	0.006
Urban Mix ^a	0.41	0.32	0.088	0.011

^aEight-component VOC mixture used to simulate NMOC emissions in an urban area.

Source: Carter and Atkinson (1989b).

3.2.5 Photochemical Production of Aerosols

The chemical processes involved in the formation of O₃ and other photochemical pollutants from the interaction of NO_x and VOCs lead to the formation of OH radicals and the formation of oxidized VOC reaction products that are often of lower volatility than the precursor VOC. The OH radicals that oxidize the VOCs and lead to the generation of RO₂ radicals and conversion of NO to NO₂ (with subsequent photolysis of NO₂ form O₃) also react with NO₂ and SO₂ to form nitric and sulfuric acids, respectively, which become incorporated into aerosols as particulate nitrate and sulfate. The low-volatility VOC reaction products can condense onto existing particles in the atmosphere to form secondary organic aerosol matter. Hence ozone formation, acid formation, and secondary aerosol formation in

the atmosphere are so related that controls aimed at reducing O₃ levels will impact (positively or negatively) acid and secondary aerosol formation in the atmosphere.

3.2.5.1 Phase Distributions of Organic Compounds

Chemical compounds are emitted into the atmosphere in both gaseous and particle-associated forms. The emissions from combustion sources (for example, vehicle exhaust) are initially at elevated temperature, and compounds that may be in the particle phase at ambient atmospheric temperature may be in the gas phase when emitted. In addition, atmospheric reactions of gas-phase chemicals can lead to the formation of products that then condense onto particles (or self-nucleate) (Pandis et al., 1991; Wang et al., 1992; Zhang et al., 1992). Measurements of ambient atmospheric gas- and particle-phase concentrations of several classes of organic compounds indicate that the phase distribution depends on the liquid-phase vapor pressure, P_L (Bidleman, 1988; Pankow and Bidleman, 1992). The available experimental data and theoretical treatments show that, as a rough approximation, organic compounds with liquid-phase vapor pressures > 10⁻⁶ torr at ambient temperature are mainly in the gas phase (Bidleman, 1988). As expected, the gas-particle phase distribution in the atmosphere depends on the ambient temperature, with the chemical being more particle-associated at lower temperatures. The gas-to-particle adsorption-desorption process can be represented as,



where A is the gas-phase compound, F is the particle-phase compound, and TSP is the total suspended particulate matter. The relationship among these three species is expressed using a particle-gas partition coefficient, K:

$$K = F/(TSP)A \quad (3-69)$$

Since K is a constant at a given temperature, if TSP increases (for example, in going from a "clean" remote atmosphere to an urban area), F/A must also increase and the chemical becomes more particle-associated (Pankow and Bidleman, 1991, 1992).

1 Gaseous and particulate species in the atmosphere are subject to wet and dry deposition.
2 Dry deposition refers to the uptake of gases and particles at the earth's surface by vegetation,
3 soil, and water, including lakes, rivers, oceans, and snow-covered ground. Wet deposition
4 refers to the removal of gases and particles from the atmosphere through incorporation into
5 rain, fog, and cloud water, followed by precipitation to the earth's surface. These processes
6 are discussed further in Section 3.6.

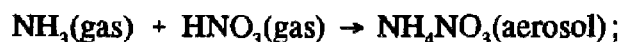
7 For gases, dry deposition is important primarily for HNO_3 , SO_2 , and H_2O_2 as well as
8 for O_3 and PAN; while wet deposition is important for water-soluble gases such as HNO_3 ,
9 H_2O_2 , phenols, and, under atmospheric conditions, SO_2 . Dry deposition of particles depends
10 on the particle size; those of mean diameter ≈ 0.1 to $2.5 \mu\text{m}$ have lifetimes with respect to
11 dry deposition of ≈ 10 days (Graedel and Weschler, 1981; Atkinson, 1988), sufficient for
12 long-range transport. However, particles are efficiently removed from the atmosphere by
13 wet deposition (Bidleman, 1988).

14 Particles can form in the atmosphere by condensation or by coagulation, occurring
15 generally by the latter in urban and regional areas. The photooxidation reactions of VOCs
16 generally lead to the formation of more oxidized and less volatile product species. When the
17 vapor pressures exceed the saturated vapor pressure, or the vapor pressure is $< 10^{-6}$ Torr,
18 the products will become particle-associated (Pandis et al., 1991, 1992). Accumulation-size
19 particles are in the size range 0.08 to $2.5 \mu\text{m}$ diameter (Whitby et al., 1972).

20 In urban areas, the major sources of particulate matter (Larson et al., 1989; Solomon
21 et al., 1989; Wolff et al., 1991; Hildemann et al., 1991a,b; Rogge et al., 1991, 1993; Chow
22 et al., 1993) are:

- 23
24 • Direct emissions of elemental carbon from, for example, diesel-powered vehicles
25 (Larson et al., 1989);
- 26
27 • Direct emissions of primary organic carbon from, for example, meat cooking
28 operations, paved road dust, and wood-burning fireplaces and other combustion
29 sources (Hildemann et al., 1991a,b; Rogge et al., 1991, 1993);
- 30
31 • Secondary organic material formed in the atmosphere from the atmospheric
32 photooxidations of gas-phase NMOC (Turpin and Huntzicker, 1991; Pandis et al.,
33 1992);
- 34

- The conversion of NO and NO₂ to nitric acid, followed by neutralization by ammonia or through combination with other cations to form aerosol nitrates:



- The conversion of SO₂ (and other sulfur-containing species) to sulfuric acid, which has sufficiently low volatility to go to the aerosol phase; and
- Emission into the atmosphere of "fine dust", for example, of crustal material.

Because the fine-particle size range is the same magnitude as the wavelength of visible light, particulate matter present in the atmosphere leads to light scattering and absorption, and hence to visibility reduction (see, for example, Larson et al., 1989; Eldering et al., 1993).

3.2.5.2 Acid Deposition

As noted above, the chemical processes involved in the formation of O₃ and other photochemical pollutants from the interaction of NMOC and NO_x also lead to the formation of acids in the atmosphere. The two major acidic species in ambient air are nitric acid and sulfuric acid, arising from the atmospheric oxidation of NO_x and SO₂, respectively. Reduced sulfur compounds emitted from biogenic sources and certain anthropogenic sources may also lead to SO₂ or sulfonic acids, or both (Tyndall and Ravishankara, 1991).

The major sulfur-containing compound emitted into the atmosphere from anthropogenic sources is sulfur dioxide, SO₂. In the troposphere, the important loss processes of SO₂ are dry deposition (Atkinson, 1988, and references therein), reactions within cloud water, and gas-phase reaction with the OH radical. The rate constant for the reaction of SO₂ with the OH radical is such that the lifetime of SO₂ with respect to gas-phase reaction with the OH radical is ≈ 15 days. The reaction proceeds by (Stockwell and Calvert, 1983; Atkinson et al., 1992a),

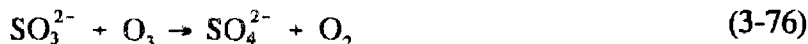
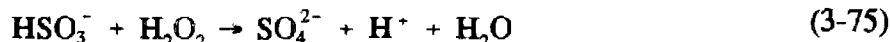
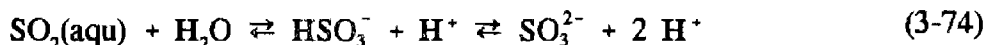




The reaction of SO_3 with water vapor is slow in the gas-phase (Atkinson et al., 1992a) and hence this may be a heterogeneous reaction. Because of its low vapor pressure, H_2SO_4 exists in the aerosol or particle phase in the atmosphere.

Dry deposition is an important atmospheric loss process for SO_2 , since SO_2 has a fairly long lifetime due to gas-phase chemical processes and has a high deposition velocity. A lifetime in relation to dry deposition of 2 to 3 days appears reasonable (Schwartz, 1989).

Sulfur dioxide is not very soluble in pure water (Schwartz, 1989). However, the presence of pollutants such as H_2O_2 or O_3 , or both, in the aqueous phase displaces the equilibrium and allows gas-phase SO_2 to be incorporated into cloud, rain, and fog water, where it is oxidized rapidly (Schwartz, 1989; Pandis and Seinfeld, 1989, and references therein):



In addition, aqueous sulfur can be oxidized in a process catalyzed by transition metals such as iron(III) [Fe^{3+}] and manganese(II) [Mn^{2+}] (Graedel et al., 1986b; Weschler et al., 1986; Pandis and Seinfeld, 1989).



The oxidation rate of aqueous sulfur by O_3 decreases as the pH decreases (i.e., as the acidity increases) and this oxidation route is therefore self-limiting and generally of minor importance in the atmosphere. The oxidation of SO_2 by H_2O_2 appears to be the dominant aqueous-phase oxidation process of SO_2 (Chandler et al., 1988; Gervat et al., 1988; Schwartz, 1989; Pandis and Seinfeld, 1989; Fung et al., 1991b), although the transition metal-catalyzed oxidation of SO_2 may also be important (Jacob et al., 1989). It should be noted that aqueous-phase H_2O_2 arises, in part, from the absorption of HO_2 radicals and H_2O_2 into the aqueous phase, with HO_2 radicals being converted into H_2O_2 (see also Zuo and Hoigne, 1993).

The oxidation of SO_2 to sulfate in clouds and fogs is often much faster than the homogeneous gas-phase oxidation of SO_2 initiated by reaction with the OH radical. The gas-phase oxidation rate is ≈ 0.5 to $1\% \text{ h}^{-1}$, while the aqueous-phase (cloud) oxidation rate may be as high as 10 to 50% h^{-1} (Schwartz, 1989).

The oxidation of NO_x to nitric acid and nitrates was discussed in Section 3.2.3 above. During daylight hours, oxidation occurs by the gas-phase reaction of NO_2 with the OH radical:



with the lifetime of NO_2 due to Reaction 3-15 calculated to be ≈ 1.4 days. Nitric acid is removed from the troposphere by wet and dry deposition, with wet deposition being efficient. During nighttime hours, NO_2 can be converted into NO_3 radicals and N_2O_5 :



1 with N₂O₅ undergoing wet or dry deposition, or both. The reader is referred to Schwartz
2 (1989) for further discussion of the conversion of NO_x to nitrate and nitric acid and acid
3 deposition.
4
5

6 **3.3 METEOROLOGICAL PROCESSES INFLUENCING OZONE** 7 **FORMATION AND TRANSPORT**

8 Day-to-day variability in ozone (O₃) concentrations is, to a first approximation, the
9 result of day-to-day variations in meteorological conditions. This section presents a succinct
10 overview of those atmospheric processes that affect the concentrations of ozone and other
11 oxidants in urban and rural areas. Included in this list of processes are the vertical structure
12 and dynamics of the planetary boundary layer (PBL); transport processes, including
13 thermally-driven mesoscale circulations such as lake and sea breeze circulations; complex
14 terrain effects on transport and dispersion; vertical exchange processes; deposition and
15 scavenging; and meteorological controls on biogenic emissions and dry deposition.
16

17 **3.3.1 Meteorological Processes**

18 **3.3.1.1 Surface Energy Budgets**

19 Knowledge of the surface energy budget is fundamental to an understanding of the
20 dynamics of the planetary boundary layer (PBL). The PBL is defined as that layer of the
21 atmosphere in contact with the surface of the earth and that is directly influenced by the
22 surface characteristics. In combination with synoptic winds, it provides the forces for the
23 vertical fluxes of heat, mass and momentum. The accounting of energy inputs and outputs
24 provides a valuable check on modeled PBL dynamics.

25 Figure 3-7 illustrates the surface radiation budget for short-wave (wavelength roughly
26 <0.4 μm) and long-wave radiation. The radiation budget for the surface can be described in
27 terms of its components as:
28

$$29 \quad Q_{sfc} = K\downarrow - K\uparrow + L\downarrow - L\uparrow + Q_H + Q_E \quad (3-78)$$

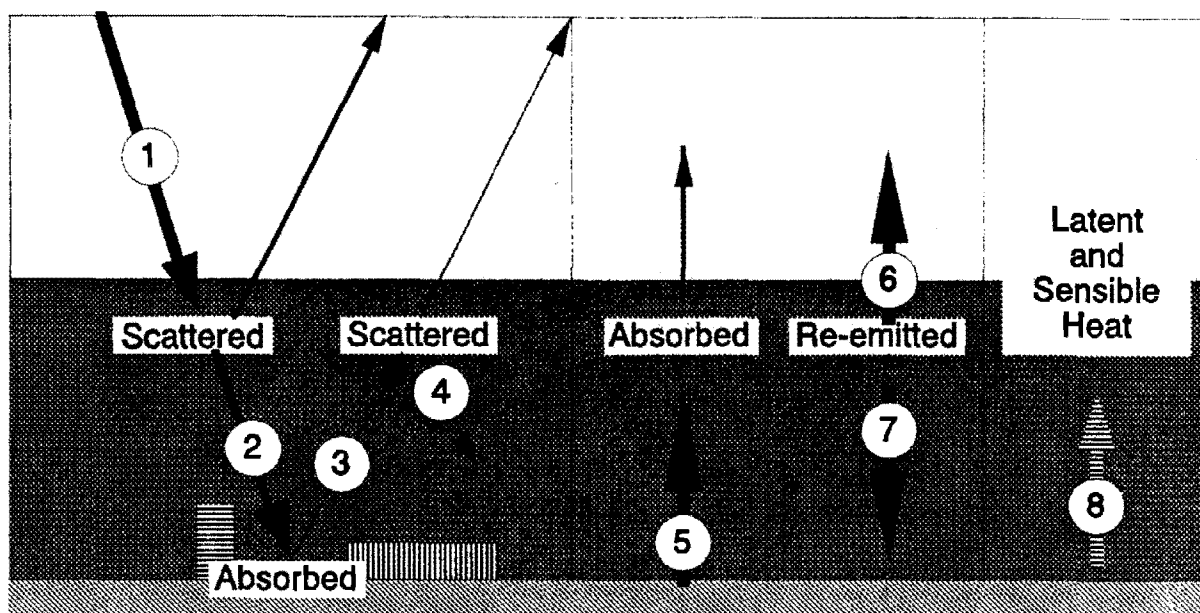


Figure 3-7. Surface radiation budget for short-wave ($\gamma > 0.4 \mu\text{m}$) and long-wave radiation. The surface radiation budget is driven by the input of short-wave radiation (1). This direct input is reduced by scatter (2) and absorption passing through the atmosphere. That amount that remains can be absorbed or reflected at the surface. The reflected light (3) can also be scattered back to the surface (4). The short-wave energy absorbed at the surface will ultimately be emitted back to the atmosphere as long-wave radiation (5). The atmosphere absorbs much of this radiation and radiates it back to the surface (7) and out to space (6). This energy cycle is completed as some of the absorbed energy is transmitted to the atmosphere as sensible and latent heat (8).

1 where $K\downarrow$ is the incoming short-wave radiation, $K\uparrow$ is the outgoing short-wave radiation,
 2 $L\downarrow$ is the incoming long-wave radiation from the atmosphere, $L\uparrow$ is the outgoing long-wave
 3 radiation, and Q_H and Q_E are the heat flux and latent heat flux to the soil, respectively.
 4 On a global annual average, Q_{sfc} is assumed to be near zero (i.e., the planet is not heating or
 5 cooling systematically, an assumption clearly being questioned with the growing debate on
 6 climatic change). On a day-to-day basis, however, Q_{sfc} will certainly vary from zero and
 7 will cause changes in surface temperature. Cloud cover, as an example, will reduce the
 8 amount of short-wave radiation reaching the surface and will modify all the subsequent
 9 components of the radiation budget. Moreover, the redistribution of energy through the PBL

1 creates thermodynamic conditions that influence vertical mixing. The treatment of energy
2 budgets has been attempted on the scale of individual urban areas. These studies are
3 summarized by Oke (1987).

4 For many of the modeling studies of the photochemical production of ozone, the
5 vertical mixing has been parameterized by a single, well-mixed layer. However, because
6 this is a great simplification of a complex structure, and because the selection of rate and
7 extent of vertical mixing may influence local control options, it behooves future modeling
8 and observational studies to address the energy balances so that more realistic simulations can
9 be made of the structure of the PBL.

11 3.3.1.2 Planetary Boundary Layer

12 The concentration of an air pollutant depends significantly on the degree of mixing that
13 occurs between the time a pollutant or its precursors are emitted and the arrival of the
14 pollutant at the receptor. Atmospheric mixing is the result of either mechanical turbulence,
15 often associated with wind shear, or thermal turbulence, associated with vertical
16 redistribution of heat energy. The potential for thermal turbulence can be characterized by
17 atmospheric stability. The more stable the air layer the more work is required to move air
18 vertically.

19 As air is moved vertically through the atmosphere, as might happen in a convective
20 thermal, its temperature will decrease with height as the result of *adiabatic* expansion. It is
21 the comparison of how the temperature *should* change with height in the absence of external
22 heating or cooling against the *actual* temperature change with height that is a measure of
23 atmospheric stability. Those layers of the atmosphere where temperature increases with
24 height (*inversion layers*) are the most stable as air, cooling as it rises, then becomes denser
25 than its new warmer environment. In an atmospheric layer with relatively low turbulence,
26 pollutants do not redistribute vertically as rapidly as they do in an unstable layer. Also,
27 because a stable layer has a relatively low rate of mixing, pollutants in a lower layer will not
28 mix through it to higher altitudes.

29 The stability of the atmosphere is often measured through computation of potential
30 temperature, q , as
31

$$\theta = \left[\frac{P}{P_0} \right]^{-R/c_p} \quad (3-79)$$

where θ is the virtual potential temperature, P is the pressure of the air parcel, P_0 is the reference pressure to which the air parcel will be moved (usually 1,000 mb), R is the gas law constant, and c_p is the specific heat of air at constant pressure. The faster θ increases with height, the less the potential for mixing.

A stable layer can also act as a trap for air pollutants lying beneath it. Hence, an elevated inversion is often referred to as a "trapping" inversion. On the other hand, if pollutants are emitted into a stable layer aloft, such as might occur from an elevated stack, the lack of turbulence will keep the effluents from reaching the ground while the inversion persists.

Traditionally, atmospheric mixing has been treated through use of a *mixing height*, which is defined as the base of an elevated inversion layer. In this model, the ozone precursors are mixed uniformly through the layer below the mixing height. As this layer grows it both entrains remnant ozone from previous days and redistributes fresh emissions aloft. The vertical mixing profile through the lower layers of the atmosphere is assumed to follow a typical and predictable cycle on a generally clear day. In such a situation a nocturnal surface inversion would be expected to form during the night as $L \uparrow$ exceeds $L \downarrow$. This surface layer inversion persists until surface heating becomes significant, probably two or three hours after sunrise. Pollutants initially trapped in the surface inversion may cause relatively high, local concentrations, but these concentrations will decrease rapidly when the surface inversion is broken by surface heating. The boundary formed between the rising, cooling air of the growing mixing layer and that of the existing PBL is often sharp and can be observed as an elevated temperature inversion.

Elevated temperature inversions, when the base is above the ground, are also common occurrences (Hosler, 1961; Holzworth, 1974). This condition can form simply as the result of rapid vertical mixing from below, but is exacerbated in regions of subsiding air when the sinking air warms to a point such that it is warmer than the rising (and cooling) underlying air. Since these circumstances are associated with specific synoptic conditions, they are less frequent than the ubiquitous nighttime radiation inversion. An elevated inversion is

1 nevertheless a very significant air pollution feature, because it may persist throughout the day
2 and thus restrict vertical mixing.

3 When compared to a source near the surface and the effects of a radiation (surface)
4 inversion, the pollutant dispersion pattern is quite different for an elevated source plume
5 trapped in a layer near the base of an elevated inversion. This plume will not be in contact
6 with the ground surface in the early morning hours because there is no mixing through the
7 surface radiation inversion. Thus, the elevated plume will not affect surface pollutant
8 concentrations until the mixing processes become strong enough to reach the altitude of the
9 plume. At that time, the plume may be mixed downward quite rapidly in a process called
10 *fumigation*. During fumigation, surface ozone concentrations will increase if the morning
11 ozone concentration is higher aloft than at the ground, and if insufficient scavenging by NO
12 occurs at ground-level. In fact, the rapid rise in ozone concentrations in the morning hours
13 is often the result of vertical (downward) transport from an elevated reservoir of ozone.
14 After this initial increase, surface concentrations can continue to increase as a result of
15 photochemistry or transport of ozone-rich air to the receptor, or both.

16 When surface heating decreases in the late afternoon and early evening, the surface
17 inversion will form again under most conditions. The fate of the elevated inversion is less
18 clear, however. While ozone and its precursors have been mixed vertically, the reduction of
19 turbulence and mixing at the end of the daylight hours leaves ozone in a remnant layer that is
20 often without a well-defined thermodynamic demarcation. This layer is then transported
21 through the night, often to regions far removed from pollution sources, where its pollutants
22 can influence concentrations at remote locations the next morning as mixing entrains the
23 elevated remnant layer. This overnight transport can be aided by the development of a
24 nocturnal jet that forms many nights at the top of the surface inversion layer.

25 Geography can have a significant impact on the dispersion of pollutants (e.g., along the
26 coast of an ocean or one of the Great Lakes). Near the coast or shore, the temperatures of
27 land and water masses can be different, as can the temperature of the air above such land and
28 water masses. When the water is warmer than the land, there is a tendency toward reduction
29 in the frequency of surface inversion conditions inland over a relatively narrow coastal strip
30 (Hosler, 1961). This in turn tends to increase pollutant dispersion in such areas. The
31 opposite condition also occurs if the water is cooler than the land, as in summer or fall.

1 Cool air near the water surface will tend to increase the stability of the boundary layer in the
2 coastal zone, and thus decrease the mixing processes that act on pollutant emissions. These
3 conditions occur frequently along the New England coast (Hosler, 1961). Similarly,
4 pollutants from the Chicago area have been observed to be influenced by a stable boundary
5 layer over Lake Michigan (Lyons and Olsson, 1972). This has been observed especially in
6 summer and fall when the lake surface is most likely to be cooler than the air that is carried
7 over it from the adjacent land.

8 Sillman et al. (1993) investigated abnormally high concentrations of O_3 observed in
9 rural locations on the shore of Lake Michigan and on the Atlantic coast in Maine, at a
10 distance of 300 km or more from major anthropogenic sources. A dynamical-photochemical
11 model was developed that represented formation of O_3 in shoreline environments and was
12 used to simulate case studies for Lake Michigan and the northeastern United States. Results
13 suggest that a broad region with elevated O_3 , NO_x , and VOC forms as the Chicago plume
14 travels over Lake Michigan, a pattern consistent with observed O_3 at surface monitoring
15 sites. Near-total suppression of dry deposition of O_3 and NO_x over the lake is needed to
16 produce high O_3 . Results for the east coast suggest that the observed peak O_3 can only be
17 reproduced by a model that includes suppressed vertical mixing and deposition over water,
18 2-day transport of a plume from New York, and superposition of the New York and Boston
19 plumes. Hence, the thermodynamics associated with the water bodies seem to play a
20 significant role in some regional-scale episodes of high ozone concentrations.

21 There is concern that the strict use of mixing height unduly simplifies the complex
22 atmospheric processes that redistribute pollutants within urban areas. There is growing
23 evidence that some ozone precursors may not be evenly redistributed over some urban areas
24 in cases where the sources are relatively close to the urban area and atmospheric mixing is
25 not strong enough to redistribute the material over a short travel time. In these cases, it is
26 necessary to treat the turbulent structure of the atmosphere directly and acknowledge the
27 vertical variations in mixing. Methods that are being used to investigate these processes
28 include the use of a diffusivity parameter to express the potential for mixing as a function of
29 height. A simple expression of how the mean concentration, $\bar{\chi}$, changes with time, t , in an
30 air parcel, assuming all concentrations are homogeneous in the horizontal, is:

$$\frac{d\bar{\chi}}{dt} = -\frac{\partial \overline{w'\chi'}}{\partial z} \quad (3-80)$$

where $\overline{w'\chi'}$ is the vertical *turbulent eddy flux* of pollutant. The term on the right hand side of the equation changes mean concentration through flux divergence; i.e., turbulence either disperses the pollutant to or from the point being considered. The problem with this representation is that the flux divergence term is virtually impossible to measure directly.

The turbulent eddy flux needed to understand the vertical distribution of ozone and its precursors is often parameterized in photochemical models, if included at all, through use of *eddy diffusivity*. The eddy diffusivity is set using an analogy to mixing length theory as

$$\overline{w'\chi'} = K_c \frac{\partial \bar{\chi}}{\partial z}, \quad (3-81)$$

which allows estimation of flux divergence from measured or estimated vertical gradients in concentration and estimation of the eddy diffusivity. The selection of diffusivity is often somewhat arbitrary, but can be related to the eddy diffusivity for heat or momentum, or both, depending on circumstances. Large values result in rapid mixing. Thus, the appropriate selection of eddy diffusivity is necessary to simulate whether elevated plumes will enter an urban airshed.

Another method uses a technique called "large-eddy simulation" to recreate the probability of redistribution within the mixing height.

Both these techniques require meteorological information that is not normally available from the National Weather Service, but that is now becoming available as part of several ozone field experiments.

3.3.1.3 Cloud Venting

Vertical redistribution of ozone out of the PBL is achieved by the venting of pollutants in clouds. Clouds represent the top-most reaches of thermals of air rising through the PBL and can act simply as chemical reactors for soluble pollutants, returning the "processed" air to the PBL; or if convection is sufficiently vigorous, they can result in physical redistribution

1 of ozone and its precursors from the PBL (Greenhut, 1986; Dickerson et al., 1987). Clouds
2 also act to influence photolysis rates and chemical transformation rates.

3 Greenhut (1986) showed that the net ozone flux in the cloud layer was a linear function
4 of the difference in ozone concentration between the boundary layer and the cloud layer.
5 Ozone fluxes between clouds were usually smaller than those found within clouds, but the
6 slower rate is at least partially offset by the larger region of cloud-free air relative to cloudy
7 air.

8 Large clouds, such as cumulonimbus, offer considerably more potential for
9 redistribution of ozone and its precursors. Additionally, the cumulonimbus clouds are also
10 associated with precipitation, a scavenger of pollutants, and with lightning, a potential source
11 for nitrogen oxides. Using carbon monoxide (CO) as a tracer, Dickerson et al. (1987) and
12 Pickering et al. (1990) have illustrated the redistribution potential of cumulonimbus cloud
13 systems. Lyons et al. (1986) provided an illustration of the potential for groups of
14 cumulonimbus clouds to vent the polluted boundary layer.

15 The role of cloud venting is thought to be largely a cleansing process for the boundary
16 layer, although a portion of the material lifted into the free troposphere could be entrained
17 back to the surface in subsequent convection. Aircraft observations have documented
18 frequently the occurrence of relatively high ozone concentrations above lower-concentration
19 surface layers (e.g., Westberg et al., 1976). This is a clear indication that ozone is
20 essentially preserved in layers above the surface and can be transported over relatively long
21 distances even when continual replenishment through precursor reactions is not a factor, such
22 as at night.

23 24 **3.3.1.4 Stratospheric-Tropospheric Ozone Exchange**

25 The fact that O₃ is formed in the stratosphere, mixed downward, and incorporated into
26 the troposphere, where it forms a more or less uniformly mixed background concentration,
27 has been known in various degrees of detail for many years (Junge, 1963). The mechanisms
28 by which stratospheric air is mixed into the troposphere have been examined by a number of
29 authors, as documented previously by EPA (U.S. Environmental Protection Agency, 1986,
30 and references therein).

1 There is little evidence that ozone from the stratosphere contributes in any substantial
2 way to either peak urban ozone values or regional episodes of elevated ozone levels (Johnson
3 and Viezee, 1981; Ludwig et al., 1977; Singh et al., 1980; and Viezee et al., 1979).
4 Johnson and Viezee (1981) concluded that the ozone-rich intrusions studied sloped downward
5 toward the south. In terms of dimensions, the average crosswind width (north to south) at an
6 altitude of 5.5 kilometers (ca. 18,000 feet or 3.4 miles) for six spring intrusions averaged
7 226 kilometers (364 miles), and for four fall tropopause fold systems, 129 kilometers
8 (208 miles). Ozone concentrations at 5.5 kilometers (ca 18,000 feet or 3.4 miles) average
9 108 ppb in the spring systems and 83 ppb in the fall systems. From this and other research
10 described in the previous criteria document for O₃ and other photochemical oxidants (U.S.
11 Environmental Protection Agency, 1986), Viezee and coworkers (Viezee and Singh, 1982;
12 Viezee et al., 1983) concluded that (1) direct ground-level impacts by stratospheric O₃ may
13 be infrequent, occurring <1% of the time; (2) that such ground-level events are short-lived
14 and episodic; and (3) that they are most likely to be associated with O₃ concentrations
15 ≤0.1 ppm. (See U.S. Environmental Protection Agency [1986] for additional details).

16 Using the ⁷Be-to-O₃ ratio as an indicator of O₃ of stratospheric origin and sulfate
17 (SO₄²⁻) concentrations as a tracer for anthropogenic sources, Altshuller (1987) estimated
18 stratospheric contributions of ozone in the range 0 to 40 ppb (0 to 95% of observed O₃) at
19 ground level at Whiteface Mountain, NY, for July 1975 and mid-June to mid-July 1977.
20 Monthly average stratospheric contributions were estimated at 5 to 10 ppb. He also
21 examined extant ⁷Be and O₃ data for a number of lower-elevation rural locations in the
22 western, midwestern, and southeastern United States, and calculated stratospheric or upper
23 tropospheric contributions at 6 to 8 ppb. He concluded that his calculated values for such
24 contributions should be viewed with caution and regarded probably as upper limits because of
25 scatter in the ⁷Be and corresponding O₃ data that hindered definition of the ⁷Be-to-O₃ ratio.
26 He also concluded that removal and dilution processes result in the loss of most stratospheric
27 O₃ before it reaches ground level (Altshuller, 1987).

28 29 **3.3.2 Meteorological Parameters**

30 This section focuses on analyses of data from previous and ongoing measurement
31 programs to address two driving questions: (1) are there meteorological parameters which

are systematically associated with ozone levels; and (2) are relationships between ozone and meteorological parameters sufficiently strong such that meteorological fluctuations can be filtered from the data to allow examination of longer-term trends?

The meteorological factors that theoretically could influence surface ozone levels include ultraviolet radiation, temperature, wind speed, atmospheric mixing and transport, and surface scavenging. The following examines the theoretical basis for each of these and identifies to what degree empirical evidence supports the hypotheses.

3.3.2.1 Sunlight

Ultraviolet (UV) radiation plays a key role in initiating the photochemical processes leading to ozone formation. Sunlight intensity (specifically the UV portion of sunlight) varies with season and latitude but the latter effect is strong only during the winter months. The importance of photolysis to the formation of O_3 provides a direct link between O_3 and time of year. However, during the summer, the maximum UV intensity is fairly constant throughout the contiguous United States and only the duration of the solar day varies to a small degree with latitude.

The effects of light intensity on individual photolytic reaction steps and on the overall process of oxidant formation have been studied in the laboratory (Peterson, 1976; Demerjian et al., 1980). Early studies, however, employed constant light intensities, in contrast to the diurnally varying intensities that occur in the ambient atmosphere. The diurnal variation of light intensity was subsequently studied as a factor in photochemical oxidant formation (e.g., Jeffries et al., 1975, 1976). Such studies showed that the effect of this factor varies with initial reactant concentrations. Most important was the observation that similar NMOC/ NO_x systems showed different oxidant-forming potential depending on whether studies of these were conducted using constant or diurnal light. This led to incorporation of the effects of diurnal or variable light into photochemical models (Tilden and Seinfeld, 1982).

There is little empirical evidence in the literature, however, linking day-to-day variations in observed UV radiation levels with variations in ozone levels. Samson et al. (1988) illustrated that the number of O_3 concentrations exceeding 120 ppb did not track well with potential solar radiation, as shown in Figure 3-8. Although variations in day-to-day concentrations could well be influenced by cloud cover or attenuated by haze, the seasonal

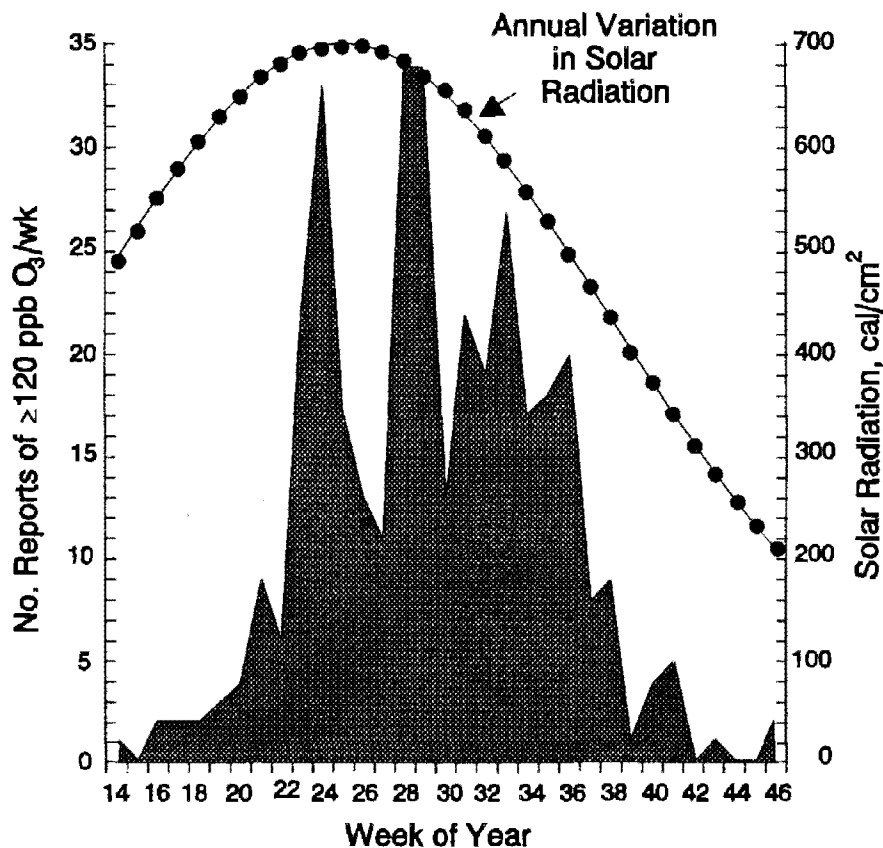


Figure 3-8. The number of reports of ozone concentrations ≥ 120 ppb at the 17 cities studied in Samson et al. (1988). (1 April = week 14, 1 May = week 18, 1 June = week 22, 1 July = week 27, 1 August = week 31, 1 September = week 35, 1 October = week 40, 1 November = week 44). A representation of the annual variation in solar radiation reaching the earth's surface at 40°N latitude (Units= cal cm^{-2}) is shown.

Source: Samson et al. (1988).

1 peak in ozone concentrations usually lags the peak in potential solar radiation that occurs at
2 the Summer Solstice on or about June 23.

3.3.2.2 Temperature

5 There is a demonstrable association between tropospheric ozone concentrations and
6 tropospheric temperature. Numerous studies done over more than a decade have reported
7 that successive occurrences or episodes of high temperatures characterize seasonally high

ozone years (e.g., Clark and Karl, 1982; Kelly et al., 1986). The relationship has been observed for the South Coast Air Basin of California (Kuntasal and Chang, 1987), and in New England (Wolff and Lioy, 1978; Atwater, 1984; Wackter and Bayly, 1988), as well as elsewhere.

Figures 3-9 and 3-10 show the daily maximum ozone concentrations versus maximum daily temperature for summer months (May to October) 1988 to 1990, for, respectively, Atlanta, Georgia, and New York City, New York; and for Detroit, Michigan, and Phoenix, Arizona. There appears to be an upper-bound on ozone concentrations that increases with temperature. Likewise, Figure 3-11 shows that a similar qualitative relationship exists between ozone and temperature even at a number of rural locations.

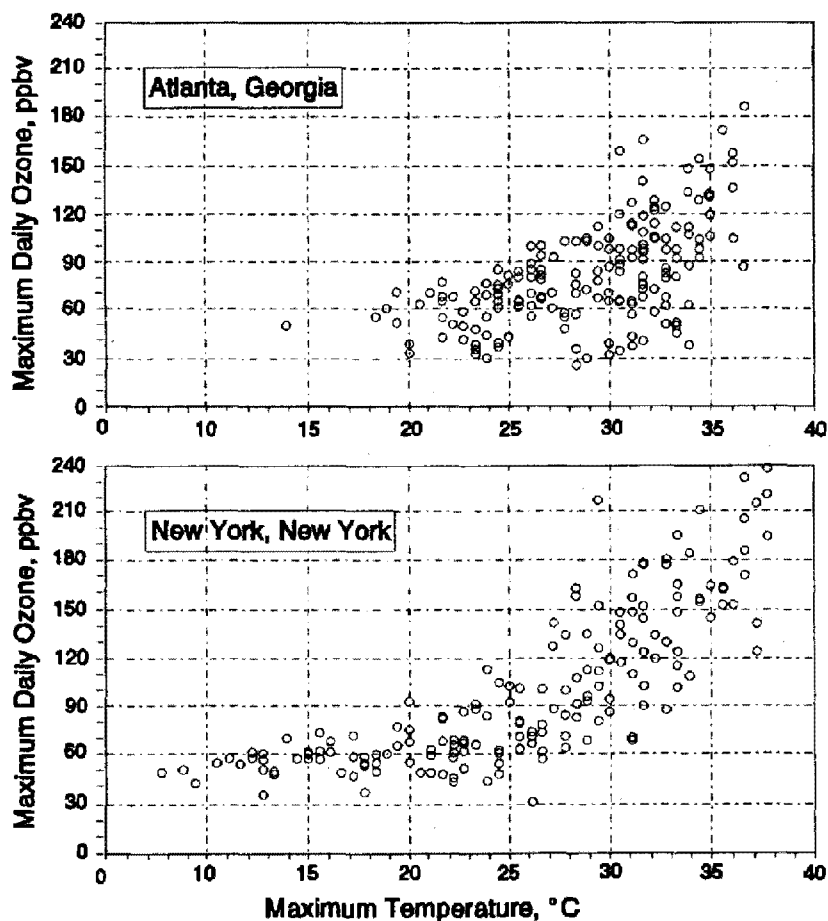


Figure 3-9. A scatter plot of maximum daily ozone concentration in Atlanta, Georgia, and New York, New York, versus maximum daily temperature.

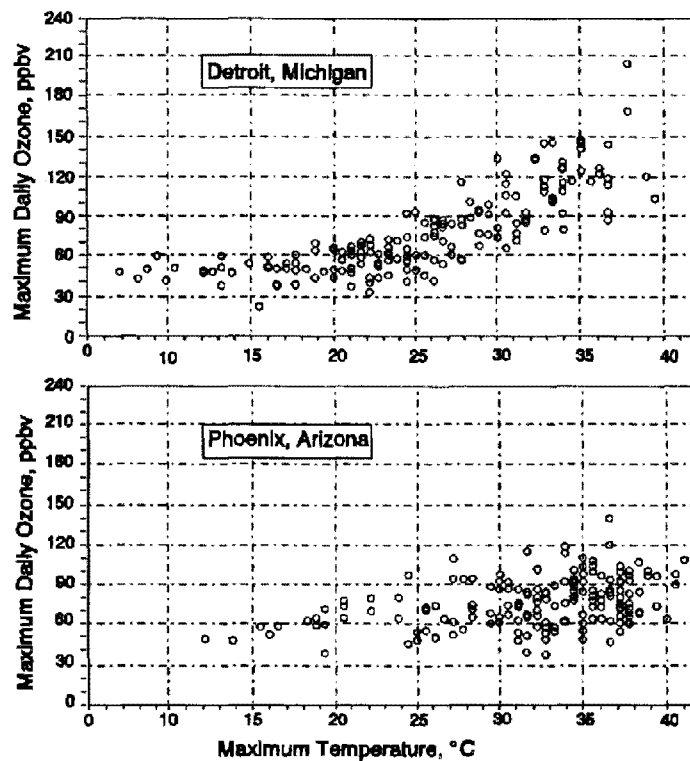


Figure 3-10. A scatter plot of maximum daily ozone concentration in Detroit, Michigan, and Phoenix, Arizona, versus maximum daily temperature.

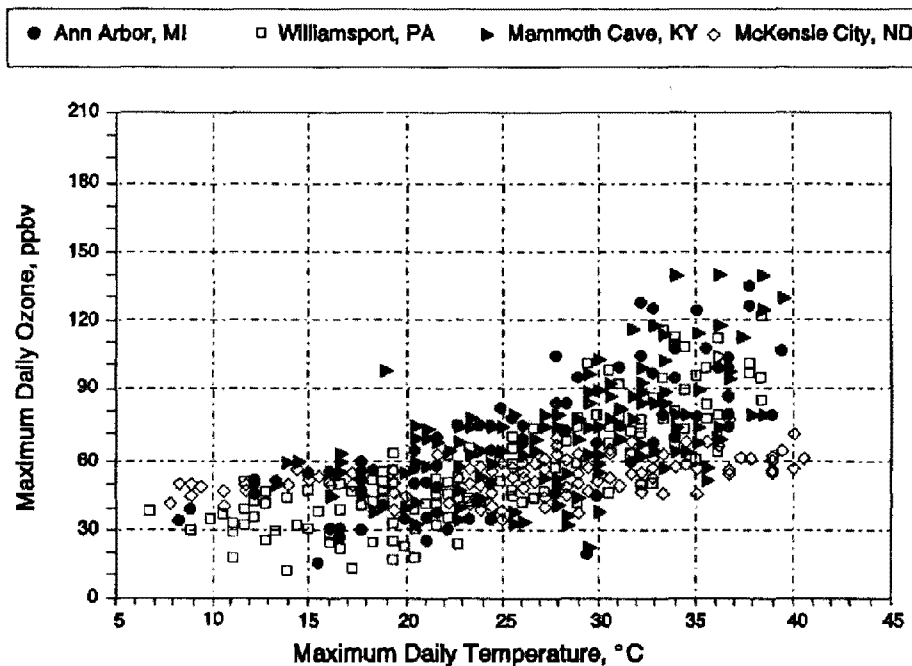


Figure 3-11. A scatter plot of maximum ozone concentration versus maximum daily temperature for four nonurban sites. The relationship with temperature is still apparent, although the slope is reduced from that of the urban areas.

1 The notable trend in these plots is the apparent upper-bound to ozone concentrations
2 because a function of temperature. It is clear that at a given temperature there is a wide
3 range of possible concentrations because other factors, (e.g., cloudiness, precipitation, wind
4 speed) can reduce the ozone production. The upper bound presumably represents the
5 maximum concentration achieved under the most favorable conditions. Table 3-4 lists the
6 results of a statistical regression performed on the paired O₃-temperature data used in
7 Figures 3-9 and 3-10 with separate slopes listed for temperatures above and below 30 °C.
8 Results show that for T > 30 °C the O₃-temperature relationship is statistically significant at
9 all sites. The rate of increase is 3 to 5 ppb/°C at rural sites and ranges from 7 to 12 ppb/°C
10 at the three eastern U.S. urban sites (New York, Detroit and Atlanta). At two western sites,
11 Williston, North Dakota, and Billings, Montana, there is a much weaker dependence on
12 temperature, possibly reflecting the lower level of anthropogenic activity. At a third western
13 site, Medford, Oregon, the O₃-temperature relationship is comparable to that at rural eastern
14 sites.

15 Relationships between peak O₃ and temperature have also been recorded by Wunderli
16 and Gehrig (1991) for three locations in Switzerland. At two sites near Zurich, peak
17 O₃ increased 3 to 5 ppb/°C for diurnal average temperatures between 10 and 25 °C, and
18 little change in peak O₃ occurred for temperatures below 10 °C. At the third site, a high-
19 altitude location removed from anthropogenic influence, showed much less variation of
20 O₃ with temperature was observed.

21 The hypotheses for this correlation include, but are not necessarily limited to:

- 22 1. Reduction in photolysis rates at low temperatures;
- 23
- 24 2. Reduction in H₂O concentrations at low temperatures
- 25
- 26 3. Thermal decomposition of PAN and its homologues;
- 27
- 28 4. Increased anthropogenic emissions of reactive hydrocarbons or NO_x or
- 29 both;
- 30
- 31 5. Increased natural emissions of reactive hydrocarbons; and
- 32
- 33 6. Relationships between high temperatures and stagnant circulation patterns.

**TABLE 3-4. RATES OF INCREASE OF PEAK OZONE WITH DIURNAL
MAXIMUM TEMPERATURE (ppb/°C) FOR T < 300 K (27 °C) AND T > 300 K,
BASED ON MEASUREMENTS FOR APRIL 1 TO SEPTEMBER 30, 1988**

Location	T < 300 K		T > 300 K	
	$\Delta O_3/\Delta T$	T-statistic	$\Delta O_3/\Delta T$	T-statistic
<i>Urbanized Regions:</i>				
NY-NJ-CT	1.5	-5.2	8.8	-7.4
Detroit	1.4	-6.4	4.4	-6.3
Atlanta	3.2	-4.2	7.1	-5.9
Phoenix	—	—	1.4	-4.1
Southern California	11.3	-8.9	—	—
<i>Nonurban Sites:</i>				
Williamsport, PA	1.2	-5	4	-7.4
Saline, MI	0.8	-3.5	3.1	-4.9
Mammoth Cave, KY	0.1	-0.3	4.4	-7.3
Kentucky, cleanest site 3	0.3	-0.7	3.4	-6.6
Williston, ND	0.2	-1	0.8	-3.7
Billings, MT	0.1	-0.5	0.7	-2.2
Medford, OR	0.5	-2.6	3.3	-13.7

Source:

The relationship with temperature is well known, but not yet reproduced by air quality models. While it has been argued that this striking relationship with temperature is an indirect result of the stagnant synoptic meteorological conditions that lead to higher ozone levels, the correlation is not strong with other parameters of stagnation, notably wind speed, as is discussed later.

3.3.2.2.1 Reduction in Photolysis Rates

It is possible that on a seasonal scale the correlation between temperature and ozone may be an indirect correlation with UV radiation variability. This is insufficient, however, to explain the day-to-day correlation between the two variables.

1 Changes in photolysis rates and in H₂O concentrations are related in that both are
2 linked to the supply of OH radicals which determines the rate of ozone production in polluted
3 environment. A reduction in either photolysis rates or H₂O would reduce the source of OH
4 radicals. Calculations by Sillman and Samson (1993) showed that the difference between
5 summer and fall photolysis rates (at 40° N latitude) has a significant impact on the rate of
6 ozone production in urban photochemical simulations, roughly equal to the impact of PAN
7 thermal decomposition (discussed below). However the impact of photolysis rates and of
8 water vapor was much lower in simulations for polluted rural environments. In the
9 simulations by Sillman et al. (1993) ozone production in urban environments was limited
10 largely by the supply of OH radicals to react with hydrocarbons; whereas in rural
11 environments the limiting factor was the source of NO_x. Consequently photolysis rates and
12 H₂O had less impact on ozone production in rural environments.

14 3.3.2.2.2 *Thermal Decomposition of Peroxyacetyl Nitrate*

15 Temperature-dependent photochemical rate constants provide a link between O₃ and
16 temperature (Sillman et al., 1990a; Cardelino and Chameides, 1990). The reason for the
17 decline in O₃ in rural areas when the PAN decomposition rate decreases is that PAN
18 apparently represents a major sink for NO_x in rural environments. When the rate of PAN
19 decomposition is decreased NO_x drops sharply while OH and HO₂ remain largely unaffected.
20 Consequently, the rate of the important HO₂ + NO reaction (see Section 3.2) shows a
21 substantial decrease.

22 The photochemical response in an urban environment is fundamentally different,
23 although the final result, a decrease in O₃ with temperature, is similar. The impact of PAN
24 in urban environments is attributable to its role as a sink for odd hydrogen rather than to its
25 effect on NO_x (Cardelino and Chameides, 1990). Sillman et al. (1990a) have shown that the
26 well-known division of ozone photochemistry into NO_x-sensitive and VOC-sensitive regimes
27 is associated with the relative magnitude of odd-hydrogen sinks. In the NO_x-sensitive
28 regime, typical of rural areas, the major sink of odd hydrogen consists of formation of
29 peroxides. Ozone formation is relatively insensitive to the magnitude of odd hydrogen
30 sources since the peroxide sink varies with the square of the HO₂ concentration and provides
31 partially buffers the effect of a change in sources. At higher NO_x concentrations or lower

VOC/NO_x ratios, the dominant sink for odd hydrogen is formation of HNO₃. The rate of odd hydrogen formation assumes a much greater importance since the buffering effect of peroxide formation and other OH-HO₂ interactions is lost. Formation of O₃ becomes strongly sensitive to odd hydrogen formation rates, and to VOC concentrations as sources of odd hydrogen.

Sillman and Samson (1993) found that the thermal decomposition of PAN was enough to explain an increase of 1 to 2 ppb peak ozone per degree C increase in temperature in rural locations in the eastern United States, based on photochemical simulations. This increase represents a significant fraction of the observed increase in peak ozone with temperature (3 ppb per degree, Figure 3-11) but is significantly less than the observed increase.

3.3.2.2.3 Increased Anthropogenic Emissions

It has recently been suggested that emission rates for anthropogenic hydrocarbons (VOC) also increase with temperature (U.S Environmental Protection Agency, 1989; Stump et al., 1992). Increased VOC emissions might be expected to cause increased rates of ozone production only in urban areas where ozone is sensitive to VOC, and would be less likely to have impact on rural areas. However, NO_x-sensitive urban areas and most rural areas would also show increased ozone production with temperature if NO_x emissions also were to increase with temperature. There is no direct evidence for an increase in NO_x emissions with temperature but power plant loads tend to be highest when temperatures are high. Because power plants are a major source of NO_x, the increased power plant load would also lead to increased NO_x emissions. Quantitative estimates are needed to determine the impact of this effect.

3.3.2.2.4 Increased Natural Emissions

Emissions of biogenic hydrocarbons increase sharply with temperature (Lamb et al., 1987). In ambient temperatures from 25 to 35 °C the rate of natural hydrocarbon emissions from isoprene-emitting deciduous trees increased by about a factor of four. From coniferous trees the increase was on the order of one and a half times.

Recently Jacob et al. (1993) found that the photochemistry of ozone production in a polluted rural environment (Blue Ridge Mountains, VA) is significantly different in

1 September and October when natural emissions from deciduous forests have ceased. The
2 difference in chemistry between summer and fall leaf production may also have an impact on
3 the ozone-temperature correlation.
4

5 **3.3.2.2.5 Correlation with Stagnation**

6 Recently Jacob et al. (1993) found that model-simulated ozone formation in the rural
7 United States shows a tendency to increase with temperature based solely on the difference in
8 atmospheric circulation between relatively warm and relatively cool days. The model-
9 simulated ozone-temperature correlation was less than observed but large enough to represent
10 a significant component of the observed correlation. However, the temperature-meteorology
11 correlation identified by Jacob et al. (1993) was based on simulated meteorology from a
12 General Circulation Model rather than on direct observations. It would be interesting to see
13 whether the correlation between ozone, temperature and atmospheric circulation predicted by
14 Jacobs et al. (1993) can be verified in terms of meteorological observations.
15

16 **3.3.2.3 Wind Speed**

17 Ozone is expected to be influenced by wind speed because lower wind speeds should
18 lead to reduced ventilation and the potential for greater buildup of ozone and its precursors.
19 Abnormally high temperatures are frequently associated with high barometric pressure,
20 stagnant circulation, and suppressed vertical mixing resulting from subsidence (Mukammal
21 et al., 1982), all of which may contribute to elevated O₃ levels. However, in reality this
22 relationship varies from one part of the country to another. Figure 3-12 shows the frequency
23 of 24-h trajectory transport distances to southern cities on days with resulting concentrations
24 of O₃ ≥ 120 ppb (Samson et al., 1988). The frequency for southern cities is biased toward
25 lower wind speeds. A similar plot for cities in the northeast United States (Figure 3-13)
26 shows an opposite pattern, in which the bias is toward higher wind speeds than normal. It is
27 unclear how much meteorological information is needed in order to perform accurate
28 urban-area ozone simulations using advanced photochemical models. To understand the
29 significance of variations between upper-air wind measurements during the Southern Oxidant
30 Study (SOS) 1992 Atlanta Intensive, an intercomparison test of the precision of upper-air
31 measurements was conducted. Collocated measurements were made at an SOS measurement

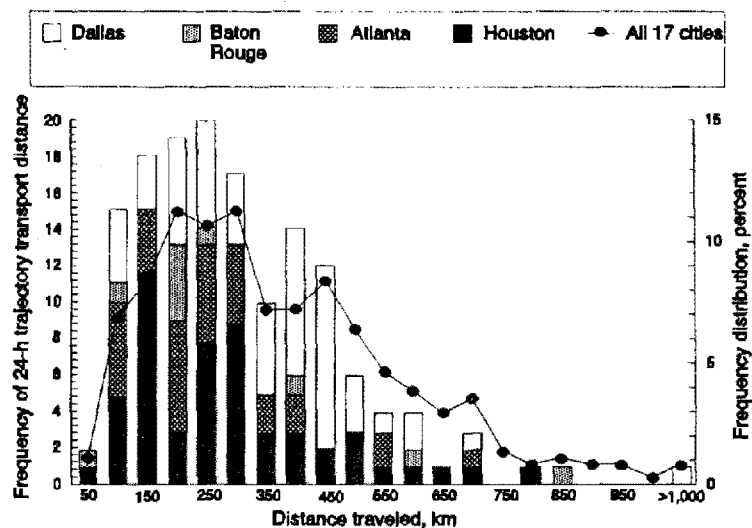


Figure 3-12. The frequency of 24-h trajectory transport distance en route to city when ozone was ≥ 120 ppb in four Southern U.S. cities compared with the percent frequency distribution for all 17 cities (scale on right) of a nationwide study, 1983 to 1985.

Source: Samson et al. (1988).

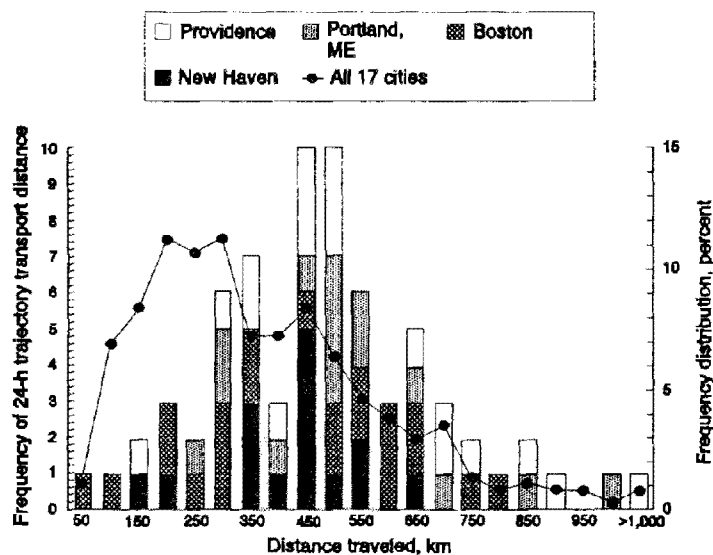


Figure 3-13. The frequency of 24-h trajectory transport distance en route to city when ozone was ≥ 120 ppb in four New England cities compared with the percent frequency distribution for all 17 cities (scale on right) of a nationwide study, 1983 to 1985.

Source: Samson et al. (1988).

1 site using a boundary-layer lidar; a wind profiler; and a rawinsonde balloon. There was
 2 generally good agreement between the profiler and rawinsonde although some large outliers
 3 existed. Figure 3-14 illustrates that the root mean square difference (RMSD) varied with
 4 altitude. The RMSD reached a minimum near 1,200 m AGL of about 2 m/sec, rising to
 5 over 3 m/sec near the surface and above 1,200 m AGL. Figure 3-15 illustrates the RMSD
 6 for the lidar comparison with CLASS observations. There is slightly greater RMSD at all
 7 heights than for the profiler-rawinsonde comparison, with a relative minimum observed at
 8 about 1,200 m.
 9

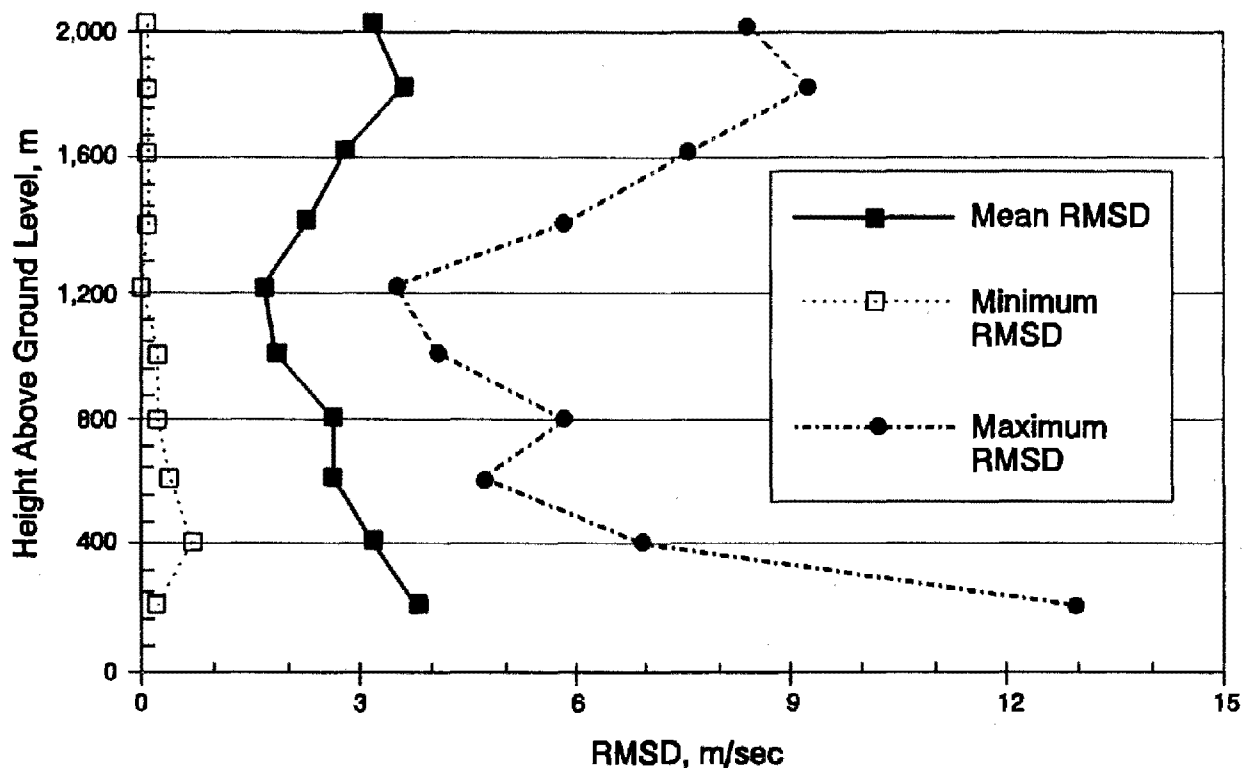


Figure 3-14. The root-mean-square-difference (RMSD) between CLASS observations
 and profiler observations as a function of height above ground level.

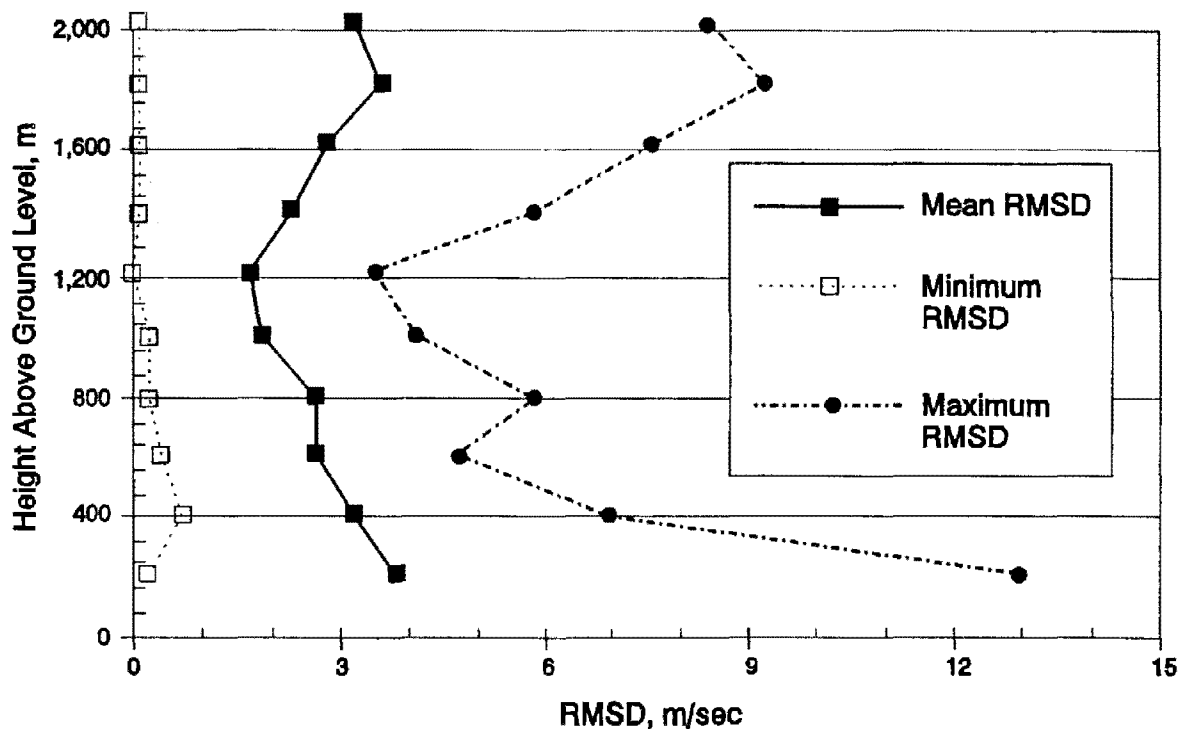


Figure 3-15. The root-mean-square-difference (RMSD) between CLASS observations and lidar observations as a function of height above ground level.

Although the measurements were significantly correlated, the results illustrate that there was still considerable disagreement between methods. The profiler had better precision than the lidar had although the differences were negligible if the first four runs were excluded from the data set for reasons stated before. The profiler obtained values biased slightly higher than the CLASS system (+0.2 m/s), while the lidar system was biased low (−0.3 m/s or −0.5 m/s). The statistical comparisons of both the profiler and the boundary-layer lidar with the rawinsonde system suggest that variations in wind speed at a particular level (based on S) must be larger than about 3 m/s to be considered significant.

3.3.2.4 Air Mass Characteristics

In meteorology, an "air mass" is a region of air, usually of multistate dimensions, that exhibits similar temperature, humidity and/or stability characteristics. Air masses are created when air becomes stagnant over a "source region" and subsequently takes on the characteristics of the source region. Similarly, when dealing with air pollution meteorology it is possible to identify a "chemical air mass" as a region of air that has become stagnant over an emissions source area. Air that was stagnant over, say, the center of Canada will exhibit relatively cold, dry conditions and will be relatively devoid of pollutants. Air that resides over the industrial regions of the midwestern United States will exhibit low visibility and, often, high ozone levels on a regional scale. Meteorological processes play an important role in determining the amount of "accumulation" of ozone and its precursors that occurs under such stagnant conditions.

Episodes of high ozone concentrations in urban areas are often associated with high concentrations of ozone in the surroundings. This accumulated ozone forms under the same atmospheric conditions that lead to high ozone levels in urban areas, and exacerbates the urban problem by supplying relatively high ozone and precursor concentrations to the urban area from upwind. The transport of ozone and its precursors beyond the urban scale (≤ 50 km) to neighboring rural and urban areas has been well documented (e.g., Wolff et al., 1977a,c; Wolff and Lioy, 1978; Clark and Clarke, 1982; Sexton, 1982; Wolff et al., 1982). A summary of these reports was given in the 1986 ozone criteria document (U.S. Environmental Protection Agency, 1986) and will not be reiterated here. The phenomena of high nonurban ozone levels was long-ago illustrated by Stasiuk and Coffey (1974) for transport within New York State; by Ripperton et al. (1977), for sites in the Middle Atlantic States; and by Samson and Ragland (1977) for the midwestern United States.

These areas of ozone accumulation are characterized by:

1. Synoptic-scale subsidence of air in the free troposphere, resulting in development of an elevated inversion layer;
2. Relatively low wind speeds associated with the weak horizontal pressure gradient around a surface high pressure system;
3. Lack of cloudiness; and
4. High temperatures.

1 On occasion, ozone at levels greater than 120 ppb can occur in rural areas far removed
2 from urban or industrial sources. Ozone levels at the summit of Whiteface Mountain
3 exceeded this value during the summer of 1988 when ozone accumulated across a wide
4 expanse of the eastern United States at levels ≥ 120 ppb. Nonetheless, even when the
5 regional accumulation is at a level below the current ozone NAAQS, the increment needed to
6 bring the level above the NAAQS in an urban area is not large.

7 The identification and understanding of the transport of photochemical ozone and other
8 oxidants and their precursors by weather systems represent a significant advance in
9 comprehending photochemical air pollution and the potential extent of its effects.
10 Considerable progress has been made in the development of long-range photochemical
11 modeling techniques so that the likely impact of synoptic systems can be anticipated. Such
12 tools are very much in the research stage, however, because the local impact of ozone and
13 other oxidants results from a complex interaction of distant and local precursor sources,
14 urban plumes, mixing processes, atmospheric chemical reactions, and general meteorology.

16 3.3.3 Normalization of Trends

17 The degree to which meteorological factors can be "normalized" out of the ozone
18 concentration and "trends" data depends in large part on the strength of the relationships
19 between ozone and meteorological components. As part of the Southern Oxidants Study
20 (SOS) Atlanta Intensive field campaign, an attempt was made to model statistically the ozone
21 levels in Atlanta to build a predictive tool for forecasting days of specialized measurement.
22 Figure 3-16 shows the fit of the data used to create the model to the model simulations.
23 Figure 3-17 shows the fit obtained from independent data collected in 1992.

24 This model was used successfully to predict next-day ozone levels in Atlanta. Ozone
25 levels in a number of American cities should be analyzed using regression tools such as this
26 to normalize meteorological variability. Through such analyses, it is possible that trends, if
27 any, represented as systematic deviations from the model may become observable.
28 A summary of other techniques for removing meteorological variability is contained in the
29 recent monograph from the National Research Council (1991). Table 3-5 lists a sample of
30 studies aimed at evaluation of ozone trends.

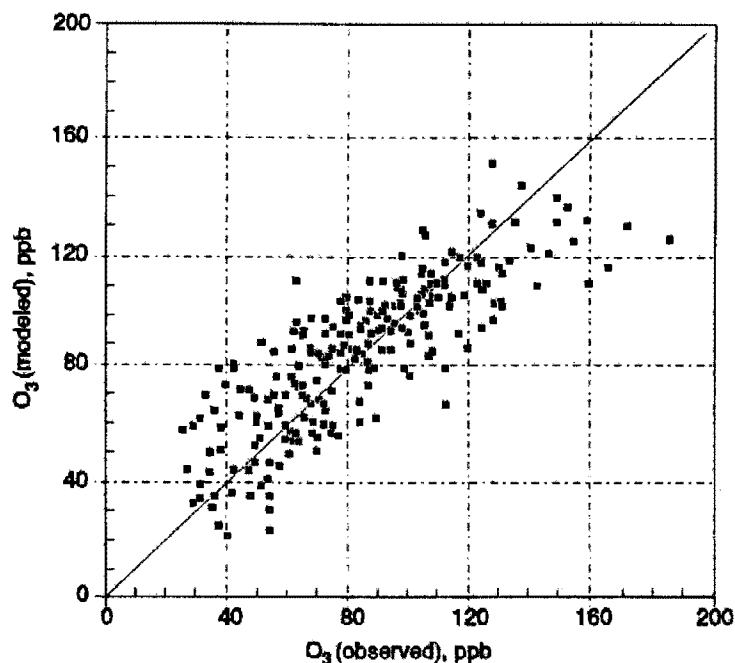


Figure 3-16. Model of ozone levels using regression techniques. The use of wind speed, temperature and previous-day ozone provided a means to forecast ozone levels.

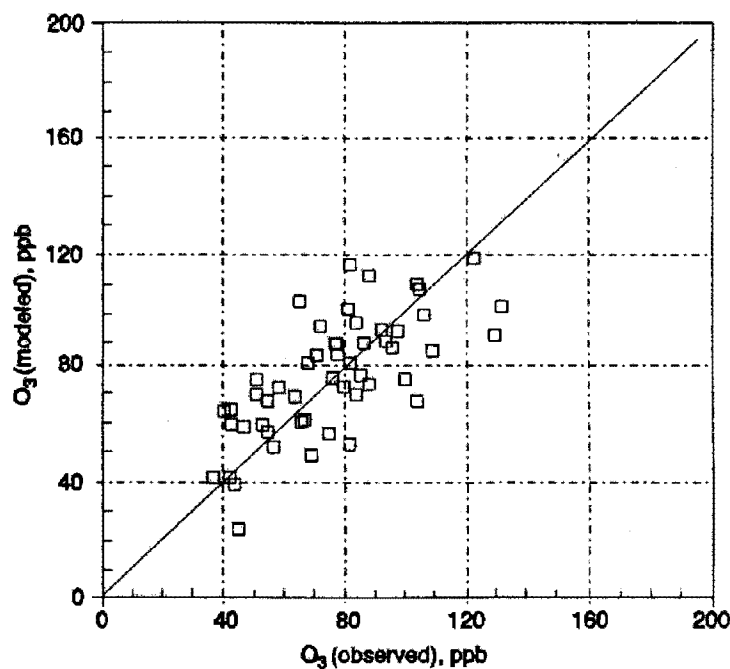


Figure 3-17. Simulated versus observed ozone levels using regression techniques on an independent data set obtained in summer 1992 in Atlanta, Georgia.

**TABLE 3-5. RECENT STUDIES EXAMINING TRENDS IN OZONE DATA
AFTER REMOVAL OF VARIABILITY ASSOCIATED
WITH METEOROLOGICAL FACTORS**

Study	Variables	Approach
Jones et al. (1988)	Surface Temperature	Compared number of days with ozone concentrations above 120 ppb to days with temperature above 30 °C.
Pollock et al. (1988)	Surface Temperature	Compared number of days with ozone concentrations above 105 ppb to days with temperature above 30 °C.
Kuntasal and Chang (1987)	850 mb Temperature	Regression of ozone versus temperature for southern California.
Wakim (1989)	Surface Temperature	Regression of ozone versus temperature for Houston, New York and Washington, DC.
Chock et al. (1982)	Surface Temperature, windspeed, relative humidity, sky cover, wind direction, dew point temperature, sea level pressure, precipitation.	Regression versus a variety of meteorological parameters.
Kumar and Chock (1984)	Surface Temperature, windspeed, relative humidity, sky cover, wind direction, dew point temperature, sea level pressure, precipitation.	Regression versus a variety of meteorological parameters.
Korsog and Wolff (1991)	Surface Temperature, windspeed, relative humidity, sky cover, wind direction, dew point temperature, sea level pressure, precipitation.	Regression versus a variety of meteorological parameters.

Source: National Research Council (1991).

3.4 PRECURSORS OF OZONE AND OTHER OXIDANTS

3.4.1 Sources and Emissions of Precursors

3.4.1.1 Introduction

As described earlier in Section 3.2, O₃ is formed in the atmosphere through a series of chemical reactions that involve volatile organic compounds (VOC) and the oxides of nitrogen (NO and NO₂ = NO_x). Control of O₃ depends on reducing emissions of VOC or NO_x or

1 both. In addition, models used to determine reductions needed require accurate emission
2 inventories. Thus, it is important to understand the sources and source strengths of these
3 precursor species in order to devise the most appropriate oxidant control strategies. In the
4 following sections, anthropogenic and biogenic NO_x and VOC sources will be described and
5 best estimates of their current emission levels and trends will be provided. Confidence levels
6 for the assigned source strengths will be discussed.

7 Both English and metric units have been utilized in emission inventories. Thousands or
8 millions of short tons are the common scales in the English system. The metric unit most
9 often employed is millions of metric tons, which is equivalent to teragrams (Tg). To convert
10 English tons to teragrams, multiply English tons by 0.907×10^{-6} . For consistency,
11 teragrams have been employed throughout the ensuing discussion.

12 13 **3.4.1.2 Nitrogen Oxides**

14 **3.4.1.2.1 Manmade Emission Sources**

15 Anthropogenic oxides of nitrogen sources are associated with combustion processes.
16 The primary pollutant is nitric oxide, which is formed from nitrogen and oxygen atoms that
17 are produced at high combustion temperatures when air is present. In addition, NO_x is
18 formed from nitrogen contained in the combustion fuel. Major NO_x source categories
19 include transportation, stationary source fuel combustion, industrial processes, solid waste
20 disposal and some miscellaneous combustion related activities. Table 3-6 provides a more
21 detailed summary of each of these source categories. The transportation category includes
22 gasoline- and diesel-powered motor vehicles, aircraft, railroads, vessels, and off-highway
23 vehicles. Electric utilities, industrial boilers, commercial/institutional boilers, and industrial
24 furnaces and space heaters comprise the Stationary Source Fuel Combustion Category.
25 Industrial processes include petroleum refining and paper, glass, steel, chemical, and cement
26 production. The incineration and open burning of wastes leads to the emissions of NO_x in
27 the solid waste disposal category. The miscellaneous sources category includes prescribed
28 forest slash burning, agricultural burning, coal refuse burning, and structure fires. It should
29 be noted at this point that, even though NO is the primary pollutant, oxides of nitrogen
30 emission inventories are quantified relative to NO_2 (mol. wt = 46).

TABLE 3-6. SOURCE CATEGORIES USED TO INVENTORY NITROGEN OXIDES EMISSIONS

Transportation	Stationary Source Fuel Combustion	Industrial Processes	Solid Waste Disposal	Miscellaneous
Highway vehicles	Coal	Pulp mills	Incineration	Forestry
Gasoline-powered	Electric utilities	Organic chemicals	Open burning	Other burning
Passenger cars	Industrial	Ammonia		
Light trucks - 1	Commercial-institutional	Nitric acid		
Light trucks - 2	Residential	Petroleum refining		
Heavy duty vehicles		Glass		
Motorcycles		Cement		
		Lime		
		Iron and steel		
Diesel-powered	Fuel oil			
Passenger cars	Electric utilities			
Light trucks	Industrial			
Heavy duty vehicles	Commercial-institutional			
	Residential			
Aircraft	Natural gas			
Railroads	Electric utilities			
Vessels	Industrial			
Farm machinery	Commercial-institutional			
Construction machinery	Residential			
Industrial machinery				
Other off-highway vehicles				
	Wood			
	Industrial			
	Residential			
	Other Fuels			
	Industrial residential			

Source: U.S. Environmental Protection Agency (1992).

Quantifying NO_x emissions in all of these categories generally requires multiplying an emission factor and an activity level. Nitrogen oxides emission factors are obtained from *Compilation of Air Pollution Factors*, AP-42 (U.S. Environmental Protection Agency, 1985), and from the current mobile source emission factor model (e.g., MOBILE5) recommended by the U.S. Environmental Protection Agency. Activity levels are derived from information sources that provide consumption levels. This takes the form of fuel type and amount consumed for stationary sources and, for transportation sources, the number of vehicle miles traveled (VMT). Point source emissions are tallied at the individual plant level. These plant-by-plant NO_x emissions are first summed at the state level and then state totals are added to arrive at the national emissions total. Data on VMT are published for three road categories—highways, rural roads, and urban streets.

Table 3-7 provides a summary of the most recent estimate of NO_x emissions from the various categories mentioned previously (U.S. Environmental Protection Agency, 1993b). The 1991 total is 21.39 Tg of NO_x emissions in the United States. Slightly less than half of the emissions (10.36 Tg) is associated with the stationary source fuel combustion category. Transportation-related activities are the second largest source, accounting for about 45% of the national total. The remaining 7% of emissions is divided between the industrial processes, solid waste disposal, and miscellaneous sources categories. The two largest single NO_x emission sources are electric power generation and highway vehicles.

Because of the dominance of the electric utility and transportation sources, the geographical distribution of NO_x emissions is related to areas with a high density of power generating stations and urban regions with high traffic densities. Figure 3-18 shows the location of the 50 largest electric power generating sources of NO_x in the United States. The majority of these power plants are concentrated in the upper Mississippi-Ohio River corridor. Because of this congregation of large point sources, 69% of U.S. NO_x emissions occur within U.S. Environmental Protection Agency Regions 3, 4, 5, and 6 (Figure 3-19). It is interesting to compare the annual NO_x emissions from a large electrical generating plant with the yearly transportation-related emissions in a major metropolitan region. The largest utility plants currently release between 0.06 and 0.09 Tg of NO_x annually, which compares to approximately 0.12 Tg of NO_x emitted by transportation sources in the Atlanta urban area (U.S. Environmental Protection Agency, 1993b).

**TABLE 3-7. 1991 EMISSION ESTIMATES FOR MANMADE SOURCES
OF NITROGEN OXIDES IN THE UNITED STATES**

Source Category	Emissions (Tg)
Transportation	<u>9.7</u>
Highway Vehicles	7.20
Off-Highway Vehicles	2.51
Stationary Fuel Combustion	<u>10.69</u>
Electric Utilities	6.74
Industrial	3.27
Other	0.68
Industrial Processes	<u>0.80</u>
Solid Waste Disposal	<u>0.07</u>
Miscellaneous	<u>0.12</u>
Forest Burning	
Other Burning	
Miscellaneous Organic Solvents	
Total of All Sources	<u>21.39</u>

Source: U.S. Environmental Protection Agency (1993b).

3.4.1.2.2 Trends in Nitrogen Oxides Emissions

Estimates of NO_x emissions date back to 1900, when approximately 2.3 Tg were emitted into the atmosphere in the United States (U.S. Environmental Protection Agency, 1992). Figure 3-20 summarizes the growth in NO_x emissions at 10-year intervals since the 1940s. Emissions grew rapidly until the 1970s and then leveled off at about 20 Tg/year. Currently, greater than 90% of the national NO_x emissions result from transportation activities and stationary fuel combustion. Figure 3-21 illustrates the growth in each of these categories over the last 50 years. Transportation-related NO_x emissions grew steadily until the 1980s and then exhibited a moderate decrease. Emissions of NO_x from fuel combustion sources have increased continually from 1940 to the present time.

Recent trends in the major NO_x emission categories are shown in Table 3-8. Between 1987 and 1991, the most recent 5 years for which NO_x emission estimates are available, transportation-related emissions have remained essentially constant, while the stationary source NO_x emissions have increased about 10%.

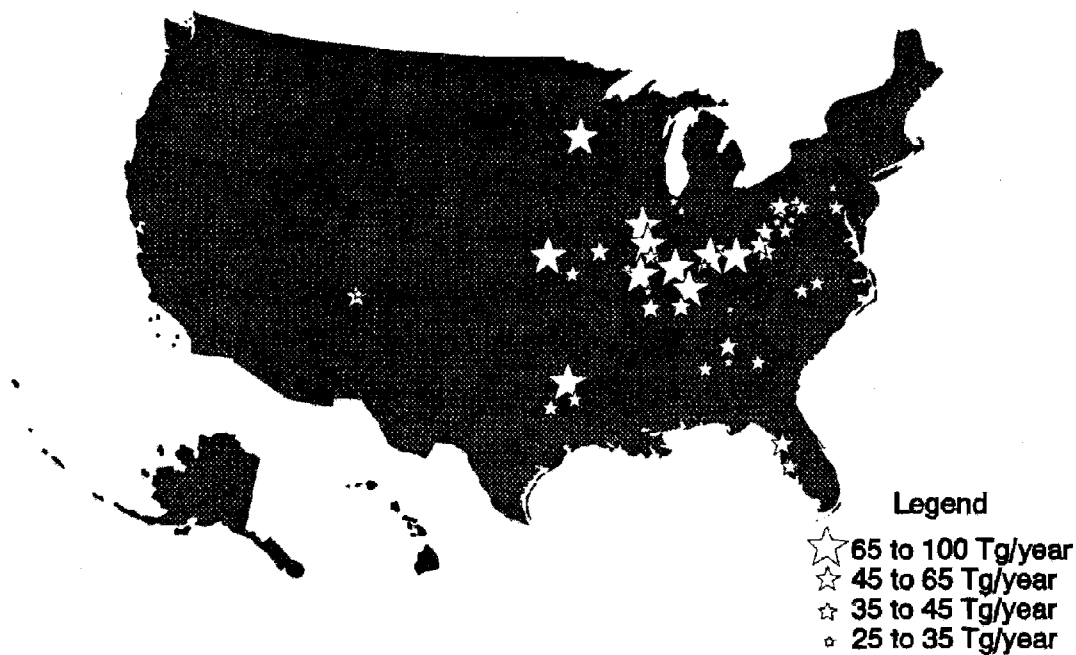


Figure 3-18. The 50 largest sources of nitrogen oxides (power plants) in the United States.

Source: U.S. Environmental Protection Agency (1992).

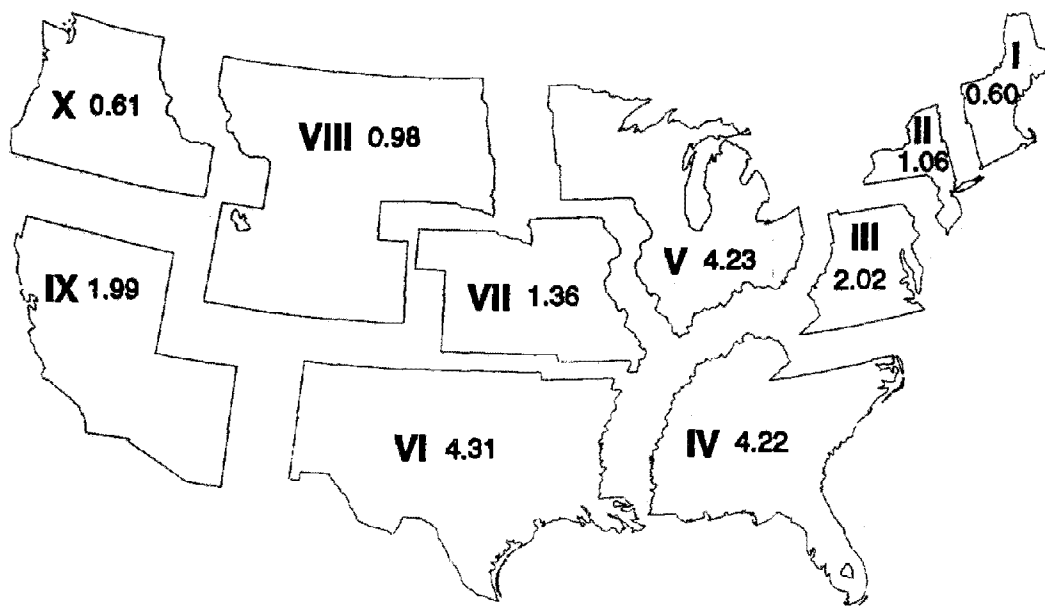


Figure 3-19. Nitrogen oxides emissions (Tg) from manmade sources in the 10 U.S. Environmental Protection Agency regions of the United States, 1991.

Source: U.S. Environmental Protection Agency (1993b).

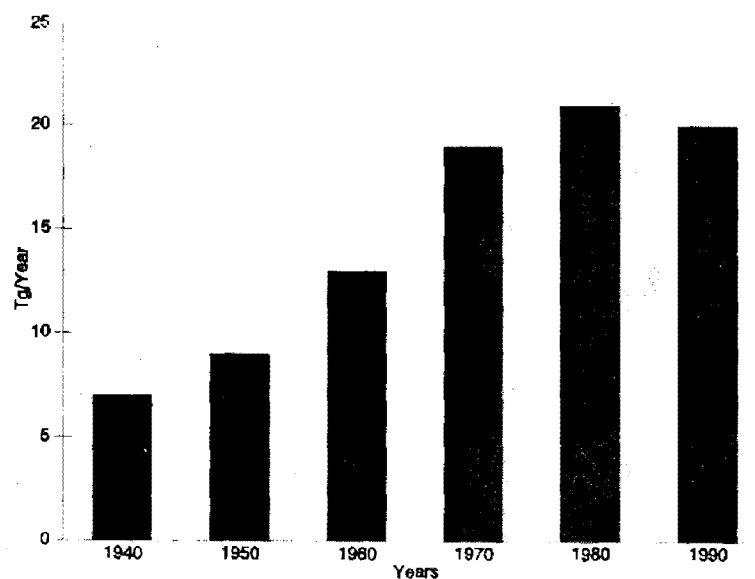


Figure 3-20. Changes in nitrogen oxides emissions from manmade sources in the United States, 10-year intervals, 1940 through 1990.

Source: U.S. Environmental Protection Agency (1992).

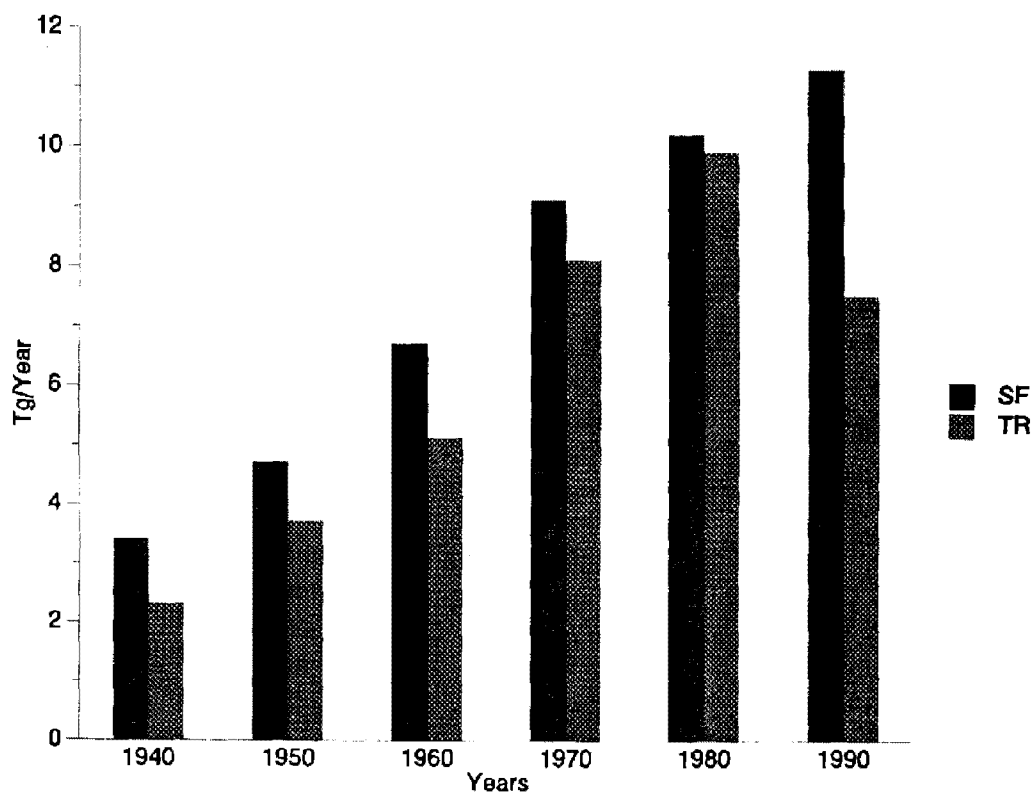


Figure 3-21. Growth in nitrogen oxides emissions from stationary source fuel combustion (SF) and transportation (TR) from 1940 through 1990.

Source: U.S. Environmental Protection Agency (1992).

TABLE 3-8. RECENT TRENDS IN NITROGEN OXIDES EMISSIONS FOR MAJOR MANMADE SOURCE CATEGORIES (Tg)

Year	Transportation	Stationary Source Fuel Combustion
1991	9.7	11.0
1990	9.9	10.7
1989	9.7	10.7
1988	9.9	10.6
1987	9.7	10.1

Source: U.S. Environmental Protection Agency (1993).

Transportation and stationary source fuel combustion will likely show downward trends in their NO_x emissions during the next 20 years. This will result from new provisions in the Clean Air Act passed in 1990. Emission limits for electric utility boilers have been prescribed to reduce acidic deposition; automobile tailpipe emission standards will be tightened; and current technology-based applications will be required for industrial boilers (non-utility) in O₃ nonattainment areas. In addition, the average grams of NO_x per mile from passenger cars is expected to decrease because of new on-board diagnostic systems and expanded inspection and maintenance requirements.

As a result of new emission limits and revised performance standards, NO_x emissions from electric utilities are expected to decrease by 16% by the year 2000. Control requirements in the industrial non-utility sector are expected to reduce NO_x emissions by 10% during the 1990 to 2000 time span. Projections based on vehicle miles traveled and emission factors from the MOBILE model suggest nearly a 50% decrease in NO_x emissions from highway vehicles between 1990 and 2000 (U.S. Environmental Protection Agency, 1992).

3.4.1.2.3 Uncertainty of Anthropogenic Nitrogen Oxides Emission Estimates

Because a large proportion of the U.S NO_x emissions are derived from distinct point sources, it is generally believed that published estimates are very reliable. For example, the NAPAP NO_x inventory for U.S. emissions in 1985 (18.6 Tg) was assigned a 90% relative

1 confidence interval in the range of 6 to 11% (Placet et al., 1991). This confidence level was
2 based on judgments used to assign uncertainty to component inputs of emission models and
3 on statistical assumptions used to aggregate uncertainty values.

4 Sources of error are associated with both the emission factors and the activity levels
5 utilized in the inventorying process. Emission factors provide quantitative estimates of the
6 average rate of emissions from many sources. Consequently, these factors are best applied
7 to a large number of sources over relatively long time periods. In other words, an NO_x
8 emission estimate for a single point source on a particular day in 1990 may be highly
9 inaccurate; but the emission value for this same source for the entire year of 1990 could be
10 very good. It appears that the emission factors assigned to the transportation sectors may be
11 the most uncertain. This results from their having been derived from mobile source models
12 that require multiple inputs. This type of model requires information on temperatures,
13 vehicle speeds, gasoline volatility, and several other parameters.

14 Recent attempts to validate NO_x emission factors or inventories, or both, have involved
15 comparing ambient NO_x concentrations with values predicted using emissions-based models.
16 These have generally taken one of two forms: (1) comparisons between NO_x concentrations
17 measured in a tunnel and those predicted from emission factors, activity levels, and dilution
18 factors in the tunnel; or (2) whole-city integration procedures in which ambient NO_x
19 concentrations are compared to ambient NO_x levels that have been predicted using a model
20 such as the Urban Airshed Model. The latter approach has been applied in the South Coast
21 Air Basin (Fujita et al., 1992). It was reported that measured and predicted NO_x
22 concentrations agreed within 20% for a 2-day period in August 1987. Likewise, the results
23 from tunnel studies have shown good agreement between predicted and measured NO_x
24 concentrations. It is important to keep in mind that ambient NO_x levels predicted using a
25 modeling method cannot be assigned true value status. There could be as much or more
26 uncertainty in the model outputs as there is in the emission inputs that are being tested. The
27 fact, however, that an emissions-based model predicts ambient concentrations that are close
28 to those measured tends to lend credence to the NO_x emission estimates.

29 In addition, NO_x inventory validation has involved comparing annual emission estimates
30 reported by different groups. Table 3-9 shows several annual U.S. NO_x emission estimates.

TABLE 3-9. COMPARISON OF ESTIMATES OF NITROGEN OXIDES EMISSIONS FROM MANMADE SOURCES IN THE UNITED STATES

Inventory ^a	Emissions/year (Tg)	
	1982	1985
NAPAP	—	18.6
EPA	19.6	19.8
MSCET	18.8	18.2
EPRI	20.7	—

^aNAPAP = National Acid Precipitation Assessment Program.
EPA = U.S. Environmental Protection Agency.
MSCET = Month and state current emissions trends.
EPRI = Electric Power Research Institute.

Source: U.S. Environmental Protection Agency (1993a).

In 1982, the estimates vary by less than 12% and this decreases to about 9% in the 1985 comparison.

3.4.1.2.4 Natural Emissions

Natural sources of NO_x include lightning, soils, wildfires, stratospheric intrusion, and the oceans. Of these, lightning and soils are the major contributors. The custom is to include emissions from all soils in the biogenic or natural category even though cultivated soil emissions are in a sense anthropogenic; cultivated soils also appear to produce higher emissions than those from undisturbed forest and prairie soils, as discussed later. Although NO_x emitted from large wildfires can be significant on a regional scale, overall this source is considered to be of minor importance for the United States. Injection of NO_x into the upper troposphere via subsidence from the stratosphere is estimated at less than 0.1 Tg/year for all of North America. Because of the relatively short lifetime of NO_x (1 to 3 days) and a small flux out of sea water, transport of NO_x from oceans is thought to be a negligible source in the United States.

1 **Lightning.** Lightning produces high enough temperatures to allow N_2 and O_2 to be
2 converted to nitric oxide. Two methods have been employed to estimate the NO_x source
3 strength from lightning:

- 4 (1) Multiply the frequency of lightning flashes by the energy dissipated per flash and
5 the NO production per unit of energy dissipated; or
6
- 7 (2) Relate NO_x production to nitrate deposition in remote areas where lightning-
8 produced NO_x is thought to be the dominant nitrate precursor.
9

10 Method (1) yields an annual NO_x production of approximately 1.2 Tg for North America
11 (Placet et al., 1991). The deposition-based estimate (Method 2) gives a somewhat larger
12 value of 1.7 Tg/year (Placet et al., 1991). The NAPAP inventory included lightning-
13 produced NO_x on a gridded $10^\circ \times 10^\circ$ latitude-longitude scale. Most of the continental
14 United States fits within 30 to 50° N latitude and 80 to 120° W longitude. The estimated
15 annual lightning-produced NO_x for this region (continental United States) is about 1.0 Tg.
16 Roughly 60% (0.6 Tg) of this NO_x is generated over the southern tier of states (30 to 40° N
17 latitude; 80 to 120° W longitude).
18

19 **Soils.** Both nitrifying and denitrifying organisms in the soil can produce NO_x . The
20 relative importance of these two pathways is probably highly variable from biome to biome.
21 Nitric oxide is the principal NO_x species emitted from soils, with emission rates depending
22 mainly on fertilization levels and soil temperature. Several reports have noted a large
23 increase in NO_x emissions from agricultural soils treated with nitrate-containing fertilizers
24 (Johansson and Granat, 1984; Kaplan et al., 1988; Johansson, 1984). Measurements of soil
25 NO_x emissions have established that the relationship with temperature is exponential,
26 consisting of approximately a two-fold increase for each $10^\circ C$ rise in temperature (Williams
27 et al., 1992; Valente and Thornton, 1993).

28 Inventorying soil NO_x emissions is difficult because of the large temporal and spatial
29 variability in emissions. The existing inventories have been developed using emission
30 algorithms that are functions of soil temperature and land-use type. Two broad, land-use
31 categories—natural and agricultural—have been assigned. The natural soils are broken down
32 into biome types, and the agricultural soils subdivided according to fertilizer applications.
33 The highest biogenic NO emissions are in corn-growing regions of the midwest (Nebraska,

Iowa, and Illinois) during summer months. Of the total U.S. biogenic emissions of NO from soils, 85% occur during the spring and summer months.

Table 3-10 provides a summary of the annual soil NO_x emissions from the ten U.S. Environmental Protection Agency regions. Approximately 60% of this NO_x is emitted in Regions 5, 7, and 8 (see Figure 3-19), which contain the central U.S. corn belt. The total estimate for U.S. soil emissions is 1.2 Tg.

TABLE 3-10. ANNUAL NITROGEN OXIDES EMISSIONS (Tg) FROM SOILS BY U.S. ENVIRONMENTAL PROTECTION AGENCY REGION

U.S. Environmental Protection Agency Region	NO _x Emissions
1, 2, and 3	0.05
4	0.11
5	0.26
6	0.18
7	0.27
8	0.21
9	0.04
10	0.01
Total	1.2

Source: Placet et al. (1991).

3.4.1.2.5 Uncertainty in Estimates of Natural Nitrogen Oxides Emissions

As indicated previously, inventorying NO_x produced from lightning requires multiplying the number of flashes by average energy factors. No attempt has been made to assign confidence limits to these variables. A measure of the uncertainty associated with lightning-produced NO_x is provided, however, by comparing emission estimates generated independently. Two estimates of the amount of lightning-generated, summertime NO_x in the southeastern United States (2.4 and 8.5×10^{-2} Tg) varied by approximately a factor of four (Placet et al., 1991).

Sources of uncertainty when inventorying NO_x emissions from soils include:

(1) land-use assignments; (2) soil temperature; and (3) emission algorithm development. Confidence levels assigned to categories 1 and 2 are about $\pm 50\%$. The emission algorithm is developed from field measurements of NO_x emission rates versus temperature for various

land-use categories. Measurement accuracy is approximately $\pm 30\%$. However, because of the natural variability of NO_x emissions within a specific soil category, uncertainty in the exponential relationship that relates emission rate to temperature is estimated to be in the range of a factor of two to four.

3.4.1.2.6 Comparison of Emissions from Manmade and Natural Sources

On an annual basis, natural sources (lightning and soils) contribute approximately 2.2 Tg of NO_x to the troposphere over the United States. This compares to the 1990 anthropogenic emission estimate of 19.4 Tg. Annual NO_x emissions from soils (1.2 Tg) are about 6% of the manmade emissions in the United States. This percentage increases to about 14% when the comparison includes only summer months (July, August, and September). Even larger biogenic contributions can occur in certain regions of the United States. For example, it is estimated that biogenic NO_x emissions from soils account for about 19% of summertime NO_x emissions in Tennessee (Valente and Thornton, 1993) and actually exceed emissions from manmade sources during the summer months in the states of Nebraska and South Dakota (Williams et al., 1992).

3.4.1.3 Volatile Organic Compounds

3.4.1.3.1 Manmade Emission Sources

Volatile organic compounds are emitted into the atmosphere by evaporative and combustion processes. Many hundreds of different organic species are released from a large number of source types. The species commonly associated with atmospheric O_3 production contain from 2 to about 12 carbon atoms. They can be true hydrocarbons, which possess only carbon and hydrogen atoms (e.g., alkanes, alkenes, and aromatics), or substituted hydrocarbons that contain a functional group such as alcohol, ether, carbonyl, ester, or halogens. Methane has been largely ignored because its atmospheric oxidation rate is very slow compared to the higher-molecular-weight organics.

In 1991, the total U.S. emissions of VOCs was estimated to be 21.0 Tg (U.S. Environmental Protection Agency, 1993b). The two largest source categories were industrial processes (10.0 Tg) and transportation (7.9 Tg). Lesser contributions were attributed to waste disposal and recycling (2.0 Tg), stationary source fuel combustion (0.7 Tg), and

miscellaneous area sources (0.5 Tg). Table 3-11 provides a more detailed breakdown of VOC source contributions. Within the industrial category, solvent utilization, petroleum product storage and transfer, and chemical manufacturing are the major contributors. Volatile organic compounds released from highway vehicles account for almost 75 % of the transportation-related emissions.

TABLE 3-11. ESTIMATED 1991 EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM MANMADE SOURCES IN THE UNITED STATES

Source Category	Emissions (Tg)
Transportation	<u>7.87</u>
Highway Vehicles	6.00
Off-Highway Vehicles	1.87
Stationary Fuel Combustion	<u>0.68</u>
Electric Utilities	0.03
Industrial	0.26
Other	0.39
Industrial Processes	<u>9.97</u>
Chemical Manufacture	1.61
Petroleum and Related Industries	0.68
Solvent Utilization	5.50
Petroleum Product Storage and Transport	1.69
Other	0.49
Waste Disposal and Recycling	<u>2.01</u>
Miscellaneous	<u>0.51</u>
TOTAL ALL SOURCES	<u>21.04</u>

Source: U.S. Environmental Protection Agency (1993).

Speciated hydrocarbon emissions from manmade sources were reported in the 1985 NAPAP Emissions Inventory. Emissions of each main hydrocarbon family exceeded 1 Tg. Alkanes comprised about 33 %, aromatics 19 %, and alkenes 11 % of anthropogenic VOC emissions in the 1985 inventory (Placet et al., 1991). None of the major oxygenated hydrocarbon groups (e.g., carbonyls, organic acids, phenols) listed in the speciated inventory exceeded 1 Tg. The carbonyl group, which included formaldehyde, higher aldehydes,

acetone, and higher ketones, was the largest contributor of oxygenated hydrocarbons at 0.73 Tg.

3.4.1.3.2 Trends in Emissions

Emissions of nonmethane VOCs peaked in the early 1970s and have decreased continually since that time. Emissions of VOCs increased from 15.5 Tg in 1940 to 27.4 Tg in 1970, and now are estimated to be back down to approximately the same level as in 1940 (U.S. Environmental Protection Agency, 1992). Figure 3-22 illustrates these changes at 10-year intervals from 1940 to 1990. Up until 1970, highway vehicles were the major source of VOC emissions. As more and better emission controls have been adopted on automobiles, however, emissions from the transportation sector have dropped below those from industrial processes, the category which is now the leading contributor of VOC emissions to the atmosphere. Transportation, industrial processes, and the miscellaneous burning and solvent use categories have accounted for 83 to 93 % of VOC emissions over the past 50 years. Figure 3-23 shows the emission trends for these three categories. The transportation-related emissions of VOCs are currently estimated to be at about the same level as in 1940. Industrial process VOC emissions nearly tripled between 1940 and 1980, followed by a small decline in more recent years. The miscellaneous category has exhibited a decrease in emissions from 4.5 Tg in 1940 to a 1990 level estimated at 2.8 Tg/year.

Trends for the dominant VOC emissions categories over the last 5 years are shown in Table 3-12. Projections for the year 2000 forecast a 62 % reduction in VOC emissions from highway vehicles compared to 1990 levels. The major reduction in the transportation area will contribute to an overall 25 % decrease in total national VOC emissions between 1990 and 2000 (U.S. Environmental Protection Agency, 1992).

3.4.1.3.5 Uncertainty in Estimates of Emissions from Manmade Sources

It has proven difficult to determine the accuracy of VOC emission estimates. Within an area source such as an oil refinery, emission factors and activity levels are assigned for thousands of individual sources (e.g., valves, flanges, meters, and processes) and emission estimates for each of these sources are summed to produce the emissions total. Since it would be impractical to determine an emission factor for each of these sources within a

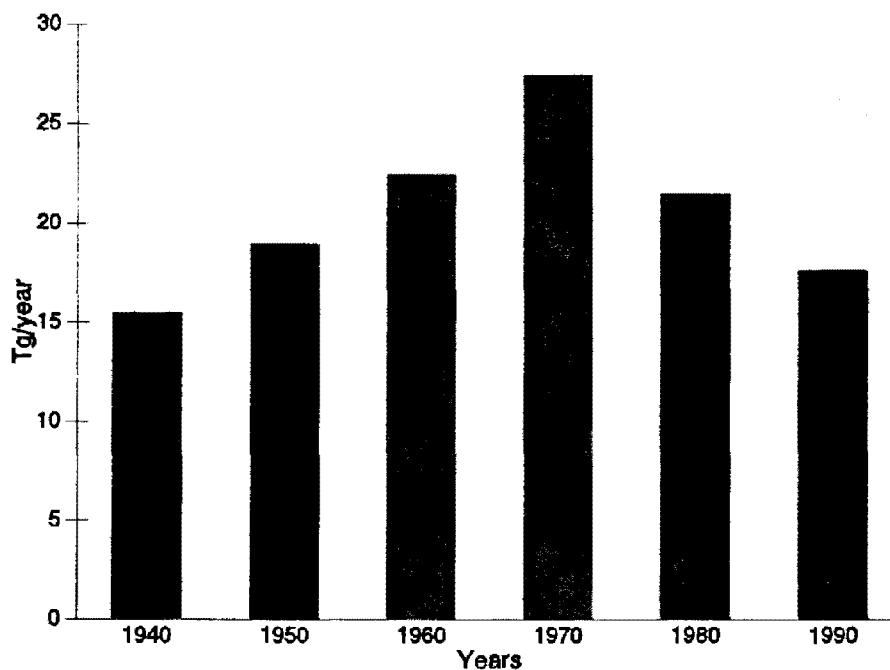


Figure 3-22. Changes in emissions of volatile organic compounds from major manmade sources in the United States, 10-year intervals, 1940 through 1990.

Source: U.S. Environmental Protection Agency (1992).

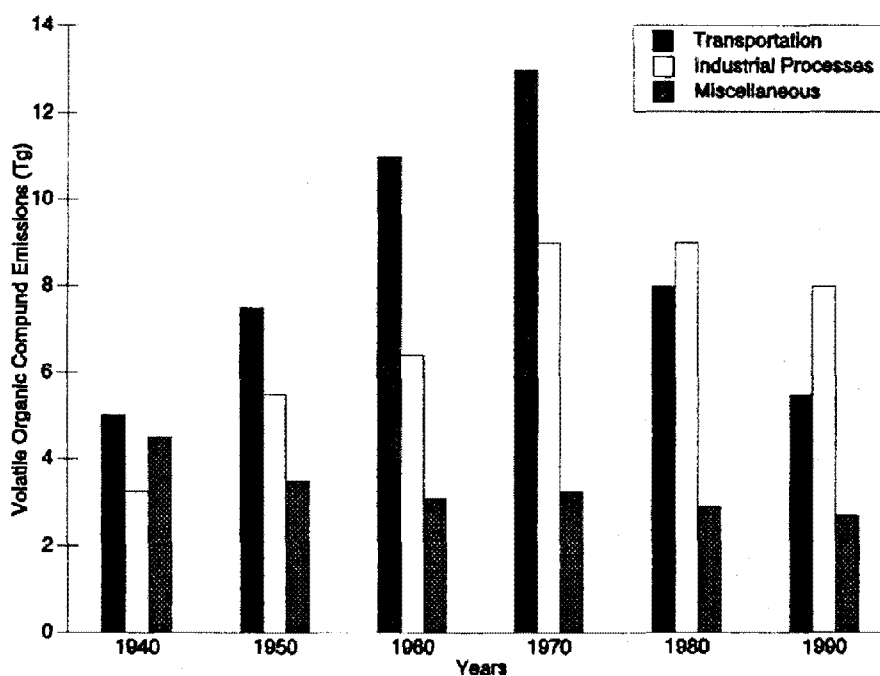


Figure 3-23. Changes in emissions of volatile organic compounds from major manmade sources, 1940 through 1990.

Source: U.S. Environmental Protection Agency (1992).

**TABLE 3-12. RECENT TRENDS IN EMISSIONS OF VOLATILE
ORGANIC COMPOUNDS FROM MAJOR CATEGORIES
OF MANMADE SOURCES (Tg)**

Year	Transportation	Industrial Processes	Waste Disposal and Recycling
1991	7.87	7.86	2.01
1990	8.07	9.96	2.05
1898	8.26	9.92	2.08
1988	9.15	10.00	2.10
1987	9.29	9.65	2.05

Source: U.S. Environmental Protection Agency (1993).

refinery individually, average emission factors for the various source categories are utilized. This can lead to substantial error if the individual sources deviate from the assigned average factor. Even more troublesome are area sources that include a large evaporative emissions component. These sources are dependent upon environmental factors such as temperature, which add to the difficulty in establishing reliable emission estimates. Such sources fall into a miscellaneous solvent evaporation category, which includes emissions from processes such as dry cleaning, degreasing, printing, autobody repair, furniture manufacture, and motor vehicle manufacture.

Assigning accurate VOC emission estimates to the mobile source category has proven troublesome, as well. Models are used that incorporate numerous input parameters, each of which has some degree of uncertainty. For example, activity models are employed to characterize the mobile source fleet. This includes the number of vehicles in various categories (e.g., gasoline fueled, diesel fueled, catalyst equipped, non-catalyst equipped, etc.), miles accumulated per year for each type of vehicle, and ages of the vehicles. Vehicle registration statistics are employed for category assignment. Errors can arise because registration data are not always up to date and unregistered vehicles are completely omitted. Military vehicles, foreign-owned automobiles, and old "junkers" that are on the highways but not registered do not get included in the inventorying process. The activity models assume vehicles of the same age accumulate mileage at the same rate. This is probably not correct,

1 and there is a need to assess the uncertainty in this assumption thorough a systematic
2 collection of vehicle type-age-mileage accumulation statistics. Recent developments in
3 remote sensing have permitted more accurate measurement of hydrocarbon exhaust emissions
4 from on-road vehicles (Stedman et al., 1990). These studies have demonstrated a highly
5 skewed distribution, with the majority of VOC emissions coming from about 20% of the
6 automobiles. Emission factors developed from laboratory dynamometer testing most likely
7 do not properly account for the high-emitting vehicle contribution (Pitchford and Johnson,
8 1993). In many cases, these high emitters are older cars that are poorly maintained.
9 In order to reduce this source of uncertainty, it may be necessary to reassess the life spans
10 assigned to vehicles. Vehicles manufactured more than 25 years prior to the present time
11 (1993) are not included in the inventory. However, these older vehicles are likely to be high
12 emitters, and if they are under-represented in the model, emissions will be underestimated.
13 Activity models provide data in terms of national averages. This can contribute to
14 inaccuracies in emissions estimates if a particular region varies from the national average in
15 terms of vehicle types, age, or vehicle miles traveled.

16 Ambient measurements of VOCs and NO_x have been employed in order to better define
17 uncertainty levels in VOC inventories. Some of the earliest work was carried out in the
18 Atlanta area in the 1980s. Using a simple model and measured ambient VOC and NO_x
19 concentrations, it was shown that ambient NO_x levels were consistent with the urban NO_x
20 emission estimates; but measured ambient VOC concentrations were as much as a factor of
21 six greater than predicted (Westberg and Lamb, 1985). More recently, experiments carried
22 out in tunnels have demonstrated a poor relationship between measured VOC emission
23 factors and those derived from automotive emission models. In a study designed to verify
24 automotive emission inventories for the South Coast Air Basin, measurements in the
25 Van Nuys Tunnel indicated that automotive VOC emissions were a factor of four larger than
26 predicted using emission models (Pierson et al., 1990). Improvements in mobile source
27 emission models have resulted in somewhat higher emission estimates that have now reduced
28 the discrepancy with ambient data to about a factor of 2.5 (Fujita et al., 1992; Cadle et al.,
29 1993). It is clear that the relationship between emission inventories and ambient
30 concentrations of NO_x and VOCs warrants further study. In addition to improving the
31 mobile source emission inventories, it will be necessary to place uncertainty bounds on

1 stationary source inventories. Whether stationary source emissions of VOC are
2 underpredicted using current emission inventory methodology is not known (Finlayson-Pitts
3 and Pitts, Jr., 1993).

4 5 **3.4.1.3.4 Biogenic Emissions**

6 Vegetation emits significant quantities of reactive VOCs into the atmosphere. Many of
7 these biogenic VOCs may contribute to O₃ production in urban (Chameides et al., 1988) and
8 rural (Trainer et al., 1987) environments. The VOC emissions of primary interest are
9 isoprene and the monoterpenes (e.g., α -pinene, β -pinene, myrcene, limonene, etc.), which
10 are hydrocarbons. Recent field measurements have shown that a variety of oxygenated
11 organics are also emitted from plants (Winer et al., 1992). A thorough discussion of
12 biogenic emissions and their implication for atmospheric chemistry has been published
13 recently by Fehsenfeld et al. (1992), who reviewed (1) the techniques used to measure VOC
14 emissions from vegetation; (2) laboratory emissions studies that have been used to relate
15 emission rates to temperature and light intensity; (3) development of emission models; and
16 (4) the use of emission models in the preparation of emission inventories.

17 Over the past 10 years, a number of regional and national biogenic emission inventories
18 have been reported (Zimmerman, 1979; Winer et al., 1983; Lamb et al., 1985; Lamb et al.,
19 1987; Lamb et al., 1993). These inventories are based on algorithms that relate VOC
20 emissions from a particular vegetation class to ambient temperature, land-use, and, in the
21 case of isoprene, photosynthetically active radiation. Most biogenic VOC emissions from
22 vegetation increase exponentially with temperature. Isoprene emissions are light-dependent,
23 being minimal at night and increasing with solar intensity during the day. Deciduous
24 vegetation is the dominant source of isoprene; whereas coniferous trees emit primarily
25 monoterpenes. Other things being equal, isoprene is emitted at a much higher rate than the
26 monoterpenes. For example, in a southern forest of mixed pine and hardwoods, the isoprene
27 emission rate from an oak tree is about 10 times larger than the flux of α -pinene from an
28 adjacent loblolly pine during the midday period.

29 The most recent biogenic VOC emissions estimate for the United States totals
30 29 Tg/year (Lamb et al., 1993). This estimate includes 5.9 Tg isoprene, 4.4 Tg α -pinene,
31 6.5 Tg other monoterpenes, and 12.3 Tg other VOCs. Table 3-13 provides a summary of

**TABLE 3-13. ANNUAL BIOGENIC HYDROCARBON EMISSION INVENTORY FOR
THE UNITED STATES (Tg)**

Compound	Land Use								U.S. Total
	Oak Forests	Other Deciduous Forests	Coniferous Forests	Scrub- lands	Grass- lands	Crop- lands	Inland Waters	Urban Areas	
Isoprene	2.31	1.01	0.61	1.17	0.49	0.2	0.02	0.08	5.9
α -pinene	0.19	0.23	2.07	0.78	0.13	0.85	0.06	0.04	4.4
Other terpenes	0.41	0.44	3.08	1.41	0.24	0.81	0.06	0.06	6.5
Other VOCs	1.12	0.88	2.72	2.49	0.45	4.51	0.07	0.08	12.3
Total	<u>4.03</u>	<u>2.56</u>	<u>8.48</u>	<u>5.85</u>	<u>1.31</u>	<u>6.37</u>	<u>0.21</u>	<u>0.26</u>	<u>29.1</u>
Percent of Total	13.9	8.8	29.2	20.1	4.5	21.9	0.7	0.9	

Source: Lamb et al. (1993).

1 the contributions from the various vegetation categories. In preparing this inventory,
2 algorithms were developed that related VOC emissions to temperature and light for each of
3 the biomass categories shown in the table. On a national scale, coniferous forests are the
4 largest vegetative contributor because of their extensive land coverage. The category, "other
5 VOCs," is the dominant biogenic hydrocarbon contributor to the national total. From the
6 standpoint of inventory accuracy, this is somewhat unfortunate because the identities of most
7 of the "other VOCs" are uncertain. This classification has carried over from the extensive
8 field measurement program conducted by Zimmerman (1979) and coworkers in the
9 mid-1970s. The category, other VOCs, includes peaks that showed up in sample
10 chromatograms at retention times that could not be matched to known hydrocarbons. It is
11 likely that if the Zimmerman study were repeated today, most of the species making up this
12 "other VOCs" category could be identified. Recent field studies have made use of GC-MS
13 techniques that were not available to Zimmerman in the 1970s.

14 Biogenic emissions vary by season because of their dependence on temperature and
15 vegetational growth. In addition, the southern tier of states is expected to produce more
16 biogenic emissions than those in the north because of higher average temperatures.
17 Table 3-14 shows a spatial and temporal breakdown of U.S. biogenic emissions.
18 Summertime emissions comprise more than half of the annual totals in all regions. Federal
19 Regions IV and VI in the southcentral and southeastern United States have the highest
20 biogenic hydrocarbon emission rates.

21 22 **3.4.1.3.5 Uncertainty in Estimates of Biogenic Emissions**

23 Sources of error in the biogenic inventorying process arise from uncertainties in
24 (1) emission measurements; (2) determination of biomass densities; (3) land-use
25 characterization; and (4) measurement of light intensity and temperature. Within each of
26 these categories the error is relatively small. However, when emission measurements are
27 combined with temperature or light intensity or both into a single algorithm, the uncertainty
28 increases greatly. This results from the fact that temperature and light are only surrogates
29 for the real physiological processes that control biogenic emissions. Emission rate and
30 ambient temperature can be highly correlated for data collected from one tree branch over a
31 24-h period; but, when these data are combined with measurements from other branches and

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**TABLE 3-14. ANNUAL BIOGENIC HYDROCARBON EMISSION INVENTORY BY MONTH AND
U.S. ENVIRONMENTAL PROTECTION AGENCY REGION FOR THE UNITED STATES (Tg)**

U.S. Environmental Protection Agency Region										
Month	3	4	5	6	7	8	9	10	Total	Percent of Total
1	0.018	0.092	0.004	0.084	0.007	0.022	0.060	0.043	0.3	1.1
2	0.017	0.139	0.004	0.123	0.007	0.02	0.054	0.039	0.4	1.4
3	0.071	0.428	0.067	0.519	0.078	0.108	0.113	0.102	1.5	5.1
4	0.169	0.460	0.189	0.567	0.211	0.303	0.320	0.202	2.4	8.3
5	0.206	0.475	0.240	0.586	0.226	0.362	0.331	0.208	2.6	9.1
6	0.427	0.874	0.550	1.146	0.508	0.809	0.710	0.424	5.5	18.7
7	0.441	0.903	0.568	1.184	0.524	0.836	0.734	0.438	5.6	19.3
8	0.439	0.903	0.568	1.184	0.524	0.820	0.734	0.438	5.6	19.3
9	0.123	0.461	0.137	0.561	0.136	0.280	0.357	0.212	2.3	7.8
10	0.069	0.286	0.066	0.394	0.026	0.290	0.369	0.219	1.7	5.9
11	0.066	0.162	0.063	0.174	0.025	0.110	0.130	0.109	0.8	2.9
12	<u>0.018</u>	<u>0.080</u>	<u>0.004</u>	<u>0.073</u>	<u>0.007</u>	<u>0.022</u>	<u>0.060</u>	<u>0.043</u>	<u>0.3</u>	<u>1.1</u>
Total	2.1	5.3	2.5	6.6	2.3	4.0	4.0	2.5	29.1	

Source: Lamb et al. (1993).

1 other trees the correlation is not nearly as good. The uncertainty associated with the
2 algorithms used to generate the U.S. inventory described previously is estimated to be a
3 factor of three (Lamb et al., 1987). Since other sources of error in the inventorying process
4 are much smaller, a factor of three is the current best estimate of the overall uncertainty
5 associated with biogenic VOC inventories. However, this may be a lower limit if it is shown
6 that oxygenated species are emitted in significant quantities by vegetation. Emission
7 measurement methods employed in the past have not been adequate for quantifying polar,
8 oxygenated organics.

10 **3.4.1.3.6 Comparison of Manmade and Biogenic Emissions**

11 The most recent anthropogenic and biogenic VOC emissions estimates for the United
12 States indicate that natural emissions (29 Tg) exceed manmade emissions (21 Tg). However,
13 in a recent National Research Council review it was concluded that emissions from manmade
14 sources are currently underestimated by a significant amount (National Research Council,
15 1991). Since uncertainty in both biogenic and anthropogenic VOC emission inventories is
16 large, it is not possible to establish at this time whether the contribution of emissions from
17 natural or manmade sources of VOCs is larger.

19 **3.4.1.4 Relationship of Summertime Precursor Emissions and Ozone Production**

20 Peak O₃ levels are recorded in most regions of the country during the summer months
21 of June, July, and August. From the foregoing discussion, it is obvious that natural
22 emissions of NO_x and VOCs peak during this same time frame. Biogenic emissions are very
23 dependent on temperature; and as ambient temperatures rise during the summer months, NO_x
24 and VOC emissions reach a maximum. Figure 3-24 clearly demonstrates this for biogenic
25 VOC emissions, and a plot of monthly biogenic NO_x emissions would show a similar
26 pattern. Well over 50% of biogenic NO_x and VOC emissions occur during the period of
27 maximum photochemical activity.

28 Seasonal changes in anthropogenic emissions of NO_x are believed to be relatively small.
29 The transportation sector produces slightly less NO_x during the warmer months, but there is
30 probably a small increase from the stationary source category because of higher summertime
31 power demands. Since these are the major U.S. sources of NO_x and changes in seasonal

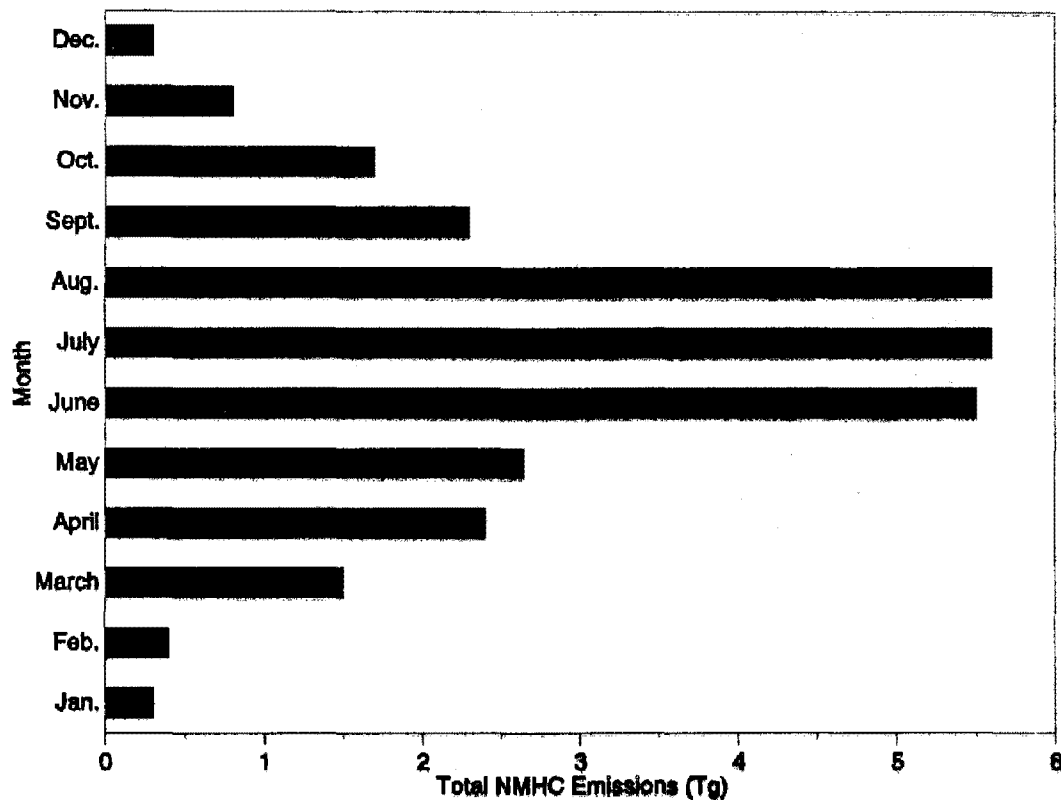


Figure 3-24. Estimated biogenic emissions of volatile organic compounds in the United States as a function of season.

Source: Fehsenfeld et al. (1992).

emissions tend to offset each other, there is no reason to expect that NO_x emissions will vary significantly by season on the national level. Evaporative emissions of VOCs are enhanced during the warm summer months. Because evaporation is an important component of anthropogenic VOC emissions, there should be a summertime increase. In 1987, U.S. VOC emissions during June, July, and August were estimated to exceed annual monthly average VOC emissions by about 17% (U.S. Environmental Protection Agency, 1992). This is a very small change relative to the uncertainty associated with VOC emission estimates. In the NAPAP inventory, VOC emissions from manmade sources were considered to be almost independent of season (Placet et al., 1991).

Increases in O_3 precursor emissions during the peak O_3 season will have a tendency to enhance O_3 production. Ozone production in rural areas is usually NO_x -limited (Fehsenfeld et al., 1992). Thus, enhanced summertime emissions of NO_x from soils and lightning will

add NO_x to the atmosphere in rural regions, which in turn will lead to the production of more O₃. Larger summertime emissions of VOCs will enhance O₃ production in urban areas. Biogenic VOC sources in the vicinity of urban areas can contribute significant quantities of reactive hydrocarbons to the urban O₃ precursor mix (Cardelino and Chameides, 1990).

3.4.2 Concentrations of Precursor Substances in Ambient Air

The volatile organic compounds (VOCs), excluding methane, often are referred to as nonmethane organic compounds (NMOCs). The class of NMOCs most frequently analyzed in air are the nonmethane hydrocarbons (NMHCs). The NMHC measurements often provide an acceptable approximation of the NMOCs. The NMHCs and the nitrogen oxides (NO_x) within urban areas tend to have morning concentration peaks. These result from vehicular traffic in combination with limited mixing depths. Later in the morning into the afternoon hours, concentrations of NMHCs and NO_x decrease, but to varying extents (Purdue et al., 1992) because of increases in mixing depths and consequent increases in dilution volumes. Photochemical atmospheric reactions also can rapidly convert nitric oxide (NO) to nitrogen dioxide, and hydrocarbons to carbonyls, PANs, and other products (Sections 3.2.4, 3.4.2.1, and 4.9). Late afternoon and early evening peaks might be expected in NMHC and NO_x concentrations because of increased vehicular traffic at urban locations, but such increases often are not discernible (Purdue et al., 1992). This effect probably results from the presence of substantial mixing depths in the warmer months that persist through these hours in many urban locations.

Because of the emphasis on early morning inputs of NMOCs and NO_x for models such as EKMA, most of the measurements available emphasize the 6 to 9 a.m. period. The variations in the concentrations of NMOCs and NO_x, their ratios, and the composition of NMOCs are important factors in the generation of O₃ and other photochemical products.

3.4.2.1 Nonmethane Organic Compounds

In earlier measurements based on gas chromatographic analyses made during a number of different studies in urban areas over the years between 1969 and 1983, the mean 6 to 9 a.m. NMHC concentrations were reported to range from 0.324 to 3.388 ppm C (U.S.

1 Environmental Protection Agency, 1986). The highest NMHC concentrations were those
2 measured at sites in Los Angeles.

3 A program for analysis for NMOCs and NO_x in the months of June through September
4 was conducted in a considerable number of U.S. cities during the 1980s. The results
5 obtained from measurements made during the 6 to 9 a.m. period at sites in 22 cities in 1984
6 and 19 cities in 1985 have been subjected to statistical analysis and interpretation (Baugues,
7 1986). The total NMOC measurements throughout the June through September periods in
8 these cities were obtained by the cryogenic preconcentration-direct flame ionization method
9 (PDFID) (McElroy et al., 1986). In addition, during about 15% of the 6 to 9 a.m. periods,
10 canister samples were collected for subsequent gas chromatographic analysis (Seila et al.,
11 1989). In 1984, the lowest median NMOC value obtained was 0.39 ppm C from
12 measurements in Charlotte, NC, while the highest median NMOC value obtained was
13 1.27 ppm C from measurements in Memphis, TN. In 1985, the lowest median NMOC value
14 obtained was 0.38 ppm C from measurements in Boston, MA, while the highest median
15 NMOC value obtained was 1.63 ppm C in Beaumont, TX. The overall median values from
16 all urban sites were approximately 0.72 ppm C in 1984 and 0.60 ppm C in 1985 (Baugues,
17 1986). The gas chromatographic analyses made on samples collected in 1984, 1985, and 1986
18 have been reported (Seila et al., 1989). The more abundant individual hydrocarbons include
19 $\text{C}_2\text{-C}_6$ alkanes, $\text{C}_2\text{-C}_5$ alkenes, $\text{C}_6\text{-C}_9$ aromatics, and acetylene. Based on the 48 most
20 abundant concentrations, the overall median concentrations by class of hydrocarbon
21 (NMHCs) were as follows: paraffins, 0.266 ppm C, 60% of total; aromatics, 0.166 ppm C,
22 26% of total; olefins, 0.047 ppm C, 11% of total; and acetylene, 0.013 ppm C, 3% of the
23 48 hydrocarbons measured (Seila et al., 1989). Additional individual NMHCs summing to
24 about 0.100 ppm C were detected at concentrations ≤ 0.002 ppm C each. Most of these
25 compounds were identified by class but not by structure.

26 Detailed hydrocarbon analyses for $\text{C}_2\text{-C}_{10}$ NMHCs were obtained during the
27 17 intensive days of the Southern California Air Quality Study (SCAQS) in 1987 (Lonneman
28 et al., 1989; Rasmussen, 1989; Stockberger et al., 1989). The average percentage ambient
29 composition from eight southern California sites during 11 intensive sampling days of the
30 summer of 1987 by class of NMHCs were as follows: paraffins, 53.4; aromatics, 27.2;
31 olefins, 12.1; carbonyls, 7.7 (Main and Lurmann, 1992).

1 In Atlanta, GA, during the summer of 1990, hydrocarbon concentrations were
2 measured at six sites with automated gas chromatographs. Results were reported on
3 54 hydrocarbons, with 24-h average concentrations ranging from 0.186 ppm C to
4 0.397 ppm C (Purdue et al., 1992).

5 A comparison of NMHC measurements made by gas chromatographic analyses over a
6 period of years in Los Angeles and in the New York City area has been reported (Lonneman
7 and Seila, 1993). In the Los Angeles area, the NMHC concentrations averaged 2.81 ppm C
8 in 1968, compared to 1.02 ppm C in 1987. In the New York City area, the NMHC
9 concentrations averaged about 1.1 ppm C in 1969, compared to 0.62 ppm C from 1986 to
10 1988. In both the Los Angeles and New York areas, there were significant decreases in
11 NMHC concentrations as well as compositional changes in NMHCs during these years, with
12 increases observed in the percentage of paraffin hydrocarbons and decreases in the
13 percentage of aromatic hydrocarbons and acetylene (Lonneman and Seila, 1993).

14 Aldehydes and ketones occur in urban air as ozone-oxidant precursors from emissions
15 such as vehicular exhaust, and as products of reactions of OH radicals with NMHCs,
16 reactions of alkenes with O₃, and, at night, reactions with NO₃ radicals. Early morning
17 aldehyde concentrations have been predicted to result to a greater extent from atmospheric
18 reactions of alkenes than from emission of vehicular exhaust (Altshuller, 1993). During the
19 day, aldehydes and ketones are rapidly produced from reactions of OH radicals with aliphatic
20 and aromatic hydrocarbons and of alkenes with O₃. Carbonyl concentrations tend to increase
21 through the daytime hours (Grosjean, 1982, 1988; Grosjean et al., 1993).

22 Measurements of ambient air concentrations of carbonyls indicate the total loading of
23 aldehydes and ketones from all processes. Ambient urban air concentrations of formaldehyde
24 and total aldehydes were tabulated for the 1960 to 1981 period (Altshuller, 1983a).
25 Subsequent studies by DNPH-HPLC techniques (Section 3.5.2.3.4) have consistently shown
26 that formaldehyde and acetaldehyde are the most abundant aldehydes; however, a number of
27 other carbonyls—including propanal, acrolein, acetone, butanal, crotonaldehyde, methyl ethyl
28 ketone, pentanal, hexanal, benzaldehyde, and tolualdehyde—also have been measured (Fung,
29 1989; Grosjean 1982, 1988, 1991; Kalabokas et al., 1988; Zweidinger et al., 1988). The
30 ratios of formaldehyde to acetaldehyde concentrations (ppbv) can vary from less than 0.5 in
31 cities in Brazil, where there is high use of ethanol fuels, up to 4.0 to 5.0 at a few urban sites

(Grosjean et al., 1993). However, at most urban sites, the ratios of formaldehyde to acetaldehyde concentrations occur in the 1.0 to 3.0 range.

A compilation of the maximum, average range of formaldehyde concentrations from many studies in Southern California carried out between 1960 and 1989 is available (Grosjean, 1991). A downward trend in formaldehyde concentrations occurs, probably because of decreased production from precursor alkenes and decreased emission in vehicular exhaust (Sigsby et al., 1987; Dodge, 1990). For example, the maximum formaldehyde concentrations decreased from above 100 ppbv in the 1960s down to the 10 to 30 ppbv range during the last decade (Grosjean, 1991). In other U.S. cities in the early 1980s, the maximum formaldehyde concentrations ranged from 5 to 45 ppb (Salas and Singh, 1986).

Several studies have reported concurrent morning hydrocarbon and carbonyl concentrations in downtown Los Angeles, CA (Grosjean and Fung, 1984); Raleigh, NC (Zweidinger et al., 1988); and Atlanta, GA (Shreffler, 1992; Grosjean et al., 1993). The average percentage of carbonyls relative to total NMHCs were reported as follows: Los Angeles, 3%; Raleigh, 2%; and Atlanta, $\geq 2\%$ (formaldehyde + acetaldehyde concentrations) at two different sampling sites. In SCAQS, carbonyls were measured at eight sites in summer and five in fall of 1987 (Fung, 1989; Fujita et al., 1992). The average percentage of C₁ to C₆ carbonyls relative to NMHCs in summer was 7.6% and in fall was 3.7%.

Compilations of NMHC concentrations of nonurban and remote locations are available (U.S. Environmental Protection Agency, 1986; Altshuller, 1989a). Total NMHC concentrations reported ranged from less than 0.01 to 0.14 ppm C. At remote locations over the Pacific, NMHC concentrations generally were less than 0.01 ppm C. Over both continental and oceanic locations there can be contributions from biogenic sources of NMHCs.

Interest in the contribution of biogenic hydrocarbons has existed for many years and earlier work has been reviewed (Altshuller, 1983b). Photochemical modeling in the United States predicts significant effects of biogenic hydrocarbons on O₃ production (Chameides et al., 1988; Roselle et al., 1991). Similar modeling of the effect of biogenic hydrocarbons on O₃ production within urban plumes over southeastern England predicted a 2 to 8 ppb increase in plume and background O₃ concentrations (MacKenzie et al., 1991). Because of

1 lower emissions of biogenic and lower overall NMOC/NO_x ratios, O₃ production over
2 southeastern England is predicted to be limited by the availability of anthropogenic
3 hydrocarbons.

4 Compilations of results of earlier measurements of isoprene and terpene concentrations
5 are available (Altshuller, 1983b; U.S. Environmental Protection Agency, 1986). Average
6 concentrations of isoprene ranged from 0.001 to 0.020 ppm C and terpenes from 0.001 to
7 0.030 ppm C. When concurrent measurements of biogenic and anthropogenic NMHCs
8 were available, the biogenic NMHCs usually constituted much less than 10% of the total
9 NMHCs (Altshuller, 1983b).

10 Among more recent studies are two investigations of terpene and isoprene emissions in
11 the central valley of California and in Louisiana (Arey et al., 1991; Khalil and Rasmussen,
12 1992). Both studies reported a large number of individual terpenes as measured using
13 enclosure methods. When ambient air measurements were made, most of the terpenes
14 measured in the enclosures were not detectable (Khalil and Rasmussen, 1992). In ambient
15 air, isoprene was the predominate hydrocarbon, accounting on average for 70% of the
16 biogenic species and 36% of NMOCs. It is concluded that the bag enclosure method can
17 lead to large overestimates in biogenic emissions (Khalil and Rasmussen, 1992).

18 In two other recent studies in deciduous forests, the isoprene oxidation products were
19 measured as well as isoprene itself (Pierotti et al., 1990; Martin et al., 1991). Both studies
20 report the ambient concentrations of methacrolein and methyl vinyl ketone. In the
21 investigation in a central Pennsylvania deciduous forest in the summer of 1988, average
22 midday concentrations of isoprene were in the 0.005 to 0.010 ppm C range; whereas the
23 corresponding concentrations of methacrolein and methyl vinyl ketone were in the 0.001 to
24 0.002 ppm C range (Martin et al., 1991). In the study conducted in California forests with
25 samples collected between 1200 and 1600 LT in late spring and summer, the upper quartile
26 of isoprene concentrations was within the 0.010 to 0.025 ppm C range, whereas methacrolein
27 concentrations were within the 0.001 to 0.003 ppm C range, and methyl vinyl ketone
28 concentrations were within the 0.0005 to 0.0015 ppm C range (Pierotti et al., 1991).

29 Higher-molecular-weight semivolatile carbonyls have been measured in a number of
30 rural-remote areas (Jüttner, 1986; Yokouchi et al., 1990; Nordek et al., 1992; Ciccioli et al.,
31 1993). The compounds identified include C₅-C₁₂ aliphatic aldehydes, aliphatic ketones, and

aromatic aldehydes. Comparisons of the measurement of these carbonyls relative to aromatic hydrocarbons in two studies indicated higher carbonyl concentrations and much lower aromatic hydrocarbon concentrations in the rural-remote sites compared to the urban areas (Yokouchi et al., 1990; Ciccioli et al., 1993). Widely varying natural sources have been associated with these carbonyls, including emissions from forest species (Nordek et al., 1992) and short vegetation (Ciccioli et al., 1993) and as secondary products of natural emissions of terpenes (Ciccioli et al., 1993) or oleic acid (Yokouchi et al., 1990). Among other oxygenates reported to be of natural origin are higher-molecular-weight alcohols (Jüttner, 1986; Nordek et al., 1992; Goldan et al., 1993). These oxygenates contribute to the "other VOCs" category in the biogenic emissions inventory (Section 3.4.1.3.4).

In an urban-scale study in Atlanta, GA, during the summer of 1990 (as part of the Southern Oxidant Study), isoprene concentrations rose in late morning and into the afternoon, with early evening peaks observed at residential and rural-residential sites (Purdue et al., 1992). A similar diurnal profile for isoprene was observed at a Pennsylvania forest site (Martin et al., 1991). The median concentration at the sampling sites in Atlanta early in the evening ranged from 0.006 to 0.020 ppm C. The isoprene as a percentage of total NMHCs in the early evening ranged among the sites from 2 to 12% (Shreffler, 1992).

3.4.2.2 Nitrogen Oxides

Measurements of NO_x were obtained with continuous NO_x analyzers at sites in 22 and 19 U.S. cities during the months of June through September of 1984 and 1985, respectively. These results have been evaluated and the 6 to 9 a.m. values tabulated (Baugues, 1986). In 1984, the lowest median NO_x concentration of 0.010 ppm was obtained from measurements in West Orange, TX; while the highest median NO_x concentration of 0.088 ppm was obtained from measurements in Memphis, TN. In 1985, the lowest median NO_x concentration of 0.005 ppm was obtained from measurements in West Orange, TX; while the highest median NO_x concentration of 0.100 ppm was obtained from measurements in Cleveland, OH. The median NO_x concentration values for sites in most of these cities in 1984 and 1985 ranged between 0.02 and 0.08 ppm. Because of high vehicular emission rates and shallow mixing depths, the median 6 to 9 a.m. concentration values in many of these cities exceeded the annual average NO_x values of 0.02 to 0.03 ppm in U.S. metropolitan

1 areas between 1980 and 1989 (U.S. Environmental Protection Agency, 1991a). In the 1990
2 Atlanta study, average summer NO_x concentration values at the six study sites ranged from
3 0.011 to 0.026 ppm (Purdue et al., 1992).

4 At nonurban sites, NO_x concentrations have been reported as mean 24-h seasonal or
5 annual NO_x values. The available results have been compiled for work reported through
6 1983 (Altshuller, 1986). The average seasonal or annual NO_x concentrations ranged from
7 less than 0.005 to 0.015 ppm. At remote sites in the earlier investigations, monthly average
8 NO_x concentrations were less than 0.001 ppm. In more recent work, the statistics on NO_x
9 concentrations have been reported for several relatively remote U.S. sites (Fehsenfeld et al.,
10 1988). The 24-h average NO_x concentrations and the range in the central 90% of values
11 were as follows: Point Arena, CA, spring 1985, 0.0004 ppm, 0.0007 to 0.001 ppm; Niwot
12 Ridge, CO, summer 1985, 0.0005 ppm, 0.0001 to 0.002 ppm; and Scotia, PA, summer
13 1986, 0.002 ppm, 0.0007 to 0.009 ppm. It should be noted that each of these sites can be
14 subject to anthropogenic influences, thus accounting for the higher NO_x values. For
15 example, at Niwot Ridge, CO, with upslope flow from the Denver-Boulder, CO, urban area,
16 higher NO_x concentrations are measured. Nitrogen oxide concentrations at or below
17 0.0001 ppm occur at other remote surface locations (Fehsenfeld et al., 1988).

19 3.4.2.3 Ratios of Concentrations of Nonmethane Organic Compounds and Nitrogen 20 Oxides

21 The ratios of 6 to 9 a.m. NMOC/NO_x have been obtained from the measurements in
22 the U.S. cities discussed above (Baugues, 1986). In 1984, the lowest median NMOC/NO_x
23 ratio of 9.1 was obtained in Cincinnati, OH, and the highest median NMOC/NO_x ratio of
24 37.7 was obtained in Texas City, TX. In 1985, the lowest median NMOC/NO_x ratio of
25 6.5 was obtained in Philadelphia, PA, whereas the highest median NMOC/NO_x ratio of
26 53.2 was obtained in Beaumont, TX. The range in daily 6 to 9 a.m. NMOC/NO_x ratios
27 within a given city is large, with 10th percentile to 90th percentile NMOC/NO_x ratios
28 varying usually by factors of 2 to 4 and at several sites by factors of 5 to 10 (Baugues,
29 1986). There appears to be a tendency for higher NMOC/NO_x ratios in the cities included in
30 the southeastern (9) and southwestern (15) United States than in the northeastern (7) and
31 midwestern United States (7) (Altshuller, 1989b). The NMOC-to-NO_x ratios at rural sites

1 tend to be higher than the mean NMOC-to-NO_x ratios in urban locations, with mean values
2 at several rural sites ranging between 20 and 40 (Altshuller, 1989b).

3 In SCAQs, the ambient NMOC (NMHCs + carbonyl)/NO_x ratios averaged 8.8 in
4 summer and 6.9 in the fall of 1987 (Fujita et al., 1992). However, the six intensive days in
5 fall between November 11 and December 11 were not characterized by elevated
6 O₃ concentrations (Zeldin, 1992). These ambient ratios were 2 to 2.5 times higher than the
7 corresponding emission inventory ratios. Discrepancies as large or larger have been
8 previously discussed for urban and rural NMHC/NO_x ambient-to-emission ratios in the
9 eastern United States (Altshuller, 1989b).

10 A trend analysis of NMHC/NO_x ratios in the South Coast Air Basin is available for the
11 1976 to 1990 period (Fujita, 1992). The ratios were consistently higher in summer than fall.
12 These ratios started decreasing slowly during the 1980s from maximum ratios of about 12 in
13 summer and 9 in fall down to 8.5 in summer and 7 in fall by 1990. The ambient-to-emission
14 inventory ratios over this period ranged from as high as 3.4 in summer to 1.7 in winter
15 (Fujita, 1992).

16 Interest in the 6 to 9 a.m. NMOC/NO_x ratios is associated with their use in the EKMA
17 type of trajectory model (Section 3.6.1.2). The analysis at 10 eastern and midwestern sites
18 of upper-quartile O₃ days relative to other O₃ days indicated a significant difference
19 ($p \leq 0.10$) by the two-sample Wilcoxon Rank Sum test at four of the 10 sites with
20 NMOC/NO_x ratios (Wolff and Korsog, 1992). However, the correlation of NMOC/NO_x
21 ratios with maximum 1-h O₃ concentrations was very weak. It was concluded that the use of
22 the 6 to 9 a.m. NMOC/NO_x ratio in EKMA will not provide sufficient information to
23 distinguish among NMOC, NO_x, or combined VOC-NO_x strategies as optimum strategies for
24 urban areas.

26 **3.4.3 Source Apportionment and Reconciliation**

27 **3.4.3.1 Source Apportionment**

28 Source apportionment refers to determining the quantitative contributions of sources to
29 ambient air pollutant concentrations. In principle, it includes two fundamentally different
30 approaches, source-oriented and receptor-oriented. In the source-oriented approach, a
31 mathematical dispersion model is applied to an emissions inventory and meteorological data

1 to produce an estimate of ambient pollutant concentrations that can be expected at a specified
2 point in space and time. In contrast, the receptor-oriented approach depends on simultaneous
3 ambient concentration measurements of a variety of pollutant species, and a knowledge of the
4 relative amounts of the species (source profiles) that are present in the emissions of the
5 sources that are potential contributors. A mathematical receptor model operates on the
6 source profile and ambient species concentration information to deconvolute the ambient
7 concentrations into their source contributions, without the need of emissions inventory or
8 meteorological information. Indeed, the desire to avoid the latter two kinds of information,
9 whose acquisition is often problematical, has been an important motivation in the
10 development of the receptor-oriented approach.

11 Although source apportionment in its general sense embraces both approaches, in recent
12 years it has come to be regarded as synonymous with the receptor-oriented approach
13 (receptor modeling). The equivalence of source apportionment and receptor modeling is
14 assumed in the following. The most recent review of the field of receptor modeling has been
15 given by Gordon (1988).

16 Because tropospheric O_3 is a secondary pollutant, the natural role of receptor modeling
17 is in determining the quantitative source contributions of the VOC precursors of O_3 .
18 Historically, receptor modeling was first developed in the 1970s for the apportionment of
19 ambient aerosol, and aerosol applications since then have been more extensive than VOC
20 applications. The aerosol and VOC areas of receptor modeling application have more
21 similarities than differences, however, so that much of the mathematical apparatus that has
22 been developed for aerosol problems is readily adaptable to VOCs.

23 For reasons that will become apparent, the separation of emissions sources into
24 anthropogenic and biogenic classes is a natural division for VOC receptor modeling and is
25 used in the following.

26 27 **3.4.3.1.1 Manmade Sources of Volatile Organic Compounds**

28 A principal approach for receptor modeling of anthropogenic VOC sources is that of
29 "mass balance". In this approach, a particular linear combination of source profiles is sought
30 that best approximates (in a linear least-squares sense) the profile of VOC species
31 concentrations measured in an ambient sample. Here a VOC source profile is defined as the

1 set of numbers giving the fractional amounts (abundances) of individual species in the
2 emissions from the source. The profile may be normalized to the sum of the abundances of
3 all VOC species emitted by the source or to a sum over some arbitrary subset of species.
4 For the linear combination of profiles that gives the best fit, the coefficients are the source
5 strengths (in the same units as the measured ambient concentrations) associated with each of
6 the included source profiles.

7 Early efforts to use various versions of the mass balance approach include Ehrenfeld
8 (1974), in Los Angeles; Mayrsohn and Crabtree (1976) and Mayrsohn et al. (1977), in
9 Los Angeles; and Nelson et al. (1983), in Sydney, Australia.

10 Of these studies, the work of Mayrsohn et al. (1977) is the most comprehensive—
11 900 samples from eight sites collected during June to September, 1974. The average results
12 were: automotive exhaust, 53%; whole gasoline evaporation, 12%; gasoline headspace
13 vapor, 10%; commercial natural gas, 5%; geogenic natural gas, 19%; liquefied natural gas,
14 1%. The percentages are for NMHCs through C₁₀ (i.e., not all of the total VOCs).

15 The estimates for the first three vehicle-related sources together account for 75% of the
16 ambient NMHCs, which is the approximate percentage estimated in the other studies listed.
17 Geogenic natural gas is obviously not anthropogenic but is included here for completeness.
18 Its strength (19%) is striking. It seems unlikely that a contribution this large would be
19 typical of other locales lacking a petroleum-related geology. In any case, accounting for the
20 urban atmospheric concentrations of ethane and propane (the main NMHC constituents of
21 natural gas) has remained an unsatisfactorily resolved problem, so that the 19% result for
22 geogenic natural gas has to be regarded skeptically.

23 Although old, these early studies are of more than just historical interest. In one
24 respect, they are superior to more recent studies in their recognition of two distinctly
25 different kinds of gasoline evaporation: (1) headspace vapor, which represents the partial
26 evaporation of gasoline in situations such as storage tank evaporation or vehicle diurnal
27 evaporation, and is characterized by an enrichment of high volatility species; and (2) whole
28 gasoline emissions, which can arise from spillage, leakage, and vehicle hot-soak emissions,
29 and has a composition resembling liquid gasoline itself. The implications of this are
30 discussed below.

1 In the mid-1980s, a useful degree of standardization was incorporated into the mass
2 balance approach by the introduction of EPA's Chemical Mass Balance (CMB) software.
3 The current version, CMB7 (Watson et al., 1990), embodies a comprehensive treatment of
4 error (including uncertainty in both ambient data and source profiles) and many diagnostics
5 (including profile collinearity), and has been used frequently in recent VOC receptor
6 modeling studies.

7 Recent studies include Wadden et al. (1986), in Tokyo; O'Shea and Scheff (1988), in
8 Chicago; Aronian et al. (1989), in Chicago; Sweet and Vermette (1992), in Chicago and East
9 St. Louis, IL; Harley et al. (1992), in Los Angeles; Kenski et al. (1993), in Chicago;
10 Beaumont, TX; Detroit; Atlanta; and Washington, DC; Spicer et al. (1993), in Columbus,
11 OH; and Lewis et al. (1993), in Atlanta.

12 The source categories covered by these studies taken together include vehicle exhaust,
13 gasoline evaporation (whole gasoline and headspace vapor), industrial emissions (refineries,
14 coke ovens, chemical plants), architectural coatings, dry cleaning, wastewater treatment, auto
15 painting, industrial solvents/degreasers, graphic arts (printing), and natural gas. Each study
16 gives estimates for the percentage contributions to measured ambient VOC (or related
17 quantity) for a selected subset of these source categories. The one exception is the work of
18 Sweet and Vermette (1992), which estimates the percentage source contributions to individual
19 species, rather than to total VOC. Such species apportionment is always available from the
20 CMB calculations, but is often not explicitly reported.

21 Usually the source profiles used were generic; that is, from compilations (e.g., U.S.
22 EPA, 1991) of source measurements taken elsewhere. The work of Lewis et al. (1993) is
23 unique in the use of profiles extracted from the ambient air data themselves.

24 Generally, for these urban-based studies, vehicle exhaust is found to be the dominant
25 contributor to ambient VOC. Exceptions are the Tokyo results of Wadden et al. (1986),
26 which show an unreasonably small average contribution of 7%, and the Beaumont results of
27 Kenski et al. (1993) at 14%. For all the rest, the average vehicle exhaust results fall in the
28 range ($45 \pm 15\%$).

29 The results for gasoline evaporation contribution estimates are much less satisfactory.
30 This is because the recent studies, with the exceptions of Harley et al. (1992) and Lewis
31 et al. (1993), included a gasoline headspace vapor profile but not a whole gasoline profile in

1 their calculations. The latter two studies suggest that this omission is a serious error. For
2 example, Harley et al. (1992) find a remarkably large whole gasoline contribution (nearly the
3 same as that of vehicle exhaust); and Lewis et al. (1993) find a whole gasoline contribution
4 that is about 20% that of vehicle exhaust. Both, however, find a whole gasoline contribution
5 about four times greater than the headspace contribution. Because vehicle exhaust and whole
6 gasoline profiles are quite similar (except for the very light species that are absent in gasoline
7 but present in exhaust as combustion products), excluding the whole gasoline profile will
8 tend to overestimate the exhaust contribution. Although this error may not greatly affect the
9 total mobile source-related emissions estimate, it is misleading with regard to implied control
10 strategies.

11 Beyond the ubiquitous vehicle-related contributions, other anthropogenic source
12 contribution estimates tend to be smaller or locale-specific.

14 **3.4.3.1.2 Biogenic Sources of Volatile Organic Compounds**

15 The possible role of biogenic VOC emissions in O₃ formation is being considered much
16 more seriously now (Chameides et al., 1988) than was the case a decade ago. Because of
17 the severe experimental problems in accurately measuring biogenic emissions directly,
18 receptor modeling approaches are of considerable interest. Compared with anthropogenic
19 sources, however, the application of receptor modeling methodology to biogenic sources has
20 been very limited. The principal reason is that it has not been possible to find VOC species
21 that are simultaneously (1) distinctive components of biogenic emissions, (2) emitted in an
22 approximately fixed proportion to the total VOC biogenic emissions, and (3) relatively
23 unreactive. Without these conditions, the construction of a credible stable biogenic source
24 profile is not possible, and, consequently, the CMB approach is unusable.

25 In this situation, a crude form of receptor modeling has been used in which the ambient
26 concentration of a VOC species, whose only source is thought to be biogenic, is divided by
27 the estimated abundance of the species in the total VOC biogenic emissions. Typical
28 candidates include isoprene (deciduous emission) and the terpenes α - and β -pinene
29 (coniferous emission), δ -caranene, and limonene. Because these are all highly reactive, any
30 such estimate can only be regarded as a lower limit of the contribution that biogenic
31 emissions make to total ambient VOC, if the loss resulting from atmospheric transformation

1 is not taken into account. As an example, Lewis et al. (1993) used isoprene, the most
2 prominent biogenic species measured in downtown Atlanta during summer 1990, to infer a
3 lower limit of 2 % (24-h average) for the biogenic percentage of total ambient VOC at that
4 location. Isoprene emissions have a strong diurnal dependence. Lower limits for biogenic
5 emissions at other hours, inferred from average isoprene concentrations, were: 1 % at 8 am,
6 5 % at noon, 6 % at 4 pm, 2 % at 9 pm.

7 The recent review article by Fehsenfeld et al. (1992) lists other prominent biogenic
8 species, and calls attention to the newly recognized importance of alcohols such as methanol
9 as biogenic primary emissions. Goldan et al. (1993) have reported the C₅ alcohol,
10 2-methyl-3-buten-2-ol ("methyl butenol"), to be the most abundant VOC of biogenic origin
11 present in a predominantly lodgepole pine forest in Colorado.

12 A more sophisticated form of biogenic receptor modeling involves the radiocarbon
13 isotope ¹⁴C. The approach depends on the fact that ¹⁴C constitutes a nearly fixed fraction
14 (approximately 10⁻¹²) of all carbon present throughout the biosphere. In contrast, the ¹⁴C in
15 dead organic material older than 40,000 years, certainly the case for fossil fuels, has been
16 reduced by at least 99 % through radioactive decay. This leads to a simple estimate of the
17 biogenic fraction of a carbon-containing sample given by f_s/f_0 , where f_s is the ¹⁴C fraction
18 in the sample, and f_0 is the ¹⁴C fraction in living material. Besides its conceptual simplicity,
19 the approach is appealing for VOC apportionment because ¹⁴C retains its identity in the
20 reaction products that may result from atmospheric transformation of reactive VOC. The
21 method appears to be reliable for particulate phase organics (Lewis et al., 1988; Lewis et al.,
22 1991a), but is still under development for VOC applications (Klouta et al., 1993).

23 24 3.4.3.2 Source Reconciliation

25 Source reconciliation refers to the comparison of measured ambient VOC concentrations
26 with emissions inventory estimates of VOC source emission rates for the purpose of
27 validating the inventories. Because concentrations and emission rates are specified in
28 different units, the comparisons are done in terms of percentages: the percentage of a
29 source's contribution to ambient total VOC as estimated by receptor modeling versus the
30 source's emission rate as a percentage of the inventory's total VOC emission rate.

1 Nearly all the receptor modeling studies listed above have included such a percentage
2 comparison. Typically, the agreement is quite good for vehicle exhaust, generally the
3 dominant VOC source in urban airsheds. Gasoline evaporation comparisons are much less
4 consistent, at least partly for the reasons already indicated. Typically, there is at least
5 qualitative agreement for the other anthropogenic sources: They are small in the inventory,
6 and the receptor-estimated contributions are small. An interesting exception is refinery
7 emissions in Chicago (Scheff and Wadden, 1993), for which the receptor estimate was 7%,
8 five times greater than the inventory estimate. Another is the significant (5 to 20%) natural
9 gas/propane contribution estimated in Los Angeles, Columbus, and Atlanta but not reflected
10 in their inventories. The few biogenic source estimates provided by receptor modeling are
11 generally smaller than those given in emissions inventories, at least partly because of the
12 reactivity problem already referred to. Credible ¹⁴C measurements on VOC samples would
13 be extremely helpful in validating the magnitude of the biogenic component of emissions
14 inventories.

15 Lewis et al. (1993) has noted that comparisons based on percentages are quite
16 insensitive for dominant source components, and the comparisons are more dependent on
17 how "total VOC" is defined than is often appreciated (the definition varies for the studies
18 listed). Thus, unfortunately, the generally good agreement (receptor versus inventory
19 estimates) found for vehicle exhaust does not translate into a definitive judgment on the
20 current concern that this source component may be significantly underestimated in existing
21 inventories. For example, if the emission rate of vehicle exhaust in a typical inventory were
22 arbitrarily doubled, the resulting change in the percentage of this component in the inventory
23 is well within the range of what can be produced in the receptor estimate by merely choosing
24 a different definition of "total VOC" from plausible alternatives. Such alternatives relate to
25 questions such as which subset of hydrocarbons are summed. Whether unidentified
26 chromatographic components are included in the sum, etc. In the future, this situation can
27 be improved by more consistency in the total VOC definition and by transforming the
28 receptor modeling results from a concentration-based representation to an emission-rate one.
29 This unavoidably involves introducing some limited meteorological information (Lewis et al.,
30 1991b).

3.5 ANALYTICAL METHODS FOR OXIDANTS AND THEIR PRECURSORS

3.5.1 Sampling and Analysis of Ozone and Other Oxidants

3.5.1.1 Ozone

3.5.1.1.1 Introduction

The measurement of O₃ in the atmosphere has been a subject of research for decades because of the importance of this compound in atmospheric chemistry and because of its potential and demonstrated effects on human health and welfare.

Because of the importance of O₃ in the air of populated regions, widespread O₃ monitoring networks have been operated for many years, and the development of measurement and calibration approaches for O₃ has been extensively reviewed (e.g., U.S. Environmental Protection Agency, 1986). This section focuses on the measurement of ozone in the ambient atmosphere at ground level, and summarizes the current state of ambient O₃ measurement and calibration. No attempt is made here to cover the full history of development of these methods, since that has been documented elsewhere (e.g., U.S. Environmental Protection Agency, 1978, 1986). Instead, this section concentrates on those methods currently used and on new developments and novel approaches to O₃ measurement.

Although no method is totally specific for O₃, current methods for O₃ must be distinguished from earlier methods that measured "total oxidants". The wet chemical methods used earlier for total oxidants have been replaced for essentially all ambient measurements by two more specific instrumental methods based on the principles of chemiluminescence and ultraviolet (UV) absorption spectrometry. These two approaches are described below. In addition, recent developments in spectroscopic measurements, in other chemical approaches, and in passive sampling devices for O₃ are described.

3.5.1.1.2 Chemiluminescence Methods

Gas-Phase Chemiluminescence. The most common chemiluminescence method for O₃ is direct gas-phase reaction of O₃ with an olefin to produce electronically excited products, which decay with the emission of light. This approach was first used nearly 30 years ago for chemical analysis by Nederbragt (Nederbragt et al., 1965), and development of a portable monitor (Warren and Babcock, 1970) and application to atmospheric

1 measurements (Stevens and Hodgeson, 1970) followed soon after. Typically, an O₃ monitor
2 based on this approach functions by mixing a constant flow of about 1 L/min of sample air
3 with a small constant flow ($\approx 50 \text{ cm}^3/\text{min}$) of ethylene. Mixing occurs in a small inert
4 reaction chamber fitted with a sealed window through which light can pass to the
5 photocathode of a photomultiplier tube. Electronically excited formaldehyde molecules,
6 generated by a small fraction of the O₃-ethylene reactions, produce a broad band of emission
7 centered at 430 nm. The emission intensity is linearly proportional to the O₃ concentration
8 over the range of 0.001 ppm to at least 1 ppm. Calibration of the monitor with a known
9 ozone source provides the relationship between monitor response and ozone concentration.
10 Detection limits of 0.005 ppm and a response time of less than 30 s are easily attained, and
11 are typical of currently available commercial instruments.

12 Although no interference has been found from common atmospheric pollutants, a
13 positive interference from atmospheric water vapor has been reported (California Air
14 Resources Board, 1976; Kleindienst et al., 1993 and references therein) and has recently
15 been confirmed (Kleindienst et al., 1993). The recent results indicate a positive interference
16 of about 3% per percent H₂O by volume at 25 °C. The results of Kleindienst et al. (1993)
17 were obtained at ozone concentrations of 0.085 to 0.32 ppm, and at H₂O concentrations of
18 1 to 3% (i.e., dew point temperatures of 9 to 24 °C). It has been estimated that the
19 interference of water in ethylene chemiluminescent measurements at 30 °C and 60% relative
20 humidity could be as high as 13 ppbv of O₃, or 11% of the O₃ reading at 120 ppbv
21 (Kleindienst et al., 1993). Calibration with known O₃ concentrations in air of temperature
22 and humidity similar to that of the sample air can minimize this source of error.

23 A separate potential problem with the ethylene chemiluminescent method is leakage of
24 the pure ethylene reagent gas. Because ozone and hydrocarbon measurements are often
25 co-located for monitoring purposes, leakage of ethylene could cause difficulty in obtaining
26 valid measurements of total nonmethane hydrocarbons (TNMHC) in ambient air.

27 The measurement principle set forth by EPA for compliance monitoring for O₃ is the
28 chemiluminescence method using ethylene (Federal Register, 1971). Methods of testing and
29 the required performance specifications that commercial O₃ monitors must meet to be
30 designated a reference or equivalent method are documented (Federal Register, 1975).
31 A monitor may be designated a *reference* method if it employs gas-phase chemiluminescence

with ethylene as the measuring principle and achieves the required performance specifications. An *equivalent* method must show a consistent relationship with the reference method and must meet the required performance specifications. Table 3-15 shows those specifications for O₃ monitors. Note that ethylene chemiluminescence monitors typically have response times far superior to that required in Table 3-15.

TABLE 3-15. PERFORMANCE SPECIFICATIONS FOR AUTOMATED METHODS OF OZONE ANALYSIS

Performance Parameter	Units	Specification
Range	ppm	0 to 0.5
Noise	ppm	0.005
Lower detectable limit	ppm	0.01
Interference equivalent		
Each interference	ppm	±0.02
Total interference	ppm	0.06
Zero drift, 12 and 24 h	ppm	±0.02
Span drift, 24 h		
20% of upper range limit	%	±20.0
80% of upper range limit	%	±5.0
Lag time	min	20
Rise time	min	15
Fall time	min	15
Precision		
20% of upper range limit	ppm	0.01
80% of upper range limit	ppm	0.01

Source: Federal Register (1975); Code of Federal Regulations (1975); cited in U.S. Environmental Protection Agency (1986).

The list of commercial O₃ monitors designated as reference or equivalent methods by EPA is shown in Table 3-16 (updated as of February 8, 1993). Details on three monitors not described in the 1986 EPA criteria document for ozone and other oxidants are presented in Table 3-17. All of the reference methods are ethylene chemiluminescence instruments, as required by the definition of a reference method. The equivalent methods are based on either gas-solid chemiluminescence or UV absorption analyzer measurements. Those methods are

**TABLE 3-16. REFERENCE AND EQUIVALENT METHODS FOR OZONE
DESIGNATED BY THE U.S. ENVIRONMENTAL PROTECTION AGENCY^a**

Method (Principle)	Designation Number	Method Code
<u>Reference Methods</u> (Ethylene Chemiluminescence)		
Beckman 950A	RFOA-0577-020	020
Bendix 8002	RFOA-0176-007	007
CSI 2000	RFOA-0279-036	036
McMillan 1100-1	RFOA-1076-014	514
McMillan 1100-2	RFOA-1076-015	515
McMillan 1100-3	RFOA-1076-016	016
Meloy OA325-2R	RFOA-1075-003	003
Meloy OA350-2R	RFOA-1075-004	004
Monitor Labs 8410E	RFOA-1176-017	017
<u>Equivalent Methods</u> (UV Absorption)		
Advanced Pollution Instr. 400	EQOA-0992-087	087
Dasibi 1003-AH,-PC,-RS	EQOA-0577-019	019
Dasibi 1008-AH,-PC,-RS	EAOA-0383-056	056
EnviroNics 300	EQOA-0990-078	078
Lear-Siegler ML9810	EQOA-0193-091	091
Monitor Labs 8810	EQOA-0881-053	053
PCI Ozone Corp. LC-12	EQOA-0382-055	055
Thermo Electron 49	EQOA-0880-047	047
<u>Equivalent Methods (Gas/Solid CL)</u>		
Philips PW9771	EQOA-0777-023	023

^aAs of February 1993.

1 described below. A gas-liquid chemiluminescence analyzer for O₃, which was submitted for
2 EPA equivalency during 1993, is also described below.

3

4 **Gas-Solid Chemiluminescence.** The reaction of O₃ with Rhodamine-B adsorbed on
5 activated silica gel produces chemiluminescence in the red region of the visible spectrum.

TABLE 3-17. LIST OF DESIGNATED REFERENCE AND EQUIVALENT METHODS FOR OZONE^a

Designation Number	Identification	Source	Manual or Auto	Ref. or Equiv.	Federal Register		Notice Date
					Vol.	Page	
EQOA-0990-078	"Environics Series 300 Computerized Ozone Analyzer," operated on the 0-0.5 ppm range, with the following parameters entered into the analyzer's computer system: Absorption Coefficient = 308 ± 4 Flue Time = 3 Integration Factor = 1 Offset Adjustment = 0.025 ppm Ozone Average Time = 4 Signal Average + 0 Temp/Press Correction = On and with or without the RS-232 Serial Data Interface	Environics, Inc. 165 River Road West Willington, CT 06279	Auto	Equiv.	55	38386	09/18/90
EQOA-0992-087	"Advanced Pollution Instrumentation, Inc. Model 400 Ozone Analyzer," operated on any full-scale range between 0-0.1 ppm ^b and 0-1 ppm, at any temperature in the range of 5 to 40 °C, with the dynamic zero and span adjustment features set OFF, with a 5-micron TFE filter element installed in the rear-panel filter assembly, and with or without any of the following options: Internal Zero/Span (IZS) Rack Mount with Slides RS-232 with Status Outputs Zero/Span Valves	Advanced Pollution Instrumentation, Inc. 8815 Production Avenue San Diego, CA 92121-2219	Auto	Equiv.	57	44565	09/28/92

TABLE 3-17 (cont'd). LIST OF DESIGNATED REFERENCE AND EQUIVALENT METHODS FOR OZONE^a

Designation Number	Identification	Source	Manual or Auto	Ref. or Equiv.	Federal Register		
					Vol.	Page	Notice Date
EQOA-0193-091	"Lear Siegler Measurement Controls Corporation Model ML9810 Ozone Analyzer," operated on any full-scale range between 0-0.050 ppm ^b and 0-1.0 ppm, with auto-ranging <i>enabled</i> or <i>disabled</i> , at any temperature in the range of 15 °C to 35 °C, with a 5-micron Teflon filter element installed in the filter assembly behind the secondary panel, the service switch on the second panel set to the <i>In</i> position; with the following menu choices selected: Calibration; <i>Manual</i> or <i>Timed</i> : Diagnostic Mode: <i>Operated</i> ; Filter Type: <i>Kalman</i> ; Pres/Temp/Flow Comp: <i>On</i> ; Span Comp: <i>Disabled</i> ; With the 50-pin I/O board installed on the rear panel configured at any of the following output range settings: Voltage, 0.1V, 1V, 5V, 10V; Current, 0-20 mA, 2-20 mA, 4-20 mA; and with or without any of the following options: Valve Assembly for External Zero/Span (EVS) Rack Mount Assembly Internal Floppy Disk Drive	Lear Siegler Measurement Controls Corp. 74 Inverness Drive East Englewood, CO 80112-5189	Auto	Equiv.	58	6964	02/03/93

^aDesignated since publication of the 1986 EPA criteria document for ozone and other photochemical oxidants.

^bUsers should be aware that designation of this analyzer for operation on any full-scale range less than 0.5 ppm is based on meeting the same absolute performance specifications required for the 0-0.5 ppm range. Thus, designation of any full-scale range lower than the 0-0.5 ppm range does not imply commensurably better performance than that obtained on the 0-0.5 ppm range.

1 This was the first chemiluminescence method ever developed for ambient O₃ measurement
2 (Regener, 1960, 1964). The emitted light intensity is linearly related to the
3 O₃ concentration, and the detection limit can be as low as 0.001 ppm. No direct
4 interferences from other gas-phase pollutants are known; however, decay of the sensitivity
5 because of surface aging can occur (Hodgeson et al., 1970). Addition of gallic acid to the
6 surface stabilizes the response characteristics, apparently by allowing direct reaction of
7 O₃ with the gallic acid, rather than with the Rhodamine-B (Bersis and Vassiliou, 1966).
8 A commercial analyzer (Phillips Model PW9771) based on this approach has been designated
9 an equivalent method for ambient ozone (see Table 3-16), but gas-solid chemiluminescence is
10 currently rarely used for ambient measurements.

11
12 *Gas-Liquid Chemiluminescence.* A recently developed commercial monitor uses the
13 chemiluminescent reaction of ozone with the dye eosin-Y in solution (Topham et al., 1993).
14 The monitor functions by exposing a fabric wick, wetted with the eosin-Y solution, to a flow
15 of sample air within view of a red-sensitive photomultiplier tube. The monitor, designated
16 the LOZ-3, is compact, portable, and requires no reagent gases. The LOZ-3 provides very
17 fast response: a lag time of 2 s, rise time of 3 s, and fall time of 2 s, all relative to a step
18 change of 400 ppbv ozone, are reported (Topham et al., 1993). Instrument noise at zero and
19 at 382 ppbv ozone is 0.05 ppbv or less, calculated as the standard deviation of 25 successive
20 2-min averages. The precision of the LOZ-3 is reported to be 0.80 ppbv at 100 ppbv ozone,
21 and as 1.87 ppbv at 400 ppbv ozone, both calculated as one standard deviation of six
22 repeated measurements at these levels (Topham et al., 1993). The instrument provides linear
23 response up to 200 ppbv, with a gradually decreasing slope of the response curve above that
24 level. Temperature and pressure sensitivity are corrected by internal circuitry (Topham
25 et al., 1993). An initial large positive interference from SO₂ is reported, which becomes
26 smaller and negative as the eosin solution ages; and a positive interference from CO₂ is also
27 present. Topham et al. (1993) report that a pretreatment technique applied to the eosin
28 reagent solution minimizes both of these interferences. Several of the performance
29 characteristics of the LOZ-3 are impressive, but verification of the reported interference
30 levels and the effectiveness of temperature and pressure corrections appears to be needed.
31 This method was submitted for EPA equivalency certification during 1993.

3.5.1.1.3 *Ultraviolet Photometry*

This method is based on the fact that O_3 has a reasonably strong absorption band with a maximum near 254 nm, coinciding with the strong emission line of a low-pressure mercury lamp. The molar absorption coefficient at the mercury line is well known, the accepted value being $134 (\pm 2) M^{-1}cm^{-1}$ in base 10 units at 0 °C and 1 atmosphere pressure (Hampson et al., 1973). Ultraviolet absorption has frequently been used to measure O_3 in laboratory chemical and kinetics studies. Ultraviolet photometry was also used for some of the first atmospheric O_3 measurements, but the early instruments suffered from poor precision because of the small absorbances being measured (U.S. Department of Health, Education, and Welfare, 1970).

Modern digital electronics have now solved the precision problems resulting from measurement of small absorbances, and several commercial O_3 monitors now employ UV photometry. Several instruments based on this principle have been designated by EPA as equivalent methods for ambient ozone (Tables 3-16 and 3-17). Ultraviolet photometry is now the predominant method for assessing compliance with the NAAQS for O_3 . The commercial monitors use pathlengths of 1 m or less, and operate in a sequential single-beam mode. Transmission of 254 nm light through the sample air is averaged over a short period of time (as short as a few seconds), and is compared to a subsequent transmission measurement on the same air stream from which O_3 has been selectively removed by a manganese dioxide scrubber. The electronic comparison of the two signals can be converted directly into a digital readout of the O_3 concentration. The method is in principle absolute, since the absorption coefficient and pathlength are accurately known and the measured absorbance can be converted directly to a concentration.

Commercial UV photometers for ambient ozone measurements have detection limits of approximately 0.005 ppm. Time response depends on the averaging time used, but is typically <1 min. Long-term precision can be within $\pm 5\%$. The method has the advantage of requiring no gas supplies, and commercial instruments are compact and reasonably portable. Sample air flow control is not critical, within the limitations of the MnO_2 scrubber. Since the measurement is absolute, UV photometry is also used to assay O_3 calibration standards as described below (Section 3.5.1.1.5). Ambient air monitors using

1 UV photometry are generally calibrated with standard O₃ mixtures to account for losses of
2 O₃ in sampling lines.

3 A potential disadvantage of UV photometry is that any atmospheric constituent that
4 absorbs 254 nm light and is removed fully or partially by the manganese dioxide scrubber
5 will be a positive interference in O₃ measurements. Potential interferents include aromatic
6 hydrocarbons, mercury vapor, and sulfur dioxide. A recent study (Kleindienst et al., 1993)
7 demonstrated that toluene and possibly aromatic reaction products, such as benzaldehyde,
8 produce positive interferences in UV photometric ozone measurements. This result was
9 found using photochemically reactive mixtures of toluene and NO_x, at concentrations a factor
10 of two to five higher than those expected in polluted urban air. Consideration of the relative
11 absorption coefficients of O₃ and the aromatics indicates that at higher humidities toluene can
12 cause an interference of 0.1 ppbv O₃ per ppbv of toluene, whereas benzaldehyde may cause
13 an interference as high as 5 ppbv O₃ per ppbv benzaldehyde (Kleindienst et al., 1993). This
14 interference may be humidity dependent. In earlier work at very low humidities, no
15 interference was observed with toluene and only a very small interference was observed with
16 benzaldehyde (Grosjean and Harrison, 1985). However, even at very low humidities these
17 investigators observed significant interferences from styrene, cresols, and nitrocresols.
18 Evaluation of aromatic interference is limited by a lack of appropriate absorption spectra in
19 the 250 nm range, and by a lack of ambient measurements of most of the aromatic
20 photochemical reaction products. The use of ethylene chemiluminescence monitors in areas
21 where aromatic concentrations are substantial is suggested (Kleindienst et al., 1993).

22 The same study found no consistent effect of ambient water vapor on measured
23 O₃ concentrations using UV photometry, in contrast to the effect noted using ethylene
24 chemiluminescence (Kleindienst et al., 1993). However, short-term disturbances in UV
25 photometric O₃ readings were observed when the humidity of the sample air was changed
26 substantially within a few seconds. This finding corroborates the observations of Meyer
27 et al. (1991) in an earlier study that indicated microscopic irregularities in the UV cell
28 windows as the cause of such disturbances. This effect should be absent in UV photometric
29 measurements of ambient O₃ at the ground, but could be important in other applications,
30 such as measuring vertical O₃ profiles from an aircraft (Kleindienst et al., 1993).

1 A different approach to evaluating potential interferences in ozone measurements has
2 been taken by Leston and Ollison (1993). These investigators examined ambient ozone data
3 from instruments of different measurement principles co-located at monitoring sites. The
4 focus of their study is the ozone "design value", the fourth highest daily maximum hourly
5 value from a monitoring station within an urban area, which is established in the 1990 Clean
6 Air Act Amendments as the basis for classification of the area relative to attainment of the
7 NAAQS for ozone. Leston and Ollison (1993) examined hourly ozone concentration data
8 from co-located UV and ethylene chemiluminescence instruments, from 1989 and 1990 at a
9 site in Madison, CT, and from shorter periods at sites in East Hartford, CT, and
10 Mobile, AL. They also examined 11 winter days of simultaneous ozone data from UV and
11 Luminox LOZ-3 instruments, from Long Beach, CA. Leston and Ollison (1993) reported
12 positive biases in the UV data of 20 to 40 ppbv O₃ during "hot, humid, hazy conditions
13 typical of design value days." They proposed that most ozone data and all design values are
14 biased high by known and suspected interferences, and that those interferences are
15 exacerbated by water vapor. Leston and Ollison (1993) argue that the interference in UV
16 measurements from benzene derivatives (e.g., styrene, cresols, benzaldehyde, nitro-
17 aromatics) is poorly accounted for. For example, of these compounds, only styrene is
18 measured in the PAMS VOC monitoring network (Leston and Ollison, 1993).

19 Interferences of the magnitude suggested by Leston and Ollison (1993) clearly would
20 have serious implications for monitoring of ambient ozone. It is difficult to estimate whether
21 interferences in the UV method could be as high as suggested, in part because data are
22 lacking on the ambient levels of potential interferents. Many potential interferents are
23 photochemically reactive, and it is questionable whether such compounds could co-exist with
24 ozone in sufficient quantities to constitute a significant interference. What is clear is that full
25 evaluation of interferences in UV and ethylene chemiluminescence methods will require
26 simultaneous measurements of ozone, humidity, temperature, and speciated organic
27 compounds, and perhaps of other meteorological parameters and potential interferents.
28

29 ***3.5.1.1.4 Spectroscopic Methods for Ozone***

30 Spectroscopic methods have the potential to provide direct, sensitive, and specific
31 measurements representative of broad areas, rather than of single monitoring sites. This

potential has led to investigation of spectroscopic approaches, primarily differential optical absorption spectrometry (DOAS), for ozone measurement. Differential optical absorption spectrometry measures the absorption through an atmospheric path (typically 0.5 to 1.5 km) of two closely spaced wavelengths of light from an artificial source. One wavelength is chosen to match an absorption line of the compound of interest, and the other is close to but off that line, and is used to account for atmospheric effects. Platt and Perner (1980) reported measurements of several atmospheric species, including ozone, by DOAS, and various investigators have applied the technique since then (Stevens et al., 1993, and references therein). Stevens et al. (1993) describe testing of a commercial DOAS instrument in North Carolina in the fall of 1989. Ozone was measured using wavelengths between 260 and 290 nm, over a 557-m path. A detection limit for ozone of 1.5 ppbv was reported, based on a 1-min averaging time (Stevens et al., 1993). Comparison of DOAS results to those from a UV absorption instrument showed (DOAS ozone) = $0.90 \times (\text{UV ozone}) - 2.5$ ppbv, with a correlation coefficient (r^2) of 0.89, at ozone levels up to 50 ppbv. The sensitivity, multiple analytical capability, stability, and speed of response of the DOAS method are attractive, though further intercomparisons and interference tests are recommended (Stevens et al., 1993).

3.5.1.1.5 Passive Samplers for Ozone

A passive sampler is one that depends on diffusion of the analyte in air to a collecting or indicating medium. In general, passive samplers are not adequate for compliance monitoring purposes because of limitations in specificity and averaging time. However, passive sampling devices (PSDs) for O₃ are of value as a means of obtaining personal human exposure data for O₃ and as a means of obtaining long-term O₃ measurements in areas where the use of instrumental methods is not feasible. Estimation of long-term population exposure and ecological monitoring for vegetation effects of ozone in remote areas are examples of the latter application. Passive sampling devices have the advantages of simplicity, small size, and low cost, but may also present disadvantages, such as poor precision, loss of effectiveness during use or storage, and interference from other atmospheric constituents. Passive samplers for measuring O₃ at ambient concentrations are now commercially

1 available. No PSD has been fully validated, however, to the point of acceptance as an
2 equivalent method for O₃.

3 The Ogawa PSD for O₃ (Ogawa, Inc., Pompano Beach, FL) contains 0.1 mL of a
4 solution of sodium nitrite and sodium carbonate in glycerine on glass fiber filter paper. The
5 nitrite ion reacts with O₃ to form nitrate. Following exposure, the PSDs are analyzed by
6 extraction of the nitrate with deionized water, followed by ion chromatographic analysis.
7 In a comparative ambient O₃ study over 24 weeks, this PSD demonstrated agreement within
8 about 10% with the weekly real-time measurements taken by a UV O₃ monitor (Mulik et al.,
9 1991). Extension of these measurements to a full year produced similar results (Mulik et al.,
10 1991). The standard deviation of weekly average measurements by three collocated PSD
11 samplers ranged from about ± 1 to ± 6 ppb, at weekly average O₃ levels of 12 to 45 ppb
12 (Mulik et al. 1991). The Ogawa PSD was also used in a study of personal exposure to
13 indoor and outdoor O₃, showing a correlation of $r = 0.91$, and relative errors of 15 %
14 (daytime) and 25 % (nighttime) relative to UV photometric data (Liu et al., 1992).

15 Another PSD for O₃ has been developed that is based on the use of a colorant that
16 fades when exposed to O₃ (Grosjean and Hisham, 1992; Grosjean and Williams, 1992). The
17 plastic badge-type PSD contains a diffusion barrier and a colorant-coated filter as the
18 O₃ trap. The colorant used is indigo carmine (5,5'-disulfonate sodium salt of indigo, λ_{max}
19 = 608 nm). With a plastic grid or Teflon filter as the diffusion barrier, detection limits of
20 30 ppb · day and 120 ppb · day, respectively, are achieved. Interferences from NO₂,
21 formaldehyde, and PAN are 15, 4, and 16%, respectively, of the ambient interferant
22 concentrations. For sampling ambient O₃ in most locations, these interferences are probably
23 negligible (Grosjean and Hisham, 1992). Following sampling, the color change is measured
24 by reflectance spectroscopy and no chemical analysis is required. The reported shelf life is
25 3 mo prior to O₃ exposure and 12 mo after O₃ exposure (Grosjean and Hisham, 1992).

26 Field tests of the indigo carmine PSD were conducted at five forest locations in
27 California in the summer of 1990 (Grosjean and Williams, 1992). During these tests,
28 ambient ozone ranged up to 250 ppbv; 3-day average ozone values at the sites ranged from
29 40 to 88 ppbv. The precision of the measurements was $\pm 12\%$ based on 42 sets of collocated
30 samplers, over sampling durations of 3 to 30 days. The color change in the PSD was highly
31 correlated ($R = 0.99$) with ozone dose as measured by UV photometry. No effect of

1 ambient temperature or humidity variations was observed, and the total interference caused
2 by other pollutants (NO₂, PAN, aldehydes) was less than 5 %.

3 A third PSD for ozone has also been recently developed, based on color formation from
4 the reaction of O₃ with an aromatic amine (Kirolos and Attar, 1991). The ChromoSense™
5 direct-read passive dosimeter is a credit-card-sized device that changes color proportionally to
6 the integrated dose of exposure of the specific toxic material for which it was designed (U.S.
7 Patent 4,772,560). The dosimeter consists of an outer polyester pouch that encloses a
8 polymeric plate with a sorbant and membrane. A filtering layer is coated on the membrane
9 to reduce the sensitivity of the detection process to nitrogen dioxide. The chromophoric
10 layer, consisting of an aromatic amine that can react with ozone and form color, is
11 encapsulated so as to create a very high surface area. A polymeric barrier separates the
12 chromophore from a UV-absorbing layer to reduce their interaction. The UV absorber (in a
13 polymeric matrix) helps stabilize the chromophore toward intense light exposure when the
14 device is used outdoors. The transparent polymeric plate keeps the wafer flat and allows
15 uninterrupted optical viewing of the color of the reference and the sample area.
16 An electronic reading device measures color on both the exposed (sample) and unexposed
17 (reference) areas, and displays a digital reading that is proportional to the log of the O₃ dose.
18 Visible color is formed at doses as low as 20 ppb·h. No interference from NO₂ is observed
19 at NO₂ concentrations up to 350 ppb, and only a small effect of ambient humidity has been
20 reported (Kirolos and Attar, 1991). No data on precision have yet been reported.

21 22 **3.5.1.1.6 Calibration Methods for Ozone**

23 Since it is an unstable molecule and cannot be stored, O₃ must be generated at the time
24 of use to produce calibration mixtures. Electrical discharges in air or oxygen readily
25 produce O₃, but at concentrations far too high for calibration of ambient monitors.
26 Radiochemical methods are expensive and require the use of radioactive sources, with
27 associated safety requirements. For calibration purposes, low levels of O₃ are nearly always
28 generated by photolysis of oxygen at wavelengths <200 nm. Placing a mercury lamp near a
29 quartz tube through which air is flowing produces small amounts of O₃ in the airstream.
30 Commercial O₃ sources based on this approach typically adjust the lamp current to control
31 the amount of light transmitted, and thus the O₃ produced.

1 Once a stable, low concentration of O₃ has been produced from a photolytic generator,
2 that O₃ output must be established by measurement with an absolute reference method. The
3 original reference calibration procedure promulgated by EPA in 1971 (Federal Register,
4 1971) was an iodometric procedure, employing 1 % aqueous neutral buffered potassium
5 iodide (NBKI). A large number of studies conducted in the 1970s revealed several
6 deficiencies with KI methods, the most notable of which were poor precision or
7 interlaboratory comparability and a positive bias of NBKI measurements relative to
8 simultaneous absolute UV absorption measurements.

9 Following investigations of problems with the NBKI method, EPA evaluated four
10 potential reference calibration procedures and selected UV photometry on the basis of
11 superior accuracy and precision and simplicity of use (Rehme et al., 1981). In 1979, UV
12 photometry was designated the reference calibration procedure by EPA (Federal Register,
13 1979).

14 The measurement principle of UV O₃ photometers used as reference standards is
15 identical to that of O₃ photometers used for ambient measurements (see Section 3.5.1.1.3).
16 A laboratory photometer used as a reference standard will typically contain a long-path cell
17 (1 to 5 m) and employ sophisticated digital techniques for making effective double-beam
18 measurements of small absorbances at low O₃ concentrations.

19 A primary reference standard is a UV photometer that meets the requirements set forth
20 in the 1979 revision designating UV photometry as the reference method (Federal Register,
21 1979). Commercially available O₃ photometers that meet those requirements may function as
22 primary standards. The EPA and the National Institute of Standards and Technology (NIST,
23 formerly National Bureau of Standards [NBS]) have established a nationwide network of
24 Standard Reference Photometers (SRPs) that are used to verify local primary standards and
25 transfer standards. A secondary or transfer standard is a device or method that can be
26 calibrated against the primary standard, and then moved to another location for calibration of
27 O₃ monitors. Commercial UV photometers for O₃ are often used as secondary or transfer
28 standards, as are commercial photolytic ozone generators and apparatus for the gas-phase
29 titration of O₃ with nitric oxide (NO).

30 The latter method, gas-phase titration (GPT) of O₃ with NO ($\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$),
31 is a direct and absolute means of determining O₃, provided NO is in excess so that no side

1 reactions occur. Under such conditions, GPT has the advantage that measurement of the NO
2 or O₃ consumed or the NO₂ produced gives a simultaneous measurement of the other two
3 species. All three modes have been used, and this method is often used for calibration of
4 NO/NO_x analyzers. Gas-phase titration has been compared to UV photometry in several
5 studies. The most detailed study is that of Fried and Hodgeson (1982), who used an NBS
6 primary standard UV photometer, highly accurate flow measurements, photoacoustic
7 detection of NO₂, and NBS (now NIST) Standard Reference Materials as sources of NO and
8 NO₂. That study showed that decreases in O₃ as measured by the UV method averaged
9 3.6% lower than the corresponding decrease in NO and increase in NO₂ measured
10 independently. Because of uncertainty about the origin of the small bias relative to UV
11 photometry, GPT is used as a transfer standard but not as a primary reference standard.
12

13 3.5.1.2 Peroxyacetyl Nitrate and Its Homologues

14 During laboratory organic photooxidation studies, Stephens et al. (1956a,b) determined
15 the presence of a number of alkyl nitrates and an unidentified species called "Compound X".
16 The presence of "Compound X" in the atmosphere of Los Angeles was confirmed by Scott
17 et al. (1957). In later work (Stephens et al., 1961) its structure was determined and
18 "Compound X" was named peroxyacetyl nitrate (PAN). Since the discovery of PAN much
19 effort has been directed toward its atmospheric measurement. In the following subsections
20 PAN measurement and calibration techniques are described. The discussion on measurement
21 techniques includes a summary description, identifies limits of detection, specificity
22 (interferences), reproducibility and accuracy of each method. The relative merits of each
23 method are also presented. The subsection on calibration techniques includes those methods
24 most often employed during ambient air measurement studies.
25

26 3.5.1.2.1 Measurement Methods

27 Two methods have been generally employed to make atmospheric measurements of
28 PAN. These methods are infrared spectroscopy (IR) and gas chromatography (GC).
29 Infrared spectroscopy permits the sampling and analysis to be conducted in real time. Since
30 PAN is very reactive in the gas phase and exhibits surface adsorptive effects, the minimal
31 contact time offered by IR makes this method very attractive. However, IR instrumentation

1 is expensive and complex and requires a good deal of space. On the other hand, gas
2 chromatography is inexpensive and requires minimal space and operator training. A PAN
3 GC can be set up to automatically sample and analyze air every 10 to 15 min. Application
4 of these methods for obtaining ambient concentrations of PAN has recently been reviewed by
5 Roberts (1990).

6
7 *Infrared Spectroscopy.* Conventional long-path infrared spectroscopy and FTIR have
8 been used to detect and measure atmospheric PAN. Sensitivity is enhanced by the use of
9 FTIR. The most frequently used IR bands have been assigned and the absorptivities reported
10 in the literature (Stephens, 1964; Bruckmann and Willner, 1983; Holdren and Spicer, 1984;
11 Niki et al., 1985; Tsalkani et al., 1989) permit the quantitative analysis of PAN without
12 calibration standards. Tuazon et al. (1978) have described an FTIR system operable at
13 pathlengths up to 2 km for ambient measurements of PAN and other trace constituents. This
14 system employed an eight-mirror multiple reflection cell with a 22.5-m base path. The
15 spectral windows available at pathlengths of 1 km were 760 to 1,300, 2,000 to 2,230 cm^{-1} .
16 Thus, PAN could be detected by the bands at 793 and 1,162 cm^{-1} . The 793 cm^{-1} band is
17 characteristic of peroxy nitrates, while the 1,162 cm^{-1} band is reportedly caused by PAN only
18 (Stephens, 1969; Hanst et al., 1982). Tuazon et al. (1981a,b) reported ambient
19 measurements with this system during a smog episode in Claremont, California, in 1978.
20 Maximum daily PAN concentrations ranged from 6 to 37 ppb over a 5-day episode.
21 A detection limit for PAN was 3 ppb at a pathlength of ~ 1 kilometer. Hanst et al. (1982)
22 modified the FTIR system used by Tuazon by changing it from an eight-mirror to a
23 three-mirror cell configuration and by considerably reducing the cell volume. A detection
24 limit for PAN was increased to 1 ppb at a similar pathlength.

25 The limited sensitivity (~ 1 ppb) and the complexity of the above FTIR systems have
26 generally limited their field use to urban areas such as Los Angeles. More recently,
27 cryogenic sampling and matrix-isolation FTIR has been used to measure PAN in 15-L
28 integrated samples of ambient air. The matrix isolation technique has a theoretical level of
29 detection of ~ 50 ppt (Griffith and Schuster, 1987).

1 ***Gas Chromatography-Electron Capture Detection.*** Peroxyacetyl nitrate is normally
2 measured by using a gas chromatograph coupled to an electron capture detector (GC/ECD).
3 The method was originally described by Darley et al. (1963) and has subsequently been
4 refined and employed by scientists over the years. Key features of the method remain
5 unchanged. The column and detector temperatures are kept relatively low ($\sim 50^\circ$ and
6 100°C , respectively) to minimize PAN thermal decomposition. Short columns of either
7 glass or Teflon are generally used (1 to 5 ft in length). Finally, column packing normally
8 includes a Carbowax stationary phase coated onto a deactivated solid support. Using packed
9 columns, detection limits of 10 ppt have been reported using direct sampling with a 20-mL
10 sample loop (Vierkorn-Rudolph et al., 1985). Detection limits were further extended to 1 to
11 5 ppt using cryogenic enrichment of samples (Vierkorn-Rudolph et al., 1985; Singh and
12 Salas, 1983). These studies have found only slight overall losses of PAN (10 to 20%)
13 associated with cryosampling, provided samples are warmed only to room temperature during
14 desorption.

15 Recently, improved precision and sensitivity have been reported using fused-silica
16 capillary columns instead of packed columns (Helmig et al., 1989; Roberts et al., 1989).
17 Signal-to-noise enhancement of 20 has been claimed (Roberts et al., 1989).

18
19 ***Gas Chromatography-Alternate Detection.*** As noted earlier, PAN is readily reduced to
20 NO in the gas phase. To separate PAN, NO, and NO_2 , Meyrahn et al. (1987) have coupled
21 a GC with a molybdenum converter; and used a chemiluminescent analyzer to measure PAN
22 as NO. Using a 10 mL sample loop, a detection limit of 10 ppb was reported.

23 A luminol-based detector has also shown sensitivity to PAN. Burkhardt et al. (1988)
24 used gas chromatography and a commercially available luminol-based instrument (i.e.,
25 Scintrex LMA-3 Luminox) to detect both NO_2 and PAN. Using a sampling interval of 40 s,
26 linear response was claimed from 0.2 to 170 ppb NO_2 and from 1 to 65 ppb PAN. Although
27 the PAN calibration was nonlinear below 1 ppb, a detection level of 0.12 ppb was reported.
28 Drummond et al. (1989) have slightly modified the above approach by converting the PAN
29 from the GC column to NO_2 and measuring the resulting NO_2 with a luminol-based
30 instrument.

3.5.1.2.2 *Peroxyacetyl Nitrate Stability*

Peroxyacetyl nitrate is an unstable gas and is subject to surface-related decomposition as well as thermal instability. Peroxyacetyl nitrate exists in a temperature-sensitive equilibrium with the peroxyacetyl radical and NO_2 (Cox and Roffey, 1977). Increased temperature favors the peroxyacetyl radical and NO_2 at the expense of PAN. Added NO_2 should force the equilibrium toward PAN and enhance its stability. In the presence of NO, peroxyacetyl radicals react rapidly to form NO_2 and acetoxy radicals, which decompose in O_2 to radicals that also convert NO to NO_2 . As a result, the presence of NO acts to reduce PAN stability and enhance its decay rate (Lonneman et al., 1982). Stephens (1969) reported that appreciable PAN loss in a metal sampling valve was traced to decomposition on a silver-soldered joint. Meyrahn et al. (1987) reported that PAN decayed according to first-order kinetics at a rate of 2 to 4%/h in glass vessels and they suggested first-order decay as the basis for a proposed method of in-field PAN calibration. In contrast, Holdren and Spicer (1984) found that without NO_2 added, 20 ppb PAN decayed in Tedlar bags according to first-order kinetics at a rate of 40%/h. The addition of 100 ppb NO_2 acted to stabilize the PAN (20 ppb) in the Tedlar bags.

A humidity-related difference in GC-ECD response has been reported (Holdren and Rasmussen, 1976). Low responses observed at humidities below 30% and PAN concentrations of 10 and 100 ppb, but not 1,000 ppb, were attributed to sample-column interactions. A humidity effect was alluded to by Nieboer and Van Ham (1976) but details were not given. No humidity effect was observed by Lonneman (1977). Watanabe and Stephens (1978) conducted experiments at 140 ppb and did not conclude that the reduced response was from faults in the detector or the instrument. They concluded that there was no column-related effect, and they observed surface-related sorption by PAN at 140 ppb in dry acid-washed glass flasks. They recommended that moist air be used to prepare PAN calibration mixtures to avoid potential surface-mediated effects.

Another surface-related effect has been reported for PAN analyses of remote marine air (Singh and Viezee, 1988). Peroxyacetyl nitrate concentrations were found to increase by 20 to 170 ppt, an average factor of 3, when the sample was stored in a glass vessel for 1 to 2 min prior to analysis. This effect remains to be explained.

3.5.1.2.3 *Preparation and Calibration*

Because PAN is unstable, the preparation of reliable calibration standards is difficult. The more promising methods are described here. The original method used the photolysis of ethyl nitrite in pure oxygen (Stephens, 1969). When pure PAN is desired, the reaction mixture must be purified, usually by chromatography, to remove the major by-products, acetaldehyde and methyl and ethyl nitrates (Stephens et al., 1965). For GC calibration, purification is unnecessary; the PAN concentration in the reactant matrix is established from the IR absorption spectrum and subsequently diluted to the parts-per-billion working range needed for calibration purposes (Stephens and Price, 1973).

Static mixtures of molecular chlorine, acetaldehyde, and NO_2 in the ratio of 2:4:4 can be photolyzed in the presence of a slight excess NO_2 to give a near-stoichiometric yield of PAN (Gay et al., 1976). This method was adapted by Singh and Salas (1983) and later by Grosjean et al. (1984) using photolytic reactors to provide continuous PAN calibration units at concentrations between 2 and 400 ppb. In the former approach, the PAN concentration is established by measuring the change in acetaldehyde concentration across the reactor. In the latter, the PAN concentration is established by measuring the acetate in an alkaline bubbler where PAN is hydrolyzed.

A static technique involving the photolysis of acetone in the presence of NO_2 and air at 250 nm has been reported to produce a constant concentration of PAN (Meyrahn et al., 1987; Warneck and Zerbach, 1992). A Penray mercury lamp is inserted into a mixture of 10 ppm NO_2 and 1% acetone and irradiated for 3 min to yield 8.9 ± 0.3 ppm PAN.

Peroxyacetyl nitrate can be synthesized in the condensed phase by the nitration of peracetic acid in hexane (Helmig et al., 1989), heptane (Nielsen et al., 1982), octane (Holdren and Spicer, 1984), or *n*-tridecane (Gaffney et al., 1984). Purification of PAN in the liquid phase is needed using the first two methods. The resulting PAN-organic solution can be stored at -20 to -80 °C with losses of less than 3.6%/mo and can be injected directly into a vessel containing air to produce a calibration mixture. The PAN concentration is normally established by FTIR analysis of the solution or the resulting PAN-air mixture.

Peroxyacetyl nitrate readily disassociates to NO , and chemiluminescence NO_x analyzers have near-quantitative response to PAN. Thus under some circumstances, chemiluminescent NO_x response can be used for PAN calibration. One method uses the difference in NO_x

1 signal measured upstream and downstream of an alkaline bubbler (Grosjean and Harrison,
2 1985a). Joos et al. (1986) have coupled a chemiluminescence NO_x analyzer with a GC
3 system to permit calibration of the ECD response by reference to the chemiluminescence
4 NO_x analyzer that has been calibrated by traditional methods.

5 As noted previously, NO in the presence of PAN is converted to NO_2 . Approximately
6 four molecules of NO can react per molecule of PAN. Lonneman et al. (1982) devised a
7 PAN calibration procedure based on the reaction of PAN with NO in the presence of
8 benzaldehyde, which is added to control unwanted radical chemistry and improve precision.
9 Using this approach and an initial NO-to-PAN ratio between 10 and 20 to 1, the change in
10 NO concentration is monitored with a chemiluminescence NO analyzer, the change in PAN
11 GC-ECD response is monitored, and the resulting ratio (i.e., $\Delta\text{NO}/\Delta\text{PAN}$) is divided by the
12 stoichiometric factor of 4.7 to arrive at a calibration factor for the ECD.

13 Peroxyacetyl nitrate and *n*-propyl nitrate (NPN) have similar ECD responses. Serial
14 dilution of the more stable compound, NPN, has been used for field operations
15 (Vierkorn-Rudolph et al., 1985). This approach is not recommended for primary calibration,
16 however, because it does not permit verification of quantitative delivery of PAN to the
17 detector (Stephens and Price, 1973).

19 3.5.1.3 Gaseous Hydrogen Peroxide

20 Although O_3 has long been considered to be the primary oxidant affecting air quality,
21 atmospheric chemists recently have identified H_2O_2 , a photochemical reaction product as
22 another oxidant that may also play a significant role in diminishing air quality. In order to
23 assess the role of atmospheric H_2O_2 , good measurement methods are needed. Early
24 measurements in the 1970s reported H_2O_2 concentrations ranging from 10 to 180 ppb (Gay
25 and Bufalini, 1972 a,b; Kok et al., 1978 a,b). However, these measurements are in error
26 because of artifact formation of H_2O_2 from reactions of absorbed gaseous O_3 (Zika and
27 Saltzman, 1982; Heikes et al., 1982, Heikes, 1984). Modeling results also indicate that
28 H_2O_2 atmospheric concentrations should be on the order of 1 ppb (Chameides and Tan,
29 1981; Logan et al., 1981).

30 In the following section, the discussion focuses on those sampling and analytical
31 methods most frequently used within the last decade to determine atmospheric levels of

H₂O₂. The measurement techniques are described and limits of detection, specificity (interferences) reproducibility and accuracy are discussed.

3.5.1.3.1 *Measurement Methods*

In-situ measurement methods that have been employed for determining gaseous H₂O₂ include both FTIR and tunable diode laser absorption spectrometry (TDLAS). Four methods involving sample collection via wet chemical means and subsequent analysis via chemiluminescent or fluorescent detection have also been frequently used. These methods are the (1) luminol; (2) peroxyoxalate; (3) enzyme-catalyzed (peroxidase); and (4) benzoic acid-fenton reagent methods. Application of most of these methods for obtaining ambient concentrations of H₂O₂ has recently been reviewed by Sakugawa et al. (1990) and Gunz and Hoffmann (1990).

In-Situ Methods. Fourier transform infrared spectroscopy was employed in the early 1980's for atmospheric measurements (Tuazon et al., 1980; Hanst et al., 1982). Even though the FTIR is very specific for H₂O₂, it saw limited use because of the high detection level of ~ 50 ppb when using a 1-km path length. The TDLAS also has very high specificity for H₂O₂ and was subsequently evaluated and shown to have a much improved detection limit of 0.1 ppb when using scan averaging times of several minutes (Slemr et al., 1986; MacKay and Schiff, 1987; Schiff et al., 1987).

Wet Chemical Methods. Numerous wet chemical techniques for measuring H₂O₂ have been reported. However, discussion in this section is limited to the four approaches most frequently used by researchers.

Luminol Method. Hydrogen peroxide concentrations in the atmosphere have been determined by the chemiluminescent response obtained from the catalyzed oxidation of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) by H₂O₂. Copper (II) (Armstrong and Humphreys, 1965; Kok et al., 1978 a,b; Das et al., 1982), as well as hemin, a blood component (Yoshizumi et al., 1984), have been reported as catalysts for the luminol-based H₂O₂ oxidation. Method sensitivity of ~0.01 ppb has been achieved. Interference from

O₃, SO₂, metal ions and high pH have been reported along with ways to mitigate these effects (Heikes et al., 1982; Zika and Saltzman, 1982; Ibusuki, 1983; Lazarus et al., 1985; Aoyanagi and Mitsushima, 1987; Hoshino and Hinze, 1987).

Peroxyoxalate Method. The peroxyoxalate chemiluminescence method has also been employed by a number of researchers (Rauhut et al., 1967; Scott et al., 1980; Klockow and Jacob, 1986). Hydrogen peroxide reacts with bis(2,4,5-trichloro-6-phenyl)-oxalate to form a high-energy dioxetanedione (Stauff and Jaeschke, 1972). The chemiluminescence is transmitted to the fluorophore, perylene, which emits light upon return to the ground state. Method sensitivity of ~0.01 ppb is achieved and no interferences are observed from O₃ and metal ions. A signal depression has been reported for trace levels of nitrite ($>10^{-5}$ M), sulfite ($>10^{-4}$ M), and formaldehyde ($>10^{-3}$ M) (Klockow and Jackob, 1986).

Enzyme-Catalyzed Method (Peroxidase). This general method involves three components: a substrate that is oxidizable; the enzyme, horseradish peroxidase (HRP); and hydrogen peroxide. The production or decay of the fluorescence intensity of the substrate or reaction product is measured as it is oxidized by H₂O₂, catalyzed by HRP. Some of the more widely used chromogenic substrates have been scopoletin (6-methoxy-7-hydroxy-1,2-benzopyrone) (Andreae, 1955; Perschke and Broda, 1961); 3-(*p*-hydroxyphenyl)propionic acid (HPPA) (Zaitsev and Okhura, 1980); leuco crystal violet (LCV) (Mottola et al., 1970); and *p*-hydroxyphenylacetic acid (POPHA) (Guilbault et al., 1968).

Of the chromogens used, POPHA is one of the better indicating substrates. Hydrogen peroxide oxidizes the peroxidase and is itself reduced by electron transfer from POPHA. The POPHA radicals form a dimer that is highly fluorescent. Since the chemical reaction is sensitive to both H₂O₂ and organic peroxides, a dual channel system with a H₂O₂ removal step (use of catalase) is used to distinguish H₂O₂ from organic peroxides (Lazarus et al., 1985; Wei and Weihs, 1987; Dasgupta and Hwang, 1985; Kok et al., 1986).

The peroxidase-POPHA-fluorescence technique has been used by several groups to measure gas-phase H₂O₂ concentrations (Lazarus et al., 1986; Tanner et al., 1986; Heikes et al., 1987; Van Valin et al., 1987; Dasgupta et al., 1988). Method detection levels range from 0.01 to 0.1 ppb. However, artifact formation does occur as a result of the reaction of

1 dissolved O_3 in the collection devices (Stachelin and Hoigne, 1982; Heikes, 1984; Gay et al.,
2 1988). To overcome the O_3 interference researchers have used NO to eliminate O_3 (Tanner,
3 1984; Tanner et al., 1986; Shen et al., 1988).

4
5 ***Fenton Reagent-Isomeric Hydroxybenzoic Acids Method.*** This technique involves the
6 formation of aqueous OH radicals from the reaction of Fenton reagent (Fe(II) complex) with
7 gaseous H_2O_2 . The OH radicals in turn react with benzoic acid (hydroxyl radical scavenger)
8 to form isomeric hydroxybenzoic acids (OHBA). The OHBA fluoresces weakly at the pH
9 necessary to carry out the above reactions. Fluorescence is enhanced by adding NaOH to the
10 product stream (Lee et al., 1990) or by using a low pH Al(III) fluorescence enhancing
11 reagent (Lee et al., 1993).

12 13 **3.5.1.3.2 Comparison of Methods**

14 The above techniques have been shown to measure H_2O_2 in the atmosphere with
15 detection levels of ≈ 0.1 ppb. Kleindienst et al. (1988) have compared several of these
16 techniques using three sources of H_2O_2 : (1) zero air in the presence and absence of common
17 interferences, (2) steady-state irradiations of hydrocarbon- NO_x mixtures, and (3) ambient air.
18 The measurements were conducted simultaneously from a common manifold. For pure
19 samples in zero air, agreement within 23 % was achieved among methods over a
20 concentration range of 0.06 to 128 ppb. A negative SO_2 interference was caused with the
21 luminol technique. During the irradiation experiment, significant concentrations of organic
22 peroxides were generated and the agreement among techniques for H_2O_2 was very poor. For
23 ambient measurements, the methods agreed reasonably well with an average deviation of
24 30 % from the mean values.

25 Atmospheric intercomparison studies have also been conducted as part of the Carbon
26 Species Methods Comparison Study (Calif, 1986). The results of the study indicated that the
27 wet chemical methods still suffer from sampling artifacts and interferences from other
28 atmospheric constituents (Dasgupta et al., 1990; MacKay et al., 1990; Kok et al., 1990;
29 Sakugawa et al., 1990; Tanner et al., 1990). It is clear from the above studies that further
30 comparisons of techniques are needed to resolve questions of errors and provide improved
31 measurement techniques.

3.5.1.3.3 Calibration Methods

The most frequently used method for generating aqueous standards is simply the serial dilution of commercial grade 30% H_2O_2 /water. The dilute solutions of H_2O_2 as low as 10^{-4} have been found to be stable for several weeks if kept in the dark (Armstrong and Humphreys, 1965). The stock H_2O_2 solution is standardized by iodometry (Allen et al., 1952; Hochanadel, 1952; Cohen et al., 1967) or, more recently, by using standardized permanganate solution (Lee et al., 1991).

Gaseous H_2O_2 standards are not as easily prepared and stability problems require use of standard mixtures immediately. One method makes use of the injection of microliter quantities of 30% H_2O_2 solution into a metered stream of air that flows into a Teflon bag. The amount of H_2O_2 in the gas phase is determined by the iodometric titration method (Cohen and Purcell, 1967). Gas-phase H_2O_2 standards have also been generated by equilibrating N_2 with an aqueous H_2O_2 solution of known concentration that is maintained at constant temperature. Equilibrium vapor pressures and corresponding gas-phase concentrations are calculated using Henry's law constant (Lee et al., 1991).

3.5.2 Sampling and Analysis of Volatile Organic Compounds

3.5.2.1 Introduction

The term volatile organic compounds (VOCs) generally refers to gaseous organic compounds that have a vapor pressure greater than 0.15 mm and generally have a carbon content ranging from C_1 through C_{12} . As discussed in Sections 3.2 and 3.4, VOCs are emitted from a variety of sources and play a critical role in the photochemical formation of O_3 in the atmosphere.

The U.S. Environmental Protection Agency (EPA) recently revised the ambient air quality surveillance regulations in Title 40 Part 58 of the Code of Federal Regulations to include, among other activities, the monitoring of volatile organic compounds. The revisions require states to establish additional air monitoring stations as part of their existing State Implementation Plan (SIP) monitoring networks. Authority for requiring the enhanced monitoring is provided for in Title I, Section 182 of the Clean Air Act Amendments of 1990.

The term nonmethane organic compounds (NMOC) is also frequently used and refers to a subset of VOCs, since it excludes the compound methane. Numerous sampling, analytical,

1 and calibration methods have been employed to determine NMOCs in ambient air. Some of
2 the analytical methods utilize detection techniques that are highly selective and sensitive to
3 specific functional groups or atoms of a compound (e.g., formyl group of aldehydes,
4 halogen), while others respond in a more universal manner; that is, to the number of carbon
5 atoms present in the organic molecule. In this overview of the most pertinent measurement
6 methods, NMOC have been arranged in three major classifications: nonmethane
7 hydrocarbons (NMHC), carbonyl species, and polar volatile organic compounds (PVOCs).
8 Measurement and calibration procedures are discussed for each classification.

10 3.5.2.2 Nonmethane Hydrocarbons

11 Nonmethane hydrocarbons (NMHC) constitute the major portion of NMOC in ambient
12 air. Traditionally, NMHC have been measured by methods that employ a flame ionization
13 detector (FID) as the sensing element. This detector was originally developed for gas
14 chromatography and employs a sensitive electrometer that measures a change in ion intensity
15 resulting from the combustion of air containing organic compounds. Ion formation is
16 essentially proportional to the number of carbon atoms present in the organic molecule
17 (Sevcik, 1975). Thus, aliphatic, aromatic, alkenic, and acetylenic compounds all respond
18 similarly to give relative responses of 1.00 ± 0.10 for each carbon atom present in the
19 molecule (e.g., 1 ppm hexane = 6 ppm C; 1 ppm benzene = 6 ppm C; 1 ppm propane =
20 3 ppm C). Carbon atoms bound to oxygen, nitrogen, or halogens give reduced relative
21 responses (Dietz, 1967). Consequently, the FID, which is primarily used as a hydrocarbon
22 measuring method, should more correctly be viewed as an organic carbon analyzer.

23 In the following sections, discussion focuses on the various methods utilizing this
24 detector to measure total nonmethane organics. Methods in which no compound speciation is
25 obtained are covered first. Methods for determining individual organic compounds are then
26 discussed.

28 3.5.2.2.1 Nonspeciation Measurement Methods

29 The original EPA reference method for nonmethane organic compounds, which was
30 promulgated in 1971, involves the gas chromatographic separation of methane (CH_4) from
31 the remaining organics in an air sample (Federal Register, 1971). A second sample is

1 injected directly to the flame ionization detector without methane separation. Subtraction of
2 the first value from the second produces a nonmethane organic concentration.

3 A number of studies of commercial analyzers employing the Federal Reference Method
4 have been reported (Reckner, 1974; McElroy and Thompson, 1975; Harrison et al., 1977;
5 Sexton et al., 1982). These studies indicated an overall poor performance of the commercial
6 instruments when either calibration or ambient mixtures containing NMOC concentrations
7 less than 1 ppm C were used. The major problems associated with using these NMOC
8 instruments have been reported in an EPA technical assistance document (U.S.
9 Environmental Protection Agency, 1981). The technical assistance document also suggests
10 ways to reduce the effects of existing problems. Other nonspeciation approaches to the
11 measurement of nonmethane organics have also been investigated. These approaches have
12 been discussed in the 1986 EPA air quality criteria document (U.S. Environmental Protection
13 Agency, 1986). Again, these approaches are also subject to the same shortcomings as the
14 EPA reference method (i.e., poor performance below 1 ppm C of NMHC).

15 More recently, a method has been developed for measuring NMOC directly and
16 involves the cryogenic preconcentration of nonmethane organic compounds and the
17 measurement of the revolatilized NMOCs using flame ionization detection (Cox et al., 1982;
18 Jayanty et al., 1982). This methodology has been formalized and is referred to as Method
19 TO-12 and is published in a compendium of methods for air toxics (Winberry et al., 1988).
20 The EPA recommends this methodology for measuring total NMOC and has incorporated it
21 into the *Technical Assistance Document for Sampling and Analysis of Ozone Precursors*
22 (U.S. Environmental Protection Agency, 1991).

23 A brief summary of the method is as follows. A whole air sample is drawn through a
24 glass bead trap that is cooled to approximately -185°C using liquid argon. The cryogenic
25 trap collects and concentrates the NMOC, while allowing the methane, nitrogen, oxygen,
26 etc., to pass through the trap without retention. After a known volume of air has been
27 drawn through the trap, carrier gas is diverted to the trap first to remove residual air and
28 methane. When the residual gases have been flushed from the trap, the cryogen is removed
29 and the temperature of the trap is ramped to approximately 100°C . The revolatilized
30 compounds pass directly to a flame ionization detector (no analytical column). The
31 corresponding signal is integrated over time (several minutes) to obtain a total FID response

1 from the NMOC species. Water vapor, which is also preconcentrated, causes a positive shift
2 in the FID signal. The effect of this shift is minimized by optimizing the peak integration
3 parameters.

4 The sensitivity and precision of Method TO-12 are proportional to the sample volume.
5 However, ice formation in the trap limits sampling volumes of ≈ 500 cc. The detection level
6 is 0.02 ppm C (with a signal-to-noise ratio, S/N, of 3) and the precision at 1 ppm C and
7 above has been determined to be $\leq 5\%$. The instrument response has been shown to be
8 linear over a range of 0 to 10 ppm C. Propane gas certified by the National Institute of
9 Standards and Technology (NIST) is normally used as the calibrant. Accuracy at the method
10 quantitation level (S/N = 10) is $\pm 20\%$.

11 12 3.5.2.2.2 *Speciation Measurement Methods*

13 The primary measurement technique utilized for NMOC speciation is gas
14 chromatography (GC). Coupled with flame ionization detection, this analytical method
15 permits the separation and identification of many of the organic species present in ambient
16 air.

17 Separation of compounds is accomplished by means of both packed and capillary GC
18 columns. If high resolution is not required and large sample volumes are to be injected,
19 packed columns are employed. The traditional packed column may contain either (1) a solid
20 polymeric adsorbent (gas-solid chromatography) or (2) an inert support, coated with a liquid
21 (gas-liquid chromatography). Packed columns containing an adsorbent substrate are normally
22 required to separate C_2 and C_3 compounds. The second type of column can be a support-
23 coated or wall-coated open tubular capillary column. The latter column has been widely
24 used for environmental analysis because of its superior resolution and broader applicability.
25 The wall-coated capillary column consists of a liquid stationary phase coated or bonded
26 (cross-linked) to the specially treated glass or fused-silica tubing. Fused-silica tubing is most
27 commonly used because of its physical durability and flexibility. When a complex mixture is
28 introduced into a GC column, the carrier gas (mobile phase) moves the sample through the
29 packed or coated capillary column (stationary phase). The chromatographic process occurs
30 as a result of repeated sorption-desorption of the sample components (solute) as they move

1 along the stationary phase. Separation occurs as a result of the different affinities that the
2 solute components have for the stationary phase.

3 As described in the previous ozone criteria document (U.S. Environmental Protection
4 Agency, 1986), the GC-FID technique has been used by numerous researchers to obtain
5 ambient NMOC data. Singh (1980) drew on the cumulative experience of these researchers
6 to prepare a guidance document for state and local air pollution agencies interested in
7 obtaining speciation data. In general, most researchers have employed two gas
8 chromatographic units to carry out analyses of NMOC species in ambient air. The more
9 volatile organic compounds (C_2 through C_5) are generally measured on one unit using
10 packed-column technology, while the other GC separates the less volatile organics using a
11 capillary column. In typical chromatograms of urban air, all major peaks are identified and,
12 on a mass basis, represent from 65 to 90% of the measurable nonmethane organic burden.

13 Identification of GC peaks is based upon matching retention times of unknown
14 compounds with those of standard mixtures. Subsequent verification of the individual species
15 is normally accomplished with gas chromatographic-mass spectrometric (GC-MS) techniques.
16 Compound-specific detection systems, such as electron capture, flame photometry, and
17 spectroscopic techniques, have also been employed to confirm peak identifications. The peak
18 matching process is far from being a trivial task. Ambient air chromatograms are often very
19 complex (> 200 peaks/run) and require a good deal of manual labor to assure that the peak
20 matching process is being carried out correctly by the resident peak identification/
21 quantification software. Efforts to improve upon the accuracy of peak assignment and
22 diminish the labor hours normally associated with the objective have recently been reported.
23 Silvestre et al. (1988) developed an off-line spreadsheet program that is menu-driven and
24 used to identify and edit a chromatogram containing 200 peaks within 15 minutes. The
25 accuracy of peak assignment was typically better than 95%. Mason et al. (1992) developed a
26 novel algorithm, which is embedded within the Harwell MatchFinder software package, and
27 have demonstrated its potential for enhancing peak identification in complex chromatograms.
28 The authors indicate that the software could be used to batch process large volumes of
29 chromatographic data. A commercial software package from Meta Four Software, Inc., was
30 recently employed during the Atlanta Ozone Precursor Monitoring Study to batch process
31 chromatographic data from over 6,000 GC runs (Purdue et al., 1992). This software was

1 also used to validate peak identities from two GC databases and was shown to improve peak
2 identities from the originally processed data by 10 to 20% (Holdren et al., 1993).

3 Because the organic components of the ambient atmosphere are present at parts-per-
4 billion levels or lower, sample preconcentration is necessary to provide sufficient material for
5 the GC-FID system. The two primary techniques utilized for this purpose are the use of
6 solid adsorbents and cryogenic collection. The more commonly used sorbent materials are
7 divided into three categories: (1) organic polymeric adsorbents, (2) inorganic adsorbents,
8 and (3) carbon adsorbents. Primary organic polymeric adsorbents used for NMOC analyses
9 include the materials Tenax®-GC and XAD-2®. These materials have a low retention of
10 water vapor and, hence, large volumes of air can be collected. These materials do not,
11 however, efficiently capture highly volatile compounds such as C₂ to C₅ hydrocarbons, nor
12 certain polar compounds such as methanol and acetone. Primary inorganic adsorbents are
13 silica gel, alumina, and molecular sieves. These materials are more polar than the organic
14 polymeric adsorbents and are thus more efficient for the collection of the more volatile and
15 polar compounds. Unfortunately, water is also efficiently collected, which in many instances
16 leads to rapid deactivation of the adsorbent. Carbon adsorbents are less polar than the
17 inorganic adsorbents and, as a result, water adsorption by carbon adsorbents is a less
18 significant problem. The carbon-based materials also tend to exhibit much stronger
19 adsorption properties than organic polymeric adsorbents; thus, lighter-molecular-weight
20 species are more easily retained. These same adsorption effects result, however, in
21 irreversible adsorption of many compounds. Furthermore, the very high thermal desorption
22 temperatures required (350 to 400 °C) limit their use and also may lead to degradation of
23 labile compounds. The commonly available classes of carbon adsorbents include:
24 (1) various conventional activated carbons; (2) carbon molecular sieves (Sphero carb®,
25 Carbosphere®, Carbosieve®); and (3) carbonaceous polymeric adsorbents (Amborsorb®
26 XE-340, XE-347, SE-348).

27 Although a number of researchers have employed solid adsorbents for the
28 characterization of selected organic species in air, only a few attempts have been made to
29 identify and quantitate the range of organic compounds from C₂ and above. Westberg et al.
30 (1980) evaluated several carbon and organic polymeric adsorbents and found that Tenax®-GC
31 exhibited good collection and recovery efficiencies for ≥ C₆ organics; the remaining

1 adsorbents tested (XAD-4®, XE-340®) were found unacceptable for the lighter organic
2 fraction. The XAD-4® retained $\geq C_2$ organic gases, but it was impossible to desorb these
3 species completely without partially decomposing the XAD-4®. Good collection and
4 recovery efficiencies were provided by XE-340® only for organics of C_4 and above. Ogle
5 et al. (1982) used a combination of adsorbents in series and designed an automated GC-FID
6 system for analyzing C_2 through C_{10} hydrocarbons. Tenax-GC® was utilized for C_6 and
7 above; whereas Carbosieve S® trapped C_3 through C_5 organics. Silica gel followed these
8 adsorbents and effectively removed water vapor while passing the C_2 hydrocarbons onto a
9 molecular-sieve 5A adsorbent. More recently, Levaggi et al. (1992) have used a
10 combination of adsorbents in series for analyzing C_2 through C_{10} hydrocarbons. Tenax GR,
11 Carbotrap, and Carbosieve S-III were evaluated. At room temperature collection, excellent
12 recovery efficiencies were obtained for all species except acetylene (breakthrough begins
13 after 220 cc). Smith et al. (1991) evaluated a commercially available GC system
14 (Chrompack, Inc.) and found that a Carbotrap C, Carbopack B, and Carbosieve S-III
15 combination was effective for all C_2 and above species if the trap temperature was
16 maintained at $-30\text{ }^{\circ}\text{C}$ during collection (600 cc). The above researchers also caution that
17 artifact peaks do occur during thermal desorption and recommend closely screening the
18 resulting data.

19 The preferred method for obtaining NMOC data is cryogenic preconcentration (Singh,
20 1980). Sample preconcentration is accomplished by directing air through a packed trap
21 immersed in either liquid oxygen (b.p. $-183\text{ }^{\circ}\text{C}$) or liquid argon (b.p. $-186\text{ }^{\circ}\text{C}$). For the
22 detection of about 1 ppb C of an individual compound, a 250-cc air sample is normally
23 processed. The collection trap is generally filled with deactivated 60/80 mesh glass beads
24 (Westberg et al., 1974), although coated chromatographic supports have also been used
25 (Lonneman et al., 1974). Both of the above cryogens are sufficiently warm to allow air to
26 pass completely through the trap, yet cold enough to collect trace organics efficiently. The
27 use of cryogenic preconcentration for collection of volatile organic compounds in general was
28 automated to allow sequential hourly updates of gas chromatographic data (McClenny et al.,
29 1984), leading to the initial configuration of what are now referred to as "auto GCs" for
30 ozone precursor monitoring. The cryogenic collection procedure also condenses water
31 vapor. An air volume of 250 cc at 50% relative humidity and $25\text{ }^{\circ}\text{C}$ contains approximately

1 2.5 mg of water, which appears as ice in the collection trap. The collected ice at times will
2 plug the trap and stop the sample flow; furthermore, water transferred to the capillary
3 column during the thermal desorption step occasionally causes plugging and other deleterious
4 column effects. To circumvent water condensation problems, Pleil et al. (1987) have
5 characterized the use of a Nafion® tube drying device to remove water vapor selectively
6 during the sample collection step. Although hydrocarbon species are not affected, polar
7 organics are partially removed when the drying device is used. Burns et al. (1983) also
8 showed that partial loss or rearrangement of monoterpenes, or both (e.g., α -pinene,
9 limonene), occur when the Nafion® tube is used to reduce water vapor.

10 The EPA has recently provided technical guidance for measuring volatile organic
11 compounds that is based on the above studies as well as emerging and developing technology
12 (U.S. Environmental Protection Agency, 1991). Guidance for the use of automated gas
13 chromatography sampling and analysis for VOCs has been derived from experience gained
14 from application of this technology during an ozone precursor study conducted by the EPA in
15 Atlanta, GA, during the summer of 1990 (Purdue et al., 1992). For that study, an
16 automated GC system developed and manufactured by Chrompack, Inc., and modified for
17 ozone precursor monitoring (McClenny et al., 1991) was used to obtain hourly VOC
18 measurements. The GC system was equipped with a preconcentration adsorption trap, a
19 cryofocusing secondary trap, and a single analytical column. The study was focused on the
20 identification and quantitation of 55 ozone precursor compounds, and resulted in accounting
21 for 65 to 80% of the total NMOC mass. Sample volumes of 600 cc were used and a
22 detection level of 0.1 ppb C was reported. External auditing indicated accuracy of $\pm 30\%$ at
23 challenge concentrations of 2 ppb C (17-component audit mixture).

24 The study also revealed several weaknesses. First of all, excessive amounts of liquid
25 cryogen were consumed in carrying out the measurements. The inferior quality of the
26 cryogen containers and poor delivery schedules resulted in reduced data capture. Secondly,
27 because of the single-column approach, numerous target species either co-eluted or were
28 poorly resolved. Finally, several significant artifact peaks co-eluted with the target species
29 and therefore biased the reported concentrations of those species as well as the total NMOC
30 (by summation of peaks).

1 Based upon these deficiencies, the EPA has challenged commercial GC instrument
2 makers with improving the current state of the art. One result has been the evolution of
3 systems that require no liquid cryogen for operation, yet provide sufficient gas
4 chromatographic resolution of target species (McClenny, 1993; Holdren et al., 1993).
5 A recent comparison study of automated gas chromatographs at Research Triangle Park with
6 five participating vendors has indicated that the newer auto GC designs use cryogens more
7 efficiently (Purdue, 1993).

8 In addition to direct sampling via preconcentration with sorbents and cryogenic
9 techniques, collection of whole air samples is frequently used to obtain NMOC data. Rigid
10 devices such as syringes, glass bulbs, or metal containers and non-rigid devices such as
11 Tedlar® and Teflon® plastic bags are often utilized during sampling. The primary purpose of
12 whole-air collection is to store an air sample temporarily until subsequent laboratory analysis
13 is performed. The major problem with this approach is assuring the integrity of the sample
14 contents prior to analysis. The advantages and disadvantages of the whole air collection
15 devices have been previously summarized in the 1986 air quality criteria document (U.S.
16 Environmental Protection Agency, 1986).

17 The canister-based method is the preferred means for collecting VOCs and is described
18 as part of the "EPA Compendium of Methods for the Determination of Toxic Organic
19 Compounds in Ambient Air" (Compendium Method TO-14). McClenny et al. (1991)
20 recently reviewed the canister-based method and have discussed basic facts about the
21 canisters, described canister cleaning procedures, contrasted the canister collection system
22 versus solid adsorbents, and discussed the storage stability of VOCs in canisters. Although
23 storage stability studies have indicated that many target VOCs can be stored with good
24 integrity over time periods of at least 7 days, there are still many VOCs for which there are
25 no stability data (Pate et al., 1992; Oliver et al., 1986; Holdren et al., 1987; Westberg et al.,
26 1981; Gholson et al., 1990; Westberg et al., 1984). Coutant (1993) has developed a
27 computer-based model for predicting adsorption behavior and vapor-phase losses in
28 multicomponent systems, based on the potential for physical adsorption as well as the
29 potential for dissolution in condensed water for canister samples collected at high humidities.
30 At present, the database for the model contains relevant physicochemical data for

1 78 compounds (including water) and provisions for inclusion of up to 120 additional
2 compounds are incorporated in the software.

3 4 **3.5.2.2.3 Calibration Methods**

5 Calibration procedures for NMOC instrumentation require the generation of dilute
6 mixtures at concentrations expected to be found in ambient air. Methods for generating such
7 mixtures are classified as static or dynamic systems.

8 As described in the previous ozone criteria document (U.S. Environmental Protection
9 Agency, 1986), static systems are generally preferred for quantitating NMOCs. The most
10 commonly used static system is a compressed gas cylinder containing the appropriate
11 concentration of the compound of interest. These cylinder gases may also be diluted with
12 hydrocarbon-free air to provide multi-point calibrations. Cylinders of calibration gases and
13 hydrocarbon-free air are available commercially. Also, some standard gases such as propane
14 and benzene, as well as a 17-component ppb mixture, are available from the National
15 Institute of Standards and Technology (NIST) as certified standard reference materials
16 (SRM). Commercial mixtures are generally referenced against these NIST standards. In its
17 recent technical assistance document for sampling and analysis of ozone precursors, EPA
18 recommended propane (or benzene)-in-air standards for calibration (U.S. Environmental
19 Protection Agency, 1991). Some commercially available propane cylinders have been found
20 to contain other hydrocarbons (Cox et al., 1982), so that all calibration data should be
21 referenced to NIST standards.

22 Because of the uniform carbon response of a GC-FID system ($\pm 10\%$) to hydrocarbons
23 (Dietz, 1967), a common response factor is assigned to both identified and unknown
24 compounds obtained from the speciation systems. If these compounds are oxygenated
25 species, an underestimation of the actual concentrations will be reported. Dynamic
26 calibration systems are employed when better accuracy is needed for these oxygenated
27 hydrocarbon species. Dynamic systems are normally employed to generate in situ
28 concentrations of the individual compound of concern and include devices such as permeation
29 and diffusion tubes and syringe delivery systems.

3.5.2.3 Carbonyl Species

Historically, the major problem in measuring concentrations of carbonyls in ambient air has been to find an appropriate monitoring technique that is sensitive to low concentrations and specific for the various homologues. Early techniques for measuring formaldehyde, the most abundant aldehyde, were subject to many interferences and lacked sensitivity at low parts-per-billion concentrations. The 1986 air quality criteria document described two methods frequently used: the chromotropic acid (CA) method for formaldehyde and the 3-methyl-2-benzothiazolone hydrazone (MBTH) technique for total aldehydes (U.S. Environmental Protection Agency, 1986). However, spectroscopic methods, on-line colorimetric methods, and the high-performance liquid chromatography (HPLC) method employing 2,4-dinitrophenylhydrazine (DNPH) derivatization are the preferred methods currently used for measuring atmospheric levels of carbonyl species.

3.5.2.3.1 Spectroscopic Methods

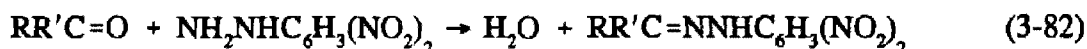
Three spectroscopic methods have been used to make measurements for atmospheric levels of formaldehyde and were recently intercompared at an urban site in California (Lawson et al., 1990). The Fourier Transform Infrared Spectroscopy (FTIR) method used gold-coated 30-cm-diameter mirrors and a total optical path of 1,150 m. The 2781.0 cm^{-1} "Q-branch" adsorption peak was used to measure HCHO. The limit of detection was 3 ppb, and the measurement errors were within ± 3 ppb. The Differential Optical Absorption Spectroscopy (DOAS) method was operated at an 800-m pathlength, and an absorption peak at 339 nm was used to measure HCHO; NO_2 and HONO spectral features were subtracted. The limit of detection was 4.5 ppb; the experimental error was $\pm 30\%$. A Tunable Diode Laser Absorption Spectroscopy (TDLAS) method was operated at a pathlength of 150 m. Laser diodes were mounted in a closed-cycle helium cryocooler with a stabilizing heater circuit for constant temperature control. Radiation from the diode was collected and focused into the sampling by reflective optics. Formaldehyde absorption was measured at $1,740\text{ cm}^{-1}$. The limit of detection was 0.1 ppb and the measurement errors were within $\pm 20\%$. Additional information on FTIR and DOAS has been reported by Winer et al., 1987; Atkinson et al., 1988; and Biermann et al., 1988. A more complete description of TDLAS is given by MacKay et al., 1987.

3.5.2.3.2 *On-line Colorimetric Method*

A wet chemical method based upon the derivatization of HCHO in aqueous solution to form a fluorescent product was recently developed by Kelly et al. (1990). The detection of fluorescent product was made more sensitive by using intense 254 nm light from a mercury lamp for excitation. This procedure allowed the use of a simple and efficient glass coil scrubber for collection of gaseous HCHO. A detection limit of 0.2 ppb was obtained when using a response time of 1 min. The instrument is portable and highly selective for HCHO.

3.5.2.3.3 *High-Performance Liquid Chromatography-2,4-Dinitrophenylhydrazine Method*

The preferred and most current method for measuring aldehydes in ambient air is one involving derivatization of the aldehydes concurrent with sample collection, followed by analysis using high-performance liquid chromatography (HPLC). This method takes advantage of the reaction of carbonyl compounds with 2,4-dinitrophenylhydrazine (DNPH) to form a 2,4-dinitrophenylhydrazone:



Because DNPH is a weak nucleophile, the reaction is carried out in the presence of acid in order to increase protonation of the carbonyl.

In this method, atmospheric sampling was initially conducted with micro-impingers containing an organic solvent and aqueous, acidified DNPH reagent (Papa and Turner, 1972; Katz, 1976; Smith and Drummond, 1979; Fung and Grosjean, 1981). After sampling was completed, the hydrazone derivatives were extracted and the extract was washed with deionized water to remove the remaining acid and unreacted DNPH reagent. The organic layer was then evaporated to dryness, subsequently dissolved in a small volume of solvent, and analyzed by reversed-phase liquid chromatographic techniques employing an ultraviolet (UV) detection system (360 nm).

An improved procedure was subsequently reported that is much simpler than the above aqueous impinger method (Lipari and Swarin, 1982; Kuntz et al., 1980; Tanner and Meng, 1984). This scheme utilizes a midjet impinger containing an acetonitrile solution of DNPH and an acid catalyst. After sampling, an aliquot of the original collection solution is directly

1 injected into the liquid chromatograph. This approach eliminates the extraction step and
2 several sample-handling procedures associated with the DNPH-aqueous solution; and
3 provides much better recovery efficiencies. This method has been formalized by the EPA as
4 Compendium Method TO-5 (Winberry et al., 1988). The TO-5 Method has been further
5 modified to include the use of DNPH-impregnated solid adsorbent rather than DNPH
6 impinger solutions as the collection medium. This modification and associated sampling
7 conditions are referred to as EPA Method TO-11. The methodology can be easily used for
8 long-term (1 to 24 h) sampling of ambient air. Sampling rates of 500 to 1,200 cc/min can be
9 achieved and detection levels of 1 ppbV can be attained with sampled volumes of 100 L.
10 The method currently calls for the use of SepPak® silica gel material as the sorbent material.
11 However, researchers have noted that O₃ present in ambient air reacted more easily with
12 carbonyl compounds collected on DNPH-coated silica gel cartridges than on DNPH-coated
13 C₁₈ bonded silica material. To eliminate this interference problem, these researchers used an
14 ozone scrubber (Arnts et al., 1989). The TO-11 Method has been included in EPA's
15 *Technical Assistance Document for Sampling and Analysis of Ozone Precursors* (U.S.
16 Environmental Protection Agency, 1991).

18 3.5.2.3.4 Calibration of Carbonyl Measurements

19 Because they are reactive compounds, it is extremely difficult to make stable calibration
20 mixtures of carbonyl species in pressurized gas cylinders. Although gas-phase standards are
21 available commercially, the vendors do not guarantee long-term stability and accuracy.

22 Formaldehyde standards are generally prepared by one of several methods. The first
23 method utilizes dilute commercial formalin (37% HCHO, w/w). Calibration is accomplished
24 by the direct spiking into sampling impingers of the diluted mixture or by evaporation into
25 known test volumes, followed by impinger collection. Formaldehyde can also be prepared
26 by heating known amounts of paraformaldehyde, passing the effluent gases through a
27 methanol-liquid nitrogen slush trap to remove impurities, and collecting the remaining
28 HCHO. Paraformaldehyde permeation tubes have also been used (Tanner and Meng, 1984).

29 For the higher-molecular-weight carbonyl species, liquid solutions can be evaporated or
30 pure vapor can be generated in dynamic gas-flow systems (permeation tubes, diffusion tubes,
31 syringe delivery systems, etc.). These test atmospheres are then passed through the

1 appropriate collection system and analyzed. A comparison of these data, with the direct
2 spiking of liquid carbonyl species into the particular collection system, provides a measure of
3 the overall collection efficiency.

4 5 **3.5.2.4 Polar Volatile Organic Compounds**

6 The VOCs discussed earlier in this chapter (Section 3.5.2.2) have included aliphatic,
7 aromatic, alkenic, and acetylenic hydrocarbons. These compounds are relatively nonpolar,
8 nonreactive species, and measurement methods have been easily applied in determining
9 ambient concentrations.

10 Recently, attention has also been directed toward the more reactive oxygen- and
11 nitrogen-containing organic compounds, in part by the inclusion of many of these compounds
12 on a list of 189 hazardous air pollutants specified in the 1990 Clean Air Act Amendments.
13 Many of these compounds are directly emitted from a variety of industrial processes, mobile
14 sources, and consumer products, and some are also formed in the atmosphere by
15 photochemical oxidation of hydrocarbons. However, as indicated earlier in this document,
16 very few ambient data exist for these species. These compounds have been collectively
17 referred to as polar VOCs (PVOCs), although it is their reactivity and water solubility, more
18 than simple polarity, that make their measurement difficult with existing methodology.

19 Two approaches have been utilized in developing analytical methods for PVOCs. One
20 approach has incorporated the use of cryogenic trapping techniques similar to those discussed
21 earlier for the nonpolar hydrocarbon species; the second approach has utilized adsorbent
22 material for sample preconcentration. To be effective for sensitive ppb measurement of
23 PVOCs, both approaches require some type of water management system to mitigate the
24 adverse effects that water has on the chromatography and detector sensitivity and reliability.
25 Several researchers have reported the use of cryogenic trapping with two-dimensional
26 chromatography to selectively remove water vapor from the analytical process (Pierotti,
27 1990; Cardin and Lin, 1991). Although this column "heart cutting" technique has been
28 successful for selected compounds, additional studies are needed to determine its potential
29 use for the wide range of PVOCs. Ogle et al. (1992) developed a novel water management
30 system based upon the condensation of moisture from the saturated carrier gas stream during
31 thermal desorption of a cryogenic trap. The moisture management system was found to be
32 effective for reducing the amount of water delivered to the column during laboratory analyses

1 of spiked mixtures. However, the system has not yet been extended to field monitoring.
2 Gordon et al. (1989) have used cryogenic trapping and gas chromatography/mass
3 spectrometry techniques to demonstrate the potential of chemical ionization (CI) within an ion
4 trap to detect PVOCs. The water vapor present in the sample served as the CI reagent gas
5 and appeared to be an effective reagent gas; however, deleterious chromatography results
6 were also encountered. The authors concluded that further laboratory work is needed before
7 this methodology can be applied to ambient air monitoring. Martin et al. (1991) also
8 reported the use of cryogenic trapping with a GC-FID system to measure ambient levels of
9 isoprene and two of its oxidation products, methacrolein and methylvinyl ketone (detection
10 level of 0.5 ppb). The water vapor was selectively removed by using a potassium carbonate
11 (K_2CO_3) trap ahead of the cryogenic trap. Frequent replacement of the K_2CO_3 trap was
12 required.

13 The use of solid adsorbents for sample preconcentration of PVOCs has been reported
14 by Kelly et al. (1993). The analytical method was used extensively at two field sites that
15 were formerly used in EPA's Toxic Air Monitoring Study (TAMS). The analytical method
16 consisted of gas chromatographic separation of PVOCs with quantification by a ion trap mass
17 spectrometer. A two-stage adsorbent trap containing Carbopack B and Carbosieve S-III
18 (Supelco catalog number 2-0321) was used to separate water vapor from the PVOCs. The
19 optimum room temperature trapping and drying procedure consisted of a 320-cc sample
20 (100 cc/min) followed by a dry nitrogen purge of 1,300 cc (100 cc/min). The trap was then
21 backflushed and thermally desorbed with helium at 220 °C. A 5-min 260 °C trap bakeout
22 followed each collection-analysis cycle. The target list contained 14 PVOCs, including
23 alcohols, ethers, esters, and nitrile species. Individual detection limits ranged from 0.2 to
24 1 ppb.

26 **3.5.3 Sampling and Analysis of Oxides of Nitrogen**

27 **3.5.3.1 Introduction**

28 The measurement of oxides of nitrogen in ambient air is of interest because of the role
29 that certain of those compounds play as precursors to ozone and because nitrogen dioxide
30 (NO_2) has been shown to elicit health effects. The primary nitrogen oxides emitted from
31 combustion sources are nitric oxide (NO) and nitrogen dioxide (NO_2). Collectively these

1 two compounds are called NO_x . They contribute to ozone formation by means of reactions
2 discussed in Section 3.2. As a result, measurement of NO_x is important in efforts to
3 understand and control ozone and NO_2 in ambient air.

4 The atmospheric photochemistry that produces ozone also results in conversion of NO
5 and NO_2 to products such as nitric acid (HNO_3), nitrous acid (HONO), peroxyacetyl nitrate
6 ($\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$; PAN), organic nitrates, and other species. The total of all of these labile
7 nitrogen species in air, NO_x included, is termed NO_y . Such compounds may be labile via
8 photolysis (e.g., HONO) or thermal decomposition (e.g., PAN), and may be toxic, irritating,
9 or acidic. However, in general they do not play the same critical role that NO_2 and NO play
10 as ozone precursors. For that reason, this section focuses on measurement methods for NO
11 and NO_2 , as the primary ozone precursors among the nitrogen oxides. The nitrogen oxides
12 other than NO_x may be important, however, as interferents in efforts to measure NO and
13 NO_2 . These non- NO_x species are considered in this section in that regard.

14 Measurements of NO_x may involve measurements of NO, of NO_2 , or of the sum of
15 NO_x . Nitrogen dioxide, but not NO, is a criteria air pollutant, and thus *reference* and
16 *equivalent* methods are specified for NO_2 measurements. In this section, the current state of
17 measurement methods for NO and NO_2 will be summarized separately. Such methods in
18 some cases rely on measurements of total NO_x , or at least an approximation of NO_x . This
19 discussion focuses on current methods and on promising new technologies; but no attempt is
20 made here to cover the extensive history of development of these methods. More detailed
21 discussions of such methods may be found elsewhere (U.S. Environmental Protection
22 Agency, 1993; National Aeronautics and Space Administration, 1983). Wet chemical
23 methods are no longer commonly used and are not discussed here; a review of such methods
24 is given by Purdue and Hauser (1980).

25 26 3.5.3.2 Measurement of Nitric Oxide

27 3.5.3.2.1 Gas-phase Chemiluminescence Methods

28 By far the most common method of NO measurement is gas-phase chemiluminescence
29 (CL) with O_3 . In this method, excess O_3 is added to air containing NO in a darkened,
30 internally reflective chamber viewed by a photomultiplier tube. A small portion of the
31 NO reactions with O_3 produce electronically excited NO_2 molecules, which decay by

1 emission of light of wavelengths longer than 600 nm. The emitted light is detected by a red-
2 sensitive photomultiplier tube, through an optical filter that prevents passage of wavelengths
3 shorter than 600 nm. This optical filtering minimizes interference from chemiluminescence
4 produced by O₃ reactions with other species (e.g., hydrocarbons). The excited NO₂ is
5 readily quenched in air, so that in typical instruments air and O₃ are mixed at reduced
6 pressure (i.e., at least 20 in. of Hg vacuum). The intensity of the emitted light is linearly
7 proportional to the NO content of the sample air over several orders of magnitude in
8 concentration.

9 Commercial CL instruments for continuous measurement of NO are available from
10 several manufacturers. The chemiluminescence approach is also an EPA-designated
11 measurement principle for measuring ambient NO₂; it requires a means of converting NO₂ to
12 NO for detection. The complexities of this conversion are discussed in Section 3.5.3.3, on
13 NO₂ methods. The commercial NO monitors typically are claimed to have detection limits
14 of a few parts per billion by volume in air (ppbv) with response time of a few minutes.
15 Field evaluations of several commercial instruments have indicated that minimum levels of
16 detection for NO₂ are 5 to 13 ppbv (Michie et al., 1983; Holland and McElroy, 1986).
17 However, more recent evaluations have indicated better performance. Rickman et al. (1989)
18 reported detection limits of 0.5 to 1 ppbv, and precision of ± 0.3 ppbv, from laboratory and
19 field evaluations of two commercial instruments operated on their 50 ppbv full-scale ranges.
20 Commercial NO analyzers are portable and quite reliable, and are now commonly used in
21 ambient air monitoring networks.

22 Commercial NO analyzers may not have sensitivity sufficient for surface measurements
23 in rural or remote areas, or for airborne measurements. As a result, several investigators
24 have devised modifications to commercial instruments to improve their sensitivity and
25 response time (Delany et al., 1982; Tanner et al., 1983, Dickerson et al., 1984, Kelly et al.,
26 1986). Those modifications include: (1) operating at low pressure and high sample flow
27 rate; (2) using a larger, more reflective reaction chamber that promotes mixing of the
28 reactants close to the photomultiplier tube; (3) increasing the O₃ supply; for example, by use
29 of oxygen in the O₃ source; (4) cooling of the photomultiplier to reduce noise; (5) adopting
30 photon counting techniques for light detection; and (6) adding a prereactor to obtain a more
31 stable and appropriate background signal. Commercial instruments modified in these ways

1 are generally reported to have detection limits of 0.1 ppbv or less, with response times of
2 30 s or less.

3 Research-grade NO instruments specially designed for ultra-high sensitivity have also
4 been built for use in remote ground-level or airborne applications (e.g, Ridley and Howlett,
5 1974; Kley and McFarland, 1980; Kelly et al., 1980; Helas et al., 1981; Drummond et al.,
6 1985; Torres, 1985; Kondo et al., 1987; Parrish et al., 1990). These instruments typically
7 have detection limits of 10 ppt (i.e., 0.01 ppbv) or less, with response times from a few
8 seconds to 1 min.

9 A number of studies indicate that the chemiluminescence method is essentially specific
10 for NO. Operation at reduced pressure prevents interference resulting from quenching by
11 water vapor (Michie et al., 1983; Drummond et al., 1985). In air sampling, no significant
12 interferences have been found in NO detection from sulfur-, chlorine-, and nitrogen-
13 containing species (Joshi and Bufalini, 1978; Sickles and Wright, 1979; Grosjean and
14 Harrison, 1985; Fahey et al., 1985). However, H₂S and possibly other sulfur-containing
15 compounds from seawater have been reported to give false NO signals (Zafiriou and True,
16 1986). This effect should not be important for ambient air measurements. Fahey et al.
17 (1985) and Drummond et al. (1985) also reported no significant NO interference from a
18 variety of other nitrogen-containing species, including NO₂, HNO₃, PAN, N₂O₅, NH₃,
19 HCN, N₂O, and HO₂NO₂; as well as no interference from methane, propylene, and
20 hydrogen peroxide.

21 Several ambient air intercomparisons have been done of chemiluminescence NO
22 instruments (Walega et al., 1984; Hoell et al., 1987; Fehsenfeld et al., 1987; Gregory et al.,
23 1990). These studies have focused on high-sensitivity research instruments, rather than the
24 commercial instruments used for widespread ambient air measurements. These studies have
25 shown excellent agreement among the CL NO instruments, even at NO levels in the low ppt
26 range (Hoell et al., 1987; Gregory et al., 1990). These results support the validity of the CL
27 approach for NO. Good agreement has also been found between CL measurements and
28 spectroscopic NO measurements in these studies (see Section 3.5.3.2.2).

3.5.3.2.2 *Spectroscopic Methods for Nitric Oxide*

Direct spectroscopic methods for NO include two-photon laser-induced fluorescence (TPLIF), tunable-diode laser absorption spectroscopy (TDLAS), and two-tone frequency-modulated spectroscopy (TTFMS). The primary characteristics of these methods are their very high sensitivity and selectivity for NO. For example, a detection limit of 10 ppt has been quoted for TPLIF with a 30-s integration time, with no significant interferences from atmospheric species (Davis et al., 1987). An accuracy of $\pm 16\%$ as a 90% confidence limit has been calculated for NO measurement by TPLIF from an aircraft (Davis et al., 1987). The TDLAS method is similarly highly selective for NO and achieves a detection limit of 0.5 ppbv (Schiff et al., 1983). The response time of the TDLAS instrument is about 1 min for NO, and is limited by stabilization of concentrations with the large surface area of the multi-pass White cell. The newest method is TTFMS, which appears in laboratory studies to be very sensitive, fast, and selective. With a 100-m path length in a 20-torr multiple-pass cell, and a 1-min averaging time, the detection limit of NO is estimated to be 4 ppt (Hansen, 1989).

Spectroscopic methods have compared well with the CL method for NO in ambient measurements. Walega et al. (1984) reported good agreement between CL and TDLAS results for NO in laboratory air, in ambient air, and even in downtown Los Angeles air. Gregory et al. (1990) reported comparisons of TPLIF and CL NO methods in airborne measurements. Agreement at levels below 20 ppt was within the expected accuracy and precision of the instruments (i.e., within 15 to 20 ppt).

The major drawbacks of these spectroscopic methods are their complexity, size, and cost. Although possessing remarkable characteristics, these methods are restricted to research applications. The TTFMS approach, in fact, is still in the laboratory development stage.

3.5.3.2.3 *Passive Samplers*

At present no passive sampler exists that directly measures NO. Instead, passive samplers developed for NO₂ have been adapted for NO measurement, using an oxidizing material that converts NO to NO₂. Palmes tubes (Palmer and Tomczyk, 1979) have been adapted for NO measurement by using two tubes in parallel. One tube collects NO₂ on a

1 triethanolamine (TEA)-coated grid, while the other collects NO₂ on a TEA grid, plus NO
2 oxidized by a chromic acid-coated surface. The grids are then extracted and analyzed for
3 NO₂⁻ ion. Nitric oxide is determined by difference between the two results, after accounting
4 for the different diffusivities of NO and NO₂. The sampling rates depend on temperature
5 and air velocity. The tubes cannot be used for periods longer than 24 h, and are intended for
6 use at ppm NO levels important in the workplace (e.g., 2 to 200 ppm·h). Applicability to
7 ambient NO levels has not been demonstrated.

8 A more sensitive passive sampler for NO has been reported (Yanagisawa and
9 Nishimura, 1982) that uses the same TEA chemistry, with CrO₃ as the NO oxidizer.
10 A detection limit of 70 ppbv·h has been reported. As with any currently available passive
11 sampler, the disadvantages of the method are the potential for interferences, relatively poor
12 precision, and low sensitivity for ambient air measurements.

14 3.5.3.3 Measurements for Nitrogen Dioxide

15 3.5.3.3.1 Gas-phase Chemiluminescence Methods

16 In 1976, the gas-phase chemiluminescence approach described above for NO detection
17 was designated as the measurement principle on which U.S. EPA reference methods for
18 ambient NO₂ must be based. The CL method thus filled the vacancy left by withdrawal of
19 the Jacobs-Hochheiser method, because of technical problems, in 1973. To be designated as
20 a reference method, an NO₂ detection method must use the CL approach and be calibrated
21 by the specified methods (gas-phase titration of NO with O₃, or use of an NO₂ permeation
22 device). In addition the instrument must meet the performance specifications shown in
23 Table 3-18. An equivalent method, either manual or automated, must meet certain
24 requirements for comparability with a reference method when measuring simultaneously in a
25 real atmosphere. Those comparability requirements are shown in Table 3-19. An automated
26 equivalent method must also meet the performance requirements shown in Table 3-18.

27 The selection of the ozone CL method as the reference measurement principle for
28 ambient NO₂ was the result of comparison tests of CL and wet chemical methods.
29 Chemiluminescence analyzers were found superior to the wet chemical methods in response
30 time, zero and span drift, and overall operation, although agreement among all the methods
31 tested was good, at the NO₂ spike levels provided (Purdue and Hauser, 1980). Table 3-20

**TABLE 3-18. PERFORMANCE SPECIFICATIONS FOR NITROGEN
DIOXIDE AUTOMATED METHODS**

Performance Parameter	Units	NO ₂
Range	ppm	0-0.5
Noise		
0% upper range limit	ppm	0.005
80% upper range limit	ppm	0.005
Lower detectable limit	ppm	0.01
Interference equivalent		
Each interferant (SO ₂ , NO, NH ₃ , H ₂ O)	ppm	±0.02
Total interferant	ppm	≤0.04
Zero drift, 12 and 24 hours	ppm	±0.02
Span drift, 24 hours		
20% upper range limit	%	±20.0
80% upper range limit	%	±5.0
Lag time	min	20
Rise time	min	15
Fall time	min	15
Precision		
20% upper range limit	ppm	0.02
80% upper range limit	ppm	0.03

Source: Code of Federal Regulations, Ambient Air Monitoring Reference and Equivalent Methods,
C.F.R. Title 40, Part 53.

**TABLE 3-19. COMPARABILITY TEST SPECIFICATIONS
FOR NITROGEN DIOXIDE**

Nitrogen Dioxide Concentration Range (ppm)		Maximum Discrepancy Specification (ppm)
Low	0.02 to 0.08	0.02
Medium	0.10 to 0.20	0.02
High	0.25 to 0.35	0.03

1 lists the methods currently designated (as of February 1993) by U.S. EPA as reference and
2 equivalent methods for ambient NO₂. Three wet chemical methods are shown as equivalent
3 methods, but these are rarely used for ambient air measurements.

4 The ozone chemiluminescence method does not measure NO₂ directly, because the
5 chemiluminescence is produced by reaction of NO with O₃. As a result, NO₂ must first be

**TABLE 3-20. REFERENCE AND EQUIVALENT METHODS FOR
NITROGEN DIOXIDE DESIGNATED BY U.S. EPA^a**

Method	Designation Number	Method Code
Reference Methods (Continuous CL Analyzers)		
Advanced Pollution Instrumentation 200	RFNA-0691-082	082
Beckman 952A	RFNA-0179-034	034
Bendix 8101-B	RFNA-0479-038	038
Bendix 8101-C	RFNA-0777-022	022
CSI 1600	RFNA-0977-025	025
Dasibi 2108	RFNA-1192-089	089
Lear Siegler ML9841	RFNA-1292-090	090
Meloy NA53OR	RFNA-1078-031	031
Monitor Labs 8440E	RFNA-0677-021	021
Monitor Labs 8840	RFNA-0280-042	042
Monitor Labs 8841	RFNA-0991-083	083
Philips PW9762/02	RFNA-0879-040	040
Thermo Electron 14B/E	RFNA-0179-035	035
Thermo Electron 14D/E	RFNA-0279-037	037
Thermo Environmental 42	RFNA-1289-074	074
Equivalent Methods (Wet Chemical)		
Sodium arsenite	EQN-1277-026	084
Sodium arsenite/Technicon II	EQN-1277-027	084
TGS-ANSA ^b	EQN-1277-028	098

^aAs of February 1993.

^bTriethanolamine-guaiacol-sulfite with 8-amino-1-naphthalene-sulfonic acid ammonium salt.

reduced to NO for detection. In principle, such a reduction should readily result in measurement of NO + NO₂ (i.e., NO_x), and allow indirect measurement of NO₂ by difference between NO and NO_x responses, measured either sequentially, or simultaneously by separate detectors. In practice, however, selective measurement of NO_x by this approach has proven very difficult.

Several methods have been employed to convert NO₂ to NO, including catalytic reduction with heated molybdenum or stainless steel, reaction with CO over a gold catalyst surface, reaction with ferrous sulfate (FeSO₄) at room temperature, reaction with carbon at 200 °C, and photolysis of NO₂ at wavelengths of 320 to 400 nm (Kelly et al., 1986). It has

1 been found in many separate investigations that the heated converters reduce NO₂ to NO
2 effectively, but also reduce other NO_y species as well (e.g., Winer et al., 1974; Cox, 1974;
3 Joseph and Spicer, 1978; Grosjean and Harrison, 1985; Fahey et al., 1985). Efficiencies of
4 conversion near 100% are reported in these studies for NO₂ and for NO_y species such as
5 HNO₃, HONO, PAN, and organic nitrates. This finding is particularly important for
6 widespread monitoring networks that use commercial instruments, because such instruments
7 without exception use heated catalytic converters (typically molybdenum). Thus, such
8 instruments measure not NO and NO_x, but more nearly NO and total NO_y. The NO₂ value
9 inferred from such measurements may be significantly in error (see below), and may in turn
10 affect the results of models of ambient ozone. The completeness of the measured NO_y value
11 is also questionable because, for example, HNO₃ is readily lost to surfaces, and, in ambient
12 sampling, may be removed within the sampling system before reaching the heated converter.

13 Other conversion methods for NO₂ have been tried in an effort to achieve higher
14 selectivity. Ferrous sulfate (FeSO₄) has been used for ambient NO₂ measurements using
15 high-sensitivity research grade CL instruments (e.g., Kelly et al., 1980; Helas et al., 1981;
16 Dickerson et al., 1984). This material is an efficient reducer of NO₂, but has also been
17 found to convert a portion of PAN, and possibly a portion of HONO and organic nitrates
18 (Fehsenfeld et al., 1987). Memory effects and reduction in efficiency can occur because of
19 humidity effects (Fehsenfeld et al., 1987). As a result of these characteristics, use of FeSO₄
20 has given high readings in comparison with spectroscopic instruments and the photolytic NO₂
21 converter, and likely results in overestimating ambient NO_x by a significant amount
22 (Fehsenfeld et al., 1987; Ridley et al., 1988a; Gregory et al., 1990). Ferrous sulfate has
23 never been used in commercial NO_x instruments, and is no longer used in research
24 measurements.

25 The most specific method for converting NO₂ to NO is photolysis (Kley and
26 McFarland, 1980). In this approach, ambient NO₂ is photolyzed to NO by a xenon arc
27 lamp. The method does not produce NO from the major potential interferents present in air
28 (i.e., HNO₃, PAN, and organic nitrates), but less abundant NO_y species such as HONO or
29 HO₂NO₂ may interfere. A detailed description of steps to minimize such interferences is
30 given by Ridley et al. (1988b). As currently used, the photolytic converter appears to be
31 essentially specific for NO₂. However, it does not provide complete conversion of NO₂.

1 Conversion efficiencies are 50 to 60% with a new lamp, and may decline to 20% over the
2 course of several weeks (Parrish et al., 1990). Thus the conversion efficiency must be
3 repeatedly calibrated. This approach has not been implemented with commercial NO
4 detectors, but has been implemented with research-grade CL NO instruments for studies of
5 NO_x and NO_y chemistry at a variety of locations (e.g., Parrish et al., 1990; Trainer et al.,
6 1991; Parrish et al., 1992). The photolytic method has compared well with other techniques,
7 including spectroscopic methods, even at NO₂ levels as low as 0.05 ppbv (Gregory et al.,
8 1990).

9 As noted above, the commercial CL analyzers used for most ambient air NO and NO_x
10 measurements actually measure more nearly NO and NO_y. The magnitude of the resulting
11 overestimation of NO₂ determined by difference obviously depends on the portion of NO_y
12 that is NO_x. The smaller the portion of NO_y that is NO_x, the greater will be the error in the
13 NO₂ determined by difference. In remote areas, where NO_x has undergone extensive
14 conversion to other products during transport from a source region, NO_x may contribute a
15 small fraction of NO_y. In urban areas, close to sources, NO_x may comprise nearly all of
16 NO_y. For example, in measurements at Point Arena, California, Parrish et al. (1992) report
17 NO_x/NO_y ratios averaging 0.3 in air of marine origin, and 0.75 in air subject to continental
18 influence. Clearly, although the commercial CL instruments are designated as reference
19 methods for NO₂, the great majority of existing ambient air data for NO₂ or NO_x are biased
20 high, because of the inclusion of some portion of other NO_y species. The magnitude of this
21 bias may not be large in urban areas, but in any case it is unknown at this time.

22 23 **3.5.3.3.2 Luminol Chemiluminescence Method**

24 This approach is based on the chemiluminescent reaction of gaseous NO₂ with the
25 surface of an aqueous solution of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione).
26 Emission occurs primarily between 380 and 520 nm. In commercial instruments, luminol
27 solution flows down a fabric wick that lies vertically on a clear window viewed by a
28 photomultiplier tube. Nitrogen dioxide in sample air passing over the wick produces light,
29 the intensity of which is proportional to the NO₂ concentration. Commercial instruments
30 using this approach are compact, light, and relatively inexpensive, and can provide detection
31 limits as low as 0.01 ppbv with response times below 30 s. The instrument has the

1 advantage of detecting NO₂ directly. However, several difficulties have had to be dealt with
2 in developing the method.

3 Original reports of the approach (Maeda et al., 1980) indicated positive interferences
4 from O₃ and SO₂ and a negative one from CO₂. Reformulation of the luminol reagent
5 solution has minimized, though not fully eliminated, those interferences (Wendel et al.,
6 1983; Schiff et al., 1986). Reported effects include a slight negative response from NO, and
7 sensitivity to PAN, HONO, and O₃ (Wendel et al., 1983; Schiff et al., 1986; Rickman et al.,
8 1989; Kelly et al., 1990; Spicer et al., 1991). Response to NO₂ may be nonlinear at low
9 concentrations (Kelly et al., 1990), although recent reformulation of the reagent has
10 apparently reduced this behavior (Busness, 1992). Evaluation of the luminol NO₂ monitor
11 indicates that great care must be taken in using and calibrating the instrument in order to
12 achieve good precision and accuracy in ambient measurements (Kelly et al., 1990). The
13 monitor has been widely used as a research tool, but has not been widely used in ambient air
14 monitoring and has not been designated an equivalent method for NO₂.

15 An O₃ scrubber is available to eliminate the O₃ interference noted above, but was also
16 found to remove a portion of the NO₂ (Kelly et al., 1990). The luminol approach has also
17 been modified to measure NO, by using a CrO₃ converter that oxidizes NO to NO₂ for
18 detection. Thus NO is detected by difference. This method has the potential for
19 measurement of total NO_x; however, evaluations of the CrO₃ converter are still underway at
20 several laboratories. Given the known interferences in the luminol approach, careful
21 evaluation of this method must be completed before it gains acceptance as an NO
22 measurement method.

23 An adaptation of the commercial luminol NO₂ detector has been reported to provide
24 measurements of total NO_y, NO₂, and NO_x (Drummond et al., 1993). This adaptation,
25 called the LNC-3M, uses a commercial luminol instrument for NO₂ detection, with a
26 CrO₃ converter for NO_x detection. The NO_x measurement must be corrected for the few
27 percent of the ambient NO₂ that is lost in the CrO₃ converter (Drummond et al., 1993). The
28 NO_y measurement is achieved using a stainless steel converter maintained at 400 °C. Tests
29 indicate that this converter provides a more complete conversion of alkyl nitrates, and
30 consequently a more complete measurement of NO_y, than is provided by either the heated
31 molybdenum converters used in commercial ozone CL NO_x detectors or the gold converters

with CO addition used in research instruments (Drummond et al., 1993). The LNC-3M adds a small amount of NO₂ to the sample to eliminate the nonlinearity at low concentrations, and uses a zeroing scrubber that greatly reduces the interference from PAN. However, this scrubber must be replaced weekly when in continuous use (Drummond et al., 1993).

3.5.3.3.3 *Spectroscopic Methods*

Several spectroscopic approaches to NO₂ detection have been developed: TDLAS, TTFMS, differential optical absorption (DOAS), and differential absorption lidar (DIAL) are absorption methods that have been used. The TDLAS method is probably the most commonly used spectroscopic NO₂ method. It can provide high selectivity for NO₂, with a detection limit of 0.1 ppbv, accuracy of ± 15 percent, and a response time on the order of 1 min because of the White cell (Mackay and Schiff, 1987). The DOAS method is an open-path long-pathlength system. The detection limit for NO₂ with a 0.8-km pathlength and 12-min averaging time has been reported as 4 ppbv, with measurement accuracy reported as $\pm 10\%$ (Biermann et al., 1988). However, recent improvements have resulted in a commercial DOAS instrument capable of an NO₂ detection limit of 0.6 ppbv, based on a 557-m path and a 1-min averaging time (Stevens et al., 1993). The detection limit for NO₂ by the DIAL technique has been reported as 10 ppbv with a 6-km pathlength (Staehr et al., 1985). The novel TTFMS method noted above for NO is reported to have an NO₂ detection limit of 0.3 ppt, but is not fully proven for ambient measurements.

Fluorescence methods have also been used for NO₂, including photofragmentation TPLIF (PF/TPLIF) (Davis, 1988). This method uses two cells in which NO is measured by TPLIF. In one of the cells, an excimer laser emitting at 353 nm photolyzes NO₂ to NO for detection. Thus NO₂ is ultimately measured, by difference, as NO, but the NO is formed directly by photolysis of NO₂. With a 2-min integration time, an NO₂ detection limit of 12 ppt is reported. The method is highly selective for NO₂, since an interferant would have to photolyze to produce NO. Several potential atmospheric species have been ruled out in this regard (Davis, 1988).

The drawbacks of most of these methods are, as noted earlier, complexity, size, and cost. At present these factors outweigh the obvious advantages of the sensitivity and selectivity of these spectroscopic methods, and have largely restricted the use of these

1 NO₂ methods to specific research applications or to their use as reference methods in
2 intercomparisons. In such intercomparisons, absorption measurements have been most
3 commonly used. The TDLAS method has been used in ground-level comparisons with
4 O₃ CL and luminol instruments to provide specific NO₂ measurements (Walega et al., 1984;
5 Sickles et al., 1990; Fehsenfeld et al., 1990), and in an airborne comparison with PF/TPLIF
6 and O₃ CL instruments (Gregory et al., 1990b). A finding of these studies was that the
7 TDLAS consistently read higher than other established methods at very low NO₂ levels (i.e.,
8 <0.4 ppbv) (Fehsenfeld et al., 1990; Gregory et al., 1990b).

9 The spectroscopic NO₂ method most fully developed beyond the research stage is the
10 DOAS technique. Stevens et al. (1993) report testing of a commercial DOAS instrument in
11 North Carolina over 17 days in the fall of 1989. The DOAS measured NO₂ using
12 wavelengths between 400 and 460 nm, and achieved a detection limit of 0.6 ppbv, as noted
13 above. Simultaneous measurements of ozone, sulfur dioxide, formaldehyde, and nitrous acid
14 were also provided by the DOAS instrument. Comparison of the DOAS NO₂ results to those
15 from a commercial CL detector showed $(\text{DOAS NO}_2) = 1.14 \times (\text{CL NO}_2) + 2.7 \text{ ppbv}$,
16 with a correlation coefficient (r^2) of 0.93, at NO₂ levels up to 50 ppbv (Stevens et al., 1993).
17 The sensitivity, stability, response time, and multicomponent capability are the primary
18 advantages of the DOAS approach. Further intercomparisons and interference tests are
19 recommended (Stevens et al, 1993).

21 3.5.3.3.4 *Passive Samplers*

22 Passive samplers are attractive, inexpensive, and simple means to obtain long-term or
23 personal exposure data for NO₂ or NO_x. The simplest passive sampler for NO₂ is the
24 nitration plate, which is essentially an open dish containing filter paper impregnated with
25 TEA. Nitrogen dioxide diffuses to the paper, and is extracted later as NO₂⁻ for analysis.
26 No diffusion barrier exists in this approach, or in a similar approach using a candle-shaped
27 absorber (Kosmus, 1985); consequently, results are very subject to ambient conditions and
28 give at best a qualitative indication of NO₂ or NO_x.

29 Addition of a diffusion barrier to the nitration plate concept has led to badge-type
30 passive samplers for NO₂ (e.g., Mulik and Williams, 1986, 1987; Mulik et al., 1989, 1991).
31 In general, such devices use perforated screens, plates, or filters as diffusion barriers on the

1 chemically reactive material, which may be exposed on one or both sides, depending on the
2 application. Extraction of the sorbent then allows measurement of the NO₂ collected,
3 typically as NO₂⁻ ion. Such a device using TEA as the active material gave very good
4 agreement relative to a CL analyzer in laboratory tests with NO₂ at 10 to 250 ppbv (Mulik
5 and Williams, 1987). However, interferences from PAN and HONO (the latter both in
6 outdoor and indoor air) are expected (Sickles and Michie, 1987). Comparison of ambient
7 NO₂ results in the 5 to 25 µg/m³ range (i.e., about 2.5 to 12.5 ppbv) from the passive
8 device to those from TDLAS showed good agreement on average values, but a correlation
9 coefficient (r) of only 0.47 on daily values (Mulik et al., 1989).

10 Badge-type personal samplers for NO₂ have also been developed by Yanagisawa and
11 Nishimura (1982) (YN) and by Cadoff and Hodgeson (1983) (CH). Triethanolamine is used
12 as the active collecting medium in both samplers, and both use colorimetry as the analytical
13 method for detection of NO₂⁻. The samplers differ in that the YN device uses TEA coated
14 on a cellulose filter with a Teflon® filter as a diffusion barrier; whereas the CH sampler uses
15 TEA coated on a glass fiber filter with a polycarbonate filter as a diffusion barrier.
16 Detection limits are reported to be 0.07 ppm·h (Yanagisawa and Nishimura, 1982) and
17 0.06 ppm·h (Cadoff and Hodgeson, 1983). Interferences from PAN and HONO are expected
18 (Sickles and Michie, 1987); likewise, the devices are sensitive to the speed of ambient air
19 movement.

20 Palmes tubes have been developed for NO₂ measurement and adapted to NO
21 measurement as described above. The device has been used for workplace and personal
22 exposure monitoring (Wallace and Ott, 1982), but not for ambient air measurements.
23 A detection limit of 0.03 ppm·h can be achieved if ion chromatography is used to determine
24 the extracted NO₂⁻ (Mulik and Williams, 1986). Adsorption of NO₂ to the tube walls may
25 raise this limit considerably (Miller, 1988), but this effect can be counteracted by use of
26 stainless steel tubes. The device is sensitive to temperature and wind speed; and PAN and
27 HONO are likely interferences (Sickles and Michie, 1987). In a comparison with two
28 commercially produced NO₂ passive samplers, the Palmes tube showed reasonable accuracy
29 and precision at loadings of 1 to 80 ppm·h. However, the commercial devices were designed
30 for use at relatively high loadings; therefore, this comparison does not support the use of
31 Palmes tubes for ambient air monitoring. The Palmes tubes have the same disadvantages as

1 other passive devices for NO₂, namely, poor precision, insufficient sensitivity, temperature
2 dependence, and considerable interferences in ambient sampling.

3 4 **3.5.3.4 Calibration Methods**

5 Calibration of NO measurement methods is done using standard cylinders of NO in
6 nitrogen. Typical NO concentrations in such cylinders are 1 to 50 ppmv. Dilution of such
7 standards with clean air using mass flow controllers can accurately provide NO
8 concentrations in the ambient (i.e., 1 to 100 ppbv) range for calibration. Nitric oxide
9 standards are available as Standard Reference Materials (SRMs) from the National Institute
10 of Standards and Technology (NIST), and as commercially available Certified Reference
11 Standards. Commercially available certified NO standards have been shown to be stable and
12 accurate in the certified concentrations.

13 Standard cylinders of NO₂ in nitrogen or air are sometimes used for NO₂ calibration.
14 These standards are commercially available, and are readily diluted to ppbv levels in the
15 same manner as for NO standards. However, instability of the NO₂ levels in such standards
16 has been reported, and caution must be used in relying on NO₂ standards as the primary
17 means of calibration.

18 Two calibration methods for NO₂ are specified in the Code of Federal Regulations
19 (1987) for calibration of ambient NO₂ measurements. Those methods are permeation tubes
20 and gas-phase titration.

21 An NO₂ permeation tube is an inert enclosure, generally of Teflon®, glass and Teflon®,
22 or stainless steel and Teflon®, that contains liquid NO₂. As long as liquid NO₂ is present,
23 NO₂ will permeate through the Teflon® at a rate that depends on the temperature of the tube.
24 Maintaining the permeation tube at a constant temperature (i.e., ±0.1 °C) results in
25 permeation of NO₂ at a constant rate. Dilution of the emitted NO₂ with a flow of dry air or
26 N₂ results in known low NO₂ concentrations for calibration. Nitrogen dioxide permeation
27 tubes are supplied as SRMs by NIST, and tubes are commercially available with a wide
28 range of permeation rates. Permeation tubes are small, simple, reliable, and relatively
29 inexpensive, although constant temperature ovens and dilution systems are required to obtain
30 good results. Nitrogen dioxide permeation tubes are susceptible to moisture, and changes in
31 permeation rate or emission of other species (HNO₃, HONO, NO) may occur if they are not

1 kept dry. As with NO₂ cylinder standards, the NO₂ permeation tube requires care as a
2 calibration method for NO₂.

3 Gas-phase titration (GPT) uses the rapid reaction of NO with O₃ to produce NO₂ with
4 1:1 stoichiometry. In practice, excess NO generated from a standard cylinder containing
5 50 to 100 ppmv NO is reacted with O₃ from a stable source. The resultant decrease in NO
6 concentration, usually measured on the NO channel of a chemiluminescence NO_x analyzer,
7 equals the concentration of NO₂ generated. Varying amounts of NO₂ can be produced by
8 varying the amount of O₃.

11 3.6 OZONE AIR QUALITY MODELS

12 To plan control strategies to achieve compliance with the National Ambient Air Quality
13 Standard (NAAQS) for ozone at some future date it is necessary to predict how ozone
14 concentrations change in response to prescribed changes in source emissions of precursor
15 species: the oxides of nitrogen (NO_x) and volatile organic compounds (VOCs). This
16 assessment requires an air quality model, which in the case of ozone prediction is often
17 called a photochemical air quality model. The model in effect is used to determine the
18 emission reductions needed to achieve the ozone air quality standard. For at least a decade,
19 the U.S. Environmental Protection Agency (EPA) has offered guidelines on the selection of
20 air quality modeling techniques for use in State Implementation Plan (SIP) revisions, new
21 source reviews, and studies aimed at the prevention of significant deterioration of air quality.

22 Ozone air quality models provide the ability to address "what if" questions, such as
23 what if emissions of VOCs or NO_x or both are reduced? The model can be used as an
24 experiment that cannot be run in the atmosphere. Sensitivity questions can be asked, such as
25 how important is emissions change A relative to emissions change B, or what is the effect of
26 an X% uncertainty in a certain chemical reaction rate constant on the ozone levels predicted.

27 Models are the ultimate integrators of our knowledge of the comprehensive chemistry
28 and physics of the atmosphere. As such, they are an indispensable tool for understanding the
29 complex interactions of transport, transformation, and removal in the atmosphere. Models
30 assist in the design of field measurement programs and are essential in the interpretation of
31 data from such programs.

1 The purpose of Section 3.6 is to review briefly the main elements of ozone air quality
2 models, to describe several of the current models, to discuss how one evaluates the
3 performance of these models, and to present examples of the use of the models for
4 determining VOC and NO_x control strategies.

6 **3.6.1 Definitions, Description, and Uses**

7 Air quality models are mathematical descriptions of the atmospheric transport,
8 diffusion, removal, and chemical reactions of pollutants. They operate on sets of input data
9 that characterize the emissions, topography, and meteorology of a region and produce outputs
10 that describe air quality in that region. Mathematical models for photochemical air pollution
11 were first developed in the early 1970s and have been improved, applied, and evaluated since
12 that time. Much of the history of the field is described in reviews by Tesche (1983),
13 Seinfeld (1988), and Roth et al. (1989).

14 Photochemical air quality models include treatments of the important physical and
15 chemical processes that contribute to ozone formation in and downwind of urban areas.
16 In particular, such models contain a representation of the following phenomena (Roth et al.,
17 1989):

- 18 • Precursor emissions. The spatial and temporal characteristics of reactive
19 hydrocarbon, carbon monoxide (CO), and NO_x emissions sources must be
20 supplied as inputs to the model. Hydrocarbon emissions are generally
21 apportioned into groups (e.g., alkanes, alkenes, aromatics, etc.) according to the
22 speciation requirements of the chemical kinetic mechanism embedded in the
23 model.
- 24 • Pollutant transport. Once the ozone precursors are emitted into the atmosphere,
25 they are transported by the wind. When ozone is formed, it is also subject to
26 transport by the wind. Grid-based models require the preparation of three-
27 dimensional, time-varying fields of the wind speed and direction. These values
28 must be specified for each grid cell. Cloud venting and cloud mixing processes
29 that are important on the regional scale can also be included in the pollutant
30 transport description.
- 31 • Turbulent diffusion. Ozone and its precursors are also subject to turbulence-
32 related dispersion processes that take place on a subgrid scale. These turbulent
33 diffusion effects are usually represented in grid-based models by the so-called
34 gradient transport hypothesis, where the pollutant flux is assumed to be
35 proportional to the spatial gradient in the concentration field. The turbulent
36 proportional to the spatial gradient in the concentration field. The turbulent
37

diffusivities employed in the model are dependent on atmospheric stability and other meteorological variables.

- Chemical reactions. Ozone results from chemical transformations involving reactive organics and NO_x (See Section 3.2). A chemical kinetics mechanism representing the important reactions that occur in the atmosphere is employed to estimate the net rate of change of each pollutant simulated by the model. Description of chemical reactions requires actinic flux, cloud cover, temperature, and relative humidity.
- Removal processes. Pollutants are removed from the atmosphere via interactions with surfaces at the ground, so-called "dry deposition," and by precipitation, called "wet deposition."

Guidelines issued by U.S. EPA (U.S. Environmental Protection Agency, 1986a) identify two kinds of photochemical model: The grid-based Urban Airshed Model (UAM) is the recommended model for modeling ozone over urban areas and the trajectory model EKMA (empirical kinetics modeling approach) is identified as an acceptable approach. The 1990 Clean Air Act Amendments mandate that three-dimensional, or grid-based, air quality models, such as UAM, be used in SIPs for ozone nonattainment areas designated as extreme, severe, serious, or multistate moderate (U.S. Environmental Protection Agency, 1991b).

3.6.1.1 Grid-Based Models

The basis for grid-based air quality models is the atmospheric diffusion equation, which expresses the conservation of mass of each pollutant in a turbulent fluid in which chemical reactions occur (Seinfeld, 1986). The region to be modeled is bounded on the bottom by the ground, on the top by some height that characterizes the maximum extent of vertical mixing, and on the sides by east-west and north-south boundaries. The choice of the size of the modeling domain will depend on the spatial extent of the ozone problem, including the distribution of emissions in the region, the meteorological conditions, and, to some extent, the computational resources available. This space is then subdivided into a three-dimensional array of grid cells. The horizontal dimensions of each cell are usually a few kilometers for urban applications up to tens of kilometers for regional applications. Some older grid-based models assumed only a single, well-mixed vertical cell extending from the ground to the inversion base; current models subdivide the region into layers. Vertical dimensions can

1 vary, depending on the number of vertical layers and the vertical extent of the region being
2 modeled. A compromise generally must be reached between the better vertical resolution
3 afforded by the use of more vertical layers and the associated increase in computing time.
4 Although aerometric data, such as the vertical temperature profile, that are needed to define
5 the vertical structure of the atmosphere are generally lacking, it is still important to use
6 enough vertical layers so that vertical transport processes are accurately represented.

7 There are practical and theoretical limits to the minimum horizontal grid cell size.
8 Increasing the number of cells increases computing and data acquisition effort and costs.
9 In addition, the choice of the dimension of a grid cell implies that the input data information
10 about winds, turbulence, and emissions, for example, are resolved to that scale. The spatial
11 resolution of the concentrations predicted by a grid-based model corresponds to the size of
12 the grid cell. Thus, effects that have spatial scales smaller than those of the grid cell cannot
13 be resolved. Such effects include the depletion of ozone by reaction with nitric oxide (NO)
14 near strong sources of NO_x like roadways and power plants.

15 Several grid-based photochemical air quality models have been developed to simulate
16 ozone production in urban areas or in larger regions. They differ primarily in their treatment
17 of specific atmospheric processes, such as chemistry, and in the numerical procedures used
18 to solve the governing system of equations. They will be reviewed in Section 3.6.3.

19 20 **3.6.1.2 Trajectory Models**

21 In the trajectory model approach, a hypothetical air parcel moves through the area of
22 interest along a path calculated from wind trajectories. Emissions are injected into the air
23 parcel and undergo vertical mixing and chemical transformations. The data requirements for
24 trajectory models include: (1) initial concentrations of all relevant pollutants and species;
25 (2) rates of emissions of VOC and NO_x precursors into the parcel along its trajectory;
26 (3) meteorological characteristics such as wind speed and direction needed to define the path
27 of the air parcel through the region; (4) mixing depth; and (5) solar ultraviolet radiation.
28 Basic limitations of trajectory models include neglect of horizontal wind shear, and neglect of
29 cell volume changes resulting from convergence and divergence of the wind field (Liu and
30 Seinfeld, 1975).

1 Trajectory models provide a dynamic description of atmospheric source-receptor
2 relationships that is simpler and less expensive to derive than that obtained from grid models.
3 Trajectory models are designed to study the photochemical production of ozone in the
4 presence of sources and vertical diffusion of pollutants; otherwise the meteorological
5 processes are highly simplified.

6 A simple trajectory model is used in the empirical kinetic modeling approach
7 (EKMA)(Dodge, 1977a). This modeling approach relates the maximum level of ozone
8 observed downwind of an urban area to the levels of VOC and NO_x observed in the urban
9 area. It is based on the use of a simple, one-cell moving box model. As the box moves
10 downwind, it encounters emissions of organics and NO_x that are assumed to be uniformly
11 mixed within the box. The height of the box is allowed to expand to account for the breakup
12 of the nocturnal inversion layer. As the height of the box increases, pollutants above the
13 inversion layer are transported into the box. The model is first used to generate a series of
14 constant ozone lines (or isopleths) as depicted in Figure 3-25. The isopleths show the
15 downwind, peak 1-h ozone levels as a function of the concentrations of VOC and NO_x for a
16 hypothetical urban area. These isopleths were generated by carrying out a large number of
17 model simulations in which the initial concentrations and anthropogenic emissions of VOC
18 and NO_x were varied systematically while all other model inputs were held constant. When
19 it was first conceived, EKMA employed a very simple, highly empirical chemical mechanism
20 and the isopleths generated were for a hypothetical situation in Los Angeles.
21 As understanding of the chemical processes responsible for ozone formation increased, the
22 EKMA model was updated to include more complete representations of atmospheric
23 chemistry. Although EKMA has employed the CBM-IV mechanism, the same mechanism
24 that is currently being used in several grid-based models, the most recent version allows the
25 input of any mechanism. The EKMA method is now used to generate city-specific isopleth
26 diagrams using information on emissions, transport, and dilution that are appropriate to the
27 particular city being modeled.

28 City-specific ozone isopleths can be used to estimate the reduction in nonmethane
29 hydrocarbon (NMHC) or NO_x levels, or both, needed to achieve the NAAQS for ozone in a
30 specific urban area. The first step is to determine the early-morning NMHC/ NO_x ratio for
31 the urban area in question and the maximum 1-h downwind O_3 concentration. Both the

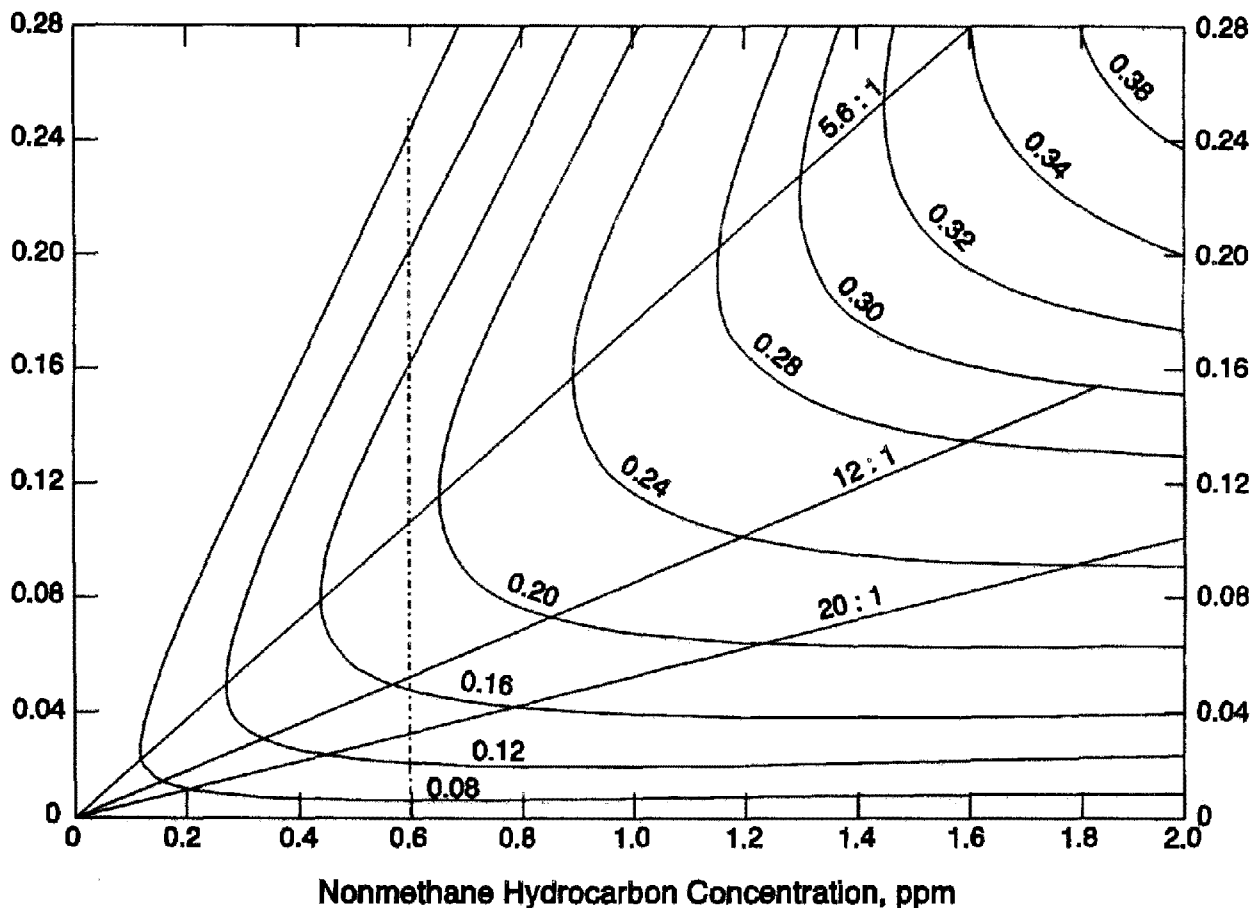


Figure 3-25. Example of EKMA diagram for high-oxidant urban area.

Source: Derived from U.S. Environmental Protection Agency (1986b).

1 NMHC/NO_x ratio and the peak ozone concentration are obtained from air monitoring data.
 2 These two values define a point on the isopleth surface and from this point, the percentage
 3 reductions in NMHC or NO_x, or both, needed to achieve the ozone NAAQS can be
 4 determined.

5 As examination of Figure 3-25 reveals, for an NMHC concentration of 0.6 ppmC, for
 6 example, increasing NO_x leads to increased O₃ until NMHC/NO_x ratios of about 5:1 to 6:1
 7 are reached; further NO_x increases, leading to lower NMHC/NO_x ratios, inhibit
 8 O₃ formation. Thus, in this example, there is a "critical" ratio (in the range of 5:1 to 6:1) at
 9 which the NO_x effect on O₃ changes direction. Besides this "critical" ratio, an "equal
 10 control" NMHC/NO_x ratio also exists, above which the reduction of NO_x is more beneficial

1 in terms of O_3 reduction than an equal percentage reduction in NMHC. This ratio, for the
2 isopleths shown in Figure 3-25, is roughly 8:1 to 9:1 for low levels of control, and as high
3 as 20:1 for the levels of control needed to reduce O_3 to 0.12 ppm. Thus, for this particular
4 case (Figure 3-25), the chemical mechanism modeling evidence suggests that (1) NO_x control
5 will increase the peak downwind O_3 concentration at NMHC/ NO_x ratios of between 5:1 and
6 6:1 or lower; (2) both NO_x control and NMHC control will be beneficial at somewhat higher
7 ratios, with control of NMHC being more effective; and (3) for ratios above 20:1, NO_x
8 control is relatively more effective in reducing O_3 to attain the ozone NAAQS.

9 The EKMA-based method for determining control strategies has some limitations, the
10 most serious of which is that predicted emissions reductions are critically dependent on the
11 initial NMHC/ NO_x ratio used in the calculations. This ratio cannot be determined with any
12 certainty and it is expected to be quite variable in an urban area. Another limitation is that
13 trajectory models have limited spatial and temporal scopes of application. They are generally
14 1-day models, simulating only one cell at a time. Another problem with the use of morning
15 NMHC/ NO_x ratios is the failure to account for photochemical evolution as urban emissions
16 are carried downwind. As demonstrated in simulations by Milford et al. (1989) and in smog
17 chamber studies by Johnson and Quigley (1989), an urban plume that is in the VOC-
18 controlling regime (low NMHC/ NO_x ratio) near city center can move increasingly into the
19 NO_x -controlling regime (high NMHC/ NO_x ratio) as the air parcels age and move downwind.
20 This progression occurs because NO_x is photochemically removed from an aging plume more
21 rapidly than VOC, causing the VOC/ NO_x ratio to increase. As demonstrated by Milford
22 et al. (1989), the implication of this evolution is that different locations in a large urban area
23 can show very different ozone sensitivities to VOC and NO_x changes. Because of this and
24 other drawbacks, the 1990 Clean Air Act Amendments require that grid-based models be
25 used in most ozone nonattainment areas.

26 27 **3.6.2 Model Components**

28 **3.6.2.1 Emissions Inventory**

29 The spatial and temporal characteristics of VOC and NO_x emissions must be supplied
30 as inputs to a photochemical air quality model. Emissions from area and point sources are
31 injected into ground-level grid cells, and emissions from large point sources are injected into

1 upper-level cells. Total VOC emissions are generally apportioned into groups of chemically
2 similar species (e.g., alkanes, alkenes, aromatics, etc.) according to the requirements of the
3 chemical mechanism. This apportionment may be accomplished using actual emission
4 sampling and analysis or be based on studies of similar emission sources. Recognition of
5 potential undercounting in existing inventories has spurred efforts to improve the accuracy of
6 emissions inventories. In fact, at present the emissions inventory is the most rapidly
7 changing component of photochemical models. It has been recognized that both mobile and
8 stationary source components have been highly uncertain, and there is significant ongoing
9 effort to improve the accuracy of emissions inventories.

10 Some emissions terminology is as follows (Tesché, 1992):

- 11 • Emissions data - the primary information used as input to emissions models.
- 12
- 13 • Emissions model - the integrated collection of calculational procedures, or
- 14 algorithms, properly encoded for computer-based computation.
- 15
- 16 • Emissions estimates - the output of emissions models; used as input to
- 17 photochemical models.
- 18
- 19 • Emissions inventory - the aggregated set of emissions estimate files.
- 20
- 21 • Emissions model evaluation - the testing of a model's ability to produce accurate
- 22 emissions estimates over a range of source activity and physicochemical and
- 23 meteorological conditions.

24
25 Emissions input requirements for the UAM, for example, include:

- 26 • Spatial allocation of precursor emissions (VOC, NO_x, CO):
 - 27 — Actual location of individual point sources;
 - 28 — Spatial allocation by gridding surrogates;
 - 29 — Assignment of surrogates to other categories.
- 30
- 31 • Stack parameters for point sources:
 - 32 — Temperature, height, diameter, exit velocity.
- 33
- 34 • Speciation of VOC emissions for CBM-IV mechanism:
 - 35 — Region-specific speciation profiles;
 - 36 — EPA default speciation profiles.
- 37
- 38 • Temporal allocation of precursor emissions:
 - 39 — Operating schedules for individual point sources;
 - 40 — Assignment of diurnal profiles for area and mobile sources.

The emissions inventory component of modeling is moving in the direction of the use of emissions models rather than inventories. Emissions models are being developed for the Lake Michigan Oxidant Study (LMOS) and the San Joaquin Valley Air Quality Study (SJVAQS) and the Atmospheric Utility Signatures, Predictions, and Experiments (AUSPEX), designated as the SJVAQS/AUSPEX Regional Model Adaptation Project (SARMAP) studies. The consistency of existing inventories was improved in 1990 when U.S. EPA released the Emissions Preprocessor System (EPS) as a component of the UAM (U.S. Environmental Protection Agency, 1990d). The EPS was updated in 1992 to EPS Version 2 (EPS2). It is an emissions model that considers spatial and temporal disaggregation factors, speciation data, and meteorological data to convert daily emissions estimates for each point source and for area source categories and mobile source emissions factors computed by the EPA MOBILE5 model into hourly, gridded speciated estimates needed by a photochemical grid model.

A step beyond the EPS is the Emissions Modeling System (EMS) (Tesché, 1992). The EMS¹ utilizes emissions estimation and information processing methods to provide gridded, temporally resolved, and chemically speciated base year emissions estimates for all relevant source categories; to provide flexibility in forecasts of future year emissions rates; and to provide modular code design facilitating module updating and replacement. The EMS provides for easy substitution of alternative assumptions, theories, or input parameters (e.g., emissions factors, activity levels, spatial distributions) and facilitates sensitivity and uncertainty testing.

3.6.2.2 Meteorological Input to Air Quality Models

Grid-based air quality models require, as input, the three-dimensional wind field for the episode being simulated. This input is supplied by a so-called meteorological module. Meteorological modules for constructing wind fields for air quality models fall into one of four categories (Tesché, 1987; Kessler, 1988):

- Objective analysis procedures that interpolate observed surface and aloft wind speed and direction data throughout the modeling domain.

¹The EMS has been renamed the GMEP (Geocoded Model of Emissions and Projections).

- Diagnostic methods in which the mass continuity equation is solved to determine the wind field.
- Dynamic, or prognostic, methods based on numerical solution of the governing equations for mass, momentum, energy, and moisture conservation along with the thermodynamic state equations on a three-dimensional, finite-difference mesh.
- Hybrid methods that embody elements from both diagnostic and prognostic approaches.

3.6.2.2.1 Objective Analysis

Objective wind-field analysis involves the interpolation and extrapolation of wind speed and direction measurements (collected at a number of unequally spaced monitoring stations) to grid points throughout the region (Goodin et al., 1980). For flat terrain settings away from complex mesoscale forcings, this class of techniques may provide an adequate method for estimating the wind field, provided that appropriate weighting and smoothing functions are used (Haltiner, 1971). For complex terrain or coastal-lake environments, however, it is tenuous to interpolate between and extrapolate from surface observational sites except with an unusually dense monitoring network. In most cases, the routinely available rawinsonde network sounding data are even more severely limited because of the large distances (300 to 500 km) between sites and because soundings are made only every 12 h. The limitations of even the best available data sets are most severe above the surface layer, where upper-level observations are less frequent and more expensive to obtain. It will remain economically unfeasible to obtain sufficiently dense atmospheric observations to allow any direct objective analysis scheme to provide the required detail and accuracy necessary for use in advanced, high-resolution photochemical models.

3.6.2.2.2 Diagnostic Modeling

In diagnostic wind modeling, the kinematic details of the flow are estimated by solving the mass conservation equation. Dynamic interactions such as turbulence production and dissipation and the effects of pressure gradients are parameterized. Various diagnostic wind models have been developed, many employing the concepts introduced by Sherman (1978) and Yocke (1981).

1 In recent years, attempts have been made to combine the best features of objective
2 analysis and pure diagnostic wind modeling. The current release of U.S. EPA's UAM-IV
3 includes the Diagnostic Wind Model (DWM) as the suggested wind-field generator for this
4 urban-scale photochemical model. The DWM (U.S. Environmental Protection Agency,
5 1990c) is representative of this class of hybrid objective-diagnostic models. The DWM
6 combines the features of the Complex Terrain Wind Model (CTWM) (Yocke, 1981) and the
7 objective wind interpolation code developed at the California Institute of Technology (Goodin
8 et al., 1980). In the DWM, a two-step procedure is normally followed. First, a
9 "domain-scale" wind is estimated from available surface and upper-air synoptic data. This
10 initial field consists of a single wind vector (e.g., horizontal homogeneity) for each elevation.
11 The domain-scale wind is adjusted using procedures derived from the CTWM for the
12 kinematic effects of terrain such as lifting, blocking, and flow acceleration.
13 Thermodynamically generated influences such as mountain-valley winds are parameterized.
14 This first step produces a horizontally varying field of wind speed and direction for each
15 vertical layer within the DWM modeling domain. Typically, 10 to 12 vertical layers are
16 used. In the second step, available hourly surface and upper air measurements are
17 objectively combined with the step 1 hourly diagnostic flow fields to produce a resultant
18 wind field that matches the observations at the monitoring points and obeys the general
19 constraints of topography in regions where data are absent. The DWM contains a number of
20 user-specified options whereby different final flow fields may be produced, depending upon
21 selection of various smoothing and weighting parameters. The final output of the DWM is a
22 set of hourly averaged horizontal wind fields for each model layer.

23 Diagnostic models may invoke scaling algorithms that propagate the influence of the
24 surface-flow field into upper levels according to the local height of the inversion and the
25 Pasquill-Gifford-Turner stability category for the hour. Once the winds are created by
26 DWM, they must be "mapped" onto the photochemical model's vertical grid structure. This
27 function is normally accomplished in a two-step process. First, the DWM winds are
28 interpolated onto the photochemical model grid using simple linear interpolation. Second,
29 the three-dimensional divergence is computed in each grid cell and an iterative scheme is
30 used to minimize this divergence to a user-specified level. Typically, the output consists of

1 "non-divergent" x- and y-direction wind components for direct input to the photochemical
2 model.

3 Among the advantages of the diagnostic modeling approach are its intuitive appeal and
4 modest computing requirements. The method generally reproduces the observed wind values
5 at the monitoring locations and provides some information on terrain-induced airflows in
6 regions where local observations are absent. In addition, one may calibrate diagnostic model
7 parameters for a particular locale based on site-specific field measurements. However, there
8 are several disadvantages. Diagnostic models cannot represent complex mesoscale
9 circulations, unless these features are well-represented by surface and aloft observations.
10 Often the vertical velocities produced by a diagnostic model are unrealistic and, in regions of
11 complex terrain, local horizontal flow velocities may often be an order of magnitude too high
12 (Tesche et al., 1987). Since the diagnostic model is not time-dependent, there is no inherent
13 dynamic consistency in the winds from one hour to the next. That is, calculation of the flow
14 field at hour 1200, for example, is not influenced by the results of the 1100 hour winds.
15 This is a particular problem in applications involving important flow regimes such as land-
16 sea breezes, mountain-valley winds, eddy circulations, and nocturnal valley jets, that take
17 several hours to develop and whose three-dimensional character is poorly characterized by
18 even the most intensive sampling networks.

19 20 3.6.2.2.3 *Prognostic Modeling*

21 In prognostic meteorological modeling, atmospheric fields are computed based on
22 numerical solutions of the coupled, nonlinear conservation equations of mass, momentum,
23 energy, and moisture. Derivations of these equations are presented extensively in the
24 literature (see, for example, Haltiner, 1971; Pielke, 1984; Seinfeld, 1986; Cotton and
25 Anthes, 1989). Many prognostic models have been developed for computing mesoscale wind
26 fields, as shown in the recent survey by Pielke (1989); and they have been applied to a
27 variety of problems, including the study of land-sea and land-lake circulations. Available
28 prognostic models range from relatively simple one-dimensional representations to complex
29 three-dimensional codes.

30 Prognostic wind models are attractive because they explicitly address the various
31 physical processes governing atmospheric flows. Consequently, they have the potential for

describing a number of wind regimes that are particularly relevant to air pollution modeling, such as flow reversal, daytime upslope flows, wind shear, and other mesoscale thermally induced circulations. Drawbacks of prognostic models include the need to gather detailed data for model performance testing and the large computational costs. Indeed, prognostic models may require as much or more computer time than regional-scale photochemical models. More intensive data sets are needed to evaluate prognostic models than for diagnostic models, but this is not necessarily a disadvantage; rather, it provides the modeler and decision-maker with a far better basis for judging the adequacy of the model than can be achieved with objective or diagnostic models.

Summaries of prognostic models available for use in air quality modeling are presented extensively in the literature (e.g., Pielke, 1989; Benjamin and Seaman, 1985; McNally, 1990; Stauffer et al., 1985; Stauffer and Seaman, 1990; Ulrickson, 1988; Wang and Warner, 1988; and Yamada et al., 1989). From these reviews, two models stand out as representing the present state-of-science in applications-oriented prognostic modeling. These are the Mesoscale Model Versions 4 and 5 (MM4/MM5) developed by Pennsylvania State University and the National Center for Atmospheric Research (NCAR) (Anthes and Warner, 1978; Anthes et al., 1987; Zhang et al., 1986; Seaman, 1990; Stauffer and Seaman, 1990), and the Coast and Lake Regional Atmospheric Modeling System (CAL-RAMS) (Tripoli and Cotton, 1982; Pielke, 1974, 1984, 1989; Lyons et al., 1991).

Two ongoing regional ozone modeling programs in the U.S. (i.e., LMOS and SARMAP) are using prognostic models to drive regional ozone models. Part of the U.S. EPA's long-range plan (in the Office of Research and Development) for model development is to construct a "third" generation modeling framework referred to as MODELS 3 (Dennis, 1991). This modeling system will consolidate all of the agency's three-dimensional models. The current plan calls for meteorological inputs to the MODELS 3 system to be supplied by prognostic models. The MM4 model (the hydrostatic version of MM5) is presently being examined by U.S. EPA for this purpose.

Activities are currently underway in the Lake Michigan Oxidant Study (LMOS) to supply prognostic model fields to U.S. EPA's Regional Oxidant Model (ROM) for use in simulating regional ozone distributions in four multiple-day ozone episodes extensively monitored during the 1991 field program in the midwest. The U.S. EPA will be exercising

1 ROM2.2 (version 2.2) with fields obtained from CAL-RAMS (Lyons et al., 1991) to
2 examine whether prognostic model output gives improved regional ozone estimates (Guinnup
3 and Possiel, 1991).

4 The SARMAP program is the modeling and data analysis component of a multiyear
5 collaboration between two projects, the San Joaquin Valley Air Quality Study (SJVAQS) and
6 the Atmospheric Utility Signatures, Predictions, and Experiments Study (AUSPEX). The
7 major near-term objective of SARMAP is to understand the processes that lead to high ozone
8 concentrations in the San Joaquin Valley of California. An overview of the regional
9 meteorological and air quality modeling approach of SARMAP is described by Tesche
10 (1993). For SARMAP, the MM5 model was chosen as the "platform" prognostic
11 meteorological model because of its broad application history, its demonstrated reliability on
12 large domains requiring spatially and temporally varying boundary conditions, and its
13 capability for four-dimensional data assimilation (FDDA) (see Section 3.6.2.2.4)—needed for
14 longer-range simulations. All of these attributes are crucial to the success of mesoscale
15 meteorological modeling.

16 Prognostic models are believed to provide a dynamically consistent, physically realistic,
17 three-dimensional representation of the wind and other meteorological variables at scales of
18 motion not resolvable by available observations. However, the meteorological fields
19 generated by a prognostic model do not always agree with observational data. Numerical
20 approximations, physical parameterizations, and initialization problems are among the
21 potential sources of error growth in model forecasts that can cause model solutions to deviate
22 from actual atmospheric behavior. Described below are methods that have been devised over
23 the past 20 years to mitigate these problems.

24 "Post-processing" refers to methods whereby output fields from prognostic models are
25 selectively adjusted through a series of objective techniques with the aim of improving the
26 realism of the resultant fields. Examples of this procedure (sometimes referred to as
27 objective combination) are given by Cassmassi et al. (1990) in the Los Angeles Basin,
28 Kessler and Douglas (1989) in the South Central Coast Air Basin, and Moore et al. (1987) in
29 the San Joaquin Valley.

30 Ideally, a prognostic model should be initialized with spatially varying, three-
31 dimensional fields (i.e., wind, temperature, moisture) that represent the state of the

1 atmosphere at the initial simulation time. A prognostic model that is initialized with such
2 fields, however, can generate large non-meteorological "waves" when the initial conditions
3 do not contain a dynamic balance consistent with the model formulation (Hoke and Anthes,
4 1976; Errico and Bates, 1988). The objective of an initialization procedure is to bring the
5 initial conditions into dynamic balance so that the model can integrate forward with a
6 minimum of noise and a maximum of accuracy (Haltiner and Williams, 1980). Dynamic
7 initialization makes use of a model's inherent adjustment mechanism to bring the wind and
8 temperature into balance prior to the initial simulation time. In this technique, a
9 "pre-simulation" integration of the model equations produces a set of dynamically balanced
10 initial conditions. By allowing the simulation to begin with a balanced initial state, this
11 technique reduces the generation of meteorological noise and thus improves the quality of the
12 simulation.

13 14 **3.6.2.2.4 Four-Dimensional Data-Assimilation Techniques**

15 Four Dimensional Data Assimilation (FDDA) refers to a class of procedures in which
16 observational data are used to enhance the quality of meteorological model predictions
17 (Harms et al., 1992). The most common use of FDDA today in applications-oriented models
18 is known as Newtonian relaxation, or simply as "nudging". With this method, model
19 estimates at a particular time interval are adjusted toward the observations by adding artificial
20 tendency terms to the governing prognostic equations. The objective of this method is to
21 improve prognostic model estimates through the use of valid, representative observational
22 data. As an example of this procedure, a linear term is added to the momentum equations to
23 "nudge" the dynamic calculation towards the observed state at each time step in regions
24 where data are available. The FDDA procedures may be thought of as the joint use of a
25 dynamic meteorological model in conjunction with observed data (or analysis fields based on
26 these data) in such a manner that the prognostic equations provide temporal continuity and
27 dynamic coupling of the hourly fields of monitored data (Seaman, 1990).

28 A recent example of the use of FDDA in regional-scale applications with the
29 MM4/RADM model is given by Stauffer and Seaman (1990). Attempts to apply FDDA in
30 support of urban-scale photochemical grid modeling are described by Tesche et al. (1990b)
31 and McNally (1990) for the San Diego Air Basin and by Stauffer et al. (1993) for the Grand

1 Canyon region of Arizona. Currently, FDDA is being used in the CAL-RAMS simulations
2 in the LMOS program (Lyons et al., 1991) and in the MM5 simulations for SARMAP
3 (Seaman, 1992).
4

5 **3.6.2.3 Chemical Mechanisms**

6 A chemical kinetic mechanism (a set of chemical reactions), representing the important
7 reactions that occur in the atmosphere, is used in an air quality model to estimate the net rate
8 of formation of each pollutant simulated as a function of time.

9 Various grid models employ different chemical mechanisms. Because so many VOCs
10 participate in atmospheric chemical reactions, chemical mechanisms that explicitly treat each
11 individual VOC component are too lengthy to be incorporated into three-dimensional
12 atmospheric models. Lumped mechanisms are therefore used (e.g., Lurmann et al., 1986;
13 Gery et al., 1989; Carter, 1990; Stockwell et al., 1990). These lumped mechanisms are
14 highly condensed and do not have the ability to follow explicit chemistry because of this
15 lumping. Lumped-molecule mechanisms group VOCs by chemical classes (alkanes, alkenes,
16 aromatics, etc.). Lumped-structure mechanisms group VOCs according to carbon structures
17 within molecules. In both cases, either a generalized (hypothetical) or surrogate (actual)
18 species represents all species within a class. Organic product and radical chemistry is limited
19 to a few generic compounds to represent all products; thus, chemistry after the first oxidation
20 step is overly uniform. Some mechanisms do not conserve carbon and nitrogen mass. Some
21 molecules do not easily "fit" the classes used in the reduced mechanisms. Because different
22 chemical mechanisms follow different approaches to "lumping," and because the developers
23 of the mechanisms made different assumptions about how to represent chemical processes
24 that are not well understood, models can produce somewhat different results under similar
25 conditions (Dodge, 1989).

26 No single chemical mechanism is currently considered "best." Both UAM-IV and
27 ROM utilize the CBM-IV mechanism, which, along with the SAPRC (Statewide Air
28 Pollution Research Center, University of California, Riverside) and RADM mechanisms, is
29 considered to represent the state-of-the-science (Tesché et al., 1992; National Research
30 Council, 1991). Agreement among mechanisms is better for ozone than for other secondary
31 pollutants (Dodge, 1989, 1990; National Research Council, 1991), raising concern that the

1 mechanisms may suffer from compensating errors. These mechanisms are at least 5 years
2 old and often tested on much older smog chamber data.

3 The chemical mechanisms used in existing photochemical ozone models contain
4 uncertainties that may limit the accuracy of their predictions. The reactions that are included
5 in these mechanisms generally fall into one of three categories:

- 6 (1) Reactions for which the magnitude of their rate constants and their product
7 distribution is well known. These include mostly the inorganic reactions and
8 those for the simple carbonyls.
9
- 10 (2) Reactions with known rate constants and known products but uncertain product
11 yields. These are mostly organic reactions, and the actual product yields
12 assumed may vary among mechanisms.
13
- 14 (3) Reactions with known rate constants but unknown products. Each mechanism
15 assumes its own set of products for reactions in this class. This class includes
16 aromatic oxidation reactions.

17
18 Most inorganic gas-phase processes are understood. Regarding classes of VOCs the
19 following general comments can be made:

- 20 • Unbranched alkanes comprise approximately one-half of the carbon emissions in
21 urban areas. Reaction rates are relatively slow. The only important reaction is
22 with the hydroxyl radical. For alkanes C4 or below, the chemistry is well
23 understood and the reaction rates are slow. For C5 and higher alkanes the
24 situation is more complex because few reaction products have been found.
25
- 26 • Branched alkanes have rates of reaction that are highly dependent on structure.
27 Rate constants have been measured for only a few of the branched alkanes and
28 reaction products for this class of organics are not well characterized.
29
- 30 • Alkenes are highly reactive with hydroxyl, ozone, and the NO_3 radical. Most
31 rate constants of these reactions are known. Alkenes make up about 15% of the
32 emitted carbon and constitute about 20% of the hydrocarbon reactions in urban
33 areas. Ozone reaction products are not well characterized, and the mechanisms
34 are poorly understood. Mechanisms for the NO_3 radical are also uncertain.
35
- 36 • Aromatics constitute about 15% of the carbon compounds emitted and 20% of
37 the hydrocarbons reacting in urban areas. Aromatics have been frequently
38 studied, but only a few reaction products have been well characterized.
39 Aromatics act as strong NO_x sinks under low NO_x conditions.
40

41 Mechanisms used in photochemical air quality models thus have uncertainties, largely
42 attributable to a lack of fundamental data on products and product yields. The missing

1 information necessitates that assumptions be made. Current mechanisms provide acceptable
2 overall simulation of ozone generation in smog chamber experiments. Specific VOCs may,
3 however, be simulated poorly, and products other than ozone may not be accurately
4 simulated. Existing mechanisms are mostly applicable to single-day, high NO_x conditions
5 because those are the conditions of almost all smog chamber experiments. Low NO_x
6 condition simulations are less well verified. Fundamental kinetic data are needed on the
7 photooxidation of aromatics, higher alkanes, and higher alkenes to fill in areas of uncertainty
8 in current mechanisms. Whereas these uncertainties are important and require continued
9 research to remove, the uncertainties are likely not such that general conclusions about the
10 relative roles of hydrocarbons and NO_x in ozone formation will be changed by new data.

11 12 **3.6.2.4 Deposition Processes**

13 Species are removed from the atmosphere by interaction with ground-level surfaces,
14 so-called dry deposition; and by absorption into airborne water droplets followed by transport
15 of the water droplets, wet deposition. Dry deposition is an important removal process for
16 ozone and other species on both the urban and regional scales and is included in all urban-
17 and regional-scale models as a contribution to the ground-level flux of pollutants. Wet
18 deposition is a key removal process for gaseous species on the regional scale and is included
19 in regional scale acid deposition models. Urban-scale photochemical models have generally
20 not included a treatment of wet deposition as ozone episodes do not occur during periods of
21 significant clouds or rain.

22 23 **3.6.2.4.1 Dry Deposition**

24 It is generally impractical to simulate, in explicit detail, the complex of multiple
25 physical and chemical pathways that result in dry deposition to individual surface elements.
26 Because of this, the usual practice has been to adopt simple parameterizations that consolidate
27 the multitude of complex processes. For example, it is generally assumed that the dry
28 deposition flux is proportional to the local pollutant concentration [at a known reference
29 height (z_r), typically 10 m], resulting in the expression $F = -v_d C$, where F represents the
30 dry deposition flux (the amount of pollutant depositing to a unit surface area per unit time)

1 and C is the local pollutant concentration at the reference height. The proportionality
2 constant, v_d , has units of length per unit time and is known as the deposition velocity.

3 It is customary to interpret the dry deposition process in terms of the electrical
4 resistance analogy, where transport of material to the surface is assumed to be governed by
5 three resistances in series: the aerodynamic resistance (r_a), the quasi-laminar layer resistance
6 (r_b), and the surface or canopy resistance (r_s) (Wu et al., 1992). The aerodynamic resistance
7 characterizes the turbulent transport through the atmosphere from reference height z_r down to
8 a thin layer of stagnant air very near the surface. The molecular-scale diffusive transport
9 across the thin quasi-laminar sublayer near the surface is characterized by r_b . The chemical
10 interaction between the surface and the pollutant of interest once the gas molecules have
11 reached the surface is characterized by r_c . The total resistance (r_t) is the sum of the three
12 individual resistances, and is, by definition, the inverse of the deposition velocity,
13 $1/v_d = r_t = r_a + r_b + r_s$. Note that the deposition velocity is small when any one of the
14 resistances is large. Hence, either meteorological factors or the chemical interactions on the
15 surface can govern the rate of dry deposition.

16 Dry deposition velocities of HNO_3 and SO_2 are typically $\approx 2 \text{ cm s}^{-1}$, and those of
17 O_3 and peroxyacetyl nitrate (PAN) are generally approximately 0.5 cm s^{-1} and $\approx 1 \text{ cm s}^{-1}$,
18 respectively (see, for example, Dolske and Gatz, 1985; Colbeck and Harrison, 1985; Huebert
19 and Robert, 1985; Shepson et al., 1992). With a 1-km-deep inversion or boundary layer, the
20 time-scale for dry deposition is of the order of 1 day for a deposition velocity of 1 cm s^{-1} ,
21 and dry deposition is important for those chemicals with high or fairly high deposition
22 velocities and long or fairly long lifetimes (≥ 10 days) due to photolysis and chemical
23 reaction (for example, HNO_3 , SO_2 , and H_2O_2 , as well as O_3 and PAN).

24 A number of researchers have reviewed the deposition literature and provided
25 summaries of deposition velocity data. The rank ordering of deposition velocity values
26 among pollutant species based on several such studies is summarized as follows:

27 McRae and Russell (1984):

28 $\text{HNO}_3 > \text{SO}_2 > \text{NO}_2 \approx \text{O}_3 > \text{PAN} > \text{NO}$

29 Derwent and Hov (1988):

30 $\text{HNO}_3 > \text{SO}_2 = \text{O}_3 > \text{NO}_2 > \text{PAN}$

1 McRae et al. (1982b):

2 $O_3 > NO_2 > PAN > NO > CO$

3 Chang et al. (1987):

4 $HNO_3 > H_2O_2 > NH_3 > HCHO > O_3 = SO_2 = NO_2 = NO > RCHO$

5
6 There is general agreement that HNO_3 is removed at the highest observed rates, which
7 is consistent with the relative deposition rates observed by Huebert and Robert (1985) and
8 which suggests that the surface resistance of HNO_3 is essentially zero. Most of the surveys
9 are roughly consistent with the relative deposition velocity ordering seen in the experiments
10 of Hill and Chamberlain (1976): diffusion-limited acids $> SO_2 > NO_2 \approx O_3 > PAN >$
11 $NO > CO$. This suggests surface resistance values should be ordered approximately as:
12 $CO > NO > PAN > O_3 \approx NO_2 > SO_2 > HNO_3 = 0$.

13 There are a significant number of other gases for which there are no surface resistance
14 data and for which values must be estimated using engineering judgment. The values should
15 be consistent with the existing experimental values for vegetative surfaces, and should
16 preserve the apparent rank ordering among the pollutant species (discussed above). For
17 ozone, surface resistance values by land-use type and season recommended by Sheih et al.
18 (1986) and Wesely (1988) are appropriate. For NO , NO_2 , NH_3 , H_2O_2 , $HCHO$, and
19 CH_3CHO , the surface resistance values for each land use can be estimated from that for SO_2
20 (Wesely, 1988), except that different proportionality factors should be used for NO and NO_2 .

21 22 **3.6.2.4.2 Wet Deposition**

23 Wet deposition refers to the removal of gases and particles from the atmosphere by
24 precipitation events, through incorporation of gases and particles into rain, cloud, and fog
25 water followed by precipitation at the earth's surface. Removal of gases and particles during
26 snow falls is also wet deposition. Wet removal of gases arises from equilibrium partitioning
27 of the chemical between the gas and aqueous phases (Bidleman, 1988; Mackay, 1991). This
28 partitioning can be defined by means of a washout ratio, Wg , with $Wg = [C]_{rain}/[C]_{air}$,
29 where $[C]_{rain}$ and $[C]_{air}$ are the concentrations of the chemical in the aqueous and gas
30 phases, respectively. Since Wg is the inverse of the air/water partition coefficient, K_{aw} , then

1 (Mackay, 1991) $W_g = RT/H$, where R is the gas constant, T is the temperature, and H is the
2 Henry's Law Constant.

3 Particles, and particle-associated chemicals, are efficiently removed from the
4 atmosphere by precipitation events, and the washout ratios for particles, W_p , are typically in
5 the range 10^4 - 10^6 (Eisenreich et al., 1981; Bidleman, 1988). Wet deposition is important for
6 particles (and particle-associated chemicals) and for those gas-phase compounds with washout
7 ratios of $W_g \geq 10^4$. Examples of such gaseous chemicals are HNO_3 , H_2O_2 , phenol, and
8 cresols, all of which are highly soluble in water. Formaldehyde is present in the aqueous
9 phase as the glycol, $\text{H}_2\text{C}(\text{OH})_2$, and has an effective washout ratio of 7×10^3 at 298 K
10 (Betterton and Hoffmann, 1988; Zhou and Mopper, 1990). Note that the importance of wet
11 deposition may depend on whether the chemical is present in the gas phase or is particle-
12 associated. For example, the gas-phase alkanes have low values of W_g and are inefficiently
13 removed by wet deposition, while the particle-associated alkanes are efficiently removed by
14 wet deposition (Bidleman, 1988), through removal of the host particles.

15 16 **3.6.2.5 Boundary and Initial Conditions**

17 When a grid-based photochemical model is applied to simulate a past pollution episode,
18 it is necessary to specify the concentration fields of all the species computed by the model at
19 the beginning of the simulation. These concentration fields are called the initial conditions.
20 Throughout the simulation it is necessary to specify the species concentrations, called the
21 boundary conditions, in the air entering the three-dimensional geographic domain.

22 Three general approaches for specifying boundary conditions for urban-scale
23 applications can be identified: (1) Use the output from a regional-scale photochemical
24 model; (2) use objective or interpolative techniques with ambient observational data; or,
25 (3) for urban areas sufficiently isolated from significant upwind sources, use default regional
26 background values and expand the area that is modeled.

27 In the ideal case, observed data would provide information about the concentrations for
28 all the predicted species at the model's boundaries. An alternative approach is to use
29 regional models to set boundary and initial conditions. This is, in fact, preferred when
30 changes in these conditions are to be forecast. In any event, simulation studies should use
31 boundaries that are far enough from the major source areas of the region that concentrations

1 approaching regional values can be used for the upwind boundary conditions. Boundary
2 conditions at the top of the area that is being modeled should use measurements taken from
3 aloft whenever they are available. Regional background values are often used in lieu of
4 measurements. An emerging technique for specifying boundary conditions is the use of a
5 nested grid, in which concentrations from a larger, coarse grid are used as boundary
6 conditions for a smaller, nested grid with finer resolution. This technique reduces
7 computational requirements compared to those of a single-size, fine-resolution grid.

8 Initial conditions are determined mainly with ambient measurements, either from
9 routinely collected data or from special studies. Where spatial coverage with data is sparse,
10 interpolation can be used to distribute the surface ambient measurements. Because few
11 measurements of air quality data are made aloft, it is generally assumed that species
12 concentrations are initially uniform in the mixed layer and above it. To ensure that the
13 initial conditions do not dominate the performance statistics, model performance should not
14 be assessed until the effects of the initial conditions have been swept out of the grid.

16 3.6.3 Urban and Regional Ozone Air Quality Models

17 Grid-based models that have been widely used to evaluate ozone and acid deposition
18 control strategies are:

- 19 • The Urban Airshed Model (UAM), developed by Systems Applications, Inc., has
20 been, and is continuing to be, applied to urban areas throughout the country.
21 It is described in Section 3.6.3.1. The current U.S. EPA-approved version is
22 UAM-IV. The UAM-V, which has been developed for the Lake Michigan
23 Oxidant Study (LMOS), is a nested regional-scale model.
- 24
25 • The California Institute of Technology/Carnegie Institute of Technology (CIT)
26 model has been applied to California's South Coast Air Basin (McRae et al.,
27 1982a,b; McRae and Seinfeld, 1983; Milford et al., 1989; Harley et al., 1993).
- 28
29 • The Regional Oxidant Model (ROM), developed by U.S. EPA, has been applied
30 to the northeastern and southeastern United States (Schere and Wayland,
31 1989a,b). It is described in Section 3.6.3.2.
- 32
33 • The Acid Deposition and Oxidant Model (ADOM) was developed by ENSR
34 Consulting and Engineering for the Ontario Ministry of the Environment and
35 Environment Canada (Venkatram et al., 1988) and the German
36 Umweltbundersamdt. Its primary application has been to acidic deposition.
- 37

- The Regional Acid Deposition Model (RADM) was developed by the National Center for Atmospheric Research (NCAR) and the State University of New York for the National Acid Precipitation Assessment Program (NAPAP). The primary objective of RADM applications is the calculation of changes in sulfur and nitrogen deposition over the eastern United States and southeastern Canada resulting from changes in emissions (National Acid Precipitation Assessment Program, 1989). See Section 3.6.3.3 for a description of RADM.

A summary of the major applications of the above air quality models, including the Sulfur Transport Eulerian Model (STEM-II), is presented in Table 3-21. All of the models are nominally based on a 1-h time resolution. The horizontal spatial resolutions vary from 5 to 120 km. Typical spatial resolutions used in past model applications are summarized in Table 3-22. It is important to note that the spatial scale at which a model is applied is governed by the manner in which physical processes are treated and the spatial scale of the inputs. The regional models can have a vertical resolution on the order of 10 to 15 layers extending up to 6 to 10 km in order to treat vertical redistribution of species above the planetary boundary layer. This increased vertical resolution often comes at the expense of decreased horizontal resolution. Urban models typically have two to five layers extending up to 1,000 to 2,000 m. The treatment of meteorological fields by the six models is summarized in Table 3-23. Generally the treatment of meteorology is separate from the air quality model itself, and models can employ wind fields prepared by different approaches as long as consistent assumptions, such as non-divergent wind field, are employed in each model. The regional models, ROM, RADM, ADOM, and STEM-II, treat the vertical redistribution of pollutants resulting from the presence of cumulus clouds. Table 3-24 summarizes the gas-phase chemical mechanisms incorporated into the six models. Generally three chemical mechanisms are used in the models: (1) CBM-IV used in ROM and UAM; (2) versions of the SAPRC mechanism used in ADOM, STEM-II, and CIT; and (3) the RADM mechanism. Of the three chemical mechanisms, RADM is the largest and CBM-IV is the smallest. Aqueous-phase chemistry is currently treated only in the regional models. Cloud processes are treated in the three regional models, RADM, ADOM, and STEM-II (Table 3-25). Cumulus venting and solar attenuation are treated in ROM. Layer 3 depths are also influenced by cloud thickness. At present, only RADM, ADOM and STEM-II treat wet deposition. The treatment of dry deposition in the models is also summarized in Table 3-25.

**TABLE 3-21. GRID-BASED URBAN AND REGIONAL AIR POLLUTION MODELS:
OVERVIEW OF THREE-DIMENSIONAL AIR QUALITY MODELS**

Model	Major Applications	Major References for Model Formulation	Selected References for Model Performance Evaluation and Application
UAM	Urban and nonurban areas in the United States and Europe	Reynolds et al. (1973, 1974, 1979) Teschke et al. (1992) U.S. Environmental Protection Agency (1990a-e) Scheffe and Morris (1993)	Teschke et al. (1992)
CIT	Los Angeles Basin	McRae et al. (1982a)	McRae and Seinfeld (1983) Russell et al. (1988a,b) Harley et al. (1993)
ROM	Eastern United States (E of 99° W longitude)	Lamb (1983)	Schere and Wayland (1989a,b) Meyer et al. (1991)
RADM	Eastern North America	Chang et al. (1987)	Middleton et al. (1988, 1993) Middleton and Chang (1990) Dennis et al. (1993a) Cohn and Dennis (1994)
ADOM	Eastern North America and Northern Europe	Venkatram et al. (1988)	Venkatram et al. (1988) Macdonald et al. (1993) Karamchandani and Venkatram (1992)
STEM-II	Philadelphia area, Kentucky, and northeastern United States, central Japan	Carmichael et al. (1986)	Carmichael et al. (1991) Saylor et al. (1991)

**TABLE 3-22. GRID-BASED URBAN AND REGIONAL AIR POLLUTION MODELS:
TREATMENT OF EMISSIONS AND SPATIAL RESOLUTION**

Model	Emitted Species	Point-Source Emissions	Area-Source Emissions	Vertical Resolution
UAM	SO ₂ , sulfate, NO, NO ₂ , CO, NH ₃ , and 8 classes of ROG and PM(4 size classes)	Released into grid cell in layer corresponding to plume rise in UAM; treated with a reactive plume model in PARIS	Grid-average with resolution ranging from 4 km × 4 km to 10 km × 10 km in past applications	Typically, 5-6 layers up to about 1.5 km
CIT	SO ₂ , sulfate, NO, NO ₂ , CO, NH ₃ , and 6 classes of ROG and PM(4 size classes)	Treated with a plume model with simple NO _x and O ₃ chemistry	Grid-average with 5 km × 5 km resolution in past applications	Five layers up to about 1.5 km
ROM	CO, NO, NO ₂ , and 8 classes of ROG	Released into grid cell in layer corresponding to plume rise	Grid-average with 18.5 km × 18.5 km resolution in present applications	Three layers up to about 4 km
RADM	SO ₂ , sulfate, NO, NO ₂ , CO, NH ₃ , and 12 classes of ROG	Released into grid cell in layer corresponding to plume rise	Grid-average with 80 km × 80 km resolution in past applications	Fifteen layers up to about 16 km
ADOM	SO ₂ , sulfate, NO, NO ₂ , NH ₃ , and 8 classes of ROG and PM	Released into grid cell in layer corresponding to plume rise	Grid-average with resolution ranging from 60 km × 60 km to about 120 km × 120 km in past applications	Twelve layers up to about 10 km
STEM-II	SO ₂ , sulfate, NO, NO ₂ , NH ₃ , and 8 classes of ROG	Released into grid cell in layer corresponding to plume rise	Grid-average with resolution ranging from 10 km × 10 km to 56 km × 56 km in past applications	Ten to 14 layers up to about 6 km

**TABLE 3-23. GRID-BASED URBAN AND REGIONAL AIR POLLUTION MODELS:
TREATMENT OF METEOROLOGICAL FIELDS, TRANSPORT AND DISPERSION**

Model	Meteorology	Transport	Turbulent Diffusion
UAM	Constructed through data interpolation or calculated with land-sea breeze or complex terrain wind model.	3-D wind field. Finite difference numerical technique.	Vertical turbulent diffusion function of atmospheric stability and friction velocity. Constant horizontal turbulent diffusion coefficient.
CIT	Constructed through data interpolation with diagnostic wind model	3-D wind field. Finite element numerical technique.	Vertical turbulent diffusion function of atmospheric stability and friction velocity. Horizontal turbulent diffusion function of mixing height and convective velocity scale.
ROM	Constructed through data interpolation.	3-D wind field with vertical transport through cumulus clouds. Finite difference numerical technique.	Vertical turbulent diffusion function of atmospheric stability. Horizontal turbulent diffusion function of atmospheric stability, convective cloud cover and velocity scale, and the depths of the boundary layer and clouds.
RADM	Calculated with Community Climate Model (CCM) and MM4	3-D wind field with vertical transport through cumulus clouds. Finite difference numerical technique	Vertical turbulent diffusion function of atmospheric stability and wind shear. No horizontal turbulent diffusion.
ADOM	Constructed through data interpolation in combination with prognostic planetary boundary-layer model.	3-D wind field with vertical transport through cumulus clouds. Cubic spline numerical technique.	Vertical turbulent diffusion calculated from planetary boundary layer model. No horizontal turbulent diffusion.
STEM-II	Calculated with dynamic wind model (MASS) or constructed through data interpolation.	3-D wind field with vertical transport through clouds. Finite element numerical technique.	Vertical turbulent diffusion function of atmospheric stability and surface roughness. Horizontal turbulent diffusion proportional to vertical turbulent diffusion.

**TABLE 3-24. GRID-BASED URBAN AND REGIONAL AIR POLLUTION MODELS:
TREATMENT OF CHEMICAL PROCESSES**

Model	Gas-Phase Chemistry	Aqueous- Phase Chemistry
UAM	Eighty-seven reactions among 36 species including NO _x , O ₃ , ROG, and SO ₂ (CBM-IV) (Gery et al., 1988, 1989)	No treatment of aqueous-phase chemistry.
CIT	One hundred-twelve reactions among 53 species including NO _x , O ₃ , ROG, and SO ₂ (Lurmann et al., 1986)	No treatment of aqueous-phase chemistry.
ROM	Eighty-seven reactions among 36 species including NO _x , O ₃ , ROG, and SO ₂ (CBM-IV)	No treatment of aqueous-phase chemistry.
RADM	One hundred fifty-seven reactions among 59 species including NO _x , O ₃ , ROG, and SO ₂ (Stockwell et al., 1990)	Forty-two equilibria and five reactions for SO ₂ oxidation.
ADOM	One hundred-twelve reactions among 53 species including NO _x , O ₃ , ROG, and SO ₂ (Lurmann et al., 1986)	Fourteen equilibria and five reactions for SO ₂ oxidation
STEM-II	One hundred-twelve reactions among 53 species including NO _x , O ₃ , ROG, and SO ₂ (Lurmann et al., 1986)	Twenty-six equilibria and about 30 reactions for SO ₂ and NO _x oxidation, radical chemistry, and transition metal chemistry.

**TABLE 3-25. GRID-BASED URBAN AND REGIONAL AIR POLLUTION MODELS:
TREATMENT OF CLOUD AND DEPOSITION PROCESSES**

Model	Cloud Processes	Wet Deposition	Dry Deposition
UAM	No treatment of cloud processes.	No treatment of wet deposition	Dry deposition velocity approach; function of wind speed, friction velocity, land type, and species.
CIT	No treatment of cloud processes.	No treatment of wet deposition.	Dry deposition velocity approach; function of atmospheric stability, wind speed, land type, and species.
ROM	No treatment of cloud processes, except vertical transport treatment.	No treatment of wet deposition	Resistance transfer approach; function of land type, wind speed, atmospheric stability, and species.
RADM	Treatment of (1) precipitating cumulus clouds, (2) precipitating stratus clouds and (3) fair-weather cumulus clouds based on precipitation amount, temperature, and relative humidity vertical profiles. Use of cloud-averaged properties for aqueous chemistry.	Calculated from precipitation rate and cloud average chemical composition. No below-cloud scavenging.	Resistance transfer approach; function of atmospheric stability, wind speed, season, land type, insolation, surface wetness, and species.
ADOM	Treatment of (1) cumulus clouds and (2) stratus clouds based on precipitation amount (for stratus clouds), temperature, and relative humidity vertical profiles. Vertical resolution for cloud chemistry.	Calculated from precipitation rate and vertically weighted cloud average chemical composition, below-cloud scavenging included.	Resistance transfer approach; function of atmospheric stability, wind speed, land type, season, insolation, and species.
STEM-II	Treatment of clouds with the Advanced Scavenging Module based on cloud base height, precipitation rate, and surface temperature.	Calculated with the Advanced Scavenging Module. Treats cloud water, rain water, and snow; below-cloud scavenging included.	Resistance transfer approach; function of atmospheric stability, land type, wind speed, and species.

More detailed descriptions will now be presented for UAM, ROM, and RADM. The UAM is described as it is officially specified by EPA as a grid-based model for urban-scale ozone control strategy determination. Its regional-scale ozone model, ROM is being used by U.S. EPA to evaluate ozone control measures for the eastern United States and to provide boundary conditions for urban area simulations using UAM. Representative of a comprehensive state-of-the-science ozone/acid deposition model, RADM has been used to evaluate combined ozone and acid deposition abatement strategies for the northeastern United States and Canada.

The U.S. Environmental Protection Agency is embarking on a project to produce the next generation of photochemical models, termed MODELS 3 (Dennis et al., 1993b). This group of models will be flexible (scalable grid and domain), will be modular (modules with interchangeable data structure), will have uniform input/output across subsystems, and will contain advanced analysis and visualization features. The models will be designed to take advantage of the latest advances in computer architecture and software.

3.6.3.1 The Urban Airshed Model

The UAM is the most widely applied and broadly tested grid-based photochemical air quality model. The model is described in a number of sources, including a multi-volume series of documents issued by the U.S. Environmental Protection Agency (U.S. Environmental Protection Agency, 1990a,b,c,d,e) and a comprehensive evaluation by Tesche et al. (1992). Current versions include provisions enabling the user to model transport and dispersion within both the mixed and inversion layers. The computer codes have been structured to allow inclusion of up to 10 vertical layers of cells and any number of cells in the horizontal directions.

The original UAM developed by Reynolds et al. (1973) simulated the dynamic behavior of six pollutants: reactive and unreactive hydrocarbons, NO, NO₂, ozone, and CO. Since 1977, the UAM has employed various versions of the Carbon-Bond Mechanism. Currently, the model utilizes the CBM-IV Mechanism (Gery et al., 1988, 1989), which treats 36 reacting species. Reactive organic compounds include alkanes, alkenes, aromatics, and aldehydes; while nitrogen-bearing species include nitrous acid (HONO), nitric acid (HNO₃), and peroxyacetyl nitrate (PAN).

3.6.3.2 The Regional Oxidant Model

The ROM was designed to simulate most of the important chemical and physical processes that are responsible for the photochemical production of O₃ over regional domains and for multiple 3-day episodes of up to 15 days in duration. These processes include (1) horizontal transport, (2) atmospheric chemistry and subgrid-scale chemical processes, (3) nighttime wind shear and turbulence associated with the low-level nocturnal jet, (4) the effects of cumulus clouds on vertical mass transport and photochemical reaction rates, (5) mesoscale vertical motions induced by terrain and the large-scale flow, (6) terrain effects on advection, diffusion, and deposition, (7) emissions of natural and anthropogenic ozone precursors, and (8) dry deposition. The processes are mathematically simulated in a three-dimensional Eulerian model with three vertical layers, including the boundary layer and the capping inversion or cloud layer. The ROM geographical domains are summarized in Table 3-26 and illustrated in Figure 3-26.

Meteorological data are used to objectively model regional winds and diffusion. The top three model layers of ROM are prognostic (predictive) and are free to locally expand and contract in response to changes in the physical processes occurring within them. During an entire simulation period, horizontal advection and diffusion and gas-phase chemistry are modeled in the upper three layers. Predictions from layer 1 are used as surrogates for surface concentrations. Layers 1 and 2 model the depth of the well-mixed layer during the day. Some special features of layer 1 include the modeling of (1) the substantial wind shear that can exist in the lowest few hundred meters above ground in local areas where strong winds exist and the surface heat flux is weak; (2) the thermal internal boundary layer that often exists over large lakes or near sea coasts; and (3) deposition onto terrain features that protrude above the layer. At night, layer 2 represents what remains of the daytime mixed layer. As stable layers form near the ground and suppress turbulent vertical mixing, a nocturnal jet forms above the stable layer and can transport aged pollutant products and reactants considerable distances. At night, emissions from tall stacks and warm cities are injected directly into layers 1 and 2. Surface emissions are specified as a mass flux through the bottom of layer 1. During the day, the top model layer, layer 3, represents the synoptic-scale subsidence inversion characteristic of high ozone-concentration periods; the base of layer 3 is typically 1 to 2 km above the ground. Relatively clean tropospheric air is assumed

TABLE 3-26. REGIONAL OXIDANT MODEL GEOGRAPHICAL DOMAINS

GENERAL INFORMATION:

ROM grid cells are 1/4° longitude and 1/6° latitude in size or approximately 18.5 km. Actual domain names are included in parenthesis after the general geographical description. In addition, all domains can be run independently or windowed from the "super" domain.

SUPER DOMAIN (SUPROXA)

99.00 W to 67.00 W Longitude
26.00 N to 47.00 N Latitude
128 × 126 Grid Cells (columns × rows)

NORTHEAST DOMAIN (NEROXA)

89.00 W to 67.00 W Longitude
35.00 N to 47.00 N Latitude
88 × 72 Grid Cells (columns × rows)

MIDWEST DOMAIN (MIDROXA)

97.00 W to 78.00 W Longitude
35.00 N to 47.00 N Latitude
76 × 72 Grid Cells (columns × rows)

SOUTHEAST DOMAIN (SEROXA)

98.75 W to 76.25 W Longitude
27.67 N to 37.67 N Latitude
90 × 60 Grid Cells (columns × rows)

SOUTHERN DOMAIN (TEXROXA)

99.00 W to 81.00 W Longitude
26.00 N to 37.67 N Latitude
72 × 70 Grid Cells (columns × rows)

NORTHEAST DOMAIN (ROMNET)

85.00 W to 69.00 W Longitude
36.33 N to 45.00 N Latitude
64 × 52 Grid Cells (columns × rows)

NORTHEAST DOMAIN (NEROS1)

84.00 W to 69.00 W Longitude
38.00 N to 45.00 N Latitude
60 × 42 Grid Cells (columns × rows)

SOUTHEAST DOMAIN (SEROS1)

97.00 W to 82.00 W Longitude
28.00 N to 35.00 N Latitude
60 × 42 Grid Cells (columns × rows)

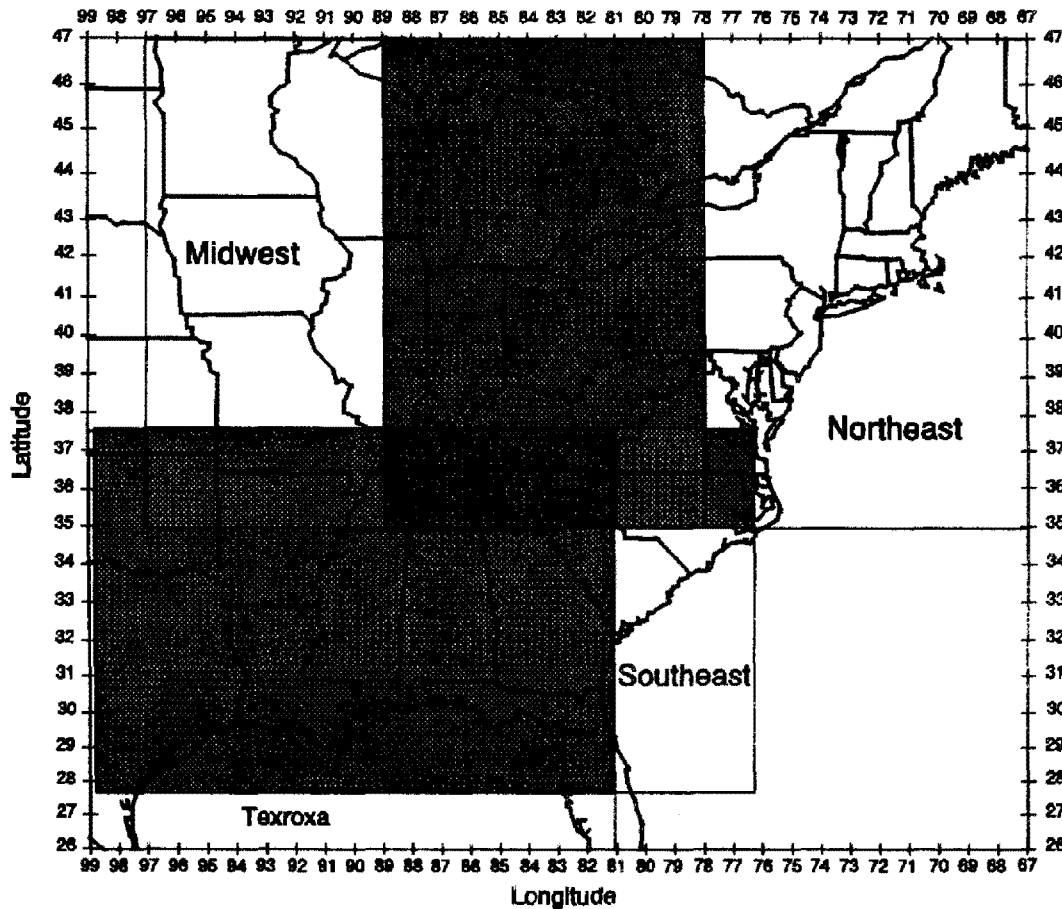


Figure 3-26. Regional oxidant model superdomain with modeling domains.

Source: R. Wayland, U.S. Environmental Protection Agency (1993).

to exist above layer 3 at all times and stratospheric intrusion of O_3 is assumed to be negligible. If cumulus clouds are present, an upward flux of O_3 and precursor species is injected into the layer by penetrative convection. At night, O_3 and the remnants of other photochemical reaction products may remain in this layer and be transported long distances downwind. These processes are modeled in layer 3.

When cumulus clouds are present in a layer 3 cell, the upward vertical mass flux from the surface is partially diverted from injection into layer 1 to injection directly into the cumulus cloud of layer 3. In the atmosphere, strong thermal vertical updrafts, primarily originating near the surface in the lowest portion of the mixed layer, feed growing fair-weather cumulus clouds with vertical air currents that extend in one steady upward motion

1 from the ground to well above the top of the mixed layer. These types of clouds are termed
2 "fair-weather cumulus" since atmospheric conditions are such that they do not grow to the
3 extent that precipitation forms. The dynamic effects of this transport process and daytime
4 cloud evolution can have significant effects on the chemical fate of pollutants. Within the
5 ROM system, a submodel parameterizes the above cloud flux process and its impact on mass
6 fluxes among all the model's layers. In the current implementation of the chemical kinetics,
7 liquid-phase chemistry is not included, and thus part of the effects from the cloud flux
8 processes are not accounted for in the simulations. The magnitude of the mass flux
9 proceeding directly from the surface layer to the cloud layer is modeled as being proportional
10 to the observed amount of cumulus cloud coverage and inversely proportional to the observed
11 depth of the clouds.

12 Horizontal transport within the ROM system is governed by hourly wind fields that are
13 interpolated from periodic wind observations made from upper-air soundings and surface
14 measurements. During the nighttime simulation period, the lowest few hundred meters of
15 the atmosphere above the ground may become stable as a radiation inversion forms. Wind
16 speeds increase just above the top of this layer, forming the nocturnal jet. This jet is capable
17 of carrying O₃, other reaction products, and emissions injected aloft considerable distances
18 downwind. This phenomenon is potentially significant in modeling regional-scale air quality
19 and is implicitly treated by the model, where the definition of layer 1 attempts to account
20 for it.

21 The ROM system requires five types of "raw" data inputs: air quality, meteorology,
22 emissions, land use, and topography.

23 Air quality data required by the ROM include initial conditions and boundary
24 conditions. The model is initialized several (usually 2 to 4) days before the start of the
25 period of interest (called an "episode," usually around 15 days long) with clean tropospheric
26 conditions for all species. Ideally, the initial condition field will have been transported out of
27 the model domain in advance of the portion of the episode of greatest interest. Upwind
28 lateral boundary conditions for O₃ are updated every 12 h based on measurements, except for
29 the large superdomain, where tropospheric background values are used. Other species
30 concentrations at the boundaries, as well as all species at the top of the modeling domain, are
31 set to tropospheric clean-air concentrations.

1 Meteorological data are assimilated by the first stage of preprocessors. These data
2 contain regular hourly observations from U.S. National Weather Service surface stations (and
3 from similar stations in Canada as necessary), including wind speed and direction, air
4 temperature and dew point, atmospheric pressure, and cloud amounts and heights. Twice-
5 daily sounding data from the upper-air observation network are also included in the
6 meteorological database. Upper-air meteorological parameters include atmospheric pressure,
7 wind speed and direction, and air temperature and dew point. Finally, both buoy and
8 Coastal Marine Automated Station data are used; parameters typically reported are wind
9 speed and direction, and air and sea temperatures.

10 Emissions data for the primary species are input to the ROM system as well.
11 Originally these data were provided from the National Acid Precipitation Assessment
12 Program 1985 emissions inventory with 18.5-km spatial resolution. Most recently, the
13 interim regional inventory is being widely used to support current applications of the ROM.
14 It represents an update and improvement to the NAPAP inventory and is being used to
15 support State Implementation Plan modeling until State inventories are approved (U.S.
16 Environmental Protection Agency, 1993a,b). Species included are CO, NO, NO₂, and ten
17 hydrocarbon reactivity categories. Natural hydrocarbons are also input, including isoprene
18 explicitly, monoterpenes divided among the existing reactivity classes, and unidentified
19 hydrocarbons. The chemical mechanism in ROM is the CBM-IV as previously described.

20 Land-use input data consist of 11 land-use categories in 1/4-degree longitude by
21 1/6-degree latitude grid cells. The data are more than 20 years old and represent a
22 weakness. Data are provided for the United States and Canada as far as 55° N. The land-
23 use categories are (1) urban land, (2) agricultural land, (3) range land, (4) deciduous forests,
24 (5) coniferous forests, (6) mixed-forest wetlands, (7) water, (8) barren land, (9) nonforested
25 wetland, (10) mixed agricultural land and range land, and (11) rocky, open places occupied
26 by low shrubs and lichens. Land-use data are used to obtain biogenic emissions estimates as
27 a function of the area of vegetative land cover, and for the determination of surface heat
28 fluxes.

29 Topography input data consist of altitude matrices of elevations in a 7.5° × 7.5° grid.
30 The data are obtained from the GRIDS database operated by U.S. EPA's Office of

1 Information Resources Management. Topography data are used in the calculation of layer
2 heights.

3 4 **3.6.3.3 The Regional Acid Deposition Model**

5 The Regional Acid Deposition Model was initially developed at the National Center for
6 Atmospheric Research (NCAR) for U.S. EPA, and subsequently refined and improved at the
7 State University of New York at Albany (SUNYA). The model is an Eulerian transport,
8 transformation, and removal model that includes a treatment of the relevant physical and
9 chemical processes leading to acid deposition and the formation of photochemical oxidants.
10 As summarized in Tables 3-21 through 3-25, these processes include atmospheric transport
11 and mixing, gas-phase and aqueous-phase chemical transformations, dry deposition, and
12 cloud mixing and scavenging.

13 Chemical trace species are transported and diffused through the three-dimensional
14 RADM grid using externally specified meteorological data. The RADM uses hourly three-
15 dimensional fields of horizontal winds, temperature, and water vapor mixing ratio calculated
16 by the meteorological model MM4 with four-dimensional data assimilation (FDDA).
17 In addition, RADM requires two-dimensional, hourly fields of surface temperature, surface
18 pressure, and precipitation rates over the model domain. Kuo et al. (1985) found that to
19 calculate accurate mesoscale trajectories, at least 3-h temporal resolution is desirable, and the
20 12-h resolution of upper air observations is inadequate. Recent verification studies with
21 30 meteorological episodes by Stauffer and Seaman (1990) further support the use of MM5
22 data with FDDA. Using meteorology generated from a dynamically consistent
23 meteorological model can introduce errors caused by simulation errors associated with the
24 meteorological model. These uncertainties can be quantified through objective verification
25 studies with observed data (Anthes et al., 1985; Stauffer and Seaman, 1990).

26 The RADM2 chemical mechanism has been described by Stockwell et al. (1990),
27 Chang et al. (1991), Carter and Lurmann (1990), and Stockwell and Lurmann (1989). For
28 RADM2, the VOCs are aggregated into 12 classes of reactive organic species. Each
29 category of VOC is represented by several model species that span the required range for
30 reaction with the OH radical. Most emitted organic compounds are lumped into surrogate
31 species of similar reactivity and molecular weight, although organic chemicals with large

emissions are treated as separate model species even though their reactivities may be similar. Categories of VOCs with large reactivity differences and complicated secondary chemistries are represented by larger numbers of intermediates and stable species. During the aggregation of organic species, the principle of reactivity weighting is followed to attempt to account for differences in reactivity.

3.6.4 Evaluation of Model Performance

Air quality models are evaluated by comparing their predictions with ambient observations. Because a model's demonstration of attainment of the ozone NAAQS is based on hypothetical reductions of emissions from a base-year-episode simulation, the accuracy of the base-year simulation is necessary, but not sufficient. An adequate model should give accurate predictions of current peak ozone concentrations and temporal and spatial ozone patterns. It should also respond accurately to changes in VOC and NO_x emissions, to differences in VOC reactivity, and to spatial and temporal changes in emissions patterns for future years.

Model performance can be evaluated at several levels. The important sub-models, the emissions model, the meteorological model, and the chemical mechanism, can be independently evaluated, and the model as a whole can be evaluated. Evaluation of emissions models can be carried out with special measurements designed to isolate the effects of emissions from a particular source category, such as tunnel studies (Pierson et al., 1990) or on-road surveillance of motor vehicles (Lawson et al., 1990) to evaluate the accuracy of motor vehicle emissions models. Meteorological sub-models can be evaluated from the results of tracer experiments. Chemical mechanisms have traditionally been developed and evaluated on the basis of smog chamber experiments. A question that merits continued attention is how well chemical mechanisms developed with reference to smog chamber data perform when simulating the ambient atmosphere. As noted in this section, comparisons of observed and predicted concentrations for all important precursors, intermediates, and products are important in assessing the accuracy of a chemical mechanism.

3.6.4.1 Model Performance Evaluation Procedures

Specific numerical and graphic procedures have been recommended for evaluation of the accuracy of grid-based photochemical models (Teschke et al., 1990b). The methods suggested include the calculation of peak prediction accuracy; various statistics based on concentration residuals; and time series of predicted and observed hourly concentrations. Four numerical measures appear to be most helpful in making an initial assessment of the adequacy of a photochemical simulation (Teschke et al., 1990b):

- The paired peak prediction accuracy.
- The unpaired peak prediction accuracy.
- The mean normalized bias.
- The mean absolute normalized gross error.

Accurate matching of ozone alone may not be sufficient to ensure that a model is performing accurately. The possibility of compensatory errors must be recognized in which two or more sources of error interact in such a way that ozone is predicted accurately, but for the wrong reasons. The inaccuracies offset each other in part. The modeling effort should be designed to minimize the likelihood of the presence of compensatory errors.

Evaluation of model performance for precursor and intermediate species as well as for product species other than ozone, when ambient concentration data for these species are available, significantly improves the chances that a flawed model will be identified. Comparisons of observed and predicted concentrations for all important precursors, intermediates, and products involved in photochemical air pollution—such as individual VOCs, nitric oxide, nitrogen dioxide, PAN, ozone, H_2O_2 , nitrous acid (HONO), and HNO_3 —are useful in model evaluation, especially with respect to the chemistry component of the model (Jeffries et al., 1992). Comparisons of predictions and observations for total organic nitrates (mainly PAN) and inorganic nitrates (HNO_3 and nitrate aerosol) can be used to test qualitatively whether the emissions inventory has the correct relative amounts of VOCs and NO_x . However, to include HNO_3 and nitrate aerosol in the data set for model comparisons,

1 the model should include an adequate description of the HNO₃ depletion process associated
2 with aerosol formation.

3 Adequate model performance for several reactive species increases the assurance that
4 correct ozone predictions are not a result of chance or fortuitous cancellation of errors
5 introduced by various assumptions. Multispecies comparisons could be the key in
6 discriminating among alternative modeling approaches that provide similar predictions of
7 ozone concentrations.

8 As noted above, photochemical models have the potential to produce nearly the right
9 ozone concentrations when performance is evaluated, but do so because two or more flaws
10 were compensating each other. The existence of compensating errors in many modeling
11 applications is suspected because most applications to date have used emission inventories
12 whose validity is now in question (National Research Council, 1991). Underestimation of
13 VOC emissions from motor vehicles may be responsible for the lack of agreement between
14 inventories and ambient concentration data (Baugues, 1986; Lawson et al., 1990; Pierson
15 et al., 1990; Fujita et al., 1992). Underestimation of emissions from other sources is also a
16 possibility. One potentially underestimated VOC source is vegetation, which naturally emits
17 VOCs. An underestimation of VOC emissions could be compensated for by underestimation
18 of mixing height or wind speed or by overestimation of boundary concentrations of ozone or
19 precursors or by inaccurate chemistry modules. Boundary concentrations (which can be
20 obtained from measurements or regional models or by assuming background concentrations,
21 as discussed in Section 3.6.2.6) are often poorly defined.

22 If only a routine database is available for modeling ozone in an urban area, then there
23 are several areas of concern that require attention (Roth, 1992):
24

- 25 • Air quality aloft - Most likely these data will not be available. These
26 measurements are important and instrumental for diagnostic analysis of model
27 simulations.
- 28 • Boundary conditions - If the possibility of significant transport into the region
29 exists, and the data are not available, the boundary conditions become a variable
30 that allows the introduction of compensatory errors if the emissions are
31 inaccurate. An approach to circumvent this problem is to define the region in a
32 way so that the boundaries become a much less significant issue.
33
34

- Ambient VOC data - These are generally not routinely available. In their absence, evaluation of model performance is hampered.
- Meteorological data aloft - Very often there are only surface measurements and a few soundings from which to extrapolate the needed data.

If any of these four areas is missing from the database, the performance evaluation and subsequent model application must be adequately planned to minimize the possibility of compensatory errors.

3.6.4.2 Performance Evaluation of Ozone Air Quality Models

3.6.4.2.1 Urban Airshed Model

The UAM has been applied to many urban areas in the United States and Europe, and most of these studies have included some form of performance evaluation. (See summary in Tesche et al., 1992, Table 6-2.) Thus, there is a growing body of information concerning the accuracy of the model's predictions. (UAM itself was continuing to undergo revision.) Evaluations of UAM's performance have been carried out for a number of geographic areas. Evaluations carried out since 1985 have indicated mean discrepancies between predicted and measured ozone values of 20 to 40% of the observations, when paired in space and time (Roth et al., 1989). The prediction of peaks exhibits relative errors that are smaller than the average error, with a tendency toward underprediction (Roth et al., 1989). The discrepancies between predicted and measured NO₂ in UAM applications are on the order of 30 to 50% with no improvement over the history of modeling applications (Roth et al., 1989). Underprediction of NO₂ by UAM has been typical, generally on the order of 20 to 40% (Roth et al., 1989).

3.6.4.2.2 Regional Oxidant Model

A primary role of the ROM model is to estimate boundary conditions for use by the Urban Airshed Model in evaluating hydrocarbon and NO_x reduction strategies for urban areas in the eastern United States, especially in areas where transport is a significant element (U.S. Environmental Protection Agency, 1990f). Analysis of regional ozone abatement strategies is also a major role of the ROM model (Possiel et al., 1990).

1 The ROM has been used in a U.S. EPA program, the Regional Ozone Modeling for
2 Northeast Transport (ROMNET) program, to assess the effectiveness of various regional
3 emission control strategies in lowering O₃ concentrations to nationally mandated levels for
4 the protection of human health, forests, and crops (Meyer et al., 1991). As part of the
5 ROMNET program, the ROM is also being used to provide regionally consistent initial and
6 upwind boundary conditions to smaller-scale urban models for simulations of future-year
7 scenarios.

8 The most complete testing of ROM2.0 was accomplished in an evaluation with the
9 50-day (July 12 to August 31, 1980) NEROS database (Schere and Wayland, 1989a,b). The
10 model underestimated the highest values and overestimated the lowest. It showed good
11 performance (an overall 2% overprediction) in predicting maximum daily O₃ concentrations
12 averaged over aggregate groups of monitoring stations. A key indicator of model
13 performance on the regional scale is the accuracy of simulating the spatial extent and
14 location, as well as the magnitude, of the pollutant concentrations within plumes from
15 significant source areas. In ROM2.0 performance analyses, plumes from the major
16 metropolitan areas of the Northeast Corridor, including Washington, DC; Baltimore;
17 New York; and Boston, could be clearly discerned in the model predictions under episodic
18 conditions. Generally the plumes were well characterized by the model, although there was
19 evidence of a westerly transport bias and underprediction of O₃ concentrations near the
20 center of the plume. Using aircraft data, ROM2.0 was found to underpredict the regional
21 tropospheric burden of ozone.

22 The evaluation of ROM2.1 (Pierce et al., 1990), unlike that of ROM2.0, was based on
23 routinely archived data from state and local agency monitoring sites rather than on an
24 intensive field-study period. The evaluation consisted of the comparison of observed and
25 predicted O₃ concentrations during selected episodes (totaling 26 days) of high ozone
26 observed during the summer of 1985. Evaluation showed that ROM2.1 underestimated the
27 highest values and slightly overestimated the lowest; underestimates of the upper percentiles
28 tended to be more prevalent in the southern and western areas of the ROMNET domain
29 (Table 3-26). The model showed good performance (an overall 1.4% overprediction) in
30 predicting maximum daily O₃ concentrations averaged over aggregate groups of monitoring
31 stations; and it appears to correct for the westerly transport bias of high-ozone plumes in the

1 Northeast Corridor seen in ROM2.0. As with ROM2.0, model performance degraded as a
2 function of increasingly complex mesoscale wind fields.

3 4 **3.6.4.3 Data Base Limitations**

5 As previously mentioned, the use of routine air quality and meteorological data requires
6 that a number of assumptions be made about key model inputs. While intensive field studies
7 are desirable during ozone episodes to acquire the full set of data required, three key
8 problems arise: such studies are expensive and, therefore, are limited in number; the time
9 required to carry out field studies usually exceeds the time available; and most field studies
10 have not captured the worst ozone episodes. Since U.S. EPA guidance emphasizes planning
11 to meet worst-case conditions, field data must often be manipulated to approximate highest
12 ozone concentrations. Such adjustments invariably increase uncertainty in model projections.

13 Studies that have, or will, provide data for model evaluation include: the St. Louis
14 Regional Air Pollution Study (RAPS) conducted in 1975-1976; the Northeast Corridor
15 Regional Modeling Project (NECRMP) conducted in 1979 and 1980; the South Central Coast
16 Cooperative Aerometric Monitoring Program (SCCCAMP) conducted in 1985; the South
17 Coast Air Quality Study (SCAQS) conducted in 1987; studies in Sacramento and San Diego
18 in 1990; SJVAQS/AUSPEX conducted in 1990; the Lake Michigan Oxidant Study (LMOS)
19 conducted in 1990 and 1991; the Southern Oxidant Study (SOS) conducted in 1991 and 1992;
20 and a Gulf Coast study planned for 1993.

21 In most cases, field studies have not coincided with periods in which ozone
22 concentrations have attained values as high as the design values. Given the low probabilities
23 of occurrence of the most adverse meteorological conditions and the fact that field studies
24 typically acquire data for two or three ozone episodes, obtaining a design value concentration
25 during the course of a field study is unlikely.

26 The U.S. EPA recommends that the five highest daily maximum ozone concentrations
27 at a design-value site, selected from the three most recent years, be modeled if EKMA is
28 used for a SIP (U.S. Environmental Protection Agency, 1989b). Because EKMA's data
29 requirements are minimal, it can be applied to the worst episodes. In contrast, the number
30 of episodes available for grid-based modeling is less than desirable in all areas. In addition,
31 any available intensive databases often do not include the worst-case meteorology; intensive

1 databases typically restrict modeling to two or three ozone episodes having a duration of 2 to
2 3 days each. Moreover, the intensive databases never encompass the full range of
3 meteorological conditions of interest (if ozone exceedances occur in an area under different
4 meteorological conditions, the relative effectiveness of different control strategies might vary
5 with the different meteorological conditions). The U.S. EPA spells out procedures for
6 episode selection for use with grid-based models (U.S. Environmental Protection Agency,
7 1991b).

8 Because the number of intensive databases is limited both in terms of episodes and
9 regions, U.S. EPA has investigated the feasibility of applying UAM without conducting
10 intensive field studies (Scheffe and Morris, 1990a,b). These studies, known as the Practice
11 for Low-cost Application in Nonattainment Regions (PLANR), were conducted for
12 New York, Philadelphia, Atlanta, Dallas-Fort Worth, and St. Louis. Of the five cities
13 studied, St. Louis, New York, and Philadelphia had intensive databases available.
14 Simulations were carried out using both routine and intensive databases for St. Louis and
15 Philadelphia. Model performance using routine data was much better for St. Louis than for
16 Philadelphia (Scheffe and Morris, 1990a,b). Scheffe and Morris (1990a,b) caution that the
17 differing results may be complicated by the quality of the databases, but they speculate that
18 model performance using routine databases for Philadelphia might have been poorer because
19 of regional transport. Performance statistics for all four applications using routine data were
20 consistent with other UAM applications (Scheffe and Morris, 1990a,b); however, the paucity
21 of data in the routine databases precluded any investigation of the possibility that
22 compensating errors occurred.

23 Scheffe and Morris (1990a,b) note that the PLANR lack of air quality data was
24 addressed by extending the length of the simulations and expanding the upwind boundary,
25 which, in effect, increased the need for accurate emissions inventories (boundary conditions
26 could also be obtained through use of ROM). For PLANR applications, gridded emissions
27 were created from routine county-level emission inventories by utilizing an emissions
28 program that made use of surrogate information, such as population distribution.
29
30

3.6.5 Use of Ozone Air Quality Models for Evaluating Control Strategies

Photochemical air quality models are used for control strategy evaluation by first demonstrating that a past episode, or episodes, can be adequately simulated and then reducing hydrocarbon or NO_x emissions or both in the model inputs and assessing the effects of these reductions on ozone in the region. Ozone concentrations can be decreased by reducing either VOC or NO_x concentrations to sufficiently low levels. Controlling VOC emissions always delays ozone formation and reduces the amount of ozone formed. Controlling highly reactive VOCs in areas exhibiting low VOC-to- NO_x ratios delays and reduces ozone formation most effectively. The effects of NO_x emissions reductions on ozone concentrations vary because NO_x is an atypical precursor: though it is necessary for ozone formation, fresh NO emissions remove ozone, and high concentrations of NO_x retard the rate of ozone formation by removing radicals. Control of NO_x tends to accelerate the rate of ozone formation; however, its effects on peak ozone concentration depend upon the location and timing of the control and upon ambient concentrations of VOCs and NO_x , which vary widely in time and space, even within a single urban area during one day.

Grid modeling applications are currently underway by or for State agencies for approximately 20 areas within the United States to support regional ozone SIP revisions.

An immediate problem faced for almost all urban areas is that even if an adequate number of episodes exist, the episodes may not include the most adverse ozone levels. An inherent question in using a less adverse episode to develop control strategies is how these strategies extrapolate to a more severe set of conditions. There is no clear answer to this question at this point. At present, control strategies, evaluated using grid-based models, are determined based on available episodes that have the largest amount of data whether or not these episodes contain the highest ozone concentration achieved. Another issue is that the form of the NAAQS for ozone does not correspond with the output from a grid-based model. The model output does not provide a direct answer to whether an area will meet the standard in its current statistically based form.

Table 3-27 summarizes a number of recent ozone control strategy evaluations for different areas of the United States. Some general observations can be made concerning issues that have arisen in control strategy exercises, particularly as they relate to problems associated with different areas of the country (Roth, 1992). In California, model results

TABLE 3-27. APPLICATIONS OF PHOTOCHEMICAL AIR QUALITY MODELS TO EVALUATING OZONE

Investigators	Region/Episode	Model Used	Strategies Evaluated
Chu et al. (1992) Chu and Cox (1993) Roselle et al. (1992) Mathur and Schere (1993)	Eastern U.S./ July 2-10, 1988	ROM2.2	Across-the-board NO _x /VOC reductions.
Possiel et al. (1993) Possiel and Cox (1993)	Northeastern U.S./ July 1-12, 1988	ROM2.2	Estimate ozone reductions per 1990 Clean Air Act Amendments
Milford et al. (1992)	Northeastern U.S./ July 2-17, 1988	ROM	Analysis of effect of NO _x reductions.
Rao (1987) Rao et al. (1989) Rao and Sistla (1993)	New York Metropolitan area/ 5 days in 1980	UAM/ROM2.1	Evaluation of 1988 SIPs and VOC/NO _x strategies
Scheffe and Morris (1990a,b)	New York St. Louis Atlanta Dallas-Ft. Worth Philadelphia	UAM	Use of UAM for demonstrating attainment with routinely available data
Possiel et al. (1990)	Northeastern U.S./ July 2-17, 1988	ROM	Ozone control strategies in Northeast
Roselle and Schere (1990) Roselle et al. (1991)	Northeast U.S./ July 12-18, 1980	ROM2.1	Sensitivity of ozone in Northeast to biogenic emissions
Dunker et al. (1992a,b)	Los Angeles New York Dallas-Ft. Worth	UAM	Effects of alternate fuels and reformulated gasolines on ozone levels
Milford et al. (1989)	South Coast Air Basin	CIT	Effects of systematic VOC and NO _x reductions
Middleton et al. (1993)	Eastern U.S. and Southeastern Canada	RADM	2010 emissions projections

1 indicate that ozone has been underestimated, most likely because VOC emissions from motor
2 vehicles have been seriously underestimated. The underestimation was hidden by adjusting
3 other model inputs within their range of uncertainty. In Atlanta, it has been estimated that
4 approximately 60% of the VOC inventory is of biogenic origin, and the variation of
5 anthropogenic emissions reductions required to achieve ozone attainment within the
6 uncertainty range of the biogenic emissions is on the order of 20%. The uncertainty range of

1 the biogenic VOC emissions needs to be reduced to obtain tighter control strategy estimates.
2 Studies with ROM and UAM tend to indicate that NO_x control is beneficial in the northeast.
3 While it is unlikely that this general conclusion will be altered by more refined data, there
4 are still significant uncertainties concerning regionwide boundary conditions and the extent of
5 influence of emissions in upwind regions on air quality in the major eastern metropolitan
6 areas.

8 **3.6.6 Conclusions**

9 The 1990 amendments to the Clean Air Act have mandated the use of photochemical
10 grid models for demonstrating how most ozone nonattainment areas can attain the NAAQS.
11 Predicting ozone is a complex problem. There are still many uncertainties in the models;
12 nonetheless models are necessary and essential for regulatory analysis and constitute one of
13 the major tools for attacking the ozone problem. These models have developed considerably
14 in the past 10 years. However, their usefulness is constrained by limited databases for
15 evaluation and from having to rely on hydrocarbon emissions data that may be inaccurate.
16 Comparison of model predictions against ozone measurements, while necessary, is not a
17 robust test of a model's accuracy. Ideally, one should evaluate performance against more
18 extensive sets of species such as individual VOCs, NO_x, and NO_y. Compensating errors in
19 input information to a model and within the model formulation can cause an ozone model to
20 generate correct ozone predictions for the wrong reasons. Therefore, model evaluation
21 indicators are needed to demonstrate the reliability of a prediction before the model can be
22 effectively used in making control strategy decisions. Models can be effectively used in a
23 relative sense to rank different control alternatives in terms of their effectiveness in reducing
24 ozone and to indicate the approximate magnitude of improvement in peak ozone levels
25 expected under various control strategies. To do so, there must be a sound emissions model
26 and data and an adequate database on which to construct the modeling. Grid-based ozone air
27 quality modeling is superior to the available alternatives for ozone control planning, but if the
28 model is not evaluated sufficiently, one can be misled. The goal is to minimize the chances
29 of its incorrect use.

3.7 SUMMARY AND CONCLUSIONS

3.7.1 Tropospheric Ozone Chemistry

3.7.1.1 Ozone in the Unpolluted Atmosphere

Ozone is found in the stratosphere, the "free" troposphere, and the planetary boundary layer (PBL) of the earth's atmosphere. In the stratosphere, the uppermost layer, O_3 is produced through cyclic reactions that are initiated by the photolysis of molecular oxygen by short-wavelength radiation from the sun and are terminated by the recombination of molecular oxygen and ground-state oxygen atoms.

In the "free" troposphere, O_3 occurs as the result of incursions from the stratosphere; upward venting from the PBL (which is the layer next to the earth, extending to altitudes of ~1 to 2 km) through certain cloud processes; and photochemical formation from precursors, notably methane, carbon monoxide, and nitrogen oxides.

Ozone is present in the PBL as the result of downward mixing from the stratosphere and free troposphere and as the result of photochemical processes occurring within the PBL. The photochemical production of O_3 and other oxidants found at the earth's surface is the result of atmospheric physical and chemical processes involving two classes of precursor pollutants, reactive volatile organic compounds (VOCs) and (NO_x). The formation of O_3 and other oxidants from its precursors is a complex, nonlinear function of many factors, including the intensity and spectral distribution of sunlight; atmospheric mixing and related meteorological conditions; the reactivity of the mixture of organic compounds in ambient air; the concentrations of precursor compounds in ambient air; and, within reasonable concentrations ranges, the ratio between the concentrations of reactive VOCs and NO_x .

In the free troposphere and in relatively "clean" areas of the PBL, methane is the chief organic precursor to in situ photochemical production of O_3 and related oxidants. The major tropospheric removal process for methane is by reaction with OH radicals. In the complex cyclic reactions that result in oxidation of methane, there can be a net increase in O_3 or a net loss of O_3 , depending mainly upon the NO concentration.

3.7.1.2 Ozone Formation in the Polluted Troposphere

The same basic processes by which methane is oxidized occur in the atmospheric oxidative degradation of other, even more reactive and more complex VOCs. The only

1 significant initiator of the photochemical formation of ozone in the troposphere is the
2 photolysis of NO_2 , yielding NO and a ground-state oxygen atom that reacts with molecular
3 oxygen to form O_3 . The O_3 thus formed reacts with NO, yielding O_2 and NO_2 . These
4 cyclic reactions attain equilibrium in the absence of VOCs. In the presence of VOCs,
5 however, the equilibrium is upset, resulting, through a complex series of chain reactions, in
6 a net increase in O_3 .

7 The key reactive species in the troposphere is the hydroxyl (OH) radical, which is
8 responsible for initiating the oxidative degradation reactions of almost all VOCs. As in the
9 methane oxidation cycle, the conversion of NO to NO_2 during the oxidation of VOCs is
10 accompanied by the production of O_3 and the efficient regeneration of the OH radical. The
11 O_3 and PANs formed in polluted atmospheres increase with the NO_2/NO concentration ratio.

12 At night, in the absence of photolysis of reactants, the simultaneous presence of O_3 and
13 NO_2 results in the formation of the nitrate radical, NO_3 . The reaction with nitrate radicals
14 appears to constitute a major sink for alkenes, cresols, and some other compounds, although
15 alkyl nitrate chemistry is not well characterized.

16 Most inorganic gas-phase processes, that is, the nitrogen cycle and its interrelationships
17 with O_3 production, are well understood. The chemistry of the VOCs in ambient air,
18 however, is not as well understood. The chemical loss processes of gas-phase VOCs, with
19 concomitant production of O_3 , include reaction with OH, NO_3 , O_3 , and photolysis.

20 The major classes of VOCs in ambient air are: alkanes, alkenes (including alkenes
21 from biogenic sources), aromatic hydrocarbons, carbonyl compounds, alcohols, and ethers.
22 A wide range of lifetimes in the atmosphere, from minutes to years, characterize the VOCs.

23 The only important reaction of alkanes is with OH radicals. For alkanes having
24 carbon-chain lengths of four or less ($\leq \text{C}_4$), the chemistry is well understood and the reaction
25 rates are slow. For $\geq \text{C}_5$ alkanes the situation is more complex because few reaction
26 products have been found. Branched alkanes (e.g., isobutane) have rates of reaction that are
27 highly dependent on structure. It is difficult to represent reactions of these VOCs
28 satisfactorily in the chemical mechanisms of air quality models. Stable products of alkane
29 photooxidation are known to include carbonyl compounds, alkyl nitrates, and
30 δ -hydroxycarbonyls. Major uncertainties in the atmospheric chemistry of the alkanes concern
31 the chemistry of alkyl nitrate formation; these uncertainties affect the amount of NO-to- NO_2

conversion occurring and hence the amounts of O₃ formed during photochemical degradation of the alkanes.

Alkenes react in ambient air with OH and NO₃ radicals and with O₃. All three processes are important atmospheric transformation processes, and all proceed by initial addition to the >C=C< bond(s). Products of alkene photooxidation include carbonyl compounds, hydroxynitrates and nitratocarbonyls, and decomposition products from the energy-rich biradicals formed in alkene-O₃ reactions. Major uncertainties in the atmospheric chemistry of the alkenes concern the products and mechanisms of their reactions with O₃, especially the radical yields (which affect the O₃ formation yields).

The only tropospherically important loss process for aromatics (benzene and the alkyl-substituted benzenes) is by reaction with the OH radical, followed by H-atom abstraction or OH radical addition. Products of aromatic hydrocarbon photooxidation include phenolic compounds, aromatic aldehydes, α-dicarbonyls (e.g., glyoxal), and unsaturated carbonyl or hydroxycarbonyl compounds or both. Aromatics appear to act as strong NO_x sinks under low NO_x conditions. Major uncertainties in the atmospheric chemistry of aromatic hydrocarbons are mainly with regard to reaction mechanisms and reaction products under ambient conditions (i.e., for NO_x concentration conditions that occur in urban and rural areas). These uncertainties impact on the representation of mechanisms in models.

Tropospherically important loss processes for carbonyl compounds not containing >C=C< bonds are photolysis and reaction with the OH radical; those that contain such bonds can undergo the same reactions as alkenes. Photolysis is the major loss process for HCHO (the simplest aldehyde) and acetone (the simplest ketone), as well as for the dicarbonyls. Reactions with OH radicals are calculated to be the dominant gas-phase loss process for the higher aldehydes and ketones. Products formed and the importance of photolysis are major uncertainties in the chemistry of carbonyl compounds.

Alcohols and ethers in ambient air react only with the OH radical, with the reaction proceeding primarily via H-atom abstraction from the C-H bonds in these compounds.

It should be noted that the photooxidation reactions of VOCs can lead to the formation of particulates in ambient air. The chemical processes involved in the formation of O₃ and other photochemical pollutants lead to the formation of OH radicals and the formation of oxidized VOC reaction products that are of low enough volatility to be present as organic

1 particulate matter. Hydroxyl radicals that oxidize VOCs also react with NO₂ and SO₂ to
2 form nitric and sulfuric acids, respectively, which become incorporated into aerosols as
3 particulate nitrate and sulfate. Controls aimed at reducing ozone will impact—positively or
4 negatively—acid and secondary aerosol formation in the atmosphere.

6 **3.7.2 Meteorological Processes Influencing Ozone Formation and** 7 **Transport**

8 **3.7.2.1 Meteorological Processes**

9 The surface energy (radiation) budget of the earth strongly influences the dynamics of
10 the planetary boundary layer (PBL). In combination with synoptic winds, it provides the
11 forces for the vertical fluxes of heat, mass, and momentum. The redistribution of energy
12 through the PBL creates thermodynamic conditions that influence vertical mixing. Energy
13 balances require study so that more realistic simulations can be made of the structure of the
14 PBL.

15 Day-to-day variability in ozone concentrations depends heavily on day-to-day variations
16 in meteorological conditions. For example, the concentration of an air pollutant depends
17 significantly on the degree of mixing that occurs between the time a pollutant or its
18 precursors are emitted and the arrival of the pollutant at the receptor. Inversion layers
19 (layers in which temperature increases with height above ground level) are prominent
20 determinants of the degree of atmospheric vertical mixing and thus the degree to which ozone
21 and other pollutants will be dispersed or accumulate. Ozone left in a layer aloft, as the result
22 of reduced turbulence and mixing at the end of daylight hours, can be transported through
23 the night, often to areas far removed from pollution sources. Downward mixing on the
24 subsequent day can result in increases in local concentrations from the transported ozone.

25 Growing evidence indicates that the strict use of mixing heights in modeling is an
26 oversimplification of the complex processes by which pollutants are redistributed within
27 urban areas; and that it is necessary to treat the turbulent structure of the atmosphere directly
28 and acknowledge the vertical variations in mixing.

29 Geography can significantly affect the dispersion of pollutants along the coast or shore
30 of oceans and lakes. Temperature gradients between bodies of water and land masses
31 influence the incidence of surface conditions. The thermodynamics of water bodies (e.g.,

1 Lake Michigan and the Atlantic Ocean off the coast of Maine) may play a significant role in
2 some regional-scale episodes of high ozone concentrations.

3 An "air mass" is a region of air, usually of multistate dimensions, that exhibits similar
4 temperature, humidity, and stability characteristics. Episodes of high ozone concentrations in
5 urban areas are often associated with high concentrations of ozone in the surroundings.

6 The transport of ozone and its precursors beyond the urban scale (≤ 50 km) to
7 neighboring rural and urban areas has been well documented and was described in the 1986
8 EPA criteria document for O_3 . Areas of ozone accumulation are characterized by:

9 (1) synoptic-scale subsidence of air in the free troposphere, resulting in development of an
10 elevated inversion layer; (2) relatively low wind speeds associated with the weak horizontal
11 pressure gradient around a surface high pressure system; (3) a lack of cloudiness; and
12 (4) high temperatures.

13 14 **3.7.2.2 Meteorological Parameters**

15 Ultraviolet (UV) radiation from the sun plays a key role in initiating the photochemical
16 processes leading to ozone formation and affects individual photolytic reaction steps. There
17 is little empirical evidence in the literature, however, linking day-to-day variations in
18 observed UV radiation levels with variations in O_3 levels.

19 An association between tropospheric ozone concentrations and tropospheric temperature
20 has been demonstrated. Plots of daily maximum ozone concentrations versus maximum daily
21 temperature for summer months of 1988 to 1990 for four urban areas, for example, show an
22 apparent upper bound on ozone concentrations that increases with temperature. A similar
23 qualitative relationship exists at a number of rural locations.

24 The relationship between wind speed and ozone buildup varies from one part of the
25 country to another. Research done during the Southern Oxidant Study (in the "Atlanta
26 intensive" field study) indicates that variations in wind speed at a particular level above
27 ground must be larger than about 3 m/s to be considered significant. This may limit the
28 accuracy of urban-area ozone simulations using photochemical models.

3.7.2.3 Normalization of Trends

Statistical techniques (e.g., regression techniques) can be used to help identify real trends in ozone concentrations, both intra-annual and inter-annual, by normalizing meteorological variability. In the Southern Oxidant Study, for example, regression techniques were successfully used to forecast ozone levels to ensure that specialized measurements were made on appropriate days.

3.7.3 Precursors

3.7.3.1 Nitrogen Oxides Emissions

Anthropogenic oxides of nitrogen are associated with combustion processes. The primary pollutant emitted is nitric oxide (NO) formed at high combustion temperatures from the nitrogen and oxygen in air and from nitrogen in the combustion fuel. Emissions of NO_x in 1991 in the United States totaled 21.39 Tg. The two largest single NO_x emission sources are electric power generation and highway vehicles. Emissions of NO_x are therefore highest in areas having a high density of electric-power-generating stations and in urban regions having high traffic densities. Between 1987 and 1991, transportation-related emissions remained essentially constant, while stationary source NO_x emissions increased about 10%.

Natural NO_x sources include stratospheric intrusion, oceans, lightning, soils, and wildfires. Lightning and soil emission are the only two significant natural sources of NO_x in the United States. The estimated annual lightning-produced NO_x for the continental United States is ~1.0 Tg, about 60% of which is generated over the southern states. Both nitrifying and denitrifying organisms in the soil can produce NO_x, principally NO. Emission rates depend mainly on fertilization levels and soil temperature. Inventorying soil NO_x emissions is difficult because of large temporal and spatial variability, but the nationwide total has been estimated at 1.2 Tg/year, of which about 85% is emitted in spring and summer. About 60% of the total soil NO_x is emitted in the area of the country containing the central corn belt.

Combined natural sources contribute about 2.2 Tg of NO_x to the troposphere over the continental United States. Uncertainties in natural NO_x inventories are much larger, however, than for anthropogenic NO_x emissions. Because a large proportion of

anthropogenic NO_x emissions come from distinct point sources, published annual estimates are thought to be very reliable.

3.7.3.2 Volatile Organic Compound Emissions

Hundreds of volatile organic compounds, commonly containing from 2 to about 12 carbon atoms, are emitted by evaporative and combustion processes from a large number of source types. Total U.S. VOC emissions in 1991 were estimated at 21.0 Tg. The two largest source categories were industrial processes (10.0 Tg) and transportation (7.9 Tg). Emissions of VOCs from highway vehicles accounted for almost 75% of the transportation-related emissions; studies have shown that the majority of these VOC emissions come from about 20% of the automobiles in service, many, perhaps most, of which are older cars that are poorly maintained.

The accuracy of VOC emission estimates is difficult to determine, both for stationary and mobile sources. Within major point sources, deviations of emission rates from individual sources from assigned average factors can result in error for the entire point source. Evaporative emissions, which depend on temperature and other environmental factors, compound the difficulties of assigning accurate emission factors. In assigning VOC emission estimates to the mobile source category, models are used that incorporate numerous input parameters (e.g., type of fuel used, type of emission controls, age of vehicle), each of which has some degree of uncertainty.

Vegetation emits significant quantities of VOCs into the atmosphere, chiefly monoterpenes and isoprene, but also oxygenated VOCs, according to recent studies. The most recent biogenic VOC emissions estimate for the United States showed annual emissions of 29.1 Tg/year. Coniferous forests are the largest vegetative contributor on a national basis, because of their extensive land coverage. Summertime biogenic emissions comprise more than half of the annual totals in all regions because of their dependence on temperature and vegetational growth. Biogenic emissions are, for those reasons, expected to be higher in the southern states than in the northern.

Uncertainties in both biogenic and anthropogenic VOC emission inventories prevent establishing the relative contributions of these two categories.

3.7.3.3 Concentrations of Volatile Organic Compounds in Ambient Air

The VOCs most frequently analyzed in ambient air are the nonmethane hydrocarbons (NMHCs). Morning concentrations (6:00 a.m. to 9:00 a.m.) have been measured most often because of the use of morning data in EKMA and in air quality simulation models. Major field studies in 22 cities in 1984 and 19 cities in 1985 produced NMHC measurements showing median values ranging from 0.39 ppm C to 1.27 ppm C for 1984; and ranging from 0.38 ppm C to 1.63 ppm C in 1985. Overall median values from all urban sites were about 0.72 ppm C in 1984 and 0.60 ppm C in 1985.

Comparative data over two decades (1960's through 1980's) in the Los Angeles and New York City areas showed decreases in NMHC concentrations in those areas. Concomitant compositional changes were observed over the two decades, with increases observed in the percentage of alkanes and decreases in the percentage of aromatic hydrocarbons and acetylene.

Concurrent measurements of anthropogenic and biogenic NMHCs have shown that biogenic NMHCs usually constituted much less than 10% of the total NMHCs. For example, average isoprene concentrations ranged from 0.001 to 0.020 ppm C and terpenes from 0.001 to 0.030 ppm C.

3.7.3.4 Concentrations of Nitrogen Oxides in Ambient Air

Measurements of NO_x at sites in 22 and 19 U.S. cities in 1984 and 1985, respectively, showed that median NO_x concentrations ranged from 0.02 to 0.08 ppm in most of these cities. The 6-to-9 a.m. median concentrations in many of these cities exceeded the annual average NO_x values of 0.02 to 0.03 ppm found in U.S. metropolitan areas between 1980 and 1989. Nonurban NO_x concentrations, reported as average seasonal or annual NO_x , range from <0.005 to 0.015 ppm.

Ratios of 6-to-9 a.m. NMOC to NO_x are higher in southeastern and southwestern U.S. cities than in northeastern and midwestern U.S. cities, according to data from EPA's multi-city studies conducted in 1984 and 1985. Median ratios ranged from 9.1 to 37.7 in 1984; in 1985, median ratios ranged from 6.5 to 53.2 in the cities studied. Rural NMOC/ NO_x ratios tend to be higher than urban ratios. Morning (6-to-9 a.m.) NMOC/ NO_x ratios are used in the EKMA-type of trajectory model. Trends from 1976 to 1990 show

decreases in these ratios in the South Coast Air Basin of California. The correlation of NMOC/NO_x ratios with maximum 1-h O₃ concentrations, however, was weak in a recent analysis.

3.7.3.5 Source Apportionment and Reconciliation

Source apportionment (now regarded as synonymous with receptor modeling) refers to determining the quantitative contributions of various sources of VOCs to ambient air pollutant concentrations. Source reconciliation refers to the comparison of measured ambient VOC concentrations with emissions inventory estimates of VOC source emission rates for the purpose of validating the inventories.

Early studies in Los Angeles employing a "mass balance" approach to receptor modeling showed the following estimated contributions of respective sources to ambient air concentrations of NMOCs through C10: automotive exhaust, 53%; whole gasoline evaporation, 12%; gasoline headspace vapor, 10%; commercial natural gas, 5%; geogenic natural gas, 19%; and liquefied natural gas, 1%. Recent studies in eight U.S. cities showed that vehicle exhaust was the dominant contributor to ambient VOCs (except in Beaumont, TX, with 14% reported). Estimates of the contributions of gasoline evaporation differ in methodology; the more appropriate methods used result in estimates of large whole gasoline contributions, i.e., equal to vehicle exhaust in one study and 20% of vehicle exhaust in a second study.

The chemical mass balance approach used for estimating anthropogenic VOC contributions to ambient air cannot be used for receptor modeling of biogenic sources. A modified approach, applied to 1990 data from a downtown site in Atlanta, indicated a lower limit of 2% (24-h average) for the biogenic percentage of total ambient VOCs at that location (isoprene was used as the biogenic indicator species). The percentage varies during the 24-h period because of the diurnal (e.g., temperature, light intensity) dependence of isoprene concentrations.

Source reconciliation data have shown disparities between emission inventory estimates and receptor-estimated contributions. For biogenics, emission estimates are greater than receptor-estimated contributions. The reverse has been true for natural gas contributions estimated for Los Angeles, Columbus, and Atlanta; and for refinery emissions in Chicago.

3.7.4 Analytical Methods for Oxidants and Their Precursors

3.7.4.1 Oxidants

Current methods used to measure O_3 are chemiluminescence (CL), ultraviolet (UV) absorption spectrometry, and newly developed spectroscopic and chemical approaches, including chemical approaches applied to passive sampling devices for O_3 .

The CL method, designated as the reference method by EPA, involves the direct gas-phase reaction of ozone with an alkene (ethylene) to produce electronically excited products, which decay with the emission of light. Detection limits of 0.005 ppm and a response time of less than 30 s are typical of currently available commercial instruments. A positive interference from atmospheric water vapor was reported in the 1970s and has recently been confirmed. Proper calibration can minimize this source of error.

Commercial UV photometers for measuring ozone have detection limits of about 0.005 ppm, long-term precision within about $\pm 5\%$, and a response time of <1 min. Ozone has a fairly strong absorption band with a maximum near 254 nm; its molar absorption coefficient at that wavelength is well known. Since the measurement is absolute, UV photometry is also used to calibrate O_3 methods.

A potential disadvantage of UV photometry is that atmospheric constituents that absorb 254 nm radiation (and that are removed fully or partially by the manganese dioxide scrubber used in UV O_3 photometers) will be a positive interference in O_3 measurements. Interferences have been reported in two recent studies but assessment of the potential importance of such interferences (e.g., toluene, styrene, cresols, nitrocresols) is hindered by lack of absorption spectra data in the 250 nm range and by lack of ambient measurements of most of the aromatic photochemical reaction products.

Differential optical absorption spectrometry (DOAS) has been used to measure ambient O_3 , but further intercomparisons with other methods and interference tests are recommended. Passive sampling devices (PSDs) permit acquisition of personal human exposure data and of ozone monitoring data in areas where the use of instrumental methods is not feasible. Three PSDs are commercially available. All employ solid absorbents that react with O_3 .

Calibration of O_3 measurement methods (other than PSDs) is done by UV spectrometry or by gas-phase titration (GPT) of O_3 with NO. Ultraviolet photometry is the reference

1 calibration method approved by EPA. Ozone is unstable and must be generated in situ at
2 time of use to produce calibration mixtures.

3 Two methods have been generally employed to measure atmospheric peroxyacetyl
4 nitrate (PAN) and its higher homologues (PANs): infrared spectroscopy (IR) and gas
5 chromatography (GC) using an electron capture detector (ECD). A third method, less often
6 used, couples GC with a molybdenum converter that reduces PAN to NO in the gas phase
7 and subsequently measures the NO with a chemiluminescence analyzer. Peroxyacetyl nitrate
8 and the higher PANs are normally measured by GC-ECD. Detection limits have been
9 extended to 1 to 5 ppt using cryogenic enrichment of samples and specified desorption
10 procedures that limit losses associated with cryosampling. Because PAN is unstable
11 (explosive, and subject to surface-related decomposition), the preparation of reliable
12 calibration standards is difficult. Methods devised to generate calibration standards include
13 photolysis of static concentrations of gases, nitration of peracetic acid in single hydrocarbons,
14 and analysis of PAN as NO under specified conditions of the dissociation of PAN into its
15 precursors.

16 Early measurements of 10 to 80 ppb hydrogen peroxide (H_2O_2) reported in the 1970s
17 have been found to be in error because of artifact formation of H_2O_2 from reactions of
18 absorbed gaseous O_3 . Modeling results also indicate that lower levels of H_2O_2 occur in the
19 atmosphere, on the order of 1 ppb.

20 In-situ measurement methods for H_2O_2 include FTIR and tunable diode laser absorption
21 spectrometry (TDLAS). The FTIR method is specific for H_2O_2 but has a high detection
22 level of ~ 50 ppb (using a 1-km path length). The TDLAS method is also specific and has a
23 detection level of 0.1 ppb over averaging times of several minutes. Four frequently used wet
24 chemical methods for measurement of H_2O_2 are available. All involve the oxidation of a
25 substrate followed by instrumental detection and quantification of the resulting
26 chemiluminescence or fluorescence. Detection limits are comparable to those of FTIR and
27 TDLAS, but interferences are common and must be obviated or minimized with specified
28 procedures.

29 Calibration of methods for gaseous H_2O_2 measurement requires the immediate use of
30 standard mixtures prepared by one of several wet chemical methods.

3.7.4.2 Volatile Organic Compounds

Increased monitoring of volatile organic compounds is required under Title I, Section 182, of the Clean Air Act Amendments of 1990 because of their role as precursors to the formation of O₃ and other photochemical oxidants. Volatile organic compounds (VOCs) are those gaseous organic compounds that have a vapor pressure greater than 0.15 mm and generally have a carbon content ranging from C1 through C12. They include methane; nonmethane organic compounds (NMOC); nonmethane hydrocarbons (NMHC); polar, oxygenated hydrocarbons (PVOC); and reactive organic gases (ROG), which can include all of the subcategories listed here.

Traditionally, NMHCs have been measured by methods that employ a flame ionization detector (FID) as the sensing element that measures a change in ion intensity resulting from the combustion of air containing organic compounds. The method recommended by EPA for total NMOC measurement involves the cryogenic preconcentration of nonmethane organic compounds and the measurement of the revolatilized NMOCs using FID. The main technique for speciated NMOC/NMHC measurements is cryogenic preconcentration followed by GC-FID. Systems for sampling and analysis of VOCs have now been developed that require no liquid cryogen for operation, yet provide sufficient resolution of species.

Stainless steel canisters have become the containers of choice for collection of whole-air samples for NMHC/NMOC data. Calibration procedures for NMOC instrumentation require the generation, by static or dynamic systems, of dilute mixtures at concentrations expected to occur in ambient air.

Preferred methods for measuring carbonyl species (aldehydes and ketones) in ambient air are spectroscopic methods; on-line colorimetric methods; and the high-performance liquid chromatography (HPLC) method employing 2,4-dinitrophenylhydrazine (DNPH) derivatization in a silica gel cartridge. The most common method in current use for measuring aldehydes in ambient air is the HPLC-DNPH method. Use of an O₃ scrubber has been recommended to prevent interference in this method by O₃ in ambient air. Carbonyl species are reactive, making preparation of stable calibration mixtures difficult; but several methods are available.

Impetus for the development of methods for measuring the more reactive oxygen- and nitrogen-containing organic compounds has come from their roles as precursors or products

1 of photochemical oxidation but also from the inclusion of many of these compounds on the
2 list of hazardous air pollutants in the 1990 Clean Air Act Amendments. Measurement of
3 these polar volatile organic compounds (PVOCs) is difficult because of their reactivity and
4 water solubility. Methods are still in development.

6 3.7.4.3 Oxides of Nitrogen

7 Nitric oxide (NO) and nitrogen dioxide (NO₂) comprise the oxides of nitrogen (NO_x)
8 involved as precursors to ozone and other photochemical oxidants.

9 The most common method of NO measurement is the gas-phase chemiluminescent
10 (CL) reaction with ozone. The CL method is essentially specific for NO. Commercial NO
11 monitors have detection limits of a few parts per billion by volume (ppbv) in ambient air.
12 Commercial NO analyzers may not have sensitivity sufficient for surface measurements in
13 rural or remote areas, or for airborne measurements. Direct spectroscopic methods for NO
14 exist that have very high sensitivity and selectivity for NO. Major drawbacks of these
15 methods are their complexity, size, and cost, which restrict these methods to research
16 applications. No passive sampling devices (PSDs) presently exist for measurement of NO.

17 Chemiluminescence (CL) analyzers are the method of choice for NO₂ measurement,
18 even though they do not measure NO₂ directly. Minimum detection levels for NO₂ have
19 been reported to be 5 to 13 ppb, but more recent evaluations have indicated detection limits
20 of 0.5 to 1 ppbv. Reduction of NO₂ to NO is required for measurement. In practice,
21 selective measurement of NO_x by this approach has proved difficult. Commercial
22 instruments that use heated catalytic converters to reduce NO₂ to NO measure not NO and
23 NO_x, but more nearly NO and total NO_y. Thus, the NO₂ value inferred from such
24 measurements may be significantly in error, which may in turn affect the results of modeling
25 of ambient ozone.

26 Several spectroscopic approaches to NO₂ detection have been developed. As noted
27 above for NO, however, these methods have major drawbacks that include their complexity,
28 size, and cost, which outweigh at present the advantages of their sensitivity and selectivity.
29 Passive samplers for NO₂ exist, but are still in the developmental stage for ambient air
30 monitoring.

1 Calibration of methods for NO measurement is done using standard cylinders of NO in
2 nitrogen. Calibration of methods for NO₂ measurement include: use of cylinders of NO₂ in
3 nitrogen or air; use of permeation tubes; and gas-phase titration.
4

5 **3.7.5 Ozone Air Quality Models**

6 **3.7.5.1 Definitions, Descriptions, and Uses**

7 Photochemical air quality models are used to predict how O₃ concentrations change in
8 response to prescribed changes in source emissions of NO_x and VOCs. They are
9 mathematical descriptions of the atmospheric transport, diffusion, removal, and chemical
10 reactions of pollutants. They operate on sets of input data that characterize the emissions,
11 topography, and meteorology of a region and produce outputs that describe air quality in that
12 region.

13 Two kinds of photochemical models are recommended in guidelines issued by EPA:
14 The grid-based Urban Airshed Model (UAM) is recommended for modeling O₃ over urban
15 areas; and EKMA (the Empirical Kinetics Modeling Approach) is identified as an acceptable
16 approach under certain circumstances. The 1990 Clean Air Act Amendments mandate the
17 use of three-dimensional (grid-based) air quality models such as UAM in developing SIPs
18 (State Implementation Plans) for areas designated as extreme, severe, serious, or multistate
19 moderate.

20 In grid-based air quality models, the region to be modeled (the modeling domain) is
21 subdivided into a three-dimensional array of grid cells. Pertinent atmospheric processes and
22 chemical reactions are represented for each cell.

23 In trajectory models, such as EKMA, a hypothetical air parcel moves through the area
24 of interest along a path calculated from wind trajectories. Emissions are injected into the air
25 parcel and undergo vertical mixing and chemical transformations. Trajectory models provide
26 a dynamic description of atmospheric source-receptor relationships that is simpler and less
27 expensive to derive than that obtained from grid models, but meteorological processes are
28 highly simplified in trajectory models

29 The EKMA-based method for determining O₃ control strategies has some limitations,
30 the most serious of which is that predicted emissions reductions are critically dependent on
31 the initial NMHC/NO_x ratio used in the calculations. This ratio cannot be determined with

any certainty and is expected to be quite variable in an urban area. Grid-based models have their limitations as well. These are pointed out subsequently.

3.7.5.2 Model Components

Spatial and temporal characteristics of VOC and NO_x emissions are major inputs to a photochemical air quality model. Greater accuracy in emissions inventories is needed, for biogenics and for both mobile and stationary source components. Grid-based air quality models also require as input the three-dimensional wind field for the photochemical episode being simulated. This input is supplied by "meteorological modules" which fall into one of four categories: (1) objective analysis procedures; (2) diagnostic methods; (3) dynamic, or prognostic, methods; and (4) hybrid methods that embody elements from both diagnostic and prognostic approaches. Prognostic models are believed to provide a dynamically consistent, physically realistic, three-dimensional representation of the wind and other meteorological variables at scales of motion not resolvable by available observations. Outputs of prognostic models do not always agree with observational data, but methods have been devised to mitigate these problems.

A chemical kinetic mechanism (a set of chemical reactions), representing the important reactions that occur in the atmosphere, is used in an air quality model to estimate the net rate of formation of each pollutant simulated as a function of time. Chemical mechanisms that explicitly treat each individual VOC component of ambient air are too lengthy to be incorporated into three-dimensional atmospheric models. "Lumped" mechanisms are therefore used. The chemical mechanisms used in existing photochemical O₃ models contain uncertainties that may limit the accuracy of their predictions. Because of different approaches to "lumping" of reactions, models can produce somewhat different results under similar conditions. Both the UAM (UAM-IV) and EPA's Regional Oxidant Model (ROM) use the Carbon-Bond Mechanism-IV (CMB-IV). The CBM-IV and the SAPRC and RADM mechanisms (Statewide Air Pollution Research Center, and Regional Acid Deposition Model, respectively) are considered to represent the state-of-the-science.

Dry deposition, the removal of chemical species from the atmosphere by interaction with ground-level surfaces, is an important removal process for ozone on both urban and regional scales; and is included in all urban- and regional-scale models. Wet deposition (the

1 removal of gases and particles from the atmosphere by precipitation events) is generally not
2 included in urban-scale photochemical models, since O₃ episodes do not occur during periods
3 of significant clouds or rain.

4 Concentration fields of all species computed by the model must be specified at the
5 beginning of the simulation; these concentration fields are called the initial conditions. These
6 initial conditions are determined mainly with ambient measurements, either from routinely
7 collected data or from special studies; but interpolation can be used to distribute the surface
8 ambient measurements.

10 **3.7.5.3 Evaluation of Model Performance**

11 Air quality models are evaluated by comparing their predictions with ambient
12 observations. An adequate model should give accurate predictions of current peak
13 O₃ concentrations and temporal and spatial O₃ patterns. It should also respond accurately to
14 changes in VOC and NO_x emissions, to differences in VOC reactivity, and to spatial and
15 temporal changes in emissions patterns for future years. Likewise, multispecies comparisons
16 could be the key in discriminating among alternative modeling approaches that provide
17 similar predictions of O₃ concentrations. Adequate model performance for several reactive
18 species increases the assurance that correct ozone predictions are not a result of chance or
19 fortuitous cancellation of errors introduced by various assumptions.

20 If only a routine database is available for modeling O₃ in an urban area, then several
21 concerns require attention relative to model performance evaluation: air quality aloft,
22 boundary conditions, ambient VOC data, and meteorological data aloft. If any of these four
23 areas is missing from the database, the performance evaluation and subsequent model
24 application must be adequately planned to minimize the possibility of compensatory errors.

26 **3.7.5.4 Use of Ozone Air Quality Model for Evaluating Control Strategies**

27 Photochemical air quality models are used for control strategy evaluation by first
28 demonstrating that a past episode, or episodes, can be adequately simulated and then
29 reducing hydrocarbon or NO_x emissions or both in the model inputs and assessing the effects
30 of these reductions on O₃ in the region. The adequacy of control strategies based on grid-
31 based models depends in part on the nature of input data for simulations and model

1 validation, on input emissions inventory data, and on the mismatch between model output
2 and the current form of the NAAQS for O₃.

3 Grid-based models that have been widely used to evaluate control strategies for O₃ or
4 acid deposition, or both, are: (1) the Urban Airshed Model; (2) the California Institute of
5 Technology/Carnegie Institute of Technology (CIT) model; (3) the Regional Oxidant Model
6 (ROM); (4) the Acid Deposition and Oxidant Model (ADOM); and (5) the Regional Acid
7 Deposition Model (RADM).

8 9 **3.7.5.5 Conclusions**

10 Urban air quality models are becoming readily available for application and have been
11 applied in recent years in several urban areas. Significant progress has also been made in the
12 development of regional models and the integration of state-of-the-art prognostic
13 meteorological models as drivers.

14 There are still many uncertainties in photochemical air quality modeling. Prime among
15 these are emission inventories. However, models are essential for regulatory analysis and
16 constitute one of the major tools for attacking the O₃ problem. Grid-based O₃ air quality
17 modeling is superior to the available alternatives for O₃ control planning, but the chances of
18 its incorrect use must be minimized.

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8

4. ENVIRONMENTAL CONCENTRATIONS, PATTERNS, AND EXPOSURE ESTIMATES

4.1 INTRODUCTION

The ubiquity and toxicity of ozone (O_3) are well documented (U.S. Environmental Protection Agency, 1986a). Its effects on humans, animals, and vegetation have received extensive examination and are discussed later in this document (Chapters 5 through 9). As indicated in the previous O_3 criteria document (U.S. Environmental Protection Agency, 1986a), most of the human and welfare effects research has focused on evaluating the impacts on health or vegetation of exposure to O_3 that mimic ambient O_3 exposures (e.g., matching the occurrence of hourly average concentrations or more prolonged times of exposure). The concentration information extensively monitored in the United States can be useful for both linking anthropogenic emissions of O_3 precursors with the protection of health and welfare (i.e., determining compliance with air standards) and also to augment exposure assessment and epidemiology studies. Therefore, as in previous criteria documents, the major emphasis in this chapter will be on characterizing and summarizing the extensive O_3 monitoring data collected under ambient conditions. Although most of the O_3 air quality data summarized were gathered for compliance and enforcement purposes, the hourly averaged O_3 information can be used for determining patterns and trends and as inputs to exposure and health assessments (e.g., U.S. Environmental Protection Agency, 1992a; Lefohn et al., 1990a). In the sections that follow, the hourly averaged ambient O_3 data have been summarized in different ways to reflect the interests of those who wish to know more about the potential for O_3 to affect humans and their environment.

Trend patterns for O_3 over several periods of time are described in Section 4.2. The trends for O_3 have been summarized by the U.S. EPA (1993) for the period 1983 to 1992. In addition, trends analysis for specific regions of the United States have been performed by several investigators. In some cases, attempts have been made to adjust for meteorological variation. In Section 4.3, the hourly averaged concentration information from several monitoring networks has been characterized for urban and rural areas. The diurnal variation (Section 4.4) occurring at urban and rural locations, as well as seasonal patterns are also

described. Specific focus is provided on O₃ monitoring sites that are isolated from anthropogenic sources of ozone precursors because these locations form the "basis for comparison" for O₃ concentrations and exposures. In many cases, it is important to know O₃ exposure regimes experienced at isolated areas so that the regimes can be compared with those that are used in control treatments in experimental studies. In Section 4.5, the seasonal patterns of exposure are discussed. The hourly average concentration information is used in Section 4.6 to compare the spatial variations that occur in urban areas with those in nonurban areas, as well as in high-elevation locations. For comparing indoor to outdoor O₃ exposures or concentrations, information is provided in Section 4.7 on the latest data on indoor/outdoor ratios.

Section 4.8 describes efforts to estimate accurately both human and vegetation exposure to O₃. Examples are provided on how both fixed-site monitoring information, as well as human exposure models, are used to estimate risks associated with O₃ exposure. A short discussion is provided on the importance of hourly average concentrations, used in the human health and vegetation experiments, mimicking as closely as possible "real world" exposures.

As indicated in the previous O₃ criteria document (U.S. Environmental Protection Agency, 1986a), O₃ is the only photochemical oxidant other than nitrogen dioxide that is routinely monitored and for which a comprehensive aerometric data base exists. Data for peroxyacetyl nitrate (PAN) and hydrogen peroxide (H₂O₂) have been obtained as part of special research investigations. Consequently, no data on nationwide patterns of occurrence are available for these non-O₃ oxidants; nor are extensive data available on the correlations of levels and patterns of these oxidants with those of O₃. Sections 4.9 and 4.10 summarize the data available for these other oxidants. Section 4.11 describes the cooccurrence patterns of O₃ with nitrogen dioxide, sulfur dioxide, acidic aerosols, acidic precipitation, and acid cloudwater.

4.1.1 Characterizing Ambient Ozone Concentrations

For purposes of using air quality data for assessing human health and vegetation effects, it is important to distinguish among concentration, exposure, and dose. For human health considerations, Sexton and Ryan (1988) provide the following definitions, as described in the Air Quality Criteria for Carbon Monoxide (U.S. Environmental Protection Agency, 1991):

- 1 1. The *concentration* of a specific air pollutant is the amount of that material
2 per unit volume of air. Air pollution monitors measure pollutant
3 concentrations, which may or may not provide accurate exposure estimates.
4
- 5 2. The term *exposure* is defined as any contact between an air contaminant of
6 a specific concentration and the outer (e.g., skin) or inner (e.g., respiratory
7 tract epithelium) surface of the human body. Exposure implies the
8 simultaneous occurrence of the two events.
9

10
11 The concentration of an airborne contaminant that is measured in an empty room is not
12 exposure. However, a concentration measured in a room with people present is considered
13 to be a measurement of exposure. A measured concentration is a surrogate for exposure
14 only to the degree to which it represents concentrations actually experienced by individuals.
15 Exposure is defined as the pollutant concentration at the point of contact between the body
16 and the external environment, while dose is defined as the amount of pollutant that actually
17 crosses one of the body's boundaries and reaches the target tissue.

18 For vegetation, similar to human health considerations, concentrations of airborne
19 contaminants are considered to represent exposure when contacts with them are experienced
20 by a plant. As indicated in Chapter 5 (see Section 5.5), dose has been defined historically by
21 air pollution vegetation researchers as ambient air quality concentration multiplied by time
22 (O'Gara, 1922). However, a more rigorous definition is required. Runeckles (1974)
23 introduced the concept of "effective dose" as the amount or concentration of pollutant that
24 was adsorbed by vegetation, in contrast to that present in the ambient air. Fowler and Cape
25 (1982) developed this concept further and proposed that the "pollutant adsorbed dose" be
26 defined in units of g m^{-2} (of ground area or leaf area) and could be obtained as the product
27 of concentration, time, and stomatal (or canopy) conductance for the gas in question. Taylor
28 et al. (1982) suggested internal flux ($\text{mg m}^{-2} \text{h}^{-1}$) as a measure of the dose to which plants
29 respond. For the purposes of vegetation, this chapter has adopted the concept that dose is
30 the amount of pollutant absorbed by the plant.

31 In order to characterize the specific doses responsible for affecting human health and
32 vegetation, there has to be a linkage between exposure and the actual dose. Unfortunately, it
33 is difficult to predict this relationship without detailed modeling. For example, the sensitivity
34 of vegetation as a function of time of day or period of growth, as well as edaphic conditions,
35 may result in plants being exposed to high O_3 concentrations with little resultant injury or

1 damage, while more moderate levels of O₃ exposures result in injury (Showman, 1991).
2 Because (1) not enough is known to quantify the links between exposure and dosage and
3 (2) routine monitoring for O₃ is summarized as hourly average concentrations (i.e., potential
4 exposure), most of the information provided in this chapter is characterized in terms of
5 concentration and exposure.

6 As indicated in the human health and vegetation chapters (Chapters 7 and 5), for many
7 years, air pollution specialists have explored alternative mathematical approaches for
8 summarizing ambient air quality information in biologically meaningful forms that can serve
9 as surrogates for dose. At present, for human health effects purposes, O₃ is usually
10 characterized in terms of the daily maximum (i.e., the highest hourly average concentration
11 for the day). In addition, recent human health concern about O₃ exposures for extended
12 periods has resulted in the summarization of hourly average concentrations of O₃ in terms of
13 4- to 8-h daily maximum concentrations (see Chapter 7 for further discussion).

14 For vegetation, as indicated in Chapter 5 (Section 5.5), extensive research has focused
15 on identifying indicators of exposure with a firm foundation on biological principles. Many
16 of these indicators have been based on research results indicating that the magnitude of
17 vegetation responses to air pollution is determined more as a function of the magnitude of the
18 concentration than the length of the exposure (U.S. Environmental Protection Agency,
19 1986b; U.S. Environmental Protection Agency, 1992b). Short-term, high concentration
20 O₃ exposures have been identified by many researchers as being more important than
21 long-term, low concentration exposures for induction of effects on vegetation (see Chapter 5
22 for further discussion). Similarly, for human health considerations, results using controlled
23 human exposures have shown the possible importance of concentration in relation to duration
24 of exposure and ventilation rate. The product of O₃ concentration multiplied by exposure
25 duration was shown to be an imprecise indicator of O₃ toxicity when the rate of O₃
26 inhalation was increased (DeLucia et al., 1978). Folinsbee et al. (1978) and Silverman et al.
27 (1976) observed that O₃ toxicity was better represented by an effective dose expressed as the
28 product of concentration, exposure duration, and ventilation. Adams et al. (1981) examined
29 the effective dose concept and concluded that O₃ concentration was of greater importance in
30 affecting pulmonary function decrement than either ventilation or exposure duration.
31 Pulmonary function research results reported by Hazucha et al. (1990) have also revealed

1 that concentration may be more important than duration. Horstman et al. (1990) reported
2 that O₃ concentration was slightly more influential than exposure duration for inducing
3 FEV_{1,0} responses. Lung function modelling results reported by Larsen et al. (1991) appears
4 to agree with previous reports that concentration is one of the most important components of
5 exposure and that the higher hourly average concentrations should be weighted differently
6 than the lower ones.

7 Long-term average concentrations initially were used to describe O₃ exposures when
8 assessing vegetation effects (Heck et al., 1982). However, as evidence began to mount that
9 higher concentrations of O₃ should be given more weight than lower concentrations (see
10 Section 5.5 for further details), the following specific concerns about the use of a long-term
11 average to summarize exposures of O₃ began appearing in the literature: (1) the use of a
12 long-term average failed to consider the impact of peak concentrations, as well as duration;
13 (2) a large number of hourly distributions within a 7-h (0900 to 1559 h) window could be
14 used to generate the same 7-h seasonal mean; and (3) high hourly average concentrations
15 (e.g., values greater than 0.10 ppm) occurred outside of a fixed 7-h window.

16 In summarizing the hourly average concentrations in this chapter, specific attention is
17 given to the relevance of the exposure indicators used. For example, for human health
18 considerations, concentration (or exposure) indicators such as the daily maximum 1-h average
19 concentrations, as well as the number of daily maximum 4-h or 8-h average concentrations
20 are used to characterize information in the population-oriented locations. For vegetation,
21 several different types of exposure indicators are used. For example, much of the National
22 Crop Loss Assessment Network (NCLAN) exposure information is summarized in terms of
23 the 7-h average concentrations. However, because peak-weighted, cumulative indicators
24 (i.e., exposure parameters that sum the products of hourly average concentrations multiplied
25 by time over an exposure period) have shown considerable promise in relating exposure and
26 vegetation response (see Section 5.5), several exposure indicators that use either a threshold
27 or a sigmoidally weighting scheme are used in this chapter to provide insight concerning the
28 O₃ exposures that are experienced at a select number of rural monitoring sites in the United
29 States. The peak-weighted cumulative exposure indicators used in this chapter are SUM06
30 (the sum of all hourly average concentrations equal to or greater than 0.06 ppm), SUM08
31 (the sum of all hourly average concentrations equal to or greater than 0.08 ppm), and W126

(the sum of the hourly average concentrations that have been weighted according to a sigmoid function [see Lefohn and Runeckles, 1987] that is theoretically based on a hypothetical vegetation response) are used.

The exposure indicators used for human health considerations are in concentration units (i.e., ppm), whereas the indicators used for vegetation are in both ppm (e.g., 7-h seasonal average concentrations) and ppm-h (e.g., SUM06, SUM08, and W126). The magnitude of the peak-weighted cumulative indicators at specific sites can be compared with those values experienced at pristine areas. In some cases, to provide more detailed information about the distribution patterns for specific O₃ exposure regime, the percentile distribution of the hourly average concentrations (in units of ppm) is given. For further clarification of the determination and rationale for the exposure indicators that are used for assessing human health and vegetation effects, the reader is encouraged to read Chapters 5 (Section 5.5) and 7.

4.1.2 The Identification and Use of Existing Ambient Ozone Data

Information is readily available from the database supported by a network of monitoring stations that were established to determine the compliance with the National Ambient Air Quality Standard for O₃. Most of the data presented in this chapter were obtained from data stored in the EPA's computerized Aerometric Information Retrieval System (AIRS) and were collected after 1978. As pointed out in the previous criteria document for O₃ and other photochemical oxidants (U.S. Environmental Protection Agency, 1986a), there was some difficulty in interpreting the O₃ data obtained at most sites across the United States prior to 1979 because of calibration problems.

In the United States, O₃ hourly average concentrations are routinely monitored through the National Air Monitoring Network, consisting of three types of sites. The National Air Monitoring Station (NAMS) sites are located in areas where the concentrations of O₃ and subsequent potential human exposures are expected to be high. Criteria for these sites have been established by regulation to meet uniform standards of siting, quality assurance, equivalent analytical methodology, sampling intervals, and instrument selection to assure consistency among the reporting agencies. For O₃, NAMS sites are located only in urban areas with populations exceeding 1 million. The other two types of sites are States and Local

1 Air Monitoring Stations (SLAMS) and Special Purpose Monitors, which meet the same rigid
2 criteria for the NAMS sites but may be located in areas which do not necessarily experience
3 high concentrations in populated areas.

4 For O₃, the reporting interval is 1 h, with the instruments operating continuously and
5 producing an integrated hourly average measurement. In many cases, the U.S.
6 Environmental Protection Agency summarizes air quality data by an O₃ "season." Table 4-1
7 summarizes the O₃ "season" for the various states in the United States.

8 In this chapter, data are analyzed for the purpose of providing focus on specific issues
9 of exposure-response relationships that are considered in later effects chapters. The analyses
10 proceed from a national picture of peak annual averages in Metropolitan Statistical Areas,
11 through national 10-year and 3-year trends, to characteristic seasonal and diurnal patterns at
12 selected stations, and a brief examination of the incidence of episodic 1-h levels. Although
13 there are O₃ data collected from monitoring stations not listed in AIRS, the major source of
14 information was derived from ambient air concentrations from monitoring sites operated by
15 the State and local air pollution agencies who report their data to AIRS. Because
16 meteorology affects the identification of trends, methodologies which adjust for meteorology
17 are described.

18 To obtain a better understanding of the potential for ambient O₃ exposures to affect
19 human health and vegetation, hourly average concentration information was summarized for
20 urban versus rural (forested and agricultural) areas in the United States. A land use
21 characterization of "rural" does not imply that any specific location is isolated from
22 anthropogenic influences. For example, Logan (1989) has noted that hourly average
23 O₃ concentrations above 0.08 ppm are common in rural areas of the eastern United States in
24 spring and summer, but are unusual at remote western sites. Consequently, for comparing
25 exposure regimes that may be characteristic of clean locations in the United States with those
26 that are urban influenced (i.e., located in either urban or rural locations), this chapter
27 characterizes data collected from those stations whose locations appear to be isolated from
28 large-scale anthropogenic influences.

29 For the most part, research on O₃ concentrations is clearly divided between ambient air
30 environments and indoor air environments, although some exposure studies use personal
31 monitors to measure continuous O₃ concentrations in both situations. Long-term

TABLE 4-1. OZONE MONITORING SEASON BY STATE

State	Begin	End	State	Begin	End
Alabama	March	November	Montana	June	September
Alaska	April	October	Nebraska	April	October
Arizona	January	December	Nevada	January	December
Arkansas	March	November	New Hampshire	April	October
California	January	December	New Jersey	April	October
Colorado	March	September	New Mexico	January	December
Connecticut	April	October	New York	April	October
Delaware	April	October	North Carolina	April	October
D.C.	April	October	North Dakota	May	September
Florida	January	December	Ohio	April	October
Georgia	March	November	Oklahoma	March	November
Hawaii	January	December	Oregon	April	October
Idaho	April	October	Pennsylvania	April	October
Illinois	April	October	Rhode Island	April	October
Indiana	April	October	South Carolina	April	October
Iowa	April	October	South Dakota	June	September
Kansas	April	October	Tennessee	April	October
Kentucky	April	October	Texas ^a	January	December
Louisiana	January	December	Texas ^b	March	October
Maine	April	October	Utah	May	September
Maryland	April	October	Vermont	April	October
Massachusetts	April	October	Virginia	April	October
Michigan	April	October	Washington	April	October
Minnesota	April	October	West Virginia	April	October
Mississippi	March	November	Wisconsin	April	October
Missouri	April	October	Wyoming	April	October

^aAQCR numbers 4, 5, 7, 10, and 11.

^bAQCR numbers 1, 2, 3, 6, 8, 9, and 12.

(multiple-year) patterns and trends are available only from stationary ambient monitors; data on indoor concentrations are collected predominantly in selected settings during comparatively short-term studies. Data from the indoor and outdoor environments are reviewed here independently.

4.2 TRENDS IN OZONE CONCENTRATIONS

4.2.1 Trends in Ambient Ozone Concentrations

Ozone concentrations and thus, exposure, change from year to year. Ambient trends during the 1980s were heavily influenced by varying meteorological conditions (U.S. Environmental Protection Agency, 1993). High O₃ levels occurred in 1983 and 1988 in some areas of the United States. These levels were more than likely attributable in part to hot, dry, stagnant conditions. However, O₃ levels in 1992 were the lowest of the 1983 to 1992 period (U.S. Environmental Protection Agency, 1993). These low levels may have been due to less favorable meteorological conditions for O₃ formation, as well as recently implemented control measures. Nationally, the summer of 1992 was the third coolest summer on record (U.S. Environmental Protection Agency, 1993). The U.S. EPA (1993) has recently reported a 21 % improvement in O₃ levels between 1983 and 1992, which in part may be attributed to relatively high levels in 1983, compared to the low O₃ exposure year from the period 1989 through 1992. However, new statistical techniques accounting for meteorological influences have been used by the U.S. EPA and they appear to suggest an improvement (independent of meteorological considerations) of 10% for the 10-year period, 1983 to 1992.

The U.S. Environmental Protection Agency summarizes trends for the National Ambient Air Quality Standards (NAAQS) for the most current 3- and 10-year periods. In order to be included in the 10-year trend analysis in the annual National Air Quality and Emissions Trend Report (U.S. Environmental Protection Agency, 1993) a station must report valid data for at least eight of the last ten years. A companion analysis of the most recent three years requires valid data in all three years. Analysis in the above report covers the periods 1983 to 1992 and 1990 to 1992, respectively; 509 sites met the 10-year period

criteria, 672 sites are included in the 1990 to 1992 data base. The NAMS sites comprise 196 of the long-term trends sites and 222 of the sites in the 3-year data base.

Figure 4-1 displays the 10-year composite average trend for the second highest daily maximum hourly average concentration during the O₃ season for the 509 trend sites and the subset of 196 NAMS sites. The 1992 composite average for the 509 trend sites is 21 % lower than the 1983 average and 20% lower for the subset of 196 NAMS sites. The 1992 value is the lowest composite average of the past ten years (U.S. Environmental Protection Agency, 1993). The 1992 composite average is significantly less than all the previous nine years, 1983 to 1991. As discussed in U.S. EPA (1992a), the relatively high O₃ concentrations in 1983 and 1988 were likely attributable in part to hot, dry stagnant conditions in some areas of the country that were especially conducive to O₃ formation.

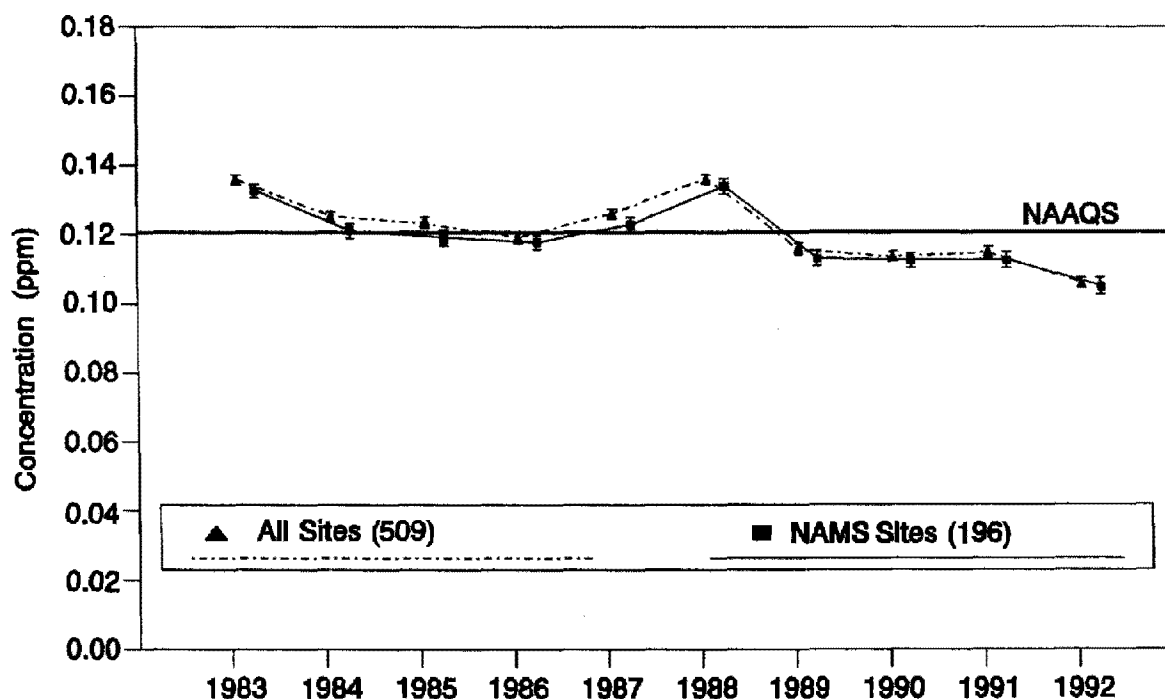


Figure 4-1. National trend in the composite average of the second highest maximum 1-h ozone concentration at both NAMS and all sites with 95% confidence intervals, 1982 to 1991.

Source: U.S. Environmental Protection Agency (1993).

1 Between 1991 and 1992, the composite mean of the second highest daily maximum
2 1-h O₃ concentrations decreased 7% at the 672 sites and 6% at the subset of 222 NAMS
3 sites. Between 1991 and 1992, the composite average of the number of estimated
4 exceedances of the O₃ standard decreased by 23% at the 672 sites, and 19% for the
5 222 NAMS sites. Nationwide VOC emissions decreased 3% between 1991 and 1992 (U.S.
6 Environmental Protection Agency, 1993).

7 The composite average of the second daily maximum concentrations decreased in eight
8 of the ten EPA Regions between 1991 and 1992, and remained unchanged in Region VII.
9 Except for Region VII, the 1992 regional composite means are lower than the corresponding
10 1990 levels.

11 Investigators have explored methods for investigating techniques for adjusting O₃ trends
12 for meteorological influences (Stoeckenius and Hudischewskyj, 1990; Wakim, 1990; Shively,
13 1991; Korsog and Wolff, 1991; Lloyd et al., 1990; Davidson, 1993; Cox and Chu, 1993).
14 Stoeckenius and Hudischewskyj (1990) used a classification method to group days into
15 categories according to the magnitude of O₃ and similarity of meteorological conditions
16 within each defined group. Adjusted O₃ statistics for each year were computed from the
17 meteorologically grouped data and the yearly frequency of occurrence of each group relative
18 to its long-term frequency was described. Wakim (1990) used standard regression analysis to
19 quantify the effect of daily meteorology on O₃. Adjusted O₃ statistics were calculated by
20 adding the expected O₃ statistic for a year with typical meteorology to the average of the
21 regression residuals obtained for the adjusted year. Shively (1991) described a model in
22 which the frequency of exceedance of various O₃ thresholds was modeled as a non-
23 homogeneous Poisson process where the parameter is a function of time and meteorological
24 variables. Kolaz and Swinford (1990) categorized O₃ days as "conductive" or "non-
25 conductive" based on selected meteorological conditions within the Chicago area. Within
26 these categories, the meteorological intensity of days conducive to daily exceedances of the
27 NAAQS for O₃ was calculated and used to establish long-term trends in the annual
28 exceedance rate.

29 Recently, Cox and Chu (1993) have modeled the daily maximum O₃ concentration
30 using a Weibull distribution with a fixed shape parameter and a scale parameter, the
31 logarithm of which varies as a linear function of several meteorological variables and a

1 yearly index. The authors tested for a statistically significant trend term to determine if an
2 underlying meteorologically adjusted trend could be detected. Overall the measured and
3 modeled predicted percentiles tracked closely in the northern latitudes but performed less
4 well in southern coastal and desert areas. The results suggested that meteorologically
5 adjusted upper percentiles of the distribution of daily maximum 1-h O₃ are decreasing in
6 most urban areas over the period 1981 through 1991. The median rate of change was
7 -1.1% per year, indicating that O₃ levels have decreased approximately 11% over this time
8 period. The authors reported that trends estimated by ignoring the meteorological component
9 appear to underestimate the rate of improvement in O₃ primarily because of the uneven year-
10 to-year distribution of meteorological conditions favorable to O₃ formation.

11 Lefohn et al. (1993a) focused on a potentially useful method for identifying monitoring
12 sites whose improvement in O₃ exposures may be attributed more to the implementation of
13 abatement control strategies than meteorological changes. As has been pointed out
14 previously, meteorology plays an important role in affecting the O₃ concentrations that are
15 contained in the tail of the 1-h distributions, as indicated by the successful predictive
16 application of the exponential-tail model to distributions (California Air Resources Board,
17 1992). Because meteorology plays such an important role in affecting the tail of the 1-h
18 distribution at a specific site, changes in "attainment" status would be expected not to affect
19 changes in the entire distribution pattern and thus, the average diurnal pattern. Lefohn et al.
20 (1993b) investigated the change in the annual averaged diurnal pattern as changes in
21 O₃ levels occurred. The authors reported that although the amplitude of the diurnal patterns
22 changed, there was little evidence for consistent changes in the shape of the annual diurnal
23 patterns (Figure 4-2). In a follow-up to this analysis, Lefohn et al. (1993a) reported that
24 25 of the 36 sites that changed compliance status across years showed no statistically
25 significant change in the shape of the average diurnal profile (averaged by O₃ season).
26 In addition, the authors reported that for 71% (10 out of 14) of the sites in southern
27 California and Dallas-Fort Worth, Texas, that showed improvement in O₃ levels (i.e.,
28 reductions in the number of exceedances over the years), but still remained in
29 "nonattainment," a statistically significant change in the shape of the seasonally averaged
30 diurnal profile occurred (Figure 4-3). Thus, the authors noted that for the southern
31 California and Dallas-Fort Worth sites, which showed improvements in O₃ levels, changes

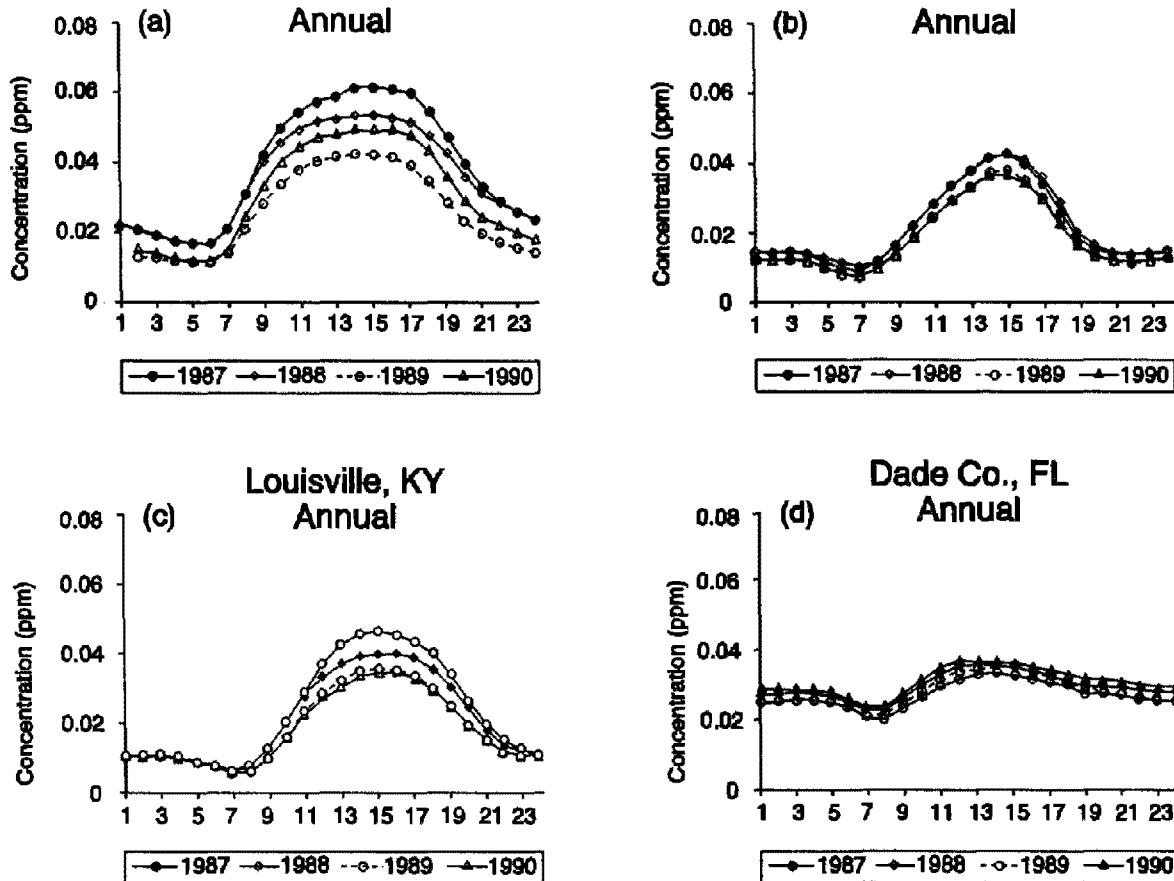


Figure 4-2. The annually averaged composite diurnal curves for the following sites that changed from nonattainment to "attainment status:" (a) Montgomery County, AL, (b) Concord, CA, (c) Louisville, KY, and (d) Dade County, FL for the period 1987 to 1990. The darkened curve in each figure identified the year in which the greatest number of daily maximum 4-h average concentrations ≥ 0.08 ppm occurred.

Source: Lefohn et al. (1993b).

were observed in the seasonally averaged diurnal profiles, while for the sites moving between "attainment" and "nonattainment" status, such a change in shape was generally not observed. Lefohn et al. (1993a) pointed out that it was possible that meteorology played a more important role in affecting attainment status than changes in emission levels.

Historically, the long-term O₃ trends in the United States characterized by the U.S. Environmental Protection Agency have emphasized air quality statistics that are closely

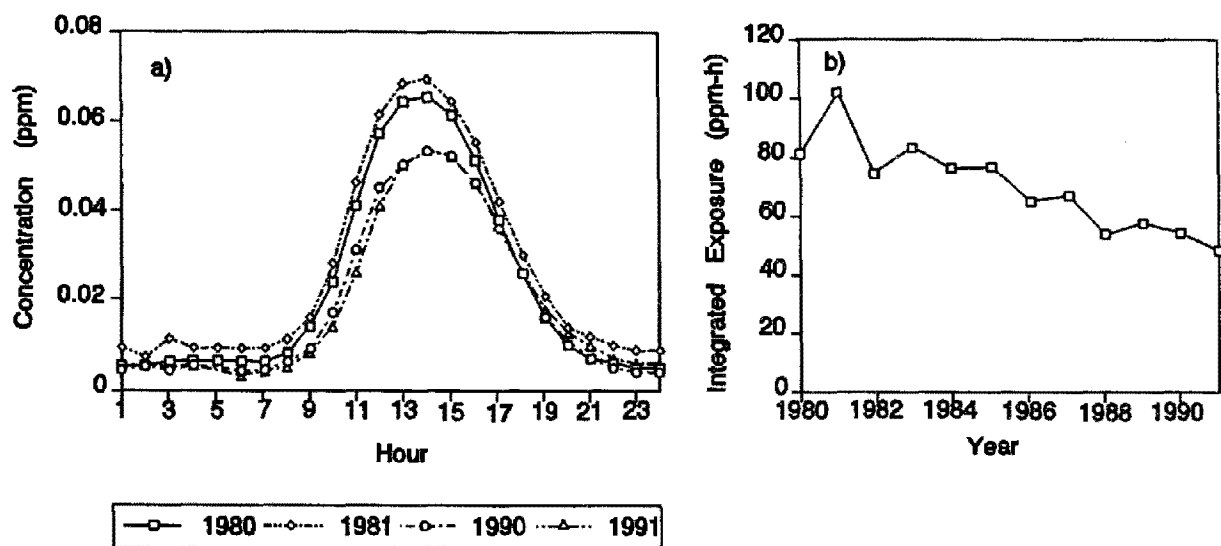


Figure 4-3. A summary of the (a) seasonal (January to December) averaged composite ozone diurnal curve and (b) integrated exposure W126 index for the Los Angeles, CA site for the period 1980 to 1991.

Source: Lefohn et al. (1993a).

related to the NAAQS. A recent report by the National Academy of Sciences (NAS) (NRC, 1991) stated that the principal measure currently used to assess O_3 trends is highly sensitive to meteorological fluctuations and is not a reliable measure of progress in reducing O_3 over several years for a given area. The NAS report recommended that "more statistically robust methods be developed to assist in tracking progress in reducing ozone." The NAS report points out that most of the trends analyses are developed from violations of standards based on lower concentration cutoffs or using percentile distributions. Because of the interest by the EPA in tracking trends in the quality of air people breathe when outdoors, most of the above measures have some association with the existing NAAQS, in the form of either threshold violations or O_3 concentrations.

Several of the alternative examples provided in the NAS report were described previously by Curran and Frank (1990). Several of the examples mentioned in the NAS report involved threshold violations: the number of days on which the maximum O_3 concentration was above 0.12 ppm (Jones et al., 1989; Kolaz and Swinford, 1990; Wakim, 1990); the number of times during the year that the daily summary statistics

1 exceeded 0.08 ppm or 0.105 ppm (Stoeckenius, 1990); and the number of days in California
2 when the O₃ concentration exceeded 0.20 ppm (Zeldin et al., 1990). Several other
3 O₃ concentration measures are described in the NAS (NRC, 1991) report.

4 As an alternative to the way in which the U.S. EPA historically implemented its trends
5 analysis, the EPA (1992a) used percentiles in the range from 50th percentile (or median) to
6 the 95th percentile. The U.S. EPA (1992a) reported that the pattern for the 10-year trends
7 (1982 to 1991) using the various alternative O₃ summary statistics were somewhat similar.
8 There was a tendency for the curves to become flatter in the lower percentiles. The peak
9 years of 1983 and 1988 were still evident in the trend lines for each indicator. The increase
10 of 8% recorded in the annual second-highest daily maximum 1-h concentration between 1987
11 and 1988 was also seen in the 95th and 90th percentile concentrations. The lower percentile
12 indicators had smaller increases of 3 to 4%. The percent change between 1982 and 1991 for
13 each of the summary statistics follows: annual daily maximum 1-h concentration (-11%),
14 annual second daily maximum 1-h concentration (-8%), 95th percentile of the daily
15 maximum 1-h concentrations (-5%), 90th percentile (-4%), 70th percentile (-1%), 50th
16 percentile, or median of the daily maximum 1-h concentrations (+1%), and the annual mean
17 of the daily maximum 1-h concentrations (-1%).

18 Besides the U.S. Environmental Protection Agency, additional investigators have
19 assessed trends at several locations in the United States (e.g., Kuntasal and Chang, 1987),
20 (Gallopoulos et al., 1988; Korsog and Wolff, 1991; Lloyd et al., 1990; Rao et al., 1992;
21 Davidson, 1993). For example, Kuntasal and Chang (1987) performed a basin-wide air
22 quality trend analysis for the South Coast Air Basin of California using multi-station
23 composite daily maximum-hour average ambient concentrations for the third quarter from
24 1968 to 1985. Basin-wide ambient O₃ concentrations appeared to show downward trends for
25 the period 1970 to 1985, but because of high fluctuations, it was difficult to delineate trends
26 for shorter periods. The meteorology (850 mb temperature)-adjusted O₃ showed a more
27 consistent downward trend than did unadjusted O₃. Korsog and Wolff (1991) examined
28 trends from 1973 to 1983 at eight major population centers in the northeastern United States,
29 using a robust statistical method. The 75th percentile was shown to be a good statistic for
30 determining trends and was used for analysis of the trends. The surface temperature and
31 upper air temperature variables were found to be the best predictors of O₃ behavior. Two

1 regression procedures were performed to remove the variability of meteorological conditions
2 conducive to high O₃ (i.e., O₃ concentrations >0.08 ppm). The results of the analysis
3 showed that there has been a decrease of a few ppb on a yearly basis for the majority of the
4 sites investigated by the authors.

5 Lloyd et al. (1989) investigated the improvement in O₃ air quality from 1976 to 1987 in
6 the South Coast Air Basin of California. The authors reported that when the trend in total
7 exceedance hours of a consistent set of Basin air monitoring stations was considered, the
8 improvement over the period of investigation was substantial. The authors reported that the
9 number of station hours at or above the Stage I Episode Level (0.20 ppm, 1-h average) had
10 decreased by about two-thirds over the period 1976 to 1987. Davidson (1993) reported on
11 the number of days on which O₃ concentrations at one or more stations in the South Coast
12 Air Basin exceeded the federal standard and the number of days reaching Stage I episode
13 levels, for the months of May through October in the years from 1976 to 1991. The author
14 reported that the number of Basin days exceeding the federal standard declined at an average
15 annual rate of 2.27 days per year over the period. In addition, the number of Basin days
16 with Stage I episodes declined at an average annual rate of 4.70 days per year over the
17 period 1976 to 1991. Rao et al. (1992) demonstrated the use of some statistical methods for
18 examining trends in ambient O₃ air quality downwind of major urban areas. The authors
19 examined daily maximum 1-h O₃ concentrations measured over New Jersey, metropolitan
20 New York City, and Connecticut for the period 1980 to 1989. The analyses indicated that
21 although there has been an improvement in O₃ air quality downwind of New York City,
22 there has been little change in O₃ levels upwind of New York City during this 10-year
23 period.

24 Lefhon and Runeckles (1987) proposed a sigmoidal weighting function that was used in
25 developing a cumulative integrated exposure index (W126):
26

$$w_i = \frac{1}{[1 + M \times \exp^{(-A \times c_i)}]} \quad (4-1)$$

27 where: M and A are positive arbitrary constants,
28 w_i = weighting factor for concentration i, and
29 c_i = concentration i.

1 Lefohn et al. (1988) reported the use of the sigmoidally weighted index with constants,
2 M and A, 4,403 and 126 ppm⁻¹, respectively. The authors referred to the index as W126.
3 The values were subjectively determined to develop a weighting function that (1) included
4 hourly average concentrations as low as 0.04 ppm, (2) had an inflection point near
5 0.065 ppm, and (3) had an equal weighting of 1 for hourly average concentrations at
6 approximately 0.10 ppm and above. To determine the value of the index, the sigmoidal
7 weighting function at c_i was multiplied by the hourly average concentration, c_i , and summed
8 over all relevant hours. The index included the lower, less biologically effective
9 concentrations in the integrated exposure summation. The weighting function has been used
10 to describe the relationship between O₃ exposure and vegetation response (e.g., Lefohn
11 et al., 1988; Lefohn et al., 1992a).

12 Lefohn and Shadwick (1991), using the W126 sigmoidally weighted exposure index,
13 assessed trends in O₃ exposures at rural sites in the United States over 5- and 10-year periods
14 (1984 to 1988 and 1979 to 1988, respectively) for forestry and agricultural regions of the
15 United States. Although their analysis did not explore the effects on trends of the lower
16 O₃ exposure period 1989 to 1992, their analysis did reflect the effect of the higher
17 O₃ exposure years (1983 and 1988). To compare the exposure index values across years, a
18 correction for missing data was applied for each pollutant. The corrections were determined
19 for each site on a monthly basis. The Kendall's K statistic (Mann-Kendall test) was used to
20 identify linear trends. Estimates of the rate of change (slope) for the index were calculated.
21 Table 4-2 summarizes the results of the analysis. For sites distributed by forestry regions,
22 there were more positive than negative slope estimates for the 5-year analysis of sites in the
23 Southern, Midwest, and Mid-Atlantic regions. For the 10-year analysis, the above was true
24 except for the Mid-Atlantic seasonal analysis, where there was one positive and one negative
25 significant trend. In the Southern region, 38% of the sites showed significant trends. For the
26 sites in the Northeastern region, few sites showed a significant trend. There were
27 considerably fewer sites in the remaining regions than in the four forestry regions above.
28 Hence, for these regions, no significance was assigned to the differences in the number of
29 negative and positive slope estimates in the tables. Similar to the results reported for the
30 forestry regions, most of the sites in the agricultural regions showed no O₃ trends.

TABLE 4-2. SUMMARY BY FORESTRY AND AGRICULTURAL REGIONS FOR OZONE TRENDS USING THE W126 EXPOSURE PARAMETER ACCUMULATED ON A SEASONAL BASIS^a

	Forestry						
	Five-Year Trends				Ten-Year Trends		
	Not Significant		Significant		Not Significant		Significant
			-	+		-	+
South	53	(16)	0	14	13	1	7
Midwest	38	(1)	0	7	20	1	6
West	10	(0)	0	3	4	2	1
Pacific Northwest	4	(2)	0	0	2	0	0
Plains	3	(0)	0	0	2	0	0
Northeast	14	(0)	1	0	7	1	1
Mid-Atlantic	12	(0)	0	3	4	1	1
Rocky Mountains	5	(2)	0	1	2	0	1
All	139	(21)	1	28	54	6	17

	Agricultural						
	Five-Year Trends				Ten-Year Trends		
	Not Significant		Significant		Not Significant		Significant
			-	+		-	+
Pacific	14	(2)	0	3	6	2	1
Mountain	5	(2)	0	1	2	0	1
Northern Plains	3	(0)	0	0	2	0	0
Lake States	10	(0)	0	1	5	0	1
Corn Belt	20	(1)	0	3	11	1	2
Northeast	26	(0)	1	3	11	2	2
Appalachian	27	(9)	0	14	8	0	8
Southeast	16	(5)	0	1	4	1	0
Delta State	9	(0)	0	2	4	0	1
Southeastern Plains	9	(2)	0	0	1	0	1
All	139	(21)	1	28	54	6	17

^aNumbers in parentheses in the "Not Significant" column under "Five-year trends" are the number of sites with exactly 3 years of data.

Source: Lefhon and Shadwick, 1991.

1 However, in the Appalachian agricultural region, as many as 50% of the sites showed a
2 pronounced indication of a trend. A predominance of positive significant trends for both the
3 5- and 10-year analyses was observed. In the other agricultural regions, there were
4 approximately an equal number of positive and negative significant 5- and 10-year trends.
5 The O₃ results produced patterns that were not pronounced enough to draw more than
6 tentative conclusions for the 10-year analysis. For the 5-year analysis, there was still not a
7 strong indication of an O₃ trend. However, when significant trends were observed, they
8 were almost always positive. This can be attributed to eastern O₃ levels that were generally
9 higher in 1988 than in previous years.

12 **4.3 SURFACE OZONE CONCENTRATIONS**

13 **4.3.1 Introduction**

14 Ozone is an omnipresent compound that is measured at levels above the minimum
15 detectable level at all monitoring locations in the world (Lefohn et al., 1990b). Stratospheric
16 sources of O₃ play an important role in determining the O₃ concentrations at remote sites that
17 are isolated from either local generation of O₃ or the transport of O₃ or its precursors (Singh
18 et al., 1978). The occasional occurrence of stratospheric injection of O₃, at specific times
19 and in certain locations, is accepted and may be responsible for some of the rare occurrences
20 of elevated levels that have been observed at both some high- and low-elevation remote sites.
21 Altshuller (1989) attributes approximately 10 ppb of surface-level O₃ concentration to
22 stratospheric intrusion.

23 For purposes of comparing how O₃ levels have changed over time, it would be
24 interesting to know how current levels compare to natural background levels. However,
25 estimations of natural background O₃ concentrations are difficult to make. The definitions of
26 natural background and use of the information are subject to much uncertainty. It is
27 difficult, if not impossible, to determine whether any geographic location on Earth is free
28 from human influence (Finlayson-Pitts and Pitts, 1986). Finlayson-Pitts and Pitts (1986)
29 have noted that photochemical production via naturally occurring NO_x-NMOC (non-methane
30 organic compounds) or carbon monoxide reactions in sunlight may be more important than
31 injection of O₃ from the stratosphere. Natural emissions can influence O₃ exposures

1 observed at remote sites (Chameides et al., 1988; Zimmerman, 1979; Trainer et al., 1987).
2 Citing indirect evidence for the possible importance of natural emissions, Lindsay et al.
3 (1989) have emphasized that additional research is required to assess the role that natural
4 hydrocarbons might play in urban and regional O₃ episodes.

5 Ozone concentrations at a specific location are influenced by local emissions and by
6 long-range transport from both natural and anthropogenic sources. In addition, levels are
7 also influenced by variables such as wind, solar insolation, vertical exchange rates, and the
8 nature of the surface. For a more complete discussion, see Chapter 3.

9 It is possible for urban emissions, as well as O₃ produced from urban area emissions,
10 to be transported to more rural downwind locations. This can result in elevated
11 O₃ concentrations at considerable distances from urban centers (Wolff et al., 1977; Husar
12 et al., 1977; Wight et al., 1978; Vukovich et al., 1977; Wolff and Lioy, 1980; Pratt et al.
13 1983; Logan, 1985; Altshuller, 1986; U.S. Environmental Protection Agency, 1986a; Kelly
14 et al., 1986; Pinkerton and Lefohn, 1986; Lefohn et al., 1987a; Logan, 1989; Lefohn and
15 Lucier, 1991; Taylor and Hanson, 1992). For example, on over 40% of the 98 days that the
16 maximum 1-h O₃ concentrations exceeded 0.120 ppm, the highest value was measured
17 downwind of St. Louis at one of the rural sites, which was located approximately 50 km
18 from downtown St. Louis (Altshuller, 1986). Urban O₃ concentration values are often
19 depressed because of titration by nitric oxide (Stasiuk and Coffey, 1974). Reagan (1984) and
20 Lefohn et al. (1987a) have observed this phenomenon where O₃ exposures at center-city sites
21 were lower than some rural locations. Because of the absence of chemical scavenging,
22 O₃ tends to persist longer in nonurban than in urban areas (U.S. Environmental Protection
23 Agency, 1986a; Coffey et al., 1977; Wolff et al., 1977; Isaksen et al., 1978).

24 The distribution of O₃ or its precursors at a rural site near an urban source is affected
25 by wind direction (i.e., whether the rural site is located up- or down-wind from the source)
26 (Kelly et al., 1986; Lindsay and Chameides, 1988). Thus, it may be difficult to apply land-
27 use designations to the generalization of exposure regimes that may be experienced in urban
28 versus rural areas. Because of this, it is difficult to identify a set of unique O₃ distribution
29 patterns that adequately describe exposures experienced at monitoring sites in rural locations
30 (Lefohn et al., 1990a).

4.3.2 Urban Area Concentrations

Figure 4-4 shows the highest second daily maximum 1-h average O_3 concentrations in 1991 across the United States. The highest second daily maximum 1-h O_3 concentrations by Metropolitan Statistical Area (MSA) for the years 1989 to 1991 are summarized in Table 4-3. The highest O_3 concentrations are observed in southern California, but high levels also persist in the Texas Gulf Coast, Northeast corridor and other heavily populated regions in the United States.

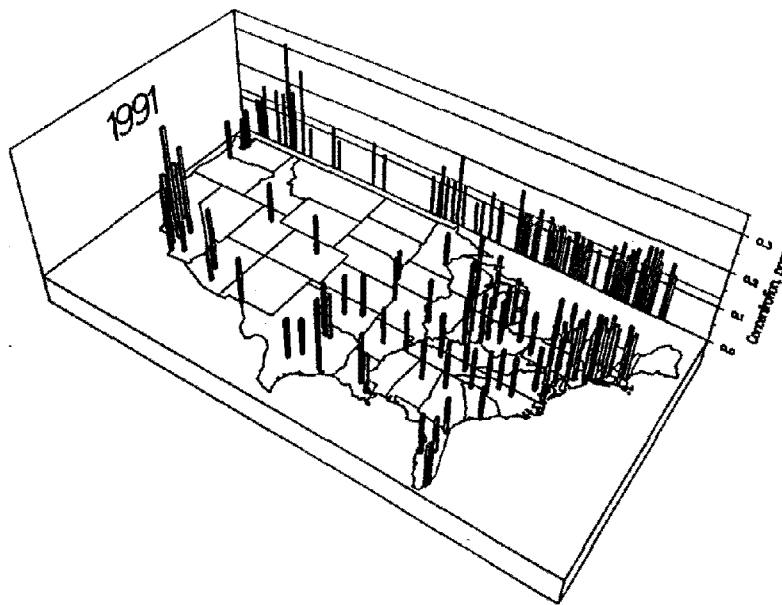


Figure 4-4. United States map of the highest second daily maximum 1-h average ozone concentration by Metropolitan Statistical Area, 1991.

Source: U.S. Environmental Protection Agency (1992a).

Lefohn (1992a) reported that for many urban sites that experience high second daily maximum 1-h average values (i.e., >0.125 ppm), most are associated with a few episodes. Monitoring sites in polluted regions tend to experience frequent hourly average O_3 concentrations at or near minimum detectable levels and high O_3 concentrations. The percentile summary information for some of these sites shows that although some of the highest hourly average concentrations occur at these locations, their occurrence is infrequent (Table 4-4). For example, O_3 monitoring sites at Delmar (CA), Stratford (CT), Madison (CT), Baton Rouge (LA), Bayonne (NJ), New York (NY), Babylon (NY), Harris County

**TABLE 4-3. THE HIGHEST SECOND DAILY MAXIMUM ONE-HOUR OZONE
CONCENTRATION BY METROPOLITAN STATISTICAL AREA (MSA) FOR
THE YEARS 1989 TO 1991
(Units are ppm)**

MSA	1989	1990	1991	MSA	1989	1990	1991
Akron, OH	0.14	0.11	0.13	Decatur, IL	0.09	0.09	0.10
Albany-Schenectady-Troy, NY	0.10	0.11	0.10	Denver, CO	0.11	0.11	0.11
Albuquerque, NM	0.10	0.10	0.09	Des Moines, IA	0.08	0.07	0.07
Allentown-Bethlehem, PA-NJ	0.10	0.11	0.12	Detroit, MI	0.14	0.12	0.13
Altoona, PA	0.10	0.10	0.11	Duluth, MN-WI	0.06		
Anaheim-Santa Ana, CA	0.24	0.21	0.20	Eau Claire, WI		0.06	
Anderson, IN	0.10			El Paso, TX	0.14	0.14	0.13
Anderson, SC			0.09	Elmira, NY	0.09	0.10	0.10
Ann Arbor, MI	0.10	0.09	0.11	Erie, PA	0.12	0.10	0.11
Appleton-Oshkosh-Neenah, WI	0.10	0.08	0.09	Eugene-Springfield, OR	0.08	0.09	0.09
Asheville, NC	0.08	0.09	0.08	Evansville, IN-KY	0.12	0.11	0.12
Atlanta, GA	0.12	0.15	0.13	Fayetteville, NC	0.11	0.10	0.10
Atlantic City, NJ	0.12	0.16	0.14	Flint, MI	0.10	0.10	0.10
Augusta, GA-SC	0.10	0.11	0.10	Fort Collins, CO	0.09	0.10	0.09
Aurora-Elgin, IL	0.11	0.09	0.13	Ft. Lauderdale-Hollywood-Pompano, FL	0.12	0.10	0.10
Austin, TX	0.11	0.11	0.10	Fort Myers-Cape Coral, FL	0.10	0.08	0.08
Bakersfield, CA	0.16	0.16	0.16	Fort Wayne, IN	0.12	0.09	0.10
Baltimore, MD	0.13	0.14	0.16	Fort Worth-Arlington, TX	0.13	0.14	0.15
Baton Rouge, LA	0.16	0.18	0.14	Fresno, CA	0.15	0.15	0.16
Beaumont-Port Arthur, TX	0.15	0.15	0.13	Galveston-Texas City, TX	0.14	0.15	0.15
Beaver County, PA	0.10	0.10	0.11	Gary-Hammond, IN	0.11	0.12	0.12
Bellingham, WA	0.05	0.08	0.07	Grand Rapids, MI	0.13	0.14	0.15
Benton Harbor, MI			0.12	Greeley, CO	0.10	0.11	0.10
Bergen-Passaic, NJ	0.12	0.13	0.14	Green Bay, WI	0.09	0.09	0.10
Billings, MT	0.08			Greensboro-Winston Salem-High Point, NC	0.10	0.12	0.11
Birmingham, AL	0.12	0.13	0.11	Greenville-Spartanburg, SC	0.10	0.11	0.11
Boston, MA	0.12	0.11	0.13	Hamilton-Middletown, OH	0.11	0.13	0.12
Boulder-Longmont, CO	0.11	0.10	0.10	Harrisburg-Lebanon-Carlisle, PA	0.11	0.12	0.11
Bradenton, FL	0.10	0.10	0.10	Hartford, CT	0.14	0.15	0.15
Brazoria, TX		0.15	0.13	Hickory, NC		0.09	
Bridgeport-Milford, CT	0.18	0.16	0.15	Honolulu, HI	0.05	0.05	0.05
Brockton, MA	0.13	0.12	0.15	Houma-Thibodaux, LA	0.11	0.12	0.10
Buffalo, NY	0.11	0.11	0.11	Houston, TX	0.23	0.22	0.20
Canton, OH	0.12	0.11	0.12	Huntington-Ashland, WV-KY-OH	0.12	0.14	0.14
Cedar Rapids, IA	0.08	0.07	0.08	Huntsville, AL	0.09	0.09	0.11
Champaign-Urbana-Rantoul, IL	0.09	0.09	0.08	Indianapolis, IN	0.12	0.11	0.11
Charleston, SC	0.09	0.10	0.09	Iowa City, IA	0.09	0.09	0.06
Charleston, WV	0.10	0.12	0.12	Jackson, MS	0.09	0.10	0.09
Charlotte-Gastonia-Rock Hill, NC-SC	0.13	0.12	0.12	Jacksonville, FL	0.11	0.11	0.10
Chattanooga, TN-GA	0.11	0.12	0.10	Jamestown-Dunkirk, NY		0.08	0.10
Chicago, IL	0.12	0.11	0.13	Janesville-Beloit, WI	0.12	0.09	0.11
Chico, CA	0.10	0.12	0.09	Jersey City, NJ	0.12	0.18	0.14
Cincinnati, OH-KY-IN	0.12	0.15	0.14	Johnson City-Kingsport-Bristol, TN-WV	0.11	0.12	0.12
Cleveland, OH	0.12	0.12	0.13	Johnstown, PA	0.10	0.10	0.11
Colorado Springs, CO	0.09	0.09	0.09	Joliet, IL	0.10	0.09	0.12
Columbia, SC	0.10	0.11	0.11	Kalamazoo, MI			0.08
Columbus, GA-AL	0.09	0.11	0.10	Kansas City MO-KS	0.11	0.11	0.12
Columbus, OH	0.11	0.11	0.12	Kenosha, WI	0.13	0.11	0.15
Corpus Christi, TX	0.10	0.10	0.11	Knoxville, TN	0.10	0.12	0.11
Cumberland, MD-WV		0.09	0.10	Lafayette, LA	0.10	0.11	0.08
Dallas, TX	0.13	0.14	0.12	Lafayette, IN	0.09	0.10	
Danbury, CT	0.13	0.15	0.14	Lake Charles, LA	0.13	0.13	0.12
Davenport-Rock Island-Moline, IA-IL	0.11	0.10	0.10	Lake County, IL	0.13	0.10	0.12
Dayton-Springfield, OH	0.15	0.12	0.12	Lancaster, PA	0.10	0.10	0.12

**TABLE 4-3 (cont'd). THE HIGHEST SECOND DAILY MAXIMUM ONE-HOUR
OZONE CONCENTRATION BY METROPOLITAN STATISTICAL
AREA (MSA) FOR THE YEARS 1989 TO 1991**
(Units are ppm)

MSA	1989	1990	1991	MSA	1989	1990	1991
Lansing-East Lansing, MI	0.10	0.10	0.11	Portland, OR-WA	0.09	0.15	0.11
Las Cruces, NM	0.11	0.10	0.10	Portsmouth-Dover-Rochester, NH-ME	0.11	0.10	0.13
Las Vegas, NV	0.11	0.11	0.09	Poughkeepsie, NY	0.08	0.12	0.13
Lawrence-Haverhill, MA-NH	0.12	0.10	0.13	Providence, RI	0.13	0.14	0.16
Lexington-Fayette, KY	0.11	0.11	0.10	Provo-Orem, UT	0.11	0.09	0.08
Lima, OH	0.10	0.10	0.10	Racine, WI	0.14	0.11	0.14
Lincoln, NE	0.06	0.07	0.07	Raleigh-Durham, NC	0.11	0.12	0.11
Little Rock-North Little Rock, AR	0.09	0.10	0.10	Reading, PA	0.11	0.11	0.12
Longview-Marshall, TX	0.10	0.13	0.11	Redding, CA	0.09	0.09	0.08
Lorain-Elyria, OH	0.12	0.09	0.10	Reno, NV	0.10	0.14	0.09
Los Angeles-Long Beach, CA	0.33	0.27	0.31	Richmond-Petersburg, VA	0.11	0.12	0.12
Louisville, KY-IN	0.11	0.13	0.13	Riverside-San Bernardino, CA	0.28	0.30	0.25
Lynchburg, VA		0.10	0.09	Roanoke, VA	0.10	0.09	0.10
Madison, WI	0.10	0.08	0.11	Rochester, NY	0.11	0.11	0.11
Manchester, NH	0.10	0.10	0.10	Rockford, IL	0.10	0.09	0.09
Medford, OR	0.09	0.10	0.07	Sacramento, CA	0.14	0.16	0.16
Melbourne-Titusville-Palm Bay, FL	0.10	0.09	0.09	St. Louis, MO-IL	0.13	0.13	0.12
Memphis, TN-AR-MS	0.12	0.12	0.11	Salinas-Seaside-Monterey, CA	0.11	0.09	0.09
Miami-Hialeah, FL	0.12	0.11	0.12	Salt Lake City-Ogden, UT	0.15	0.12	0.11
Middlesex-Somerset-Hunterdon, NJ	0.13	0.15	0.13	San Antonio, TX	0.11	0.10	0.11
Middletown, CT	0.17	0.16	0.17	San Diego, CA	0.19	0.17	0.18
Milwaukee, WI	0.15	0.13	0.18	San Francisco, CA	0.09	0.06	0.07
Minneapolis-St. Paul, MN-WI	0.10	0.10	0.09	San Jose, CA	0.13	0.12	0.12
Mobile, AL	0.10	0.11	0.09	San Juan, PR	0.06	0.07	0.08
Modesto, CA	0.13	0.12	0.11	Santa Barbara-Santa Maria-Lompoc, CA	0.16	0.13	0.10
Monmouth-Ocean, NJ	0.14	0.14	0.15	Santa Cruz, CA	0.08	0.08	0.10
Montgomery, AL	0.08	0.10	0.09	Santa Fe, NM	0.05	0.08	0.08
Muskegon, MI	0.14	0.13	0.15	Santa Rosa-Petaluma, CA	0.10	0.08	0.10
Nashua, NH	0.09	0.10	0.11	Sarasota, FL	0.10	0.10	0.10
Nashville, TN	0.14	0.13	0.12	Scranton-Wilkes-Barre, PA	0.11	0.11	0.13
Nassau-Suffolk, NY	0.15	0.14	0.18	Seattle, WA	0.09	0.13	0.11
New Bedford, MA	0.12	0.13	0.13	Sharon, PA	0.11	0.10	0.11
New Haven-Meriden, CT	0.15	0.16	0.18	Sheboygan, WI	0.11	0.11	0.16
New London-Norwich, CT-RI	0.14	0.16	0.14	Shreveport, LA	0.12	0.12	0.11
New Orleans, LA	0.11	0.11	0.11	South Bend-Mishawaka, IN	0.10	0.10	0.11
New York, NY	0.13	0.16	0.18	Spokane, WA		0.07	0.08
Newark, NJ	0.13	0.13	0.14	Springfield, IL	0.11	0.10	0.10
Niagara Falls, NY	0.10	0.10	0.10	Springfield, MO	0.09	0.08	0.08
Norfolk-Virginia Beach-Newport News, VA	0.10	0.11	0.11	Springfield, MA	0.13	0.12	0.13
Oakland, CA	0.13	0.12	0.12	Stamford, CT	0.16	0.14	0.15
Oklahoma City, OK	0.11	0.11	0.11	Steubenville-Weirton, OH-WV	0.11	0.09	0.12
Omaha, NE-IA	0.10	0.08	0.08	Stockton, CA	0.11	0.12	0.11
Orlando, FL	0.11	0.12	0.10	Syracuse, NY	0.10	0.11	0.11
Owensboro, KY	0.10	0.11	0.09	Tacoma, WA	0.09	0.13	0.09
Oxnard-Ventura, CA	0.17	0.15	0.16	Tallahassee, FL	0.07		0.05
Parkerburg-Marietta, WV-OH	0.12	0.11	0.12	Tampa-St. Petersburg-Clearwater, FL	0.10	0.11	0.11
Pascagoula, MS	0.10	0.11	0.10	Terre Haute, IN	0.11	0.11	0.10
Pensacola, FL	0.09	0.12	0.11	Toledo, OH	0.11	0.10	0.12
Peoria, IL	0.11	0.09	0.10	Trenton, NJ	0.14	0.14	0.15
Philadelphia, PA-NJ	0.16	0.14	0.16	Tucson, AZ	0.10	0.10	0.09
Phoenix, AZ	0.11	0.14	0.12	Tulsa, OK	0.12	0.12	0.12
Pittsburgh, PA	0.13	0.11	0.12	Utica-Rome, NY	0.09	0.10	0.10
Pittsfield, MA	0.09	0.11	0.10	Vallejo-Fairfield-Napa, CA	0.11	0.10	0.11
Portland, ME	0.13	0.13	0.14	Vancouver, WA	0.09	0.11	0.10

**TABLE 4-3 (cont'd). THE HIGHEST SECOND DAILY MAXIMUM ONE-HOUR
OZONE CONCENTRATION BY METROPOLITAN STATISTICAL
AREA (MSA) FOR THE YEARS 1989 TO 1991
(Units are ppm)**

MSA	1989	1990	1991	MSA	1989	1990	1991
Victoria, TX	0.10	0.07	0.10	Wilmington, DE-NJ-MD	0.13	0.14	0.15
Vineland-Millville-Bridgeton, NJ	0.13	0.13	0.12	Wilmington, NC		0.09	
Visalia-Tulare-Porterville, CA	0.15	0.14	0.12	Worcester, MA	0.10	0.12	0.14
Washington, DC-MD-VA	0.13	0.13	0.14	York, PA	0.10	0.12	0.11
W. Palm Beach-Boca Raton-Delray, FL	0.11	0.09	0.09	Youngstown-Warren, OH	0.11	0.10	0.12
Wheeling, WV-OH	0.11	0.11	0.11	Yuba City, CA	0.01	0.09	0.10
Wichita, KS	0.09	0.10	0.10	Yuma, AZ		0.09	0.09
Williamsport, PA	0.08	0.09	0.10				

(TX), and Bayside (WI) exhibit maximum hourly average concentrations above 0.125 ppm; however, only 1 % of the hourly average concentrations generally exceed 0.100 ppm. Although for human health considerations, the occurrence of a second daily maximum hourly average concentration is important, the table illustrates the point that, for the sites listed, the occurrence of high hourly average concentrations is infrequent and that they are associated with occasional episodes.

As indicated in the Introduction, interest has been expressed in characterizing O₃ exposure regimes for sites experiencing daily maximum 8-h concentrations above specific thresholds (e.g., 0.08 or 0.10 ppm). Table 4-5 summarizes the highest second daily maximum 8-h average O₃ concentrations by MSA for the years 1989 to 1991. The data have been reported for the O₃ season as summarized in Table 4-1. In some cases, high concentrations occur in the fall and winter periods as well as the summertime. Analyses reported by Rombout et al. (1986, 1989), Berglund et al. (1988), and Lioy and Dyba (1989) documented the occurrence, at some sites, of multihour periods within a day of O₃ at levels of potential health effects. While most of these analyses were made using monitoring data collected from sites in or near nonattainment areas, the analysis of Berglund et al. (1988) showed that at five sites, two in New York state, two in rural California, and one in rural Oklahoma, an alternative O₃ standard of an 8-h average of 0.10 ppm would be exceeded even though the existing 1-h standard would not be. Berglund et al. (1988) described the occurrence at these five sites, none of which was in or near a nonattainment area, of O₃ concentrations showing only moderate peaks but showing multihour levels above

**TABLE 4-4. SUMMARY OF PERCENTILES OF HOURLY AVERAGE
CONCENTRATIONS FOR THE APRIL-TO-OCTOBER PERIOD
(Units are ppm)**

AIRS Site	Name	Year	Min.	10	30	50	70	90	95	99	Max.	Number of Observations
060370016	Glendora, CA	1989	0.000	0.000	0.020	0.030	0.060	0.120	0.150	0.220	0.340	4,874
		1990	0.000	0.000	0.010	0.030	0.050	0.110	0.140	0.200	0.290	4,888
		1991	0.000	0.000	0.010	0.020	0.050	0.100	0.140	0.200	0.320	4,907
060595001	La Habra, CA	1989	0.000	0.000	0.010	0.030	0.040	0.070	0.090	0.140	0.260	4,875
		1990	0.000	0.000	0.010	0.020	0.040	0.070	0.090	0.140	0.210	4,887
		1991	0.000	0.000	0.010	0.020	0.040	0.070	0.090	0.130	0.210	4,899
060710005	San Bernardino County, CA	1989	0.000	0.020	0.050	0.060	0.090	0.140	0.160	0.200	0.270	4,871
		1990	0.000	0.020	0.040	0.060	0.080	0.120	0.150	0.180	0.330	4,899
		1991	0.000	0.020	0.040	0.060	0.080	0.120	0.140	0.190	0.270	4,905
060731001	Del Mar, CA	1989	0.000	0.020	0.040	0.040	0.050	0.070	0.080	0.120	0.250	4,814
		1990	0.000	0.020	0.030	0.040	0.050	0.060	0.070	0.100	0.170	5,060
		1991	0.000	0.020	0.040	0.050	0.050	0.060	0.070	0.100	0.150	5,017
090013007	Stratford, CT	1989	0.001	0.008	0.024	0.036	0.046	0.064	0.077	0.115	0.202	4,673
		1990	0.001	0.010	0.023	0.033	0.044	0.059	0.068	0.100	0.176	3,853
		1991	0.000	0.007	0.019	0.030	0.042	0.060	0.074	0.110	0.157	4,794
090093002	Madison, CT	1989	0.001	0.008	0.022	0.033	0.043	0.059	0.070	0.103	0.149	4,272
		1990	0.000	0.008	0.023	0.033	0.043	0.063	0.075	0.107	0.197	4,477
		1991	0.000	0.007	0.023	0.034	0.045	0.065	0.082	0.123	0.193	4,814
220330003	Baton Rouge, LA	1989	0.000	0.001	0.009	0.021	0.034	0.059	0.069	0.094	0.168	4,964
		1990	0.000	0.000	0.011	0.023	0.038	0.063	0.079	0.109	0.187	5,000
		1991	0.000	0.002	0.010	0.020	0.031	0.054	0.067	0.092	0.134	4,905
340170006	Bayonne, NJ	1989	0.001	0.001	0.008	0.021	0.036	0.059	0.074	0.099	0.147	4,815
		1990	0.001	0.001	0.009	0.022	0.036	0.058	0.073	0.106	0.185	4,939
		1991	0.001	0.002	0.011	0.024	0.038	0.065	0.082	0.110	0.167	4,943
360610063	New York, NY	1989	0.000	0.015	0.028	0.040	0.051	0.073	0.086	0.110	0.134	4,825
		1990	0.000	0.014	0.029	0.039	0.051	0.074	0.090	0.116	0.175	4,707
		1991	0.002	0.015	0.029	0.041	0.056	0.082	0.096	0.123	0.177	4,910

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**TABLE 4-4 (cont'd). SUMMARY OF PERCENTILES OF HOURLY AVERAGE
CONCENTRATIONS FOR THE APRIL-TO-OCTOBER PERIOD
(units are ppm)**

AIRS Site	Name	Year	Min.	10	30	50	70	90	95	99	Max.	Number of Observations
361030002	Babylon, NY	1989	0.001	0.004	0.015	0.027	0.039	0.060	0.073	0.101	0.156	4,407
		1990	0.000	0.006	0.017	0.027	0.040	0.060	0.075	0.105	0.146	4,876
		1991	0.001	0.005	0.018	0.030	0.044	0.067	0.081	0.111	0.217	4,873
482010024	Harris County, TX	1989	0.000	0.000	0.010	0.020	0.030	0.060	0.070	0.110	0.230	4,728
		1990	0.000	0.000	0.010	0.020	0.040	0.070	0.090	0.130	0.220	4,274
		1991	0.000	0.000	0.000	0.020	0.030	0.060	0.080	0.110	0.170	4,322
550790085	Bayside, WI	1989	0.002	0.006	0.024	0.035	0.046	0.066	0.077	0.101	0.151	4,376
		1990	0.002	0.009	0.025	0.034	0.044	0.061	0.071	0.094	0.130	4,395
		1991	0.002	0.008	0.025	0.035	0.047	0.070	0.081	0.113	0.189	4,303

**TABLE 4-5. THE HIGHEST SECOND DAILY MAXIMUM EIGHT-HOUR
AVERAGE OZONE CONCENTRATION BY METROPOLITAN STATISTICAL
AREA (MSA) FOR THE YEARS 1989 TO 1991**
(Units are ppm)

MSA	1989	1990	1991	MSA	1989	1990	1991
Akron, OH	0.109	0.097	0.102	Davenport-Rock Island-Moline, IA-IL	0.102	0.071	0.086
Albany-Schenectady-Troy, NY	0.087	0.091	0.089	Dayton-Springfield, OH	0.122	0.096	0.107
Albuquerque, NM	0.078	0.089	0.077	Decatur, IL	0.084	0.077	0.087
Alexandria, LA	0.077	0.076	0.074	Denver, CO	0.089	0.086	0.080
Allentown-Bethlehem, PA-NJ	0.091	0.098	0.112	Des Moines, IA	0.073	0.051	0.056
Altoona, PA	0.077	0.090	0.094	Detroit, MI	0.103	0.091	0.111
Anaheim-Santa Ana, CA	0.146	0.135	0.110	Duluth, MN-WI	0.073	0.051	
Anderson, IN	0.084			Eau Claire, WI		0.049	
Anderson, SC			0.081	El Paso, TX	0.083	0.087	0.080
Ann Arbor, MI	0.093	0.087	0.096	Elmira, NY	0.075	0.080	0.094
Appleton-Oshkosh-Neenah, WI	0.091	0.078	0.082	Erie, PA	0.092	0.088	0.093
Asheville, NC	0.083	0.074	0.064	Eugene-Springfield, OR	0.061	0.077	0.070
Atlanta, GA	0.096	0.125	0.102	Evansville, IN-KY	0.097	0.094	0.107
Atlantic City, NJ	0.104	0.135	0.112	Fayetteville, NC	0.089	0.088	0.085
Augusta, GA-SC	0.078	0.092	0.081	Flint, MI	0.093	0.086	0.090
Aurora-Elgin, IL	0.088	0.077	0.100	Fort Collins, CO	0.076	0.076	0.077
Austin, TX	0.099	0.103	0.084	Ft. Lauderdale-Hollywood-Pompano, FL	0.089	0.078	0.064
Bakersfield, CA	0.124	0.120	0.118	Fort Myers-Cape Coral, FL	0.084	0.070	0.062
Baltimore, MD	0.103	0.111	0.127	Fort Wayne, IN	0.105	0.091	0.096
Baton Rouge, LA	0.095	0.134	0.100	Fort Worth-Arlington, TX	0.098	0.116	0.116
Beaumont-Port Arthur, TX	0.110	0.100	0.101	Fresno, CA	0.116	0.105	0.119
Beaver County, PA	0.095	0.085	0.095	Galveston-Texas City, TX	0.102	0.096	0.094
Bellingham, WA	0.038	0.068	0.059	Gary-Hammond, IN	0.102	0.122	0.101
Benton Harbor, MI			0.098	Grand Rapids, MI	0.119	0.107	0.124
Bergen-Passaic, NJ	0.093	0.097	0.106	Greeley, CO	0.080	0.080	0.081
Billings, MT	0.56			Green Bay, WI	0.095	0.074	0.079
Biloxi-Gulfport, TX			0.089	Greensboro-Winston Salem-High Point, NC	0.083	0.100	0.087
Birmingham, AL	0.088	0.105	0.088	Greenville-Spartanburg, SC	0.088	0.091	0.085
Bismark, ND	0.086	0.062	0.061	Hamilton-Middletown, OH	0.095	0.111	0.105
Bloomington-Normal, IL	0.081	0.071	0.095	Harrisburg-Lebanon-Carlisle, PA	0.091	0.108	0.100
Boston, MA	0.109	0.105	0.118	Hartford, CT	0.114	0.109	0.112
Boulder-Longmont, CO	0.082	0.084	0.083	Hickory, NC		0.080	
Bradenton, FL	0.086	0.075	0.074	Honolulu, HI	0.020	0.037	0.042
Brazoria, TX		0.101	0.107	Houma-Thibodaux, LA	0.082	0.084	0.077
Bridgeport-Milford, CT	0.139	0.114	0.121	Houston, TX	0.121	0.141	0.115
Brockton, MA	0.110	0.106	0.107	Huntington-Ashland, WV-KY-OH	0.102	0.109	0.124
Buffalo, NY	0.085	0.096	0.097	Huntsville, AL	0.072	0.080	0.082
Canton, OH	0.098	0.098	0.099	Indianapolis, IN	0.097	0.099	0.100
Carson City, NV	0.070			Iowa City, IA	0.078	0.084	0.060
Cedar Rapids, IA	0.078	0.057	0.066	Jackson, MS	0.086	0.083	0.075
Champaign-Urbana-Rantoul, IL	0.084	0.080	0.077	Jacksonville, FL	0.090	0.084	0.077
Charleston, SC	0.094	0.084	0.074	Jamestown-Dunkirk, NY		0.068	0.082
Charleston, WV	0.087	0.083	0.099	Janesville-Beloit, WI	0.097	0.081	0.090
Charlotte-Gastonia-Rock Hill, NC-SC	0.089	0.100	0.094	Jersey City, NJ	0.105	0.128	0.117
Charlottesville, VA	0.076	0.089	0.091	Johnson City-Kingsport-Bristol, TN-WV	0.083	0.100	0.080
Chattanooga, TN-GA	0.091	0.094	0.083	Johnstown, PA	0.082	0.090	0.099
Chicago, IL	0.101	0.084	0.106	Joliet, IL	0.082	0.070	0.091
Chico, CA	0.081	0.083	0.074	Kalamazoo, MI		0.071	
Cincinnati, OH-KY-IN	0.106	0.119	0.115	Kansas City MO-KS	0.090	0.089	0.089
Cleveland, OH	0.099	0.096	0.101	Kenosha, WI	0.113	0.093	0.118
Colorado Springs, CO	0.072	0.065	0.068	Knoxville, TN	0.088	0.105	0.091
Columbia, SC	0.079	0.094	0.083	Lafayette, LA	0.080	0.086	0.075
Columbus, GA-AL	0.068	0.075	0.083	Lafayette, IN	0.077	0.092	0.090
Columbus, OH	0.097	0.098	0.112	Lake Charles, LA	0.088	0.084	0.096
Corpus Christi, TX	0.083	0.085	0.075	Lake County, IL	0.092	0.082	0.102
Cumberland, MD-WV		0.070	0.076	Lancaster, PA	0.085	0.089	0.096
Dallas, TX	0.101	0.115	0.095	Lansing-East Lansing, MI	0.093	0.083	0.087
Danbury, CT	0.098	0.105	0.116	Las Cruces, NM	0.074	0.082	0.074

**TABLE 4-5 (cont'd). THE HIGHEST SECOND DAILY MAXIMUM
EIGHT-HOUR AVERAGE OZONE CONCENTRATION BY METROPOLITAN
STATISTICAL AREA (MSA) FOR THE YEARS 1989 TO 1991**
(Units are ppm)

MSA	1989	1990	1991	MSA	1989	1990	1991
Las Vegas, NV	0.084	0.082	0.075	Provo-Orem, UT	0.094	0.070	0.071
Lawrence-Haverhill, MA-NH	0.104	0.077	0.106	Racine, WI	0.110	0.090	0.118
Lewiston-Auburn, ME	0.089	0.090	0.101	Raleigh-Durham, NC	0.099	0.094	0.091
Lexington-Fayette, KY	0.097	0.097	0.088	Reading, PA	0.095	0.101	0.109
Lima, OH	0.088	0.086	0.091	Redding, CA	0.080	0.100	0.093
Lincoln, NE	0.057	0.060	0.060	Reno, NV	0.081	0.109	0.075
Little Rock-North Little Rock, AR	0.077	0.083	0.089	Richmond-Petersburg, VA	0.094	0.101	0.097
Longview-Marshall, TX	0.076	0.089	0.086	Riverside-San Bernardino, CA	0.196	0.193	0.189
Lorain-Elyria, OH	0.096	0.082	0.091	Roanoke, VA	0.077	0.075	0.078
Los Angeles-Long Beach, CA	0.188	0.170	0.178	Rochester, NY	0.094	0.097	0.103
Louisville, KY-IN	0.096	0.093	0.119	Rockford, IL	0.085	0.073	0.081
Lynchburg, VA		0.083	0.079	Sacramento, CA	0.105	0.125	0.124
Madison, WI	0.089	0.079	0.089	St. Louis, MO-IL	0.105	0.098	0.107
Manchester, NH	0.084	0.098	0.087	Salinas-Seaside-Monterey, CA	0.082	0.074	0.071
Medford, OR	0.063	0.076	0.055	Salt Lake City-Ogden, UT	0.114	0.086	0.086
Melbourne-Titusville-Palm Bay, FL	0.082	0.082	0.069	San Antonio, TX	0.100	0.080	0.085
Memphis, TN-AR-MS	0.099	0.100	0.093	San Diego, CA	0.139	0.135	0.128
Miami-Hialeah, FL	0.087	0.076	0.072	San Francisco, CA	0.064	0.056	0.054
Middlesex-Somerset-Hunterdon, NJ	0.108	0.111	0.111	San Jose, CA	0.094	0.075	0.086
Middletown, CT	0.119	0.117	0.125	San Juan, PR	0.043	0.042	0.044
Milwaukee, WI	0.115	0.100	0.118	Santa Barbara-Santa Maria-Lompoc, CA	0.129	0.129	0.075
Minneapolis-St. Paul, MN-WI	0.090	0.077	0.079	Santa Cruz, CA	0.066	0.058	0.067
Mobile, AL	0.079	0.098	0.062	Santa Fe, NM	0.049	0.069	0.076
Modesto, CA	0.101	0.106	0.091	Santa Rosa-Petaluma, CA	0.083	0.061	0.076
Monmouth-Ocean, NJ	0.118	0.107	0.122	Sarasota, FL	0.085	0.083	0.080
Montgomery, AL	0.066	0.081	0.071	Scranton-Wilkes-Barre, PA	0.088	0.096	0.111
Muskegon, MI	0.139	0.100	0.119	Seattle, WA	0.078	0.099	0.087
Nashua, NH	0.072	0.095	0.110	Sharon, PA	0.098	0.095	0.094
Nashville, TN	0.093	0.102	0.107	Sheboygan, WI	0.103	0.088	0.103
Nassau-Suffolk, NY	0.099	0.115	0.121	Shreveport, LA	0.098	0.102	0.087
New Bedford, MA	0.104	0.101	0.106	South Bend-Mishawaka, IN	0.089	0.089	0.093
New Haven-Meriden, CT	0.108	0.122	0.128	Spokane, WA		0.060	0.060
New London-Norwich, CT-RI	0.128	0.127	0.115	Springfield, IL	0.085	0.082	0.087
New Orleans, LA	0.075	0.086	0.079	Springfield, MO	0.075	0.061	0.069
New York, NY	0.111	0.119	0.133	Springfield, MA	0.123	0.113	0.117
Newark, NJ	0.108	0.107	0.119	Stamford, CT	0.113	0.112	0.115
Niagara Falls, NY	0.082	0.092	0.095	Steubenville-Weirton, OH-WV	0.094	0.075	0.098
Norfolk-Virginia Beach-Newport News, VA	0.089	0.095	0.089	Stockton, CA	0.086	0.093	0.090
Oakland, CA	0.091	0.091	0.083	Syracuse, NY	0.090	0.093	0.098
Oklahoma City, OK	0.089	0.090	0.089	Tacoma, WA	0.077	0.094	0.077
Omaha, NE-IA	0.075	0.075	0.073	Tallahassee, FL	0.072		
Orlando, FL	0.096	0.082	0.075	Tampa-St. Petersburg-Clearwater, FL	0.088	0.085	0.083
Owensboro, KY	0.096	0.104	0.077	Terre Haute, IN	0.087	0.095	0.089
Oxnard-Ventura, CA	0.147	0.119	0.129	Toledo, OH	0.093	0.084	0.107
Parkersburg-Marietta, WV-OH	0.094	0.088	0.104	Trenton, NJ	0.119	0.112	0.131
Pascagoula, MS	0.082	0.092	0.077	Tucson, AZ	0.074	0.084	0.080
Pensacola, FL	0.080	0.098	0.082	Tulsa, OK	0.093	0.094	0.097
Peoria, IL	0.087	0.075	0.088	Utica-Rome, NY	0.082	0.094	0.091
Philadelphia, PA-NJ	0.118	0.110	0.123	Vallejo-Fairfield-Napa, CA	0.076	0.074	0.078
Phoenix, AZ	0.086	0.096	0.094	Vancouver, WA	0.058	0.080	0.042
Pittsburgh, PA	0.107	0.100	0.106	Victoria, TX	0.093	0.056	0.086
Pittsfield, MA	0.075	0.094	0.095	Vineland-Millville-Bridgeton, NJ	0.122	0.106	0.108
Portland, ME	0.124	0.109	0.134	Visalia-Tulare-Porterville, CA	0.114	0.103	0.104
Portland, OR-WA	0.071	0.111	0.092	Washington, DC-MD-VA	0.106	0.110	0.114
Portsmouth-Dover-Rochester, NH-ME	0.107	0.086	0.123	W. Palm Beach-Boca Raton-Delray, FL	0.081	0.067	0.059
Poughkeepsie, NY	0.079	0.085	0.101	Wheeling, WV-OH	0.086	0.089	0.093
Providence, RI	0.107	0.112	0.127	Wichita, KS	0.079	0.089	0.081

**TABLE 4-5 (cont'd). THE HIGHEST SECOND DAILY MAXIMUM
EIGHT-HOUR AVERAGE OZONE CONCENTRATION BY METROPOLITAN
STATISTICAL AREA (MSA) FOR THE YEARS 1989 TO 1991
(Units are ppm)**

MSA	1989	1990	1991	MSA	1989	1990	1991
Williamsport, PA	0.065	0.072	0.087	York, PA	0.091	0.108	0.103
Wilmington, DE-NJ-MD	0.105	0.110	0.118	Youngstown-Warren, OH	0.088	0.085	0.101
Wilmington, NC		0.086		Yuba City, CA	0.084	0.076	0.084
Worcester, MA	0.097	0.089	0.107	Yuma, AZ	0.080	0.075	0.070

0.10 ppm. Lefohn et al. (1993) have identified those areas in the United States for the period 1987 to 1989 where more than one occurrence of an 8-h daily maximum average concentration of 0.08 ppm was experienced, while an hourly average concentration equal to or greater than 0.12 ppm never occurred.

A follow-up to the points made above is whether an improvement in O₃ levels may produce distributions of 1-h O₃ that result in a broader diurnal profile than those seen in high-oxidant urban areas where O₃ regimes contain hourly average concentrations with sharper peaks. The result would be an increase in the number of exceedances of daily maximum 8-h average concentrations ≥ 0.08 ppm, when compared to those sites, experiencing sharper peaks. Lefohn et al. (1993b), using aerometric data at specific sites, observed how O₃ concentrations change when the sites change compliance status. One of the parameters examined was 4-h daily maxima. The number of exceedances for a specific daily maximum average concentration tended to decrease as fewer exceedances of the current 1-h standard were observed at a given site. The number of occurrences of the daily maximum 4-h average concentration ≥ 0.08 ppm and the number of exceedances of the current form of the standard had a positive, weak correlation ($r = 0.51$). Lefohn et al. (1993a,b) reported few changes in the shape of the average diurnal patterns as sites changed attainment status; this may have explained why Lefohn et al. (1993b) could not find evidence that the number of occurrences of the daily maximum 4-h average concentration ≥ 0.08 ppm increased when the sites experienced few high hourly average concentrations.

There has been considerable interest in possibly substituting one index for another when attempting to relate O₃ exposure with an effect. For example, using O₃ ambient air quality data, McCurdy (1988) compared the number of exceedances of 0.125 ppm and the number of

1 occurrences of the daily maximum 8-h average concentrations ≥ 0.08 ppm and reported that
2 a positive correlation ($r = 0.79$) existed between the second-highest 1-h daily maximum in a
3 year and the expected number of days with an 8-h daily maximum average concentration
4 > 0.08 ppm O_3 . In this case, the predictive strength of using one O_3 exposure index to
5 predict another is not strong.

6 Similar to analysis performed by McCurdy (1988), all of the hourly averaged data from
7 rural agricultural and forested sites in the AIRS database were summarized into maximum
8 3-mo SUM06, second highest daily maximum hourly average concentration, and second
9 highest daily maximum 8-h average concentration exposure indices per year for the period
10 1980 to 1991. For the rural agricultural sites, the correlation coefficient between the 3-mo
11 SUM06 and (a) second highest daily maximum hourly average concentration and (b) second
12 highest daily maximum 8-h average concentration was 0.650 and 0.739, respectively
13 (Figure 4-5). For the rural forested sites, the correlation coefficient between the 3-mo
14 SUM06 and (a) second highest daily maximum hourly average concentration and (b) second
15 highest daily maximum 8-h average concentration was 0.585 and 0.683, respectively
16 (Figure 4-6).

17 One of the difficulties in attempting to use correlation analysis between indices for
18 rationalizing the substitution of one exposure index for another for predicting an effect (e.g.,
19 SUM06 versus the second highest daily maximum hourly average concentration) is the
20 introduction of the error associated with estimating levels of one index from another. Lefohn
21 et al. (1989) have recommended that if a different exposure index (e.g., second highest daily
22 maximum hourly average concentration) is to be compared to, for example, the SUM06 for
23 adequacy in predicting crop loss, then the focus should be on how well the two exposure
24 indices predict crop loss using the effects model that is a function of the most relevant index
25 and not on how well the indices predict one another. Using data from both urban and rural
26 O_3 monitoring sites in the midwestern United States that were located near agricultural/
27 forested areas, Lefohn et al. (1989) reported a large amount of scatter between the second
28 highest daily maximum hourly average concentration and the SUM06 indices. This large
29 scatter indicated considerable uncertainty when attempting to predict a value for SUM06,

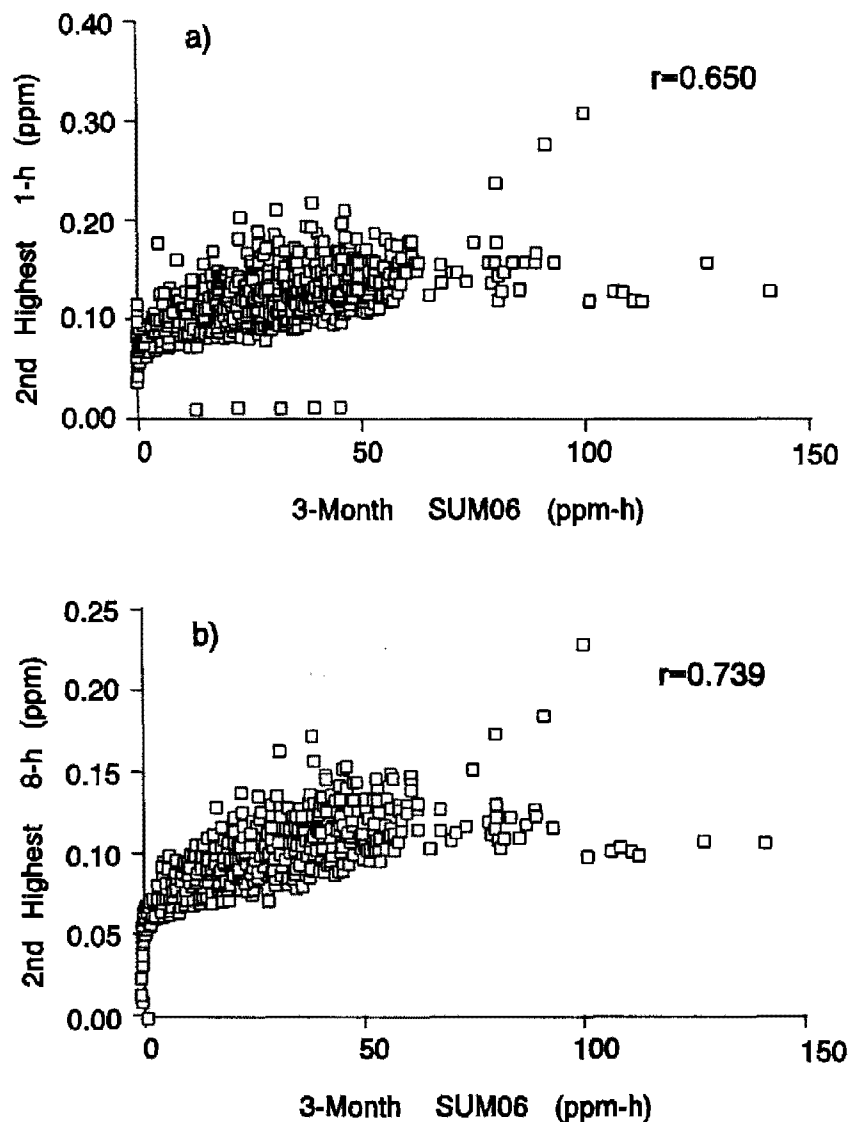


Figure 4-5. The relationship between the (a) second highest daily maximum hourly average O₃ concentration and the maximum 3-mo SUM06 value and (b) the second highest daily maximum 8-h average concentration and the maximum 3-mo SUM06 value for specific site years at rural agricultural sites for the 1980-to-1991 period.

1 given a specific second highest daily maximum hourly average concentration value. The
 2 authors reported that for a given second highest daily maximum hourly average
 3 concentration, the SUM06 values varied over a large range. Lefohn et al. (1989) concluded
 4 that such large uncertainty would introduce additional uncertainty when attempting to use the
 5 predicted exposure index to estimate an effect. The authors concluded that less error would

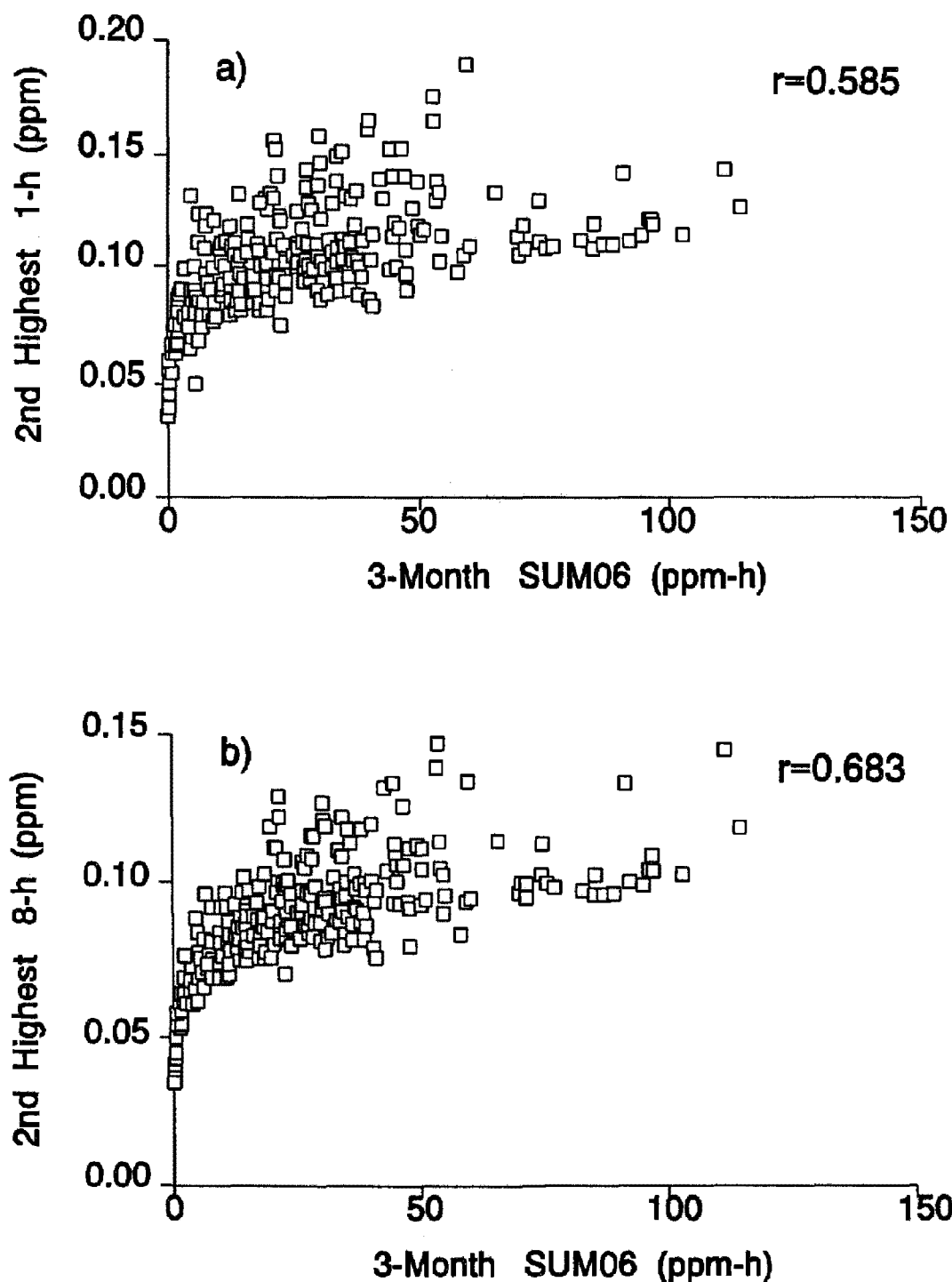


Figure 4-6. The relationship between the (a) second highest daily maximum hourly average O₃ concentration and the maximum 3-mo SUM06 value and (b) the second highest daily maximum 8-h average concentration and the maximum 3-mo SUM06 value for specific site years at rural forested sites for the 1980-to-1991 period.

1 be introduced if either of the two indices were used directly in the development of an
2 exposure-response model.

3 As pointed out by the U.S. EPA (1986a), a familiar measure of O₃ air quality is the
4 number or percentage of days on which some specific concentration is equalled or exceeded.
5 This measure, however, does not shed light on one of the more important questions
6 regarding the effects of O₃ on both people and plants; that is, the possible significance of
7 high concentrations lasting 1 h or longer and then recurring on 2 or more successive days.

1 The recurrence of high O₃ concentrations on consecutive days was examined for one
2 site in four cities by the U.S. EPA (1986a). The numbers of multiple-day events were tallied
3 by length of event (i.e., how many consecutive days) using data for the daylight hours (0600
4 to 2000 h) in the second and third quarters of 1979 through 1981. These sites were selected
5 because they included areas known to experience high O₃ concentrations (California), and
1 because they represent different geographic regions of the country (west, southwest, and
2 east).

3 Because of the importance of episodes and respites, EPA (1986a) commented on the
4 occurrences of the length of episodes and the time between episodes (respites). The agency
5 concluded that its analysis showed variations among sites in the lengths of episodes, as well
6 as the respite periods. In its discussion, the U.S. EPA (1986a) defined a day or series of
7 days on which the daily 1-h maximum reached or exceeded the specified level as an
8 "exposure"; the intervening day or days when that level was not reached was called a
9 "respite." Four O₃ concentrations were selected: 0.06, 0.12, 0.18, and 0.24 ppm. At the
10 Dallas site, for example, the value equalled or exceeded 0.06 ppm for more than 7 days in a
11 row. The Pasadena site experienced 10 such exposures, but these 10 exposure events
12 spanned 443 days; in Dallas, the 11 exposures involved only 168 days. At the lowest
13 concentration (≥ 0.06 ppm), the Dallas station recorded more short-term (≤ 7 days)
14 exposures (45) involving more days (159) than the Pasadena station (14 exposures over
15 45 days) because the daily 1-h maximum statistic in Pasadena remained above 0.06 ppm for
16 such protracted periods. At concentrations ≥ 0.12 ppm, the lengthy exposures at the
17 Pasadena site resolved into numerous shorter exposures, whereas in Dallas the exposures
18 markedly dwindled in number and duration.

4.3.3 Nonurban Area Concentrations

4.3.3.1 Pristine Areas

For those attempting to compare O₃ exposures experienced under ambient or experimental conditions with a reference point, it is important to identify the hourly average concentration regimes that occur in pristine areas. The U.S. EPA (1989) has indicated that a reasonable estimate of annual average natural O₃ background concentration near sea-level in the United States today is from 0.020 to 0.035 ppm. This estimate included a 0.010 to 0.015 ppm contribution from the stratosphere and a 0.01 ppm contribution from photochemically-affected biogenic non-methane hydrocarbons. In addition, the U.S. EPA (1989) estimated that an additional 0.010 ppm is possible from the photochemical reaction of biogenic methane. The U.S. EPA concluded that a reasonable estimate of natural O₃ background concentration for a 1-h daily maximum at sea-level in the United States during the summer is on the order of 0.03 to 0.05 ppm (U.S. Environmental Protection Agency, 1989).

Using measurements at a remote site in South Dakota, Kelly et al. (1982) estimated the background O₃ in air masses entering the Midwest and eastern United States to be 0.020 to 0.050 ppm. Pratt et al. (1983), using data from low-elevation rural sites in Minnesota and North Dakota, reported that annual average concentrations for an O₃ monitoring site in LaMoure County, ND, (400 m) for 1978 through 1981, ranged from 0.030 to 0.035 ppm, while an O₃ monitoring site in Traverse County, MN (311 m), had a range of 0.029 to 0.035 ppm. Bower et al. (1989) reported that the remote northern Scotland site, Strath Vaich (270 m), had a 1987 to 1988 annual average O₃ concentration of 0.031 ppm.

Lefohn and Jones (1986) have characterized several O₃ monitoring sites, which appeared to be isolated from major anthropogenic activities, independent of land use designations (i.e., remote, rural, or urban), and reported that the data collected at these sites show a tendency of few hourly mean O₃ concentrations at or near the minimum detectable level and few occurrences of hourly average concentrations above 0.08 ppm. At these sites, more than 90% of the hourly average concentrations are greater than 0.015 ppm. The infrequent minimally detectable hourly mean concentrations occur because of weak surface sink effects. The authors referred to these sites as being located in clean areas.

1 Lefohn and Foley (1992) summarized O₃ exposures experienced at several clean sites in
2 the United States (Table 4-6). Redwood NP (CA), Olympic NP (WA), Glacier NP (MT),
3 Sand Dunes NM (CO), Yellowstone NP (WY), Badlands NP (SD), and Theodore Roosevelt
4 NP (ND) experienced no hourly average concentration ≥ 0.08 ppm for the period April to
5 October. Logan (1989) has noted that O₃ hourly average concentrations above 0.08 ppm are
6 rarely exceeded at remote western sites. In almost all cases for the above sites, the
7 maximum hourly average concentration was ≤ 0.07 ppm. In 1989, the maximum hourly
8 average concentration experienced at the Redwood NP (CA) site was 0.046 ppm.

9 Evans et al. (1983) summarized O₃ hourly averaged data collected at eight stations
10 located in eight National Forests across the United States. The first three stations began
11 operations in 1976 (Green Mountain NF, Vermont; Kisatchie NF, Louisiana; and Custer NF,
12 Montana); the second three in 1978 (Chequamegon NF, Wisconsin; Mark Twain NF,
13 Missouri; and Croatan NF, North Carolina); and the last two in 1979 (Apache NF, Arizona;
14 and Ochoco NF, Oregon). For the period 1979 to 1983, hourly maximum average
15 concentrations occurring at the clean sites, Custer National Forest (MT), Ochoco National
16 Forest (OR), and Apache National Forest (AZ), were similar to the exposures determined for
17 6 of the 7 clean sites characterized by Lefohn and Foley (1992). In almost all cases,
18 (1) none of the sites experienced hourly average concentrations ≥ 0.08 ppm and (2) the
19 maximum hourly average concentrations were in the range from 0.060 to 0.075 ppm.
20 Table 4-7 summarizes the percentile distributions for the three national forest sites.

21 Several clean sites were characterized by Lefohn et al. (1990b), using various exposure
22 indices. One of the indices used was a sigmoidally weighted cumulative exposure index
23 (W126), which was described in Section 4.1. The sigmoidal exposure (W126) values,
24 calculated over an annual period, are provided in Table 4-8. The W126 values for Theodore
25 Roosevelt National Park, ND were in the range 6.48 to 8.03 ppm-h. The maximum hourly
26 average concentration reported at the site was 0.068 ppm. The W126 values at the Custer
27 National Forest, MT and Ochoco National Forest, OR sites ranged from 5.79 to
28 22.67 ppm-h. The maximum hourly average concentrations measured at each site were
29 0.075 and 0.080 ppm, respectively. The W126 values calculated for the Custer National
30 Forest and Ochoco National Forest sites showed greater variability from year-to-year than the
31 values calculated for the South Pole, Barrow, and Theodore Roosevelt National Park sites.

**TABLE 4-6. SEASONAL (APRIL TO OCTOBER) PERCENTILE DISTRIBUTION
OF HOURLY OZONE CONCENTRATIONS, NUMBER OF HOURLY MEAN OZONE
OCCURRENCES ≥ 0.08 AND ≥ 0.10 , SEASONAL SEVEN-HOUR AVERAGE
CONCENTRATIONS, AND W126 VALUES FOR SITES IN
SELECTED CLASS I AREAS WITH DATA CAPTURE $\geq 75\%$
(All concentrations are in ppm units)**

Class I Area	Site/AIRS ID	Year	Min.	Percentiles (ppm)							Max.	No. of Obs.	Hours			Seasonal W126 (ppm-h)
				10	30	50	70	90	95	99			≥ 0.08	≥ 0.10	7-h (ppm)	
Redwood, CA	Redwood NP 06015002	1989	0.000	0.010	0.017	0.022	0.027	0.034	0.038	0.041	0.046	4,624	0	0	0.024	1.0
		1990	0.000	0.011	0.018	0.023	0.027	0.035	0.038	0.043	0.053	4,742	0	0	0.025	1.1
		1991	0.001	0.012	0.019	0.025	0.031	0.038	0.041	0.045	0.054	4,666	0	0	0.027	1.7
Olympic, WA	Olympic NP 530090012	1982	0.000	0.000	0.010	0.010	0.020	0.030	0.030	0.040	0.060	4,704	0	0	0.020	7.4
		1984	0.000	0.000	0.010	0.010	0.020	0.020	0.020	0.030	0.050	4,872	0	0	0.015	1.6
		1986	0.000	0.000	0.010	0.020	0.020	0.040	0.040	0.040	0.060	4,776	0	0	0.025	13.7
		1989	0.000	0.003	0.010	0.015	0.022	0.030	0.035	0.046	0.065	4,220	0	0	0.021	0.7
		1990	0.000	0.005	0.012	0.018	0.023	0.030	0.034	0.043	0.064	4,584	0	0	0.022	0.8
		1991	0.000	0.006	0.014	0.019	0.024	0.033	0.036	0.044	0.056	4,677	0	0	0.025	0.9
Glacier, MT	Glacier NP 300298001	1989	0.000	0.003	0.015	0.026	0.036	0.046	0.050	0.058	0.067	4,770	0	0	0.036	5.9
		1990	0.000	0.001	0.014	0.026	0.035	0.044	0.047	0.052	0.066	5,092	0	0	0.036	4.1
		1991	0.000	0.001	0.014	0.027	0.036	0.046	0.049	0.056	0.062	5,060	0	0	0.036	5.3
Yellowstone, WY	Yellowstone NP 560391010	1989	0.002	0.018	0.027	0.036	0.044	0.051	0.056	0.063	0.071	4,079	0	0	0.042	10.7
		1990	0.000	0.015	0.023	0.029	0.036	0.043	0.046	0.053	0.060	4,663	0	0	0.034	3.7
		1991	0.004	0.020	0.030	0.037	0.042	0.048	0.051	0.057	0.064	4,453	0	0	0.042	7.7
Badlands, SD	Badlands NP 460711001	1989	0.006	0.020	0.027	0.034	0.041	0.049	0.053	0.060	0.071	4,840	0	0	0.040	9.0
		1990	0.006	0.019	0.027	0.032	0.037	0.044	0.048	0.054	0.063	4,783	0	0	0.037	4.7
		1991	0.005	0.020	0.028	0.034	0.040	0.047	0.050	0.056	0.066	4,584	0	0	0.038	6.2
Great Sand Dunes, CO	Sand Dunes NM 08003002	1989	0.011	0.031	0.037	0.041	0.045	0.050	0.051	0.056	0.063	4,436	0	0	0.044	10.5
		1990	0.010	0.030	0.037	0.041	0.045	0.051	0.055	0.061	0.070	4,624	0	0	0.044	13.3
		1991	0.008	0.029	0.037	0.043	0.048	0.055	0.058	0.065	0.077	4,130	0	0	0.046	17.0
Theodore Roosevelt, ND North Unit	Theodore Roosevelt NP 380530002	1984	0.000	0.017	0.025	0.032	0.039	0.047	0.050	0.059	0.068	4,923	0	0	0.038	7.0
		1985	0.000	0.019	0.026	0.032	0.038	0.046	0.049	0.054	0.061	4,211	0	0	0.038	5.0
		1986	0.004	0.017	0.027	0.033	0.039	0.047	0.050	0.056	0.062	4,332	0	0	0.039	5.5
		1989	0.004	0.023	0.032	0.039	0.045	0.054	0.058	0.065	0.073	4,206	0	0	0.046	14.2
Point Reyes, CA	Point Reyes, NP 060410002	1989	0.006	0.020	0.025	0.031	0.036	0.041	0.045	0.058	0.080	4,577	1	0	0.033	4.7
		1990	0.006	0.017	0.022	0.025	0.029	0.036	0.040	0.046	0.063	4,856	0	0	0.028	1.8
		1991	0.006	0.019	0.025	0.030	0.034	0.040	0.043	0.048	0.072	4,588	0	0	0.031	3.0
Arches, UT	Arches NP 490190101	1989	0.000	0.031	0.040	0.045	0.050	0.056	0.059	0.065	0.083	4,260	2	0	0.047	20.6
		1990	0.000	0.020	0.025	0.027	0.031	0.036	0.039	0.045	0.055	4,639	0	0	0.030	1.7
Rocky Mountains, CO	Rocky Mountain NP 080690007	1989	0.003	0.025	0.034	0.039	0.043	0.051	0.055	0.070	0.098	4,366	9	0	0.043	13.6
		1990	0.006	0.022	0.029	0.034	0.038	0.046	0.049	0.058	0.070	4,091	0	0	0.038	5.5
		1991	0.004	0.026	0.037	0.043	0.048	0.055	0.059	0.074	0.095	4,730	21	0	0.048	22.3

TABLE 4-7. SEASONAL (APRIL TO OCTOBER) PERCENTILE DISTRIBUTION OF HOURLY OZONE CONCENTRATIONS, NUMBER OF HOURLY MEAN OZONE OCCURRENCES ≥ 0.08 AND ≥ 0.10 , SEASONAL SEVEN-HOUR AVERAGE CONCENTRATIONS, AND W126 VALUES FOR THREE "CLEAN" NATIONAL FOREST SITES WITH DATA CAPTURE $\geq 75\%$
(All concentrations are in ppm units)

Site	AIRS ID	Year	Percentiles (ppm)									No. of Obs.	Hours		Seasonal W126	
			Min.	10	30	50	70	90	95	99	Max.		$\geq .08$	$\geq .10$	7-h (ppm)	(ppm-h)
Custer NF, MT	300870101	1978	0.000	0.010	0.020	0.035	0.040	0.050	0.055	0.060	0.070	4,759	0	0	0.033	8.3
		1979	0.010	0.025	0.035	0.040	0.045	0.050	0.055	0.060	0.075	5,014	0	0	0.043	13.2
		1980	0.010	0.025	0.035	0.040	0.050	0.055	0.060	0.065	0.070	4,574	0	0	0.043	19.7
		1983	0.010	0.025	0.035	0.040	0.045	0.050	0.055	0.060	0.065	4,835	0	0	0.042	10.7
Ochoco NF, OR	410130111	1980	0.010	0.030	0.035	0.040	0.045	0.055	0.055	0.065	0.080	4,759	5	0	0.044	16.5
		1981	0.010	0.025	0.030	0.035	0.040	0.045	0.045	0.055	0.075	4,459	0	0	0.035	4.7
		1982	0.010	0.025	0.030	0.035	0.040	0.045	0.050	0.055	0.065	4,697	0	0	0.038	7.6
		1983	0.010	0.025	0.035	0.035	0.040	0.045	0.050	0.055	0.060	4,423	0	0	0.039	6.8
Apache NF, AZ	040110110	1981	0.010	0.025	0.030	0.035	0.040	0.045	0.050	0.055	0.065	4,806	0	0	0.039	7.6
		1982	0.015	0.030	0.040	0.045	0.050	0.055	0.060	0.065	0.075	4,714	0	0	0.047	21.9
		1983	0.004	0.025	0.035	0.040	0.045	0.055	0.055	0.065	0.070	4,788	0	0	0.042	14.6

**TABLE 4-8. THE VALUE OF THE W126 SIGMOIDAL EXPOSURE
PARAMETER CALCULATED OVER THE ANNUAL PERIOD
(Units in ppm-h)**

Site	Elevation (m)	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987
South Pole, Antarctica	2,835					2.65	3.72	3.01	2.41	3.54	2.76	4.09	
Bitumount, Alberta, Canada	350				2.99								
Barrow, AK	11					2.60	2.60	3.15	2.36	2.79	2.03	2.46	3.69
Theodore Roosevelt NP, ND	727									8.03	6.69	6.48*	
Custer National Forest, MT	1,006				14.08	22.67			12.18				
Ochoco National Forest, OR	1,364					19.54	5.79	9.10	8.02				
Birch Mountain, Alberta, Canada	850				19.73								
White River Oil Shale Project, UT, U-4 1600								19.98	32.10				
Fortress Mountain, Alberta, Canada	2,103											25.04	83.89
Apache National Forest, AZ	2,424					81.39	10.24	27.18	17.48				
Mauna Loa, HI	3,397					27.48	45.68	33.68	48.90	19.18	32.66	24.48	
Whiteface Mountain, NY	1,483				86.50	68.30	33.75	32.03	37.82	42.94	41.36	32.07	58.33
Hohenpeissenberg, FRG	975	61.28	25.04	35.64	21.76	18.53	29.53	49.00	19.85	40.43			
American Samoa	82					0.28	0.24	0.25	0.28	0.30	0.26	0.30	0.32

* Collection did not occur during the months of October, November, and December.

Source: Lefohn et al. (1990b).

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1 As the W126 values increased, the magnitude of the year-to-year variability also
2 increased. For 2 years of data, the W126 values calculated for the White River U-4 Oil
3 Shale (UT) site were 19.98 and 32.10 ppm-h. The maximum hourly concentration recorded
4 was 0.079 ppm. The W126 values calculated for the Apache National Forest, AZ site
5 ranged from 10.24 to 81.39 ppm-h. The highest hourly average concentration was
6 0.090 ppm.

7 The 7-h (0900 to 1559 h) average concentration has been used by vegetation researchers
8 to characterize O₃ exposures experienced in plant chamber experiments (see Chapter 5).
9 Because O₃ concentrations are highest during the warm-season months and, at many low-
10 elevation sites, during daylight hours, the 7-mo seasonal, 7-h (0900 to 1559 h) average
11 concentration is higher than annual average values. Most remote sites outside North America
12 experience seasonal 7-h averages of 0.025 ppm (Table 4-9) (Lefohn et al., 1990b). The
13 seasonal average of the daily 7-h average values for the South Pole, Antarctica, range from
14 0.024 to 0.027 ppm. The values range from 0.022 to 0.026 ppm at Barrow, Alaska. In the
15 continental United States and southern Canada, values range from approximately 0.028 to
16 0.050 ppm (Lefohn, 1990b). At an O₃ monitoring site at the Theodore Roosevelt National
17 Park in North Dakota, a 7-mo (April to October) average of the 7-h daily average
18 concentrations of 0.038, 0.039, and 0.039 ppm, respectively, was experienced in 1984,
19 1985, and 1986. These 7-mo seasonal averages (i.e., 0.038 and 0.039 ppm) appear to be
20 representative of values that may occur at other fairly clean sites located in the United States
21 and other locations in the northern hemisphere. In earlier investigations, Lefohn (1984)
22 reported 3-mo (June to August), 7-h averages of 0.048, 0.044, and 0.059 ppm at remote
23 national forest sites at Custer, MT, Ochoco, OR, and Apache, AZ, respectively.

24 25 **4.3.3.2 Urban-Influenced Nonurban Areas**

26 It is difficult to identify a set of unique O₃ distribution patterns that adequately
27 describes exposures experienced at monitoring sites in nonurban locations because, as
28 indicated earlier, many nonurban sites in the United States are influenced by local sources of
29 pollution or long-range transport of O₃ or its precursors. Unlike the clean sites characterized
30 by Lefohn and Jones (1986), Lefohn et al. (1990b), and Lefohn and Foley (1992),

**TABLE 4-9. THE VALUE OF THE OZONE SEASON (SEVEN-MONTH) AVERAGE OF
THE DAILY SEVEN-HOUR (0900 TO 1559 HOURS) CONCENTRATION
(Units in ppm)**

Site	Elevation (m)	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987
South Pole, Antarctica	2,835					0.025	0.027		0.026	0.027	0.024	0.025	
Bitumount, Alberta, Canada	350				0.028								
Barrow, AK	11					0.022	0.025	0.024	0.024	0.022	0.026	0.022	0.026
Theodore Roosevelt NP, ND	727									0.038	0.039	0.039*	
Custer National Forest, MT	1,006				0.043	0.044			0.042				
Ochoco National Forest, OR	1,364					0.043	0.035	0.038	0.038				
Birch Mountain, Alberta, Canada	850				0.036								
White River Oil Shale Project, UT, U-4 1600								0.045	0.045				
Fortress Mountain, Alberta, Canada	2,103											0.041	0.050
Apache National Forest, AZ	2,424					0.054	0.039	0.047	0.040				
Mauna Loa, HI	3,397					0.035	0.039	0.034	0.038	0.035	0.035	0.034	
Whiteface Mountain, NY	1,483				0.049	0.046	0.040	0.034	0.041	0.044	0.043	0.043	0.045
Hohenpeissenberg, FRG	975	0.047	0.040	0.044	0.040	0.037	0.043	0.047	0.040	0.043			
American Samoa	82					0.010	0.010	0.011	0.009	0.012	0.010	0.011	

* Collection did not occur during the months of October, November, and December.

Source: Lefohn et al. (1990b).

urban-influenced nonurban sites sometimes show frequent hourly average concentrations near the minimum detectable level, but almost always show occurrences of hourly average concentrations above 0.10 ppm. The frequent occurrence of hourly average concentrations near the minimum detectable level is indicative of scavenging processes (i.e., NO_x); the presence of high hourly average concentrations can be attributable to the influence of either local generation or the long-range transport of O₃. For example, Evans et al. (1983) reported that the Green Mt. (VT) and Mark Twain (MO) national forest sites were influenced by long-range transport of O₃. Environmental Protection Agency (1986a) reported that the maximum hourly average concentrations at Green Mt. (for the period 1977 to 1981) and Mark Twain (for the period 1979 to 1983) were 0.145 and 0.155 ppm, respectively. Using hourly averaged data from the AIRS database for a select number of rural monitoring sites, Table 4-10 summarizes the percentiles of the hourly average O₃ concentrations, the number of occurrences of the hourly average concentration ≥ 0.10 ppm, and the 3-mo sum of all hourly average concentrations ≥ 0.06 ppm.

As part of a comprehensive air monitoring project sponsored by the Electric Power Research Institute (EPRI), O₃ measurements were made by the chemiluminescence method from 1977 through 1979 at nine "nonurban" Sulfate Regional Experiment Sites (SURE) and Eastern Regional Air Quality Study (ERAQS) sites in the eastern United States. On the basis of diurnal NO_x patterns that indicated the influence of traffic emissions, five of the sites were classed as "suburban;" the other four were classed as "rural." The O₃ data from these nine stations are summarized in Table 4-11. The sites are either influenced by local sources or transport of O₃ or its precursors. The maximum hourly average concentrations are generally higher than 0.125 ppm and the occurrence of hourly average concentrations near minimum detectable levels indicates NO_x scavenging processes.

As part of its effort to provide long-term estimates of dry acidic deposition across the United States, the National Dry Deposition Network (NDDN) operated more than 50 sites, which include 41 in the eastern United States and 9 in the western United States, that routinely recorded hourly average O₃ concentrations. Figure 4-7 shows the locations of the NDDN sites. Edgerton and Lavery (1992) have summarized the O₃ exposures at some of the sites for the period 1988 to 1990. Table 4-12 summarizes the 7-h (0900 to 1559 h) growing season average concentration (May to September) for selected sites in the Midwest and East.

**TABLE 4-10. SUMMARY OF PERCENTILES, NUMBER OF HOURLY OCCURRENCES ≥ 0.10 ppm,
AND THREE-MONTH SUM06 VALUES FOR SELECTED RURAL OZONE MONITORING SITES
IN 1989 (APRIL TO OCTOBER)
(Concentration values in ppm)**

AIRS Site	Name	Percentiles (ppm)									Number of Hourly Values	Number of Occurrence ≥ 0.10	Max. Uncorrected 3-mo SUM06 Value (ppm-h)
		Min.	10	30	50	70	90	95	99	Max.			
RURAL AGRICULTURAL													
170491001	Effingham County, IL	0.000	0.009	0.023	0.036	0.046	0.063	0.070	0.081	0.104	4,600	1	25.3
180970042	Indianapolis, IN	0.001	0.006	0.021	0.034	0.046	0.063	0.072	0.085	0.103	4,592	3	25.4
240030014	Anne Arundel, MD	0.000	0.006	0.021	0.032	0.045	0.064	0.073	0.090	0.120	4,360	10	25.5
310550032	Omaha, NE	0.002	0.021	0.030	0.037	0.047	0.062	0.067	0.075	0.098	4,160	0	24.9
420070003	New Brighton, PA	0.000	0.008	0.021	0.032	0.043	0.062	0.070	0.087	0.102	5,055	4	29.4
510610002	Fauquier County, VA	0.000	0.009	0.021	0.033	0.045	0.061	0.069	0.084	0.122	5,050	5	24.6
RURAL FOREST													
060430004	Yosemite NP, CA	0.000	0.008	0.022	0.035	0.049	0.065	0.072	0.083	0.111	4,853	3	37.6
360310002	Essex County, NY	0.016	0.031	0.040	0.049	0.056	0.066	0.072	0.086	0.106	4,792	4	45.6
470090101	Smoky Mountain NP, TN	0.000	0.025	0.036	0.044	0.053	0.065	0.070	0.081	0.098	4,764	0	35.9
511870002	Shen NP (Dky Rdg), VA	0.004	0.027	0.037	0.045	0.054	0.065	0.071	0.082	0.100	4,454	1	33.5
RURAL OTHER													
040132004	Scottsdale, AZ	0.000	0.006	0.018	0.031	0.045	0.062	0.071	0.084	0.107	5,070	4	31.7
350431001	Sandoval County, NM	0.000	0.010	0.020	0.030	0.040	0.060	0.060	0.070	0.090	5,059	0	25.1
370810011	Guilford County, NC	0.004	0.010	0.023	0.034	0.046	0.063	0.070	0.083	0.113	4,853	2	27.7
371470099	Farmville, NC	0.000	0.010	0.023	0.034	0.044	0.062	0.070	0.083	0.100	4,833	2	26.4
550270001	Horicon, WI	0.002	0.019	0.029	0.037	0.047	0.062	0.070	0.088	0.111	4,142	11	24.6
551390007	Oshkosh, WI	0.002	0.016	0.028	0.038	0.048	0.063	0.070	0.084	0.121	4,206	3	27.9

TABLE 4-11. SUMMARY OF PERCENTILES OF HOURLY AVERAGE CONCENTRATIONS FOR ELECTRIC POWER RESEARCH INSTITUTE SULFATE REGIONAL EXPERIMENT SITES (SURE)/ERAQS OZONE MONITORING SITES
(Units are ppm)

SURE/ERAQS Name	Year	Percentiles									Number of Observations
		Min.	10	30	50	70	90	95	99	Max.	
Montague, MA	1978	0.000	0.002	0.018	0.032	0.043	0.061	0.075	0.119	0.202	7,138
	1979	0.000	0.000	0.013	0.025	0.035	0.056	0.070	0.103	0.149	8,485
Scranton, PA	1978	0.000	0.015	0.031	0.040	0.048	0.062	0.073	0.094	0.126	5,461
	1979	0.000	0.011	0.022	0.030	0.040	0.061	0.074	0.097	0.132	8,313
Indian River, DE	1978	0.000	0.010	0.024	0.035	0.049	0.072	0.085	0.103	0.134	6,874
	1979	0.000	0.008	0.020	0.031	0.042	0.063	0.073	0.092	0.138	8,527
Duncan Falls, OH	1978	0.000	0.005	0.022	0.034	0.049	0.071	0.081	0.110	0.144	5,125
	1979	0.000	0.010	0.021	0.029	0.042	0.060	0.069	0.086	0.110	7,595
Rockport, IN	1978	0.000	0.008	0.021	0.032	0.044	0.066	0.078	0.101	0.145	6,849
	1979	0.000	0.008	0.019	0.028	0.038	0.055	0.064	0.083	0.104	8,391
Giles County, TN	1978	0.000	0.000	0.018	0.032	0.046	0.066	0.075	0.087	0.110	6,034
	1979	0.000	0.000	0.014	0.024	0.036	0.055	0.065	0.081	0.130	8,439
Roanoke, IN	1978	0.000	0.004	0.019	0.032	0.044	0.067	0.079	0.106	0.160	5,874
	1979	0.000	0.004	0.017	0.026	0.038	0.061	0.074	0.098	0.133	8,001
Research Triangle Park, NC	1978	0.000	0.001	0.017	0.032	0.049	0.076	0.087	0.108	0.142	7,081
	1979	0.000	0.001	0.012	0.024	0.037	0.058	0.068	0.084	0.131	8,652
Lewisburg, WV	1978	0.002	0.020	0.034	0.045	0.056	0.072	0.079	0.091	0.115	7,019
	1979	0.000	0.013	0.022	0.029	0.039	0.056	0.065	0.080	0.099	7,849

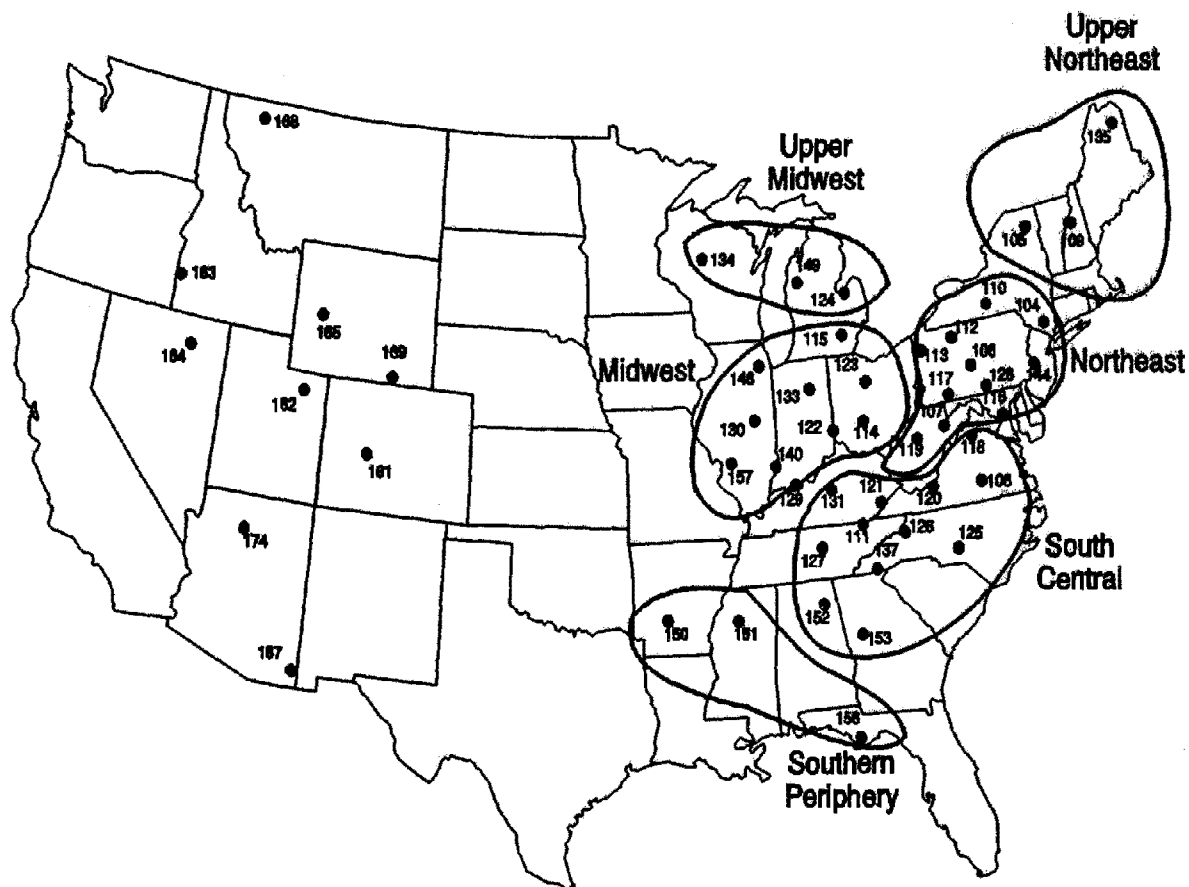


Figure 4-7. The location of National Dry Deposition Network monitoring sites as of December 1990.

Source: Edgerton and Lavery (1992).

1 Fifty-nine percent of the monitoring sites listed in the table have been classified as
 2 agricultural and 36% as forested. One site was classified as commercial. As noted by the
 3 U.S. EPA (1992a), 1988 was an exceptionally high O₃ concentration year, when compared
 4 with 1989 and 1990. The number of hourly O₃ concentrations ≥ 0.08 ppm is presented in
 5 the table. Edgerton and Lavery (1992) have summarized O₃ hourly average concentration
 6 data for several sites using the cumulative integrated exposure index, W126, as proposed by
 7 Lefohn and Runeckles (1987). Based on evidence presented in the literature relating
 8 O₃ exposure with agricultural yield reduction, the index was proposed as a way to weight the
 9 higher hourly average concentrations greater than the lower values. The data in the table
 10 illustrate the large differences in cumulative exposure between those that occurred in 1988

**TABLE 4-12. SEVEN-HOUR GROWING SEASON MEAN, W126 VALUES, AND NUMBER ≥ 80 ppb FOR
SELECTED EASTERN NATIONAL DRY DEPOSITION NETWORK SITES**

Subregion	State	Site	Land Class *	7-h Mean (ppb)			W126 (ppm-h)			SUM06 (ppm-h)			SUM08 (ppm-h)		
				1988	1989	1990	1988	1989	1990	1988	1989	1990	1988	1989	1990
NORTHEAST															
Connecticut Hill	NY	110	RF	55.0	48.3	45.3	75.5	40.3	36.8	86.8	47.2	35.8	44.3	5.5	3.3
Washington's Crossing	NJ	144	RA	—	52.8	52.4	—	46.0	43.7	—	52.1	48.4	—	21.2	21.3
Pennsylvania State University	PA	106	RA	59.0	46.0	51.0	63.5	25.4	42.7	65.6	28.1	45.0	32.3	5.0	11.6
Laurel Hill State Park	PA	117	RF	62.7	48.4	48.6	68.8	29.1	31.0	75.5	30.8	32.1	41.6	7.0	8.0
Beltsville	MD	116	RA	—	54.6	55.5	—	45.4	45.7	—	48.6	49.4	—	22.9	21.9
Cedar Creek State Park	WV	119	RA	59.8	44.9	48.2	50.4	19.6	24.3	56.3	19.0	23.2	27.0	4.1	6.5
UPPER NORTHEAST															
Whiteface Mountain	NY	105	RF	43.5	45.7	42.3	37.8	25.3	31.2	40.9	25.2	29.0	17.0	2.6	8.4
Ashland	ME	135	RA	—	37.9	35.3	—	9.1	8.7	—	5.4	5.8	—	0.6	0.8
MIDWEST															
Argonne National Lab	IL	146	RA	61.1	51.4	46.3	59.1	29.6	21.6	69.4	35.0	25.7	32.3	10.4	3.6
Vincennes	IN	140	RA	62.0	51.1	50.9	68.1	36.4	35.8	78.5	40.3	41.2	36.7	8.7	11.8
Oxford	OH	122	RA	65.3	53.5	51.7	91.8	48.4	46.4	103.2	55.3	51.7	56.8	15.8	17.2
UPPER MIDWEST															
Unionville	MI	124	RA	—	51.5	47.4	—	35.4	30.7	—	41.6	31.6	—	9.0	7.1
Perkinstown	WI	134	RA	—	44.2	38.8	—	19.0	11.6	—	18.3	7.6	—	0.2	0.0
SOUTH CENTRAL															
Sand Mountain	AL	152	RA	—	52.6	63.6	—	40.6	68.7	—	33.2	83.4	—	3.4	24.0
Georgia Station	GA	153	RA	—	48.1	62.6	—	28.1	69.7	—	21.8	77.7	—	4.6	28.4
Perryville	KY	129	RA	65.2	50.8	—	103.6	39.7	—	99.6	38.9	—	39.7	5.2	—
Research Triangle Park	NC	101	RC	62.3	50.8	—	62.3	31.7	—	71.0	35.5	—	20.5	6.6	—
Coweeta	NC	137	RF	55.6	41.0	47.9	44.3	16.1	21.3	—	—	—	—	—	—
Edgar Evins State Park	TN	127	RF	—	47.2	56.1	—	26.9	44.5	—	24.4	49.2	—	1.5	8.2
Horton Station	VA	120	RF	62.3	51.4	54.4	127.6	61.2	70.6	150.7	64.0	82.8	60.2	8.5	9.2

**TABLE 4-12 (cont'd). SEVEN-HOUR GROWING SEASON MEAN, W126 VALUES, AND NUMBER ≥ 80 ppb FOR
SELECTED EASTERN NATIONAL DRY DEPOSITION NETWORK SITES**

Subregion	State	Site	Land Class *	7-h Mean (ppb)			W126 (ppm-h)			SUM06 (ppm-h)			SUM08 (ppm-h)		
				1988	1989	1990	1988	1989	1990	1988	1989	1990	1988	1989	1990
SOUTHERN PERIPHERY															
Caddo Valley	AR	150	RF	—	46.2	49.5	—	18.5	21.0	—	15.6	25.2	—	0.2	2.3
Sumatra	FL	156	RF	—	39.8	46.3	—	17.8	20.0	—	16.5	17.4	—	1.0	0.9

— = No data or insufficient data.

*RA = Rural agricultural.

RF = Rural forest.

RC = Rural commercial.

Source: Edgerton and Lavery (1992).

1 and those that were experienced in 1989 and 1990. The percentile of the hourly average
2 concentrations is summarized in Table 4-13. Although several of the monitoring sites are
3 located in fairly remote locations in the eastern United States (based on land use
4 characterization) the maximum hourly average concentrations reflect the transport of O₃ or
5 its precursors into the area.

6 Taylor et al. (1992) have summarized the O₃ exposures that were experienced at
7 10 EPRI Integrated Forest Study sites in North America. The authors reported that in 1988
8 all sites experienced maximum hourly average concentrations ≥ 0.08 ppm. In almost all
9 cases, the sites experienced multiple occurrences above 0.08 ppm. This implies that although
10 the sites were located in remote forested areas, the sites experienced elevated O₃ exposures
11 that were more than likely due to long-range transport of O₃ or its precursors.

12 Ozone concentrations on a seasonal basis in the Shenandoah National Park exhibit some
13 features in common with both urban and rural areas. During some years, maximum hourly
14 average concentrations exceed 0.12 ppm, although some sites in the Park exhibit a lack of
15 hourly average concentrations near minimum detectable level. Taylor and Norby (1985)
16 have characterized O₃ episodes, which they defined as any day in which a 1-h mean
17 O₃ concentration was > 0.08 ppm. Based on a 4-year monitoring period in the Park, the
18 probability was 80% that any given episode during the growing season would last 2 or more
19 days, while the probabilities of episodes lasting for periods > 3 , 4, and 5 days were 30, 10,
20 and 2%, respectively. Single-day O₃ episodes were infrequent. Taylor and Norby (1985)
21 noted that, given the frequency of respites, there was a 50% probability that a second
22 episode would occur within 2 weeks.

23 Because of a lack of air quality data collected at rural and remote locations, it has been
24 necessary to use interpolation techniques to estimate O₃ exposures in nonurban areas. In the
25 absence of actual O₃ data, interpolation techniques have been applied to the estimation of
26 O₃ exposures across the United States (Reagan, 1984; Lefohn et al., 1987a; Knudsen and
27 Lefohn, 1988). Kriging, a mathematical interpolation technique, has been used to provide
28 estimates of seasonal O₃ values for the National Crop Loss Assessment Network (NCLAN)
29 for 1978 through 1982 (May to September for each year) (Reagan, 1984). These values,
30 along with updated values, coupled with exposure-response models, were used to predict
31

TABLE 4-13. SUMMARY OF PERCENTILES FOR NATIONAL DRY DEPOSITION NETWORK MONITORING SITES
(Units are ppm)

Site No.	Name	Year	Min.	Percentiles							Max.	Number of Observations
				10	30	50	70	90	95	99		
RURAL AGRICULTURAL SITES												
106	Pennsylvania State University, PA	1988	0.000	0.013	0.026	0.036	0.049	0.073	0.086	0.114	0.143	4,716
		1989	0.000	0.010	0.022	0.033	0.043	0.059	0.066	0.082	0.104	5,089
		1990	0.000	0.015	0.027	0.038	0.048	0.065	0.074	0.090	0.120	5,056
116	Beltsville, MD	1989	0.002	0.003	0.014	0.029	0.044	0.068	0.081	0.096	0.131	5,062
		1990	0.000	0.001	0.015	0.027	0.041	0.067	0.080	0.103	0.137	4,597
119	Cedar Creek, WV	1988	0.000	0.008	0.017	0.029	0.044	0.069	0.082	0.108	0.134	4,938
		1989	0.001	0.006	0.013	0.024	0.037	0.056	0.065	0.082	0.172	5,044
		1990	0.001	0.007	0.014	0.024	0.038	0.057	0.067	0.085	0.116	5,025
122	Oxford, OH	1988	0.001	0.019	0.032	0.044	0.058	0.083	0.096	0.117	0.221	4,746
		1989	0.001	0.017	0.029	0.039	0.050	0.069	0.077	0.092	0.109	5,073
		1990	0.000	0.015	0.028	0.037	0.048	0.067	0.077	0.092	0.116	5,077
124	Unionville, MI	1989	0.003	0.021	0.031	0.038	0.047	0.063	0.071	0.086	0.113	5,041
		1990	0.004	0.020	0.029	0.036	0.044	0.061	0.069	0.084	0.105	5,065
129	Perryville, KY	1988	0.002	0.024	0.038	0.049	0.062	0.080	0.094	0.110	0.143	4,061
		1989	0.001	0.020	0.033	0.043	0.052	0.066	0.072	0.086	0.102	4,787
134	Perkinstown, WI	1989	0.007	0.023	0.032	0.038	0.046	0.057	0.062	0.071	0.085	5,029
		1990	0.006	0.020	0.028	0.035	0.041	0.050	0.056	0.065	0.074	5,063
135	Loring AFB/Ashland, ME	1989	0.002	0.017	0.026	0.032	0.039	0.049	0.055	0.063	0.103	5,067
		1990	0.002	0.014	0.023	0.029	0.036	0.046	0.051	0.068	0.088	5,080
140	Vincennes, IN	1988	0.000	0.007	0.024	0.036	0.052	0.076	0.089	0.104	0.120	4,908
		1989	0.000	0.009	0.025	0.036	0.047	0.064	0.072	0.085	0.112	5,065
		1990	0.000	0.009	0.025	0.035	0.045	0.062	0.073	0.089	0.110	5,084
144	Washington Crossing, NJ	1989	0.000	0.006	0.021	0.033	0.046	0.067	0.078	0.100	0.159	5,053
		1990	0.001	0.008	0.021	0.032	0.043	0.065	0.079	0.104	0.148	5,058

**TABLE 4-13 (cont'd). SUMMARY OF PERCENTILES FOR NATIONAL DRY DEPOSITION NETWORK
MONITORING SITES**
(Units are ppm)

Site No.	Name	Year	Min.	Percentiles							Max.	Number of Observations
				10	30	50	70	90	95	99		
RURAL AGRICULTURAL SITES (cont'd)												
146	Argonne National Laboratory, IL	1988	0.000	0.004	0.019	0.032	0.046	0.073	0.085	0.103	0.146	5,037
		1989	0.000	0.005	0.019	0.029	0.041	0.061	0.070	0.088	0.126	5,055
		1990	0.000	0.004	0.017	0.028	0.039	0.057	0.065	0.077	0.097	5,033
152	Sand Mountain, AL	1989	0.000	0.020	0.031	0.041	0.051	0.065	0.072	0.082	0.097	4,509
		1990	0.000	0.021	0.035	0.045	0.057	0.074	0.080	0.093	0.117	5,068
153	Georgia Station, GA	1989	0.002	0.014	0.025	0.034	0.045	0.062	0.069	0.082	0.118	3,540
		1990	0.002	0.021	0.034	0.044	0.056	0.073	0.084	0.102	0.144	4,814
RURAL FOREST SITES												
105	Whiteface Mountain, NY	1988	0.000	0.016	0.026	0.034	0.044	0.062	0.074	0.098	0.129	5,051
		1989	0.003	0.022	0.030	0.038	0.047	0.059	0.066	0.078	0.093	4,698
		1990	0.005	0.018	0.028	0.036	0.046	0.060	0.069	0.086	0.115	5,016
110	Ithaca, NY	1988	0.005	0.025	0.034	0.043	0.055	0.080	0.090	0.103	0.126	4,827
		1989	0.002	0.025	0.036	0.044	0.052	0.065	0.071	0.081	0.101	5,064
		1990	0.001	0.022	0.033	0.041	0.049	0.063	0.069	0.081	0.093	5,075
117	Laurel Hill, PA	1988	0.001	0.012	0.025	0.036	0.050	0.076	0.092	0.119	0.156	5,007
		1989	0.000	0.009	0.020	0.031	0.043	0.061	0.069	0.087	0.110	4,697
		1990	0.001	0.009	0.020	0.030	0.042	0.060	0.071	0.086	0.109	5,032
120	Horton Station, VA	1988	0.010	0.031	0.045	0.057	0.067	0.084	0.096	0.114	0.145	5,012
		1989	0.002	0.032	0.043	0.050	0.059	0.070	0.076	0.085	0.103	4,976
		1990	0.004	0.032	0.044	0.052	0.059	0.071	0.075	0.084	0.097	5,066
127	Edgar Evins State Park, TN	1989	0.000	0.017	0.028	0.037	0.047	0.062	0.067	0.077	0.090	5,060
		1990	0.001	0.019	0.032	0.041	0.052	0.067	0.073	0.085	0.109	5,027

**TABLE 4-13 (cont'd). SUMMARY OF PERCENTILES FOR NATIONAL DRY DEPOSITION NETWORK
MONITORING SITES
(Units are ppm)**

Site No.	Name	Year	Min.	Percentiles							Max.	Number of Observations
				10	30	50	70	90	95	99		
RURAL FOREST SITES (cont'd)												
137	Coweeta, NC	1988	0.001	0.010	0.022	0.034	0.047	0.065	0.072	0.094	0.145	4,182
		1989	0.001	0.007	0.016	0.025	0.037	0.055	0.061	0.071	0.094	4,275
		1990	0.000	0.008	0.018	0.029	0.043	0.059	0.064	0.072	0.085	5,046
150	Caddo Valley, AR	1989	0.002	0.005	0.016	0.028	0.041	0.057	0.063	0.075	0.102	5,046
		1990	0.002	0.004	0.015	0.029	0.041	0.057	0.065	0.077	0.094	5,078
156	Sumatra, FL	1989	0.001	0.012	0.022	0.030	0.040	0.057	0.065	0.075	0.098	4,700
		1990	0.000	0.011	0.023	0.033	0.043	0.057	0.063	0.072	0.118	4,444
RURAL COMMERCIAL SITE												
101	Research Triangle Park, NC	1988	0.000	0.004	0.020	0.035	0.050	0.072	0.084	0.111	0.137	5,030
		1989	0.000	0.004	0.019	0.030	0.042	0.063	0.071	0.083	0.121	4,893

1 agriculturally related economic benefits anticipated by lower O₃ levels in the United States
2 (Adams et al., 1985; Adams et al., 1989).

3 Kriging is a statistical tool developed by Matheron (1963) and named in honor of D.G.
4 Krige. Although originally developed specifically for ore reserve estimation, kriging has
5 been used for other spatial estimation applications, such as analyzing and modeling air
6 quality data (Grivet, 1980; Faith and Sheshenski, 1979). At its simplest, kriging can be
7 thought of as a way to interpolate spatial data much as an automatic contouring program
8 would. In a more precise manner, kriging can be defined as a best linear unbiased estimator
9 of a spatial variable at a particular site or geographic area. Kriging assigns low weights to
10 distant samples and vice versa, but also takes into account the relative position of the samples
11 to each other and the site or area being estimated.

12 Figure 4-8 shows the average for the 1985 through 1987 period for the seasonal (April
13 to October) average of the daily maximum 7- and 12-h values across the United States. The
14 estimates made for the Rocky Mountain region had large uncertainties associated with them
15 because of a lack of monitoring sites.

16 Because of the importance of the higher hourly average concentrations in eliciting
17 injury and yield reduction for agricultural crops (U.S. Environmental Protection Agency,
18 1986b; 1992b), kriging was used to predict O₃ exposures in the eastern United States, using
19 the sigmoidally weighted W126 exposure index as described earlier in this section. Lefohn
20 et al. (1992b) used the W126 index in its kriging to characterize the O₃ exposures that
21 occurred during the period 1985-1989. Figure 4-9 illustrates the integrated O₃ exposure for
22 the 1988 and 1989 periods (data derived from work described in Lefohn et al., 1992b).
23 Using the kriged data in the East, the 1988 exposures were the highest for the 5-year period,
24 while 1989 exhibited the lowest exposures. The O₃ gradient pattern analyses described by
25 Lefohn et al. (1992b) identified contiguous areas of persistent relatively high seasonal
26 O₃ values. The largest area extended from New Jersey south to northern Georgia and South
27 Carolina. This area was roughly bounded on the west by the Appalachian Mountains.
28 A second area, which exhibited persistent relatively high seasonal O₃ exposures, was
29 centered over the Ohio River Valley in the region near the Kentucky-Indiana-Ohio borders.
30 Relatively low O₃ exposures were found in Minnesota, Iowa, Wisconsin, Maine, Vermont,
31

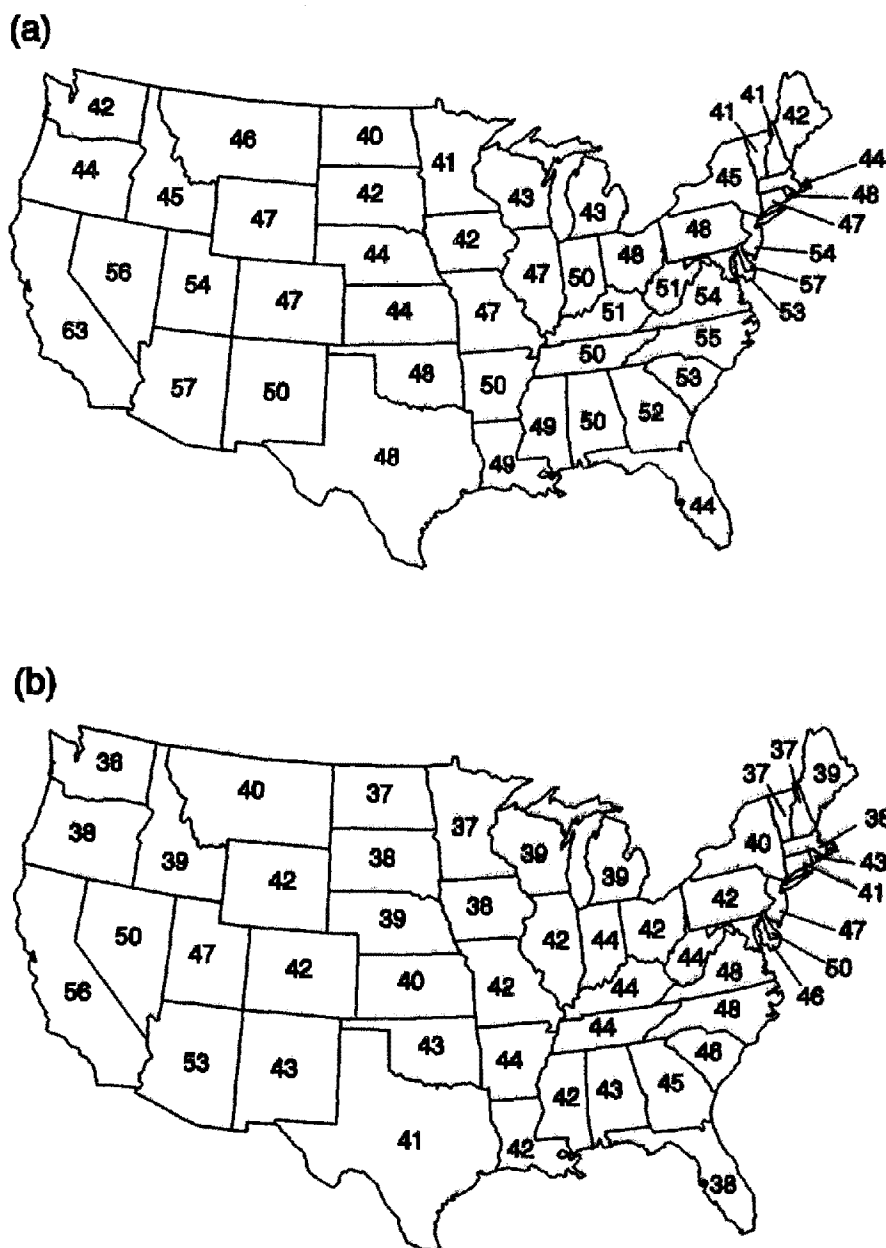


Figure 4-8. The kriged 1985 to 1986 maximum (a) 7-h and (b) 12-h average concentrations of ozone across the United States.

Source: Lefohn et al. (1990a).

- 1 New Hampshire, and Florida. On a year-to-year basis, the analysis by Lefohn et al. (1992b)
- 2 showed that regions that tended to be high for a specific year continued to experience
- 3 O₃ exposures that were higher when compared to other regions.
- 4

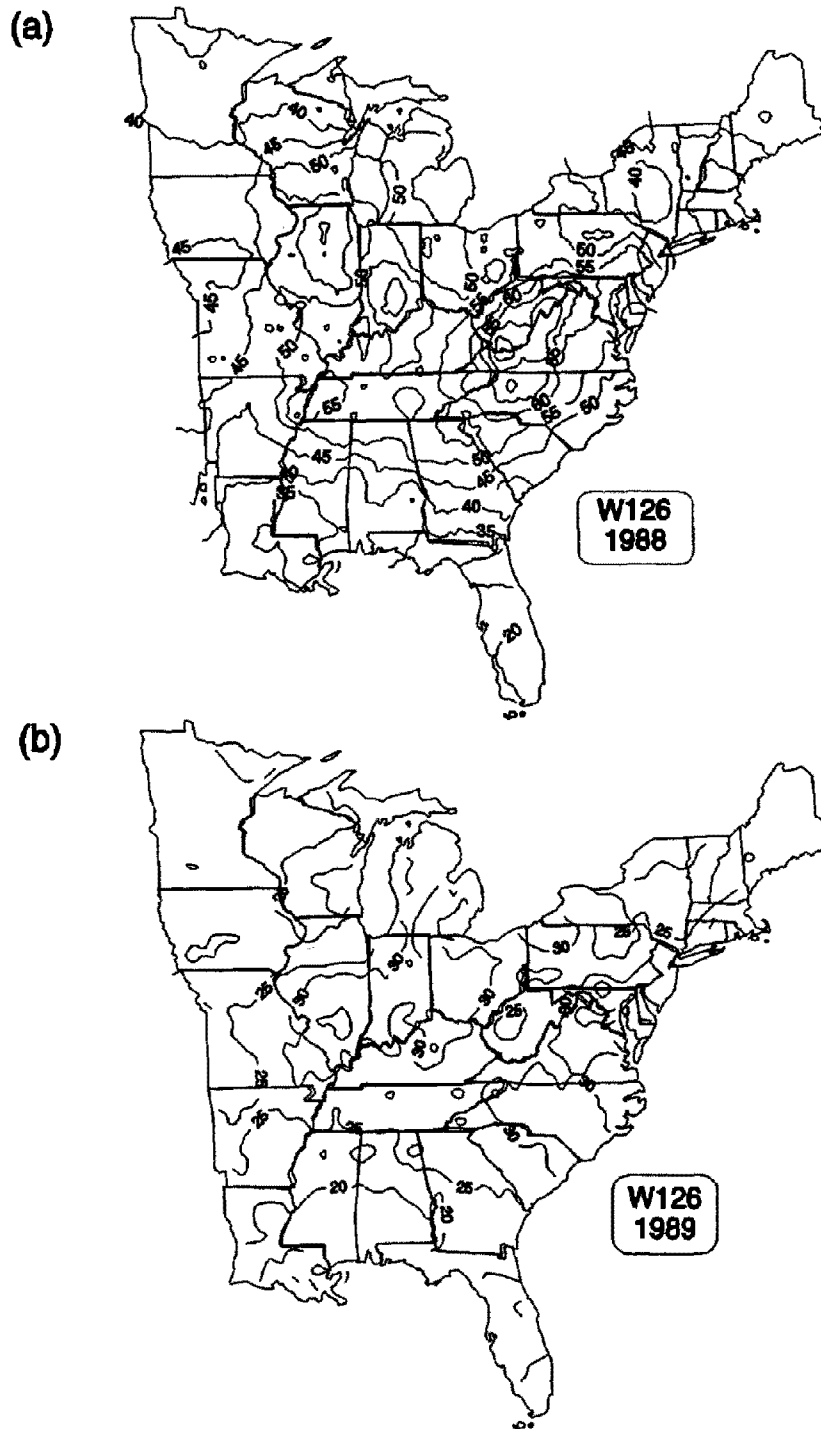


Figure 4-9. The kriged estimates of the W126 integrated ozone exposure index for the eastern United States for (a) 1988 and (b) 1989.

Source: Lefohn et al. (1992b).

4.4 DIURNAL VARIATIONS IN OZONE CONCENTRATIONS

4.4.1 Introduction

By definition, diurnal variations are those that occur during a 24-h period. Diurnal patterns of O_3 may be expected to vary with location, depending on the balance among the many factors affecting O_3 formation, transport, and destruction. Although they vary with locality, diurnal patterns for O_3 typically show a rise in concentration from low or levels near minimum detectable amounts to an early afternoon peak. The 1978 criteria document (U.S. Environmental Protection Agency, 1978) ascribed the diurnal pattern of concentrations to three simultaneous processes: (1) downward transport of O_3 from layers aloft; (2) destruction of O_3 through contact with surfaces and through reaction with nitric oxide at ground level; and (3) in situ photochemical production of O_3 (U.S. Environmental Protection Agency, 1978; Coffey et al., 1977; Mohnen et al., 1977; Reiter, 1977a).

The form of an average diurnal pattern may provide information on sources, transport, and chemical formation/destruction effects at various sites (Lefohn, 1992b). Non transport conditions will produce early afternoon peaks. However, long-range transport processes will influence the actual timing of a peak from afternoon to evening or early morning hours. Investigators have utilized diagrams that illustrate composite diurnal patterns as a means to describe qualitatively the differences in O_3 exposures between sites (Lefohn and Jones, 1986; Böhm et al., 1991). Although it might appear that composite diurnal pattern diagrams could be used to quantify the differences in O_3 exposures between sites, Lefohn et al. (1990a) cautioned their use for this purpose. The average diurnal patterns are derived from long-term calculations of the hourly average concentrations, and the resulting diagram cannot adequately identify, at most sites, the presence of high hourly average concentrations and thus may not adequately be able to distinguish O_3 exposure differences among sites. Logan (1989) noted that diurnal variation of O_3 did not reflect the presence of high hourly average concentrations.

Unique families of diurnal average profiles exist and it is possible to distinguish between two types of O_3 monitoring sites. A seasonal diurnal diagram provides the investigator with the opportunity to identify whether a specific O_3 monitoring site has more scavenging than any other site. Ozone is rapidly depleted near the surface below the nocturnal inversion layer (Berry, 1964). Mountainous sites, which are above the nocturnal

1 inversion layer, do not necessarily experience this depletion (Stasiuk and Coffey, 1974).
2 Taylor and Hanson (1992) reported similar findings using data from the Integrated Forest
3 Study. For the low-elevation sites, the authors reported that intra-day variability was most
4 significant due to the pronounced daily amplitude in O_3 concentration between the pre-dawn
5 minimum and mid-afternoon-to-early evening maximum. The authors reported that the inter-
6 day variation was more significant in the high-elevation sites. Ozone trapped below the
7 inversion layer is depleted by dry deposition and chemical reactions if other reactants are
8 present in sufficient quantities (Kelly et al., 1984). Above the nocturnal inversion layer, dry
9 deposition generally does not occur and the concentration of O_3 scavengers is generally lower
10 so that O_3 concentration remains fairly constant (Wolff et al., 1987). A flat diurnal pattern
11 is usually interpreted as indicating a lack of efficient scavenging of O_3 and/or a lack of
12 photochemical precursors, whereas a varying diurnal pattern is taken to indicate the opposite.
13 With the composite diagrams alone, it is difficult to quantify the daily or long-term exposures
14 of O_3 . For example, the diurnal patterns for two such sites are illustrated in Figure 4-10.
15 The Jefferson County (KY) site is urban-influenced and experiences elevated levels of O_3 and
16 NO_x . The Oliver County (ND) site is fairly isolated from urban-influenced sources and
17 hourly average O_3 concentrations are mostly below 0.09 ppm. The flat diurnal pattern
18 observed for the Oliver County site is usually interpreted as indicating a lack of efficient
19 scavenging of O_3 and/or a lack of photochemical precursors, whereas the varying diurnal
20 pattern observed at the Jefferson County site may be interpreted to indicate the opposite.
21 Logan (1989) has described the diurnal pattern for several rural sites in the United States
22 (Figure 4-11) and noted that average daily profiles showed a broad maximum from about
23 noon until about 1800 LT at all the eastern sites, except for the peak of Whiteface Mountain.
24 Logan (1989) noted that the maximum concentrations were higher at the SURE sites than at
25 the NAPBN sites in the east because the latter were situated in more remote or coastal
26 locations.

28 4.4.2 Urban Area Diurnal Patterns

29 The U.S. EPA (1986a) has discussed diurnal patterns for urban sites. Figure 4-12,
30 reproduced from the previous document, shows the diurnal pattern of O_3 concentrations on
31 July 13, 1979, in Philadelphia, Pennsylvania. On this day a peak 1-h average concentration

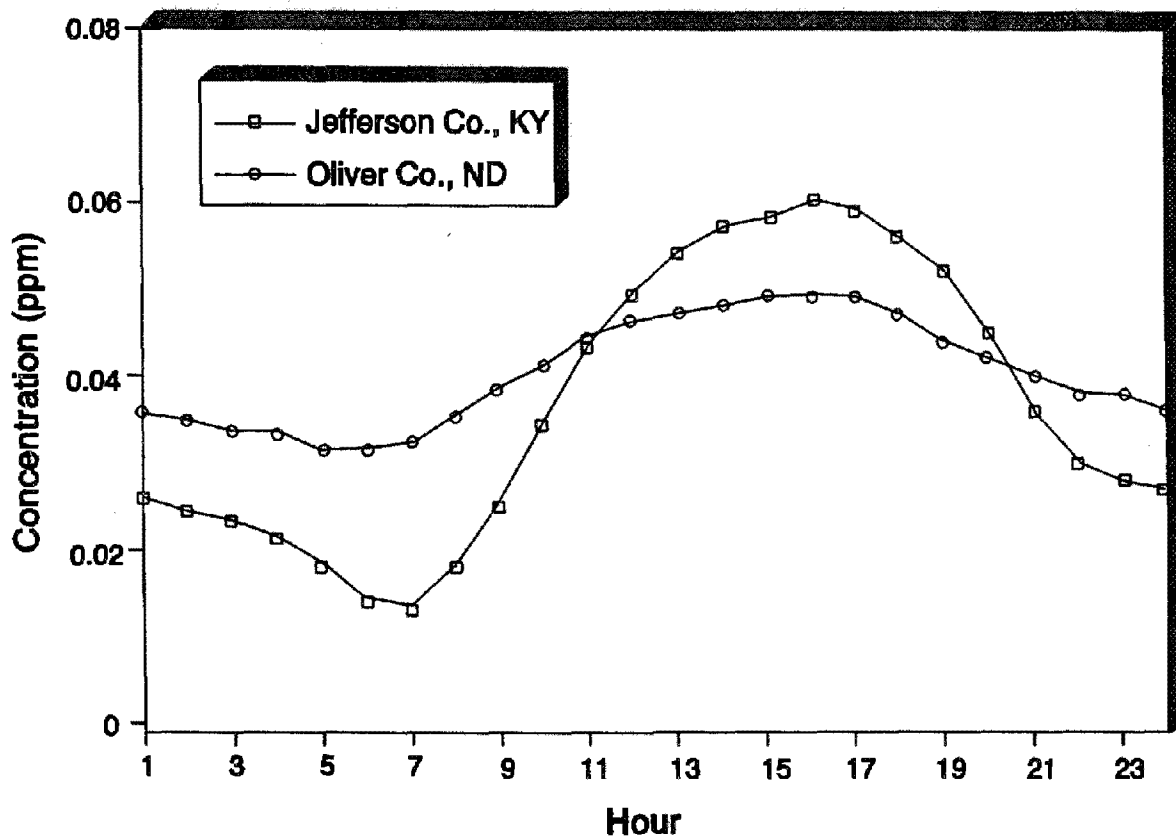


Figure 4-10. The comparison of the seasonal diurnal patterns using 1988 data for Jefferson County, KY and Oliver County, ND.

of 0.20 ppm, the highest for the month, was reached at 2:00 p.m., presumably as the result of meteorological factors, such as atmospheric mixing and local photochemical processes. The severe depression of concentrations to below detection limits (less than 0.005 ppm) between 3:00 and 6:00 a.m. is usually explained as resulting from the scavenging of O_3 by local nitric oxide emissions. In this regard, this station is typical of most urban locations.

Diurnal profiles of O_3 concentrations can vary from day to day at a specific site, however, because of changes in the various factors that influence concentrations. Composite diurnal data (that is, concentrations for each hour of the day averaged over multiple days or months) often differ markedly from the diurnal cycle shown by concentrations for a specific day. In Figures 4-13 through 4-15, reproduced from the previous document, diurnal data for 2 consecutive days are compared with composite diurnal data (1-mo averages of hour-by-hour measurements) at three different kinds of sites: center city-commercial

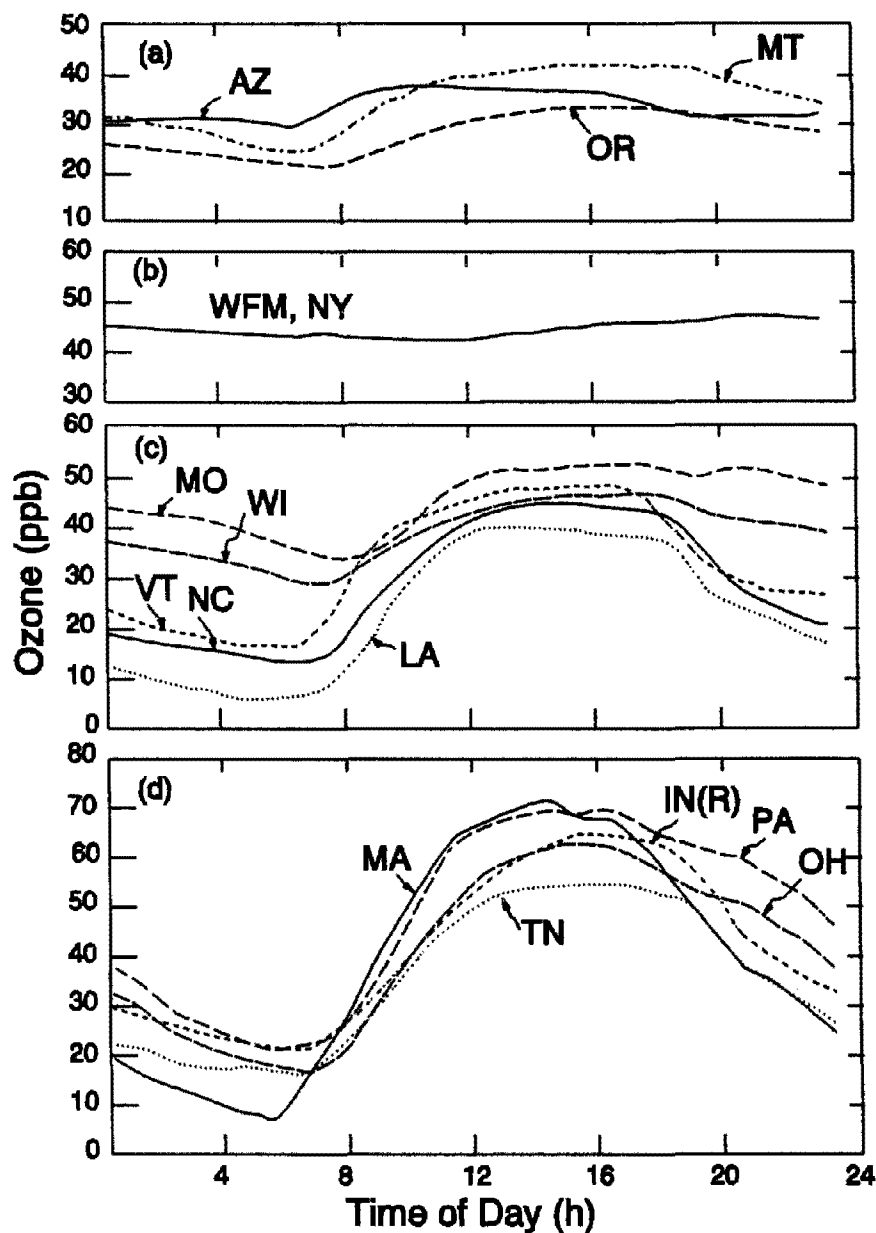


Figure 4-11. Diurnal behavior of ozone at rural sites in the United States in July. Sites are identified by the state in which they are located. (a) Western National Air Pollution Background Network (NAPBN); (b) Whiteface Mountain (WFM) located at 1.5 km above sea level; (c) eastern NAPBN sites; and (d) sites selected from the Electric Power Research Institute's Sulfate Regional Air Quality study. IN (R) refers to Rockport.

Source: Logan (1989).

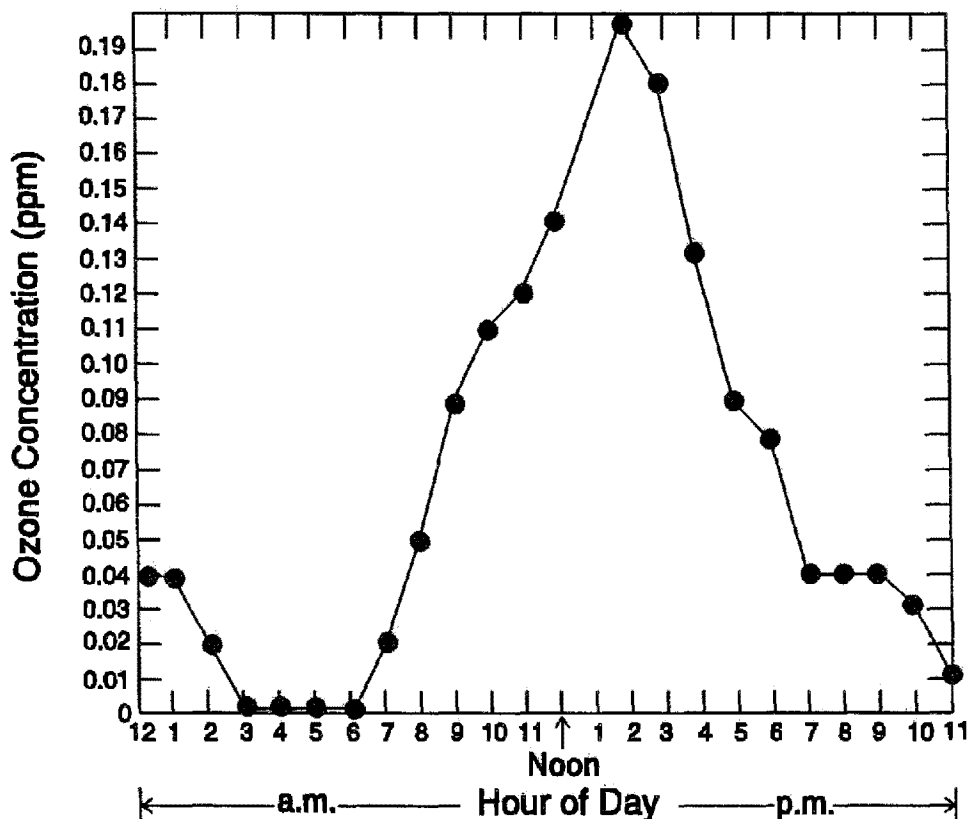


Figure 4-12. Diurnal pattern of 1-h ozone concentrations on July 13, 1979, Philadelphia, PA.

Source: U.S. Environmental Protection Agency (1986a).

(Washington, DC), rural-near urban (St. Louis, MO), and suburban-residential (Alton, IL). Several obvious points of interest present themselves in these figures: (1) at some sites, at least, peaks can occur at virtually any hour of the day or night but these peaks may not show up strongly in the longer-term average data; (2) some sites may be exposed to multiple peaks during a 24-h period; and (3) disparities, some of them large, can exist between peaks (the diurnal data) and the 1-mo average (the composite diurnal data) of hourly O_3 concentrations.

When diurnal or short-term composite diurnal O_3 concentrations are compared with longer-term composite diurnal O_3 concentrations, the peaks are smoothed as the averaging period is lengthened. Figure 4-16 demonstrates the effects of lengthening the period of time

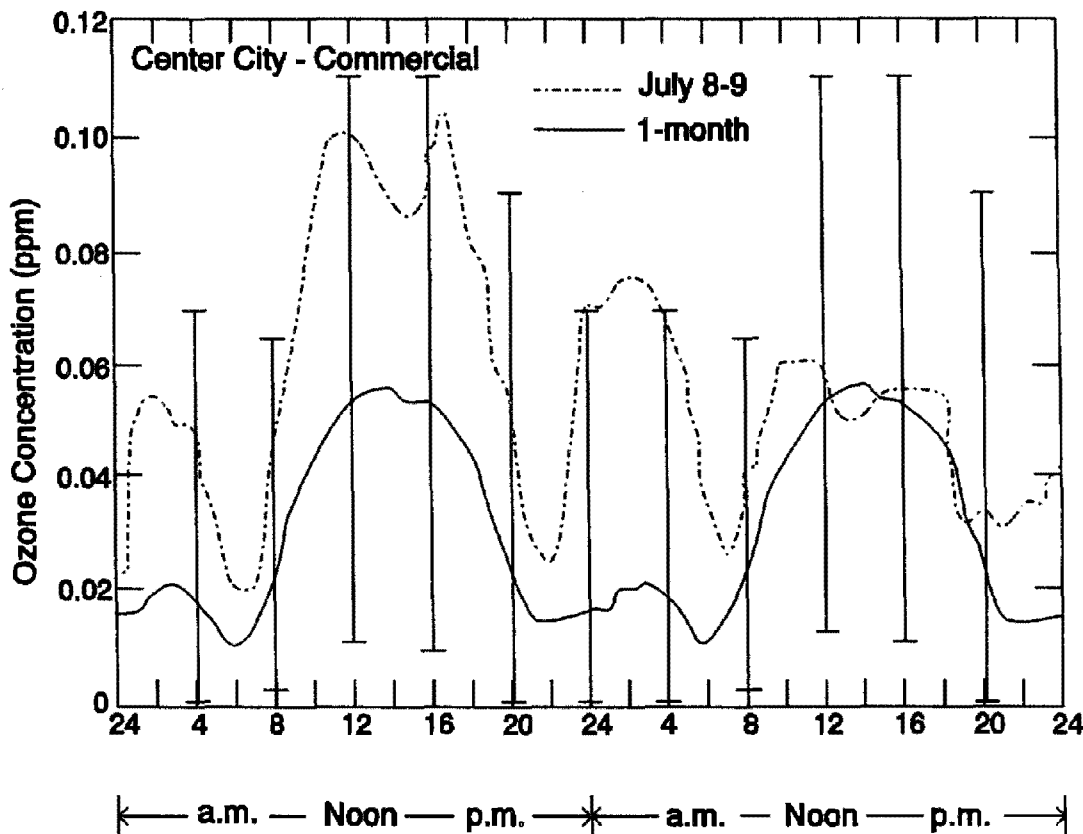


Figure 4-13. Diurnal and 1-mo composite diurnal variations in ozone concentrations, Washington, DC, July 1981.

Source: U.S. Environmental Protection Agency (1986a).

over which values are averaged. This figure shows a composite diurnal pattern calculated on the basis of 3 mo. While seasonal differences are observed, the comparison of 3-mo (Figure 4-16) with 1-mo composite diurnal concentrations (Figure 4-15) at the Alton, IL, site readily demonstrates the smoothing out of peak concentrations as the averaging period is lengthened. As indicated in the previous version of the document (U.S. Environmental Protection Agency, 1986a), although this is an obvious and familiar result in the statistical treatment of monitoring data, it is highly pertinent to the protection of human health and welfare from the effects of O_3 .

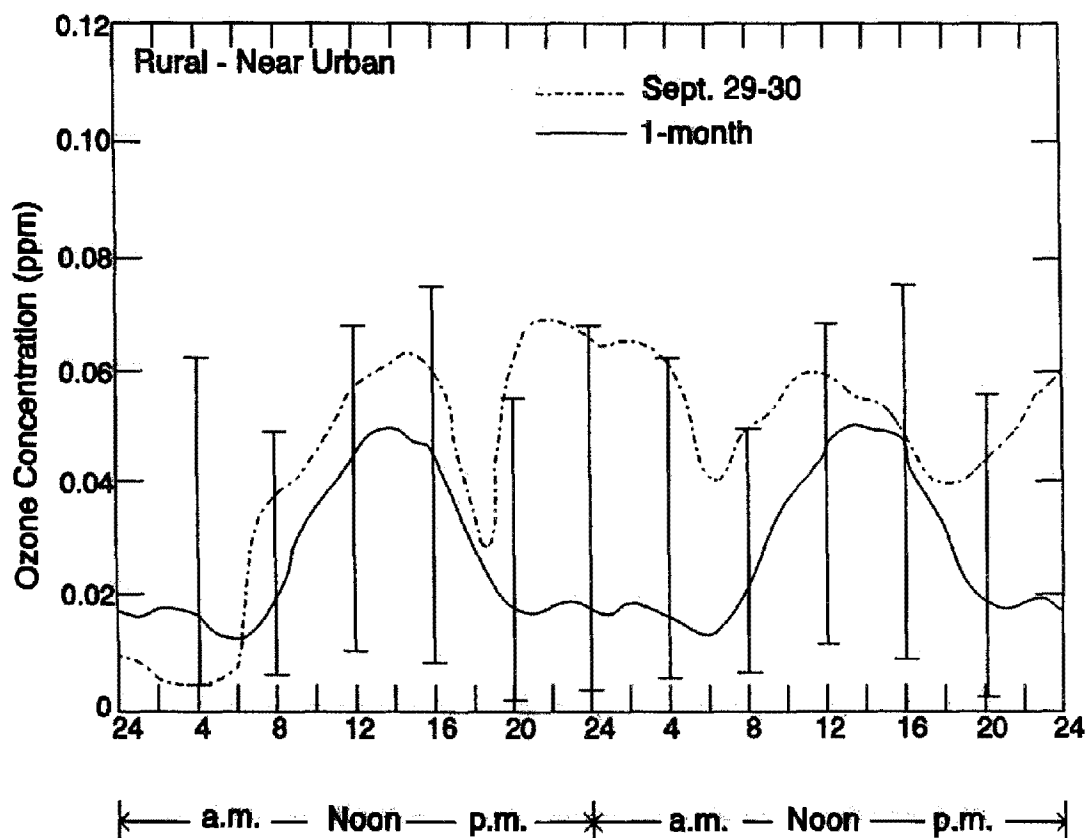


Figure 4-14. Diurnal and 1-mo composite diurnal variations in ozone concentrations, St. Louis County, MO, September 1981.

Source: U.S. Environmental Protection Agency (1986a).

4.4.3 Nonurban Area Diurnal Patterns

Non-urban areas only marginally affected by transported O_3 usually have a flatter diurnal profile than sites located in urban areas. Nonurban O_3 monitoring sites experience differing types of diurnal patterns (Böhm et al., 1991; Lefohn, 1992b). As indicated earlier, O_3 concentrations at a specific location are influenced by local emissions and by long-range transport from both natural and anthropogenic sources. Thus, considerable variation of O_3 exposures among sites characterized as agricultural or forested is found and there is no preference for maximum diurnal patterns to occur in either the second or third quarter.

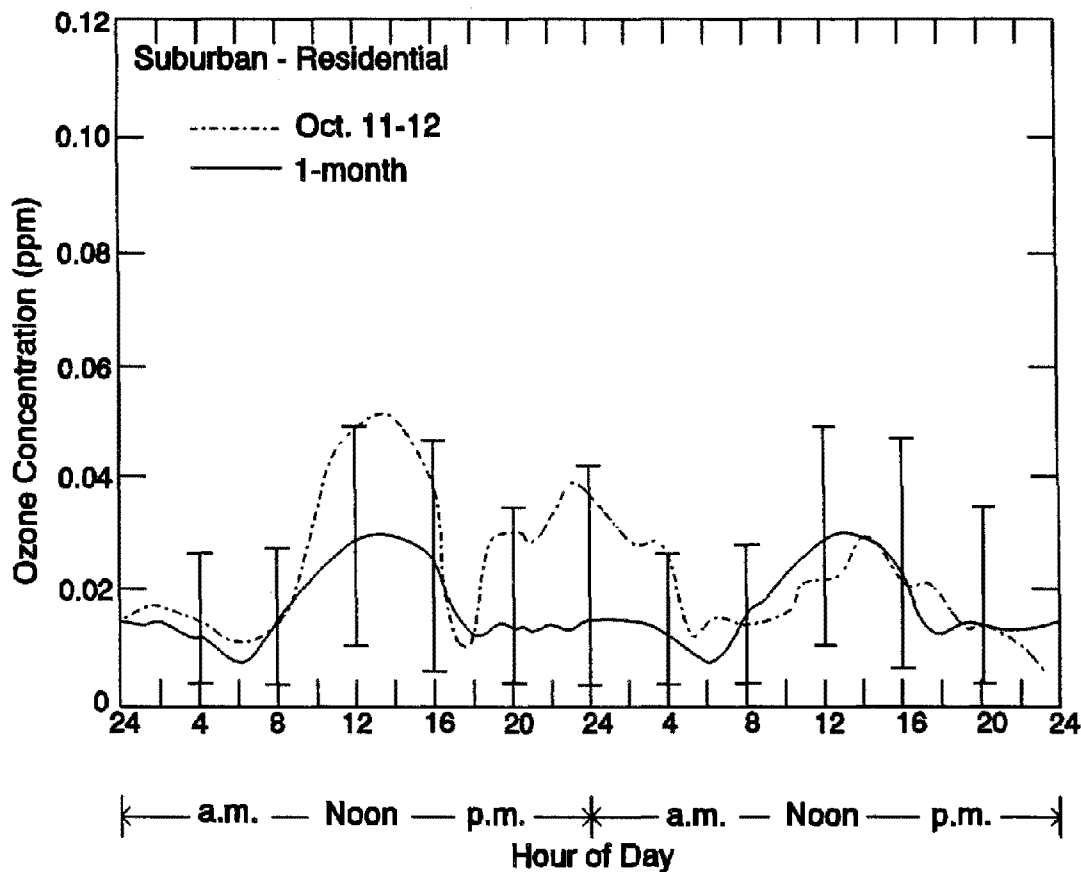


Figure 4-15. Diurnal and 1-mo composite diurnal variations in ozone concentrations, Alton, IL, October 1981 (fourth quarter).

Source: U.S. Environmental Protection Agency (1986a).

The diurnal patterns for several agricultural sites have been characterized (U.S. Environmental Protection Agency, 1986a). Figures 4-17 and 4-18 show some typical patterns of exposure. As discussed by U.S. EPA (1986a), the six sites, whose diurnal patterns are illustrated in Figure 4-16, represent counties with high soybean, wheat, or hay production. The figures show a distinct afternoon maximum with the lowest concentrations occurring in the early morning and evening hours. Quarterly composite diurnal patterns clearly show the division of the afternoon O_3 concentrations into two seasonal patterns, the low "winter" levels in the first and fourth quarters and the high "summer" levels in the second and third quarters of the year.

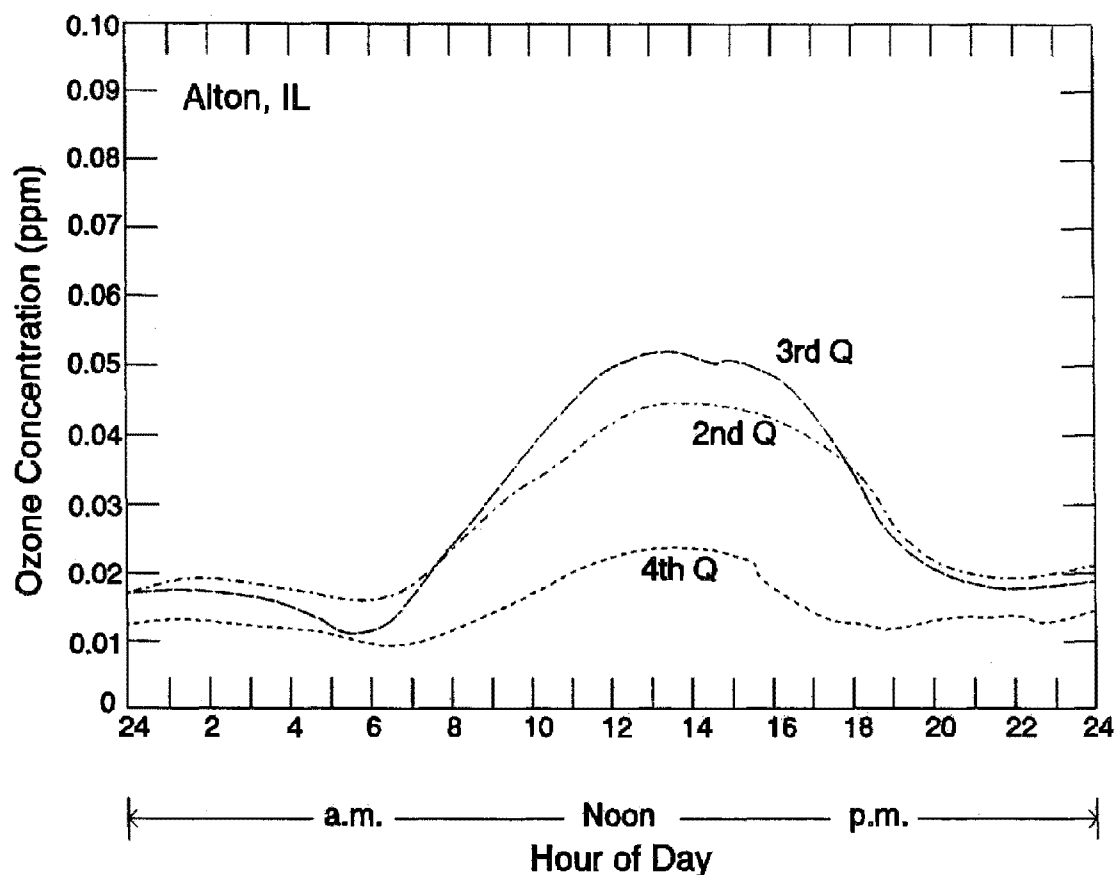


Figure 4-16. Composite diurnal patterns of ozone concentrations by quarter, Alton, IL, 1981.

1 Remote forested sites experience unique patterns of O_3 exposures (Evans et al., 1983;
 2 Lefohn, 1984). These sites tend to experience a weak diurnal pattern, with hourly average
 3 O_3 concentrations that occur frequently in the range of 0.04 to 0.05 ppm. Figure 4-19 shows
 4 diurnal patterns for several sites in the NDDN network that are located in forested areas.
 5 Several of the NDDN sites analyzed by Edgerton and Lavery (1992) exhibit fairly flat
 6 average diurnal patterns. Such a pattern is based on average concentrations calculated over
 7 an extended period. On a daily basis, some variation in O_3 concentration does occur from
 8 hour to hour and, in some cases, high hourly average concentrations are experienced either
 9 during daytime or nighttime periods (Lefohn and Mohnen, 1986; Lefohn and Jones, 1986;
 10 Logan, 1989; Lefohn et al., 1990c; Taylor et al., 1992).

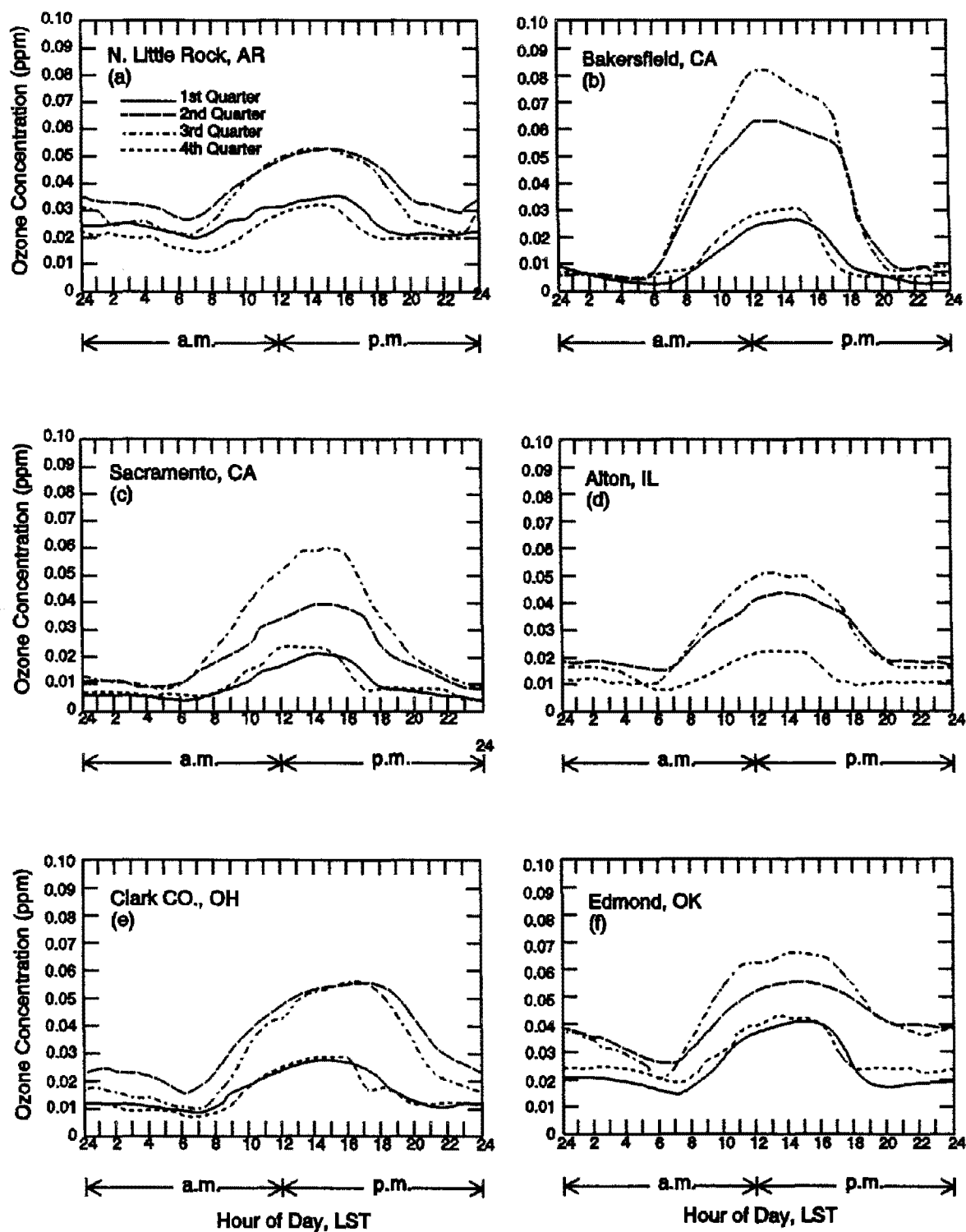


Figure 4-17. Quarterly composite diurnal patterns of ozone concentrations at selected sites representing potential for exposure of major crops, 1981.

Source: U.S. Environmental Protection Agency (1986a).

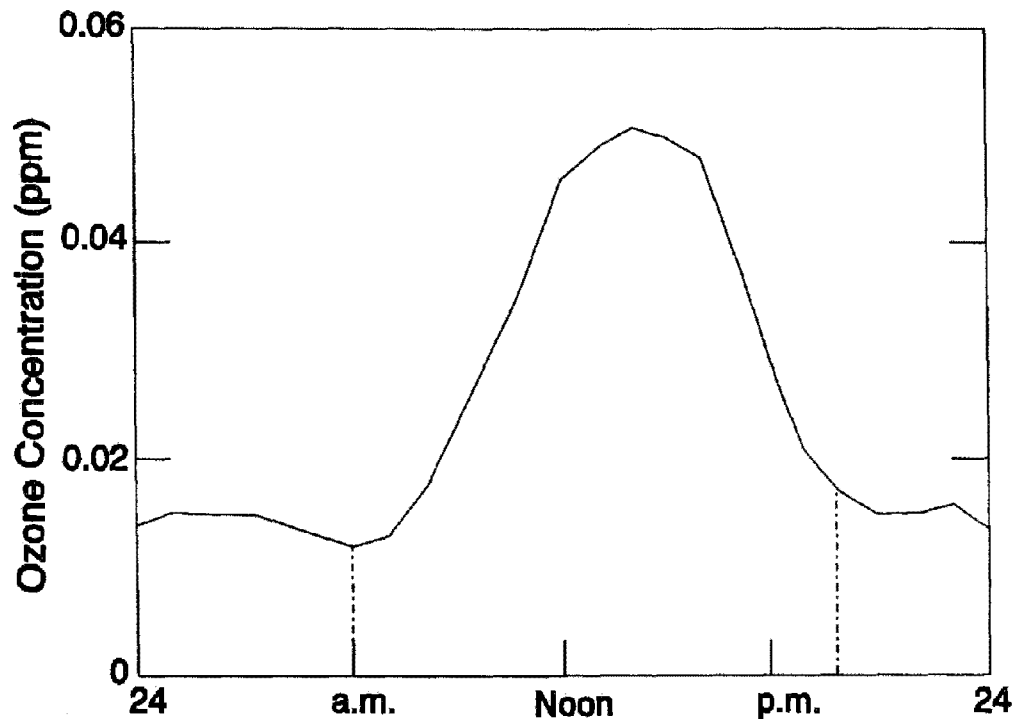


Figure 4-18. Composite diurnal ozone pattern at a rural National Crop Loss Assessment Network site in Argonne, IL, August 6 through September 30, 1980.

Source: U.S. Environmental Protection Agency (1986a).

Lefohn et al. (1990c) characterized O_3 exposures at high-elevation monitoring sites. The authors reported that a fairly flat diurnal pattern for the Whiteface Mountain summit site (WF1) was observed (Figure 4-20a), with the maximum hourly average concentrations occurring in the late evening or early morning hours. A similar pattern was observed for the mid-elevation site at Whiteface Mountain (WF3). The site at the base of Whiteface Mountain (WF4) showed the typical diurnal pattern expected from sites that experience some degree of O_3 scavenging. More variation in the diurnal pattern for the highest Shenandoah National Park sites occurred than for the higher elevation Whiteface Mountain sites, with the typical variation for urban-influenced sites in diurnal pattern at the lower elevation Shenandoah National Park site (Figure 4.20b). Aneja and Li (1992), in their analysis of the 5 high-elevation Mountain Cloud Chemistry Program sites (see Section 4.6.2 for site descriptions), noted the flat diurnal pattern typical of high-elevation sites that has been described previously in the literature. Aneja and Li (1992) noted that the peak of the diurnal

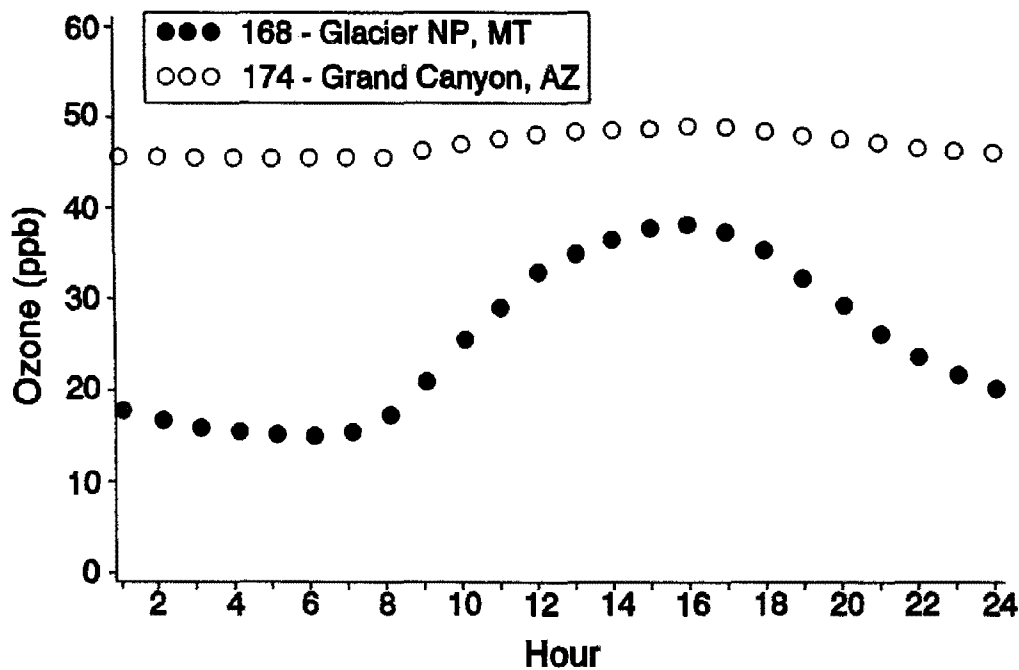
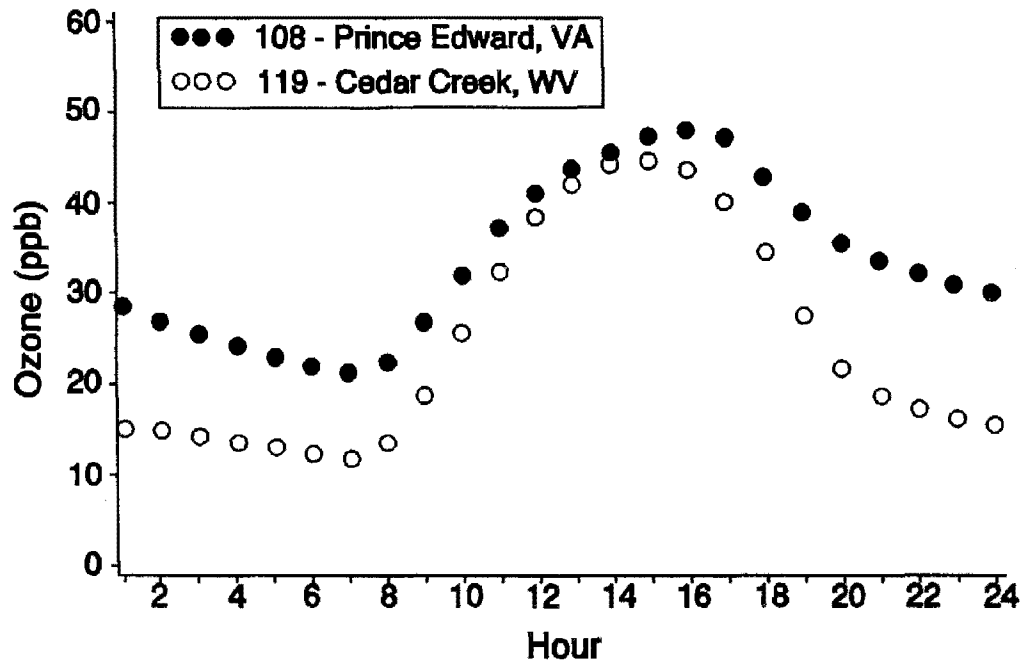


Figure 4-19. Composite diurnal ozone pattern at selected National Dry Deposition Network sites.

Source: Edgerton and Lavery (1992).

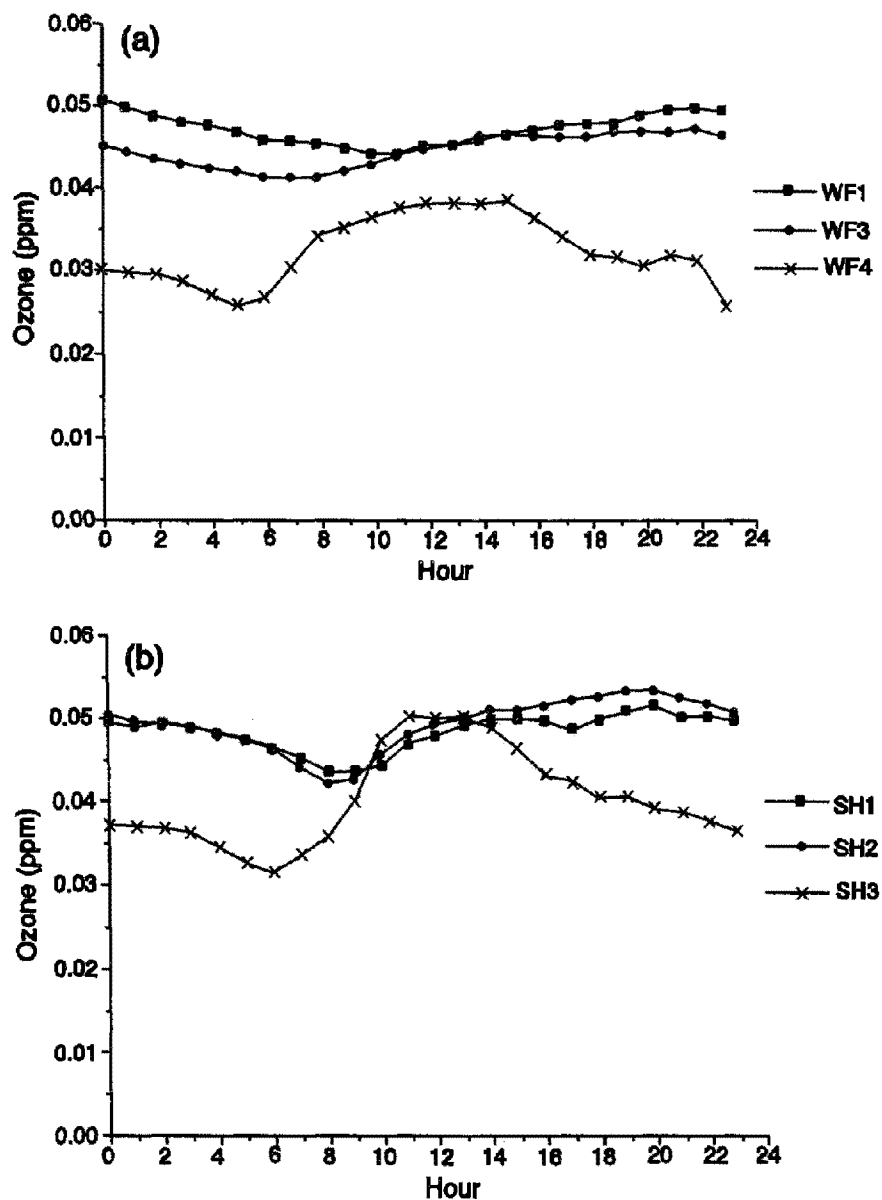


Figure 4-20. Composite diurnal pattern at (a) Whiteface Mountain, NY, and (b) Mountain Cloud Chemistry Program's Shenandoah National Park site for May to September 1987.

Source: Lefohn et al. (1990c).

patterns over the period May to October (1986 to 1988) for the 5 sites occurred between 1800 and 2400 h, while the minimum was observed between 0900 and 1200h. However, it is important to note that as indicated by Lefohn et al. (1990), the flat diurnal pattern is not observed for all high-elevation sites.

4.5 SEASONAL PATTERNS IN OZONE CONCENTRATIONS

4.5.1 Urban Area Seasonal Patterns

Seasonal variations in O_3 concentrations in 1981 were described by the U.S. EPA (1986a). Figure 4-21 shows the 1-mo averages and the single 1-h maximum concentrations within the month for eight sites across the nation. The data from most of these sites exhibit the expected pattern of high O_3 in late spring or in summer and low levels in the winter. Data from Pomona (Figure 4-21c) and Denver (Figure 4-21d) show summer maxima. Tampa shows a late spring maximum but with concentrations in the fall (i.e., October) approaching those of spring (June) (Figure 4-21f). Dallas data also tend to be skewed toward higher spring concentrations; but note that November concentrations are also relatively high (Figure 4-21h). Because of seasonal changes in temperature, relative humidity, and storm tracks from year to year, the general weather conditions in a given year may be more favorable for the formation of O_3 and other oxidants than during the prior or following year. For example, 1988 was a hot and dry year during which some of the highest O_3 concentrations of the last decade occurred, while 1989 was a cold and wet year in which some of the lowest concentrations occurred (U.S. Environmental Protection Agency, 1992a).

4.5.2 Nonurban Area Seasonal Patterns

In the literature, several investigators have reported on the tendency for average O_3 concentrations to be higher in the second versus the third quarter of the year for many isolated rural sites (Evans et al., 1983; Singh et al., 1978). This observation has been attributed to either stratospheric intrusions or an increasing frequency of slow-moving, high-pressure systems that promote the formation of O_3 . Lefohn et al. (1990b) reported that for several clean sites, the highest exposures occurred in the third quarter rather than in the second. The results of this analysis will be discussed in the Section 4.5.3. Taylor et al.

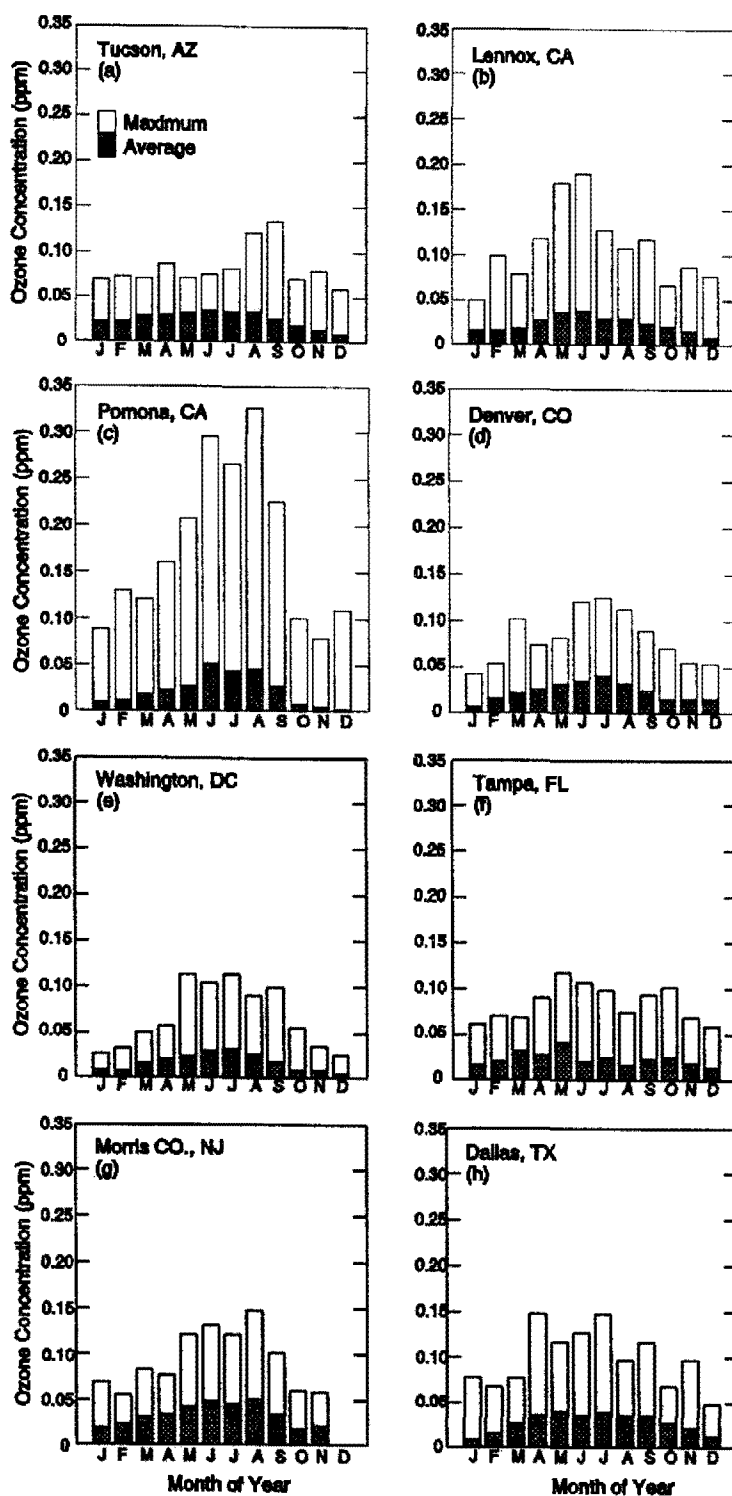


Figure 4-21. Seasonal variations in ozone concentrations as indicated by monthly averages and the 1-h maximum in each month at selected sites, 1981.

Source: U.S. Environmental Protection Agency (1986a).

(1992) reported that for 10 forest sites in North America, the temporal patterns of O_3 on quarterly or annual periods exhibited less definitive patterns. Based on the exposure index selected, different patterns were reported. The different patterns may be associated with the observations by Logan (1989) that rural O_3 in the eastern United States in the spring and summer is severely impacted by anthropogenic and possibly natural emissions of NO_x and hydrocarbons and that O_3 episodes occur when the weather is particularly conducive to photochemical formation of O_3 . Meagher et al. (1987) reported for rural O_3 sites in the southeastern United States that the daily maximum 1-h average concentration was found to peak during the summer months. Taylor and Norby (1985) reported that in the Shenandoah National Park, the probability of a day occurring in which a 1-h mean O_3 concentration was >0.08 ppm was the same during the months of May, June, and July, while the probability was nearly 40% less in August. The probability of an episode during each of the remaining months of the growing season was $<5\%$. The month of July experienced both the highest frequency of episodes and the highest mean duration of exposure events.

Aneja and Li (1992) reported that the maximum monthly ozone levels occurred in either the spring or the summer (May to August), and the minimum occurred in the fall (September and October). The timing of the maximum monthly values differed across sites and years. However, in 1988, an exceptionally high concentration O_3 year, for almost all of the 5 sites, June was the month in which the highest monthly average concentration occurred. This was the month in which the greatest number of O_3 episodes occurred in the eastern United States.

4.5.3 Seasonal Pattern Comparisons with "Pristine" Sites

Lefohn et al. (1990b) have characterized the O_3 concentrations that occurred at several clean sites in the United States. The Theodore Roosevelt National Park, ND site experienced its maximum in July for 1984 and 1985 and in May for 1986. Of the three western national forest sites evaluated by Lefohn et al. (1990b), only Apache National Forest experienced its maximum monthly mean concentration in the Spring. The Apache National Forest site was above mean nocturnal inversion height and no decrease of concentrations occurred during the evening hours. This site also experienced the highest hourly maximum concentration, as well as the highest W126 O_3 exposures. The Custer and Ochoco National Forest sites experienced most of their maximum monthly mean concentrations in the summer. The White

1 River Oil Shale site in Colorado experienced its maximum monthly mean during the spring
2 and summer months.

3 The W126 sigmoidal weighting function index was also used to identify the month of
4 highest O₃ exposure. A somewhat more variable pattern was observed than when the
5 maximum monthly average concentration was used. For some sites, the winter/spring
6 pattern was represented; for others, it was not. In some cases, the highest W126 exposures
7 occurred earlier in the year than was indicated by the maximum monthly concentration. For
8 example, in 1979, the Custer National Forest site experienced its highest W126 exposure in
9 April, although the maximum monthly mean occurred in August. In 1980, the reverse
10 occurred.

11 There was no consistent pattern for those sites located in the continental United States.
12 The Theodore Roosevelt National Park, Custer National Forest, Ochoco National Park, and
13 White River Oil Shale sites experienced their maximum O₃ exposures during the spring and
14 summer months. The sites experiencing their highest O₃ exposures in the fall to spring
15 period did not necessarily experience the lowest O₃ exposures.

18 **4.6 SPATIAL VARIATIONS IN OZONE CONCENTRATIONS**

19 **4.6.1 Urban-Nonurban Area Concentration Differences**

20 Diurnal concentration data presented earlier indicate that peak O₃ concentrations can
21 occur later in the day in rural areas than in urban, with the distances downwind from urban
22 centers generally determining how much later the peaks occur. Meagher et al. (1987)
23 reported that for five rural sites in the Tennessee Valley region of the southeastern United
24 States, O₃ levels were found to equal or exceed urban values for the same region. Data
25 presented in the 1978 criteria document demonstrated that peak concentrations of O₃ in rural
26 areas are generally lower than those in urban areas, but that average concentrations in rural
27 areas are comparable to or even higher than those in urban areas (U.S. Environmental
28 Protection Agency, 1978). Reagan (1984) noted that O₃ concentrations measured near
29 population-oriented areas were depressed in comparison with data collected in more isolated
30 areas. As noted earlier, urban O₃ values are often depressed because of titration by nitric
31 oxide (Stasiuk and Coffey, 1974). In reviewing the National Crop Loss Assessment

1 Network's use of kriging to estimate the 7-h seasonal average O₃ levels, Lefohn et al.
2 (1987a) found that the 7-h values derived from kriging for sites located in rural areas tended
3 to be lower than the actual values because of the effect of using data from urban areas to
4 estimate rural values. In addition to the occurrence of higher average concentrations and
5 occasionally higher peak concentrations of O₃ in nonurban areas than in urban, it is well
6 documented that O₃ persists longer in nonurban than in urban areas (Coffey et al., 1977;
7 Wolff et al., 1977; Isaksen et al., 1978). The absence of chemical scavengers appears to be
8 the main reason.

10 **4.6.2 Concentrations Experienced at High-Elevation Sites**

11 The distributions of hourly average concentrations experienced at high-elevation urban
12 sites are similar to those experienced at low-elevation areas. For example, the distribution of
13 hourly average concentrations for several O₃ sites located in Denver were similar to
14 distributions observed at many low-elevation sites in the United States. However, as will be
15 discussed in Section 4.6.3, for assessing the possible impacts of O₃ at high-elevation sites,
16 the use of absolute concentration (e.g., in units of micrograms per cubic meter) instead of
17 mixing ratios (e.g., ppm) may be an important consideration.

18 Lefohn et al. (1990c) have summarized the characterization of gaseous exposures at
19 rural sites in 1986 and 1987 at several Mountain Cloud Chemistry Program (MCCP) high-
20 elevation sites. Aneja and Li (1992) have reported the ozone exposures for 1986 to 1988.
21 Table 4-14 summarizes the sites characterized by Lefohn et al. (1990c). Table 4-15
22 summarizes the exposures that occurred at several of the sites for the period 1987 to 1988.
23 In 1987, the 7- and 12-h seasonal means were similar at the Whiteface Mountain WF1 and
24 WF3 sites (Figure 4-22a). The 7-h mean values were 0.0449 and 0.0444 ppm, respectively;
25 the 12-h mean values were 0.0454 and 0.0444 ppm, respectively. Note that, in some cases,
26 the 12-h mean was slightly higher than the 7-h mean value. This resulted when the 7-h mean
27 period (0900 to 1559 h) did not capture the period of the day when the highest hourly mean
28 O₃ concentrations were experienced. A similar observation was made, using the 1987 data,
29 for the MCCP Shenandoah National Park sites. The 7- and 12-h seasonal means were
30 similar for the SH1 and SH2 sites (Figure 4-22b). Based on cumulative indices, the
31 Whiteface Mountain summit site (WF1) experienced a slightly higher exposure than the WF3

**TABLE 4-14. DESCRIPTION OF MOUNTAIN CLOUD CHEMISTRY
PROGRAM SITES**

Site	Elevation (m)	Latitude			Longitude		
Howland Forest (HF1), ME	65	45°	11'		68°	46'	
Mt. Moosilauke (MS1), NH	1,000	43°	59'	18"	71°	48'	28"
Whiteface Mountain (WF1), NY	1,483	44°	23'	26"	73°	51'	34"
Shenandoah Park (SH1), VA	1,015	38°	37'	12"	78°	20'	48"
Shenandoah Park (SH2), VA	716	38°	37'	30"	78°	21'	13"
Shenandoah Park (SH3), VA	524	38°	37'	45"	78°	21'	28"
Whitetop Mountain (WT1), VA	1,689	36°	38'	20"	81°	36'	21"
Mt. Mitchell (MM1), NC	2,006	35°	44'	15"	82°	17'	15"
Mt. Mitchell (MM2), NC	1,760	35°	45'		82°	15'	

1 site (Figure 4-22c). Both the sum of the concentrations ≥ 0.07 ppm (SUM07) and the
2 number of hourly concentrations ≥ 0.07 ppm were higher at the WF1 site than at the WF3
3 site. The site at the base of the mountain (WF4) experienced the lowest exposure of the
4 three O₃ sites. Among the MCCC Shenandoah National Park sites, the SH2 site experienced
5 marginally higher O₃ exposures, based on the index that sums all of the hourly average
6 concentrations (i.e., referred to as total dose in the figure) and sigmoidal values, than the
7 high-elevation site (SH1; Figure 4-22d); the reverse was true for the sums of the
8 concentrations ≥ 0.07 ppm and number of hourly concentrations ≥ 0.07 ppm.

9 When the Big Meadows, Dickey Ridge, and Sawmill Run Shenandoah National Park
10 data for 1983 to 1987 were compared, it was again found that the 7- and 12-h seasonal
11 means were insensitive to the different O₃ exposure patterns. A better resolution of the
12 differences was observed when the cumulative indices were used (Figure 4-23). There was
13 no evidence that the higher elevation, Big Meadows, site had consistently experienced higher
14 O₃ exposures than the lower elevation sites. In 2 of the 5 years, the higher elevation site
15 experienced lower exposures than the Dickey Ridge and Sawmill Run sites, based on "total
16 dose" or sigmoidal indices. For 4 of the 5 years, the SUM07 index yielded the same result.

17 Taylor et al. (1992) indicate that forests experienced marked quantitative and qualitative
18 differences in O₃ exposure. The principal spatial factors underlying this variation were

**TABLE 4-15. SEASONAL (APRIL TO OCTOBER) PERCENTILES, SUM06, SUM08, AND W126
VALUES FOR THE MOUNTAIN CLOUD CHEMISTRY PROGRAM SITES**

Site	Year	Min.	10	30	50	70	90	95	99	Max.	No. Obs.	SUM06	SUM08	W126
Howland Forest, ME (HF1)	1987	0.000	0.013	0.021	0.028	0.035	0.046	0.052	0.065	0.076	4,766	5.9	0.0	7.7
	1988	0.000	0.012	0.021	0.028	0.036	0.047	0.054	0.076	0.106	4,786	10.9	2.9	11.6
Mt. Moosilauke, NH (MS1)	1987	0.006	0.027	0.036	0.045	0.053	0.065	0.074	0.086	0.102	4,077	45.0	9.5	40.1
	1988	0.010	0.026	0.033	0.043	0.055	0.076	0.087	0.113	0.127	2,835	51.9	21.2	43.4
Whiteface Mountain, NY (WF1) (36-031-0002)	1987	0.011	0.029	0.037	0.046	0.053	0.067	0.074	0.087	0.104	4,704	62.0	12.2	49.5
	1988	0.014	0.025	0.033	0.043	0.056	0.078	0.089	0.110	0.135	4,673	65.8	40.8	56.5
Whiteface Mountain, NY (WF3)	1987	0.010	0.025	0.033	0.039	0.047	0.064	0.075	0.091	0.117	4,755	45.4	14.4	40.3
Whiteface Mountain, NY (WF4)	1987	0.000	0.011	0.023	0.031	0.041	0.056	0.065	0.081	0.117	4,463	23.8	5.1	21.3
Mt. Mitchell, NC (MM1)	1987	0.008	0.034	0.044	0.051	0.058	0.067	0.074	0.085	0.105	3,539	59.4	7.8	46.5
	1988	0.011	0.038	0.054	0.065	0.075	0.095	0.106	0.126	0.145	2,989	145.1	69.7	116.6
	1989	0.010	0.038	0.047	0.054	0.059	0.068	0.072	0.081	0.147	2,788	54.8	3.5	40.7
	1992	0.005	0.036	0.043	0.048	0.053	0.063	0.069	0.081	0.096	3,971	37.8	4.4	36.7
Mt. Mitchell, NC (MM2)	1987	0.017	0.032	0.042	0.049	0.056	0.067	0.073	0.083	0.096	3,118	47.0	5.1	37.4
	1988	0.009	0.029	0.041	0.050	0.060	0.080	0.092	0.110	0.162	2,992	68.7	28.1	57.7
Shenandoah Park, VA (SH1)	1987	0.000	0.023	0.036	0.044	0.054	0.069	0.076	0.085	0.135	3,636	54.2	8.5	42.0
	1988	0.006	0.024	0.036	0.047	0.058	0.077	0.087	0.103	0.140	3,959	80.9	29.6	67.2
Shenandoah Park, VA (SH2)	^a 1987	0.003	0.027	0.040	0.049	0.059	0.071	0.077	0.086	0.145	2,908	55.7	7.8 55.8	41.8
Shenandoah Park, VA (SH3)	1987	0.000	0.018	0.029	0.037	0.047	0.061	0.068	0.080	0.108	3,030	23.1	2.6	19.2
	1988	0.006	0.020	0.031	0.040	0.051	0.067	0.076	0.097	0.135	4,278	52.3	15.6	44.2
Whitetop Mountain, VA (WT1)	1987	0.011	0.038	0.051	0.059	0.066	0.078	0.085	0.096	0.111	4,326	147.7	32.4	105.7
	1988	0.000	0.030	0.046	0.058	0.068	0.084	0.094	0.119	0.163	3,788	133.8	51.0	102.8

^aCalculations based on a May to September season.

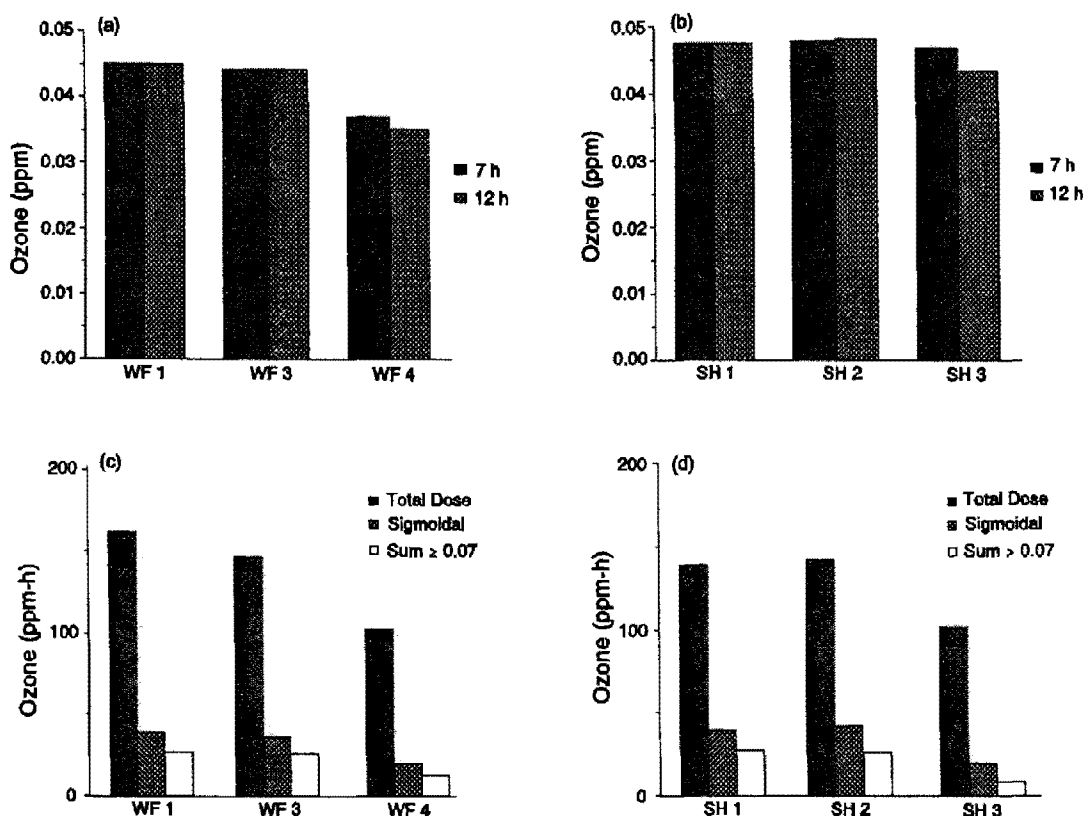


Figure 4-22. Seven- and 12-h means at (a) Whiteface Mountain and (b) Shenandoah National Park for May to September 1987 and integrated exposures at (c) Whiteface Mountain and (d) Shenandoah National Park for May to September 1987.

Source: Lefohn et al. (1990c).

elevation, proximity to anthropogenic sources of oxidant precursors, regional-scale meteorological conditions, and airshed dynamics between the lower free troposphere and the surface boundary layer. Table 4-16 summarizes the exposure values for the ten EPRI Integrated Forest Study Sites located in North America.

4.6.3 Other Spatial Variations in Ozone Concentrations

Despite relative intraregional homogeneity, evidence exists for intracity variations in concentrations that are pertinent to potential exposures of human populations and to the assessment of actual exposures sustained in epidemiologic studies. Two illustrative pieces of

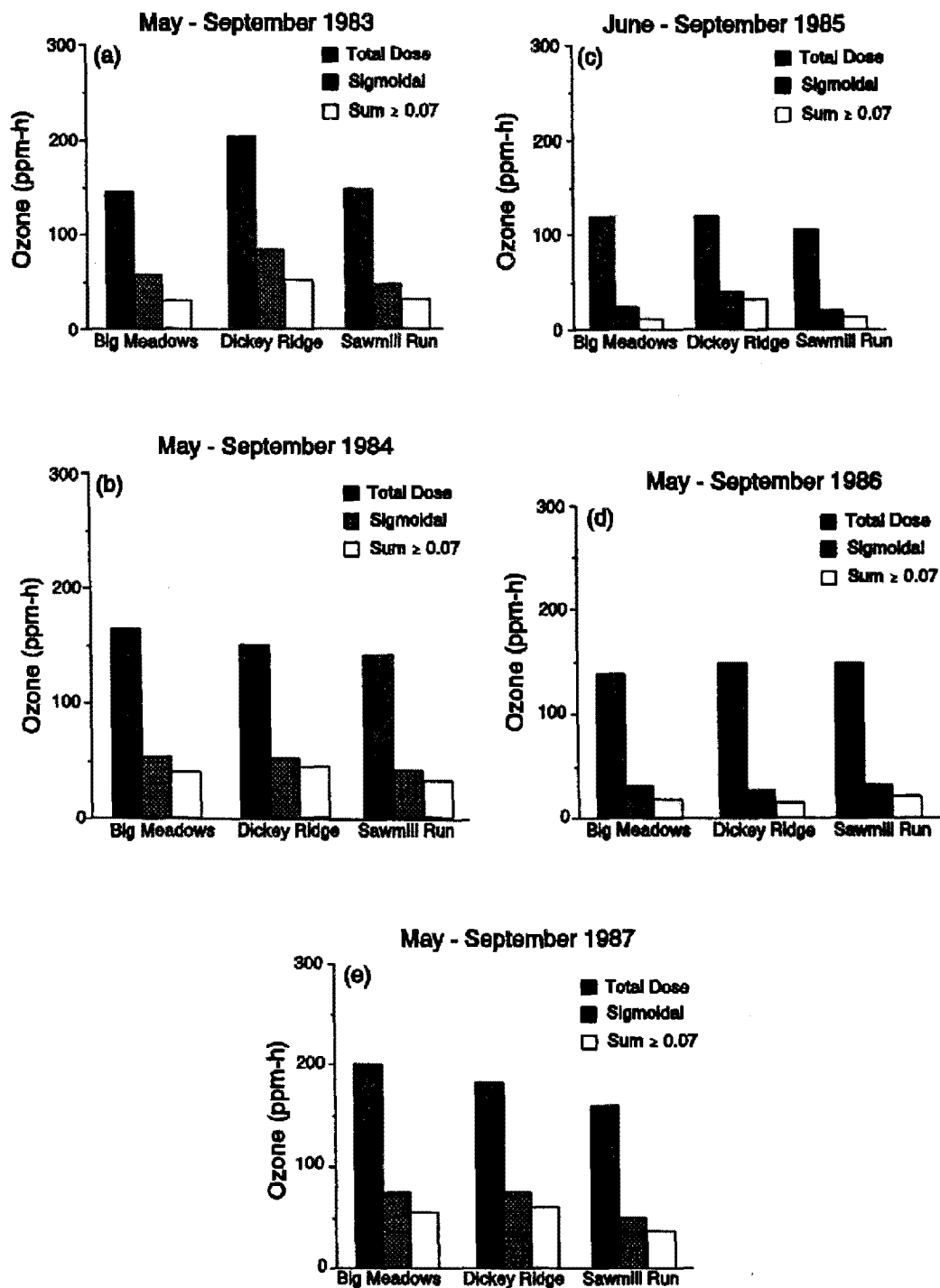


Figure 4-23. Integrated exposures for three non-Mountain Cloud Chemistry Program's Shenandoah National Park sites, 1983 to 1987.

Source: Lefohn et al. (1990c).

TABLE 4-16. SUMMARY STATISTICS FOR 11 INTEGRATED FOREST STUDY SITES
(All units are in ppb)

Site	Year	Quarter	24-h (ppb)	12-h (ppb)	7-h (ppb)	1-h Max. (ppb)	SUM06 (ppm-h)	SUM08 (ppm-h)
HIGH ELEVATION SITES								
Whiteface Mountain, NY	1987	2	42	43	42	104	13.2	2.5
	1987	3	45	44	43	114	30.1	11.8
	1988	2	49	50	49	131	33.5	13.9
	1988	3	44	43	43	119	22.6	10.4
Great Smoky Mountain NP	1987	2	54	52	49	99	57.1	10.9
	1987	3	53	51	49	95	34.3	8.8
	1988	2	71	70	68	119	126.3	61.2
	1988	3	59	57	55	120	74.7	22.2
Coweeta Hydrologic Lab, NC	1987	2	50	48	47	85	32.4	2.6
	1987	3	47	44	42	95	24.1	2.4
	1988	2	61	59	59	104	81.6	18.5
	1988	3	57	54	51	100	63.6	19.8
LOW ELEVATION SITES								
Huntington Forest, NY	1987	2	36	42	42	88	9.8	0.9
	1987	3	24	32	33	76	5.4	0.2
	1988	2	40	46	46	106	19.2	6.1
	1988	3	37	46	48	91	18.6	2.7
Howland, MA	1987	2	34	39	39	69	1.9	0.0
	1987	3	26	32	31	76	3.8	0.0
	1988	2	36	41	41	90	8.1	2.9
	1988	3	24	30	30	71	1.7	0.0

TABLE 4-16 (cont'd). SUMMARY STATISTICS FOR 11 INTEGRATED FOREST STUDY SITES
(All units are in ppb)

Site	Year	Quarter	24-h	12-h	7-h	1-h Max.	SUM06 (ppm-h)	SUM08 (ppm-h)
LOW ELEVATION SITES (cont'd)								
Oak Ridge, TN	1987	2	42	53	50	112	39.5	13.5
	1987	3	29	44	41	105	24.3	9.0
	1988	2	40	57	58	104	26.4	9.8
	1988	3	32	47	51	122	19.7	7.7
Thompson Forest, WA	1987	2	36	43	41	103	10.7	3.6
	1987	3	30	36	34	94	10.3	2.1
	1988	2	32	39	37	103	8.1	2.3
	1988	3	32	39	36	140	13.5	6.7
B.F. Grant Forest, GA	1987	2	32	46	48	99	26.1	5.1
	1987	3	33	52	54	102	31.3	10.3
	1988	2	47	63	64	127	53.1	21.9
	1988	3	32	47	48	116	24.1	7.4
Gainseville, FL	1987	2	42	53	50	a	a	a
	1987	3	29	44	41	a	a	a
	1988	2	35	48	51	84	23.4	0.5
	1988	3	20	29	30	70	1.9	0.1
Duke Forest, NC	1987	2	38	48	52	100	29.2	7.8
	1987	3	52	59	50	124	a	a
	1988	2	54	69	75	115	a	a
	1988	3	38	51	54	141	52.9	23.4
Nordmoen, Norway	1987	2	32	40	41	75	2.4	0.0
	1987	3	14	18	20	32	0.0	0.0
	1988	2	22	28	29	53	0.0	0.0
	1988	3	11	15	16	30	0.0	0.0

^aData were insufficient to calculate statistic.

Source: Adapted from Taylor et al. (1992).

data are presented in this section, one a case of relative homogeneity in a city with a population under 500,000 (New Haven, Connecticut) and one a case of relative in homogeneity of concentrations in a city of greater than 9 million population (New York City).

As described in the previous version of the criteria document (U.S. Environmental Protection Agency, 1986a), the general similarity of the percentiles of the hourly average concentrations for a New Haven site, and two other monitoring stations in the county that were operating at the time, one in Derby, Connecticut, 9 miles west of New Haven, and one in Hamden, Connecticut, 6 miles north of New Haven, is evident. Table 4-17 shows that the data and time of the maximum hourly concentrations by quarter at these three sites are similar.

TABLE 4-17. QUARTERLY MAXIMUM 1-H OZONE VALUES AT SITES IN AND AROUND NEW HAVEN, CONNECTICUT, 1976
(Chemiluminescence method, hourly values in ppm)

	Quarter of Year			
	1	2	3	4
New Haven, CT				
No. measurements	10	1,964	2,079	66
Max 1-h, ppm	0.045	0.274	0.235	0.066
Hour of day	11:00 a.m.	2:00 p.m.	2:00 p.m.	10:00 p.m.
Date	3/29	6/24	8/12	10/3
Derby, CT				
No. measurements	11	2,140	2,187	1,360
Max 1-h, ppm	0.015	0.280	0.290	0.060
Hour of day	11:00 p.m.	2:00 p.m.	2:00 p.m.	7:00 p.m.
Date	3/31	6/24	8/12	12/20
Hamden, CT				
No. measurements	56	2,065	1,446	286
Max 1-h, ppm	0.050	0.240	0.240	0.065
Hour of day	12:00 p.m.	3:00 p.m.	1:00 p.m.	3:00 p.m.
Date	3/29	6/24	7/20	10/7

Source: U.S. Environmental Protection Agency (1986a).

1 The source of much of the O₃ experienced in the New Haven, Connecticut, area is the
2 greater New York area (e.g., Wolff et al., 1975; Cleveland et al., 1976a,b) and an urban
3 plume transported over the distance from New York City to New Haven would tend to be
4 relatively well-mixed and uniform, such that intracity variations in New Haven would
5 probably be minimal.

6 As indicated in the previous version of the Criteria Document (U.S. Environmental
7 Protection Agency, 1986a), intracity differences in O₃ concentrations have also been reported
8 by Kelly et al. (1986) for a 1981 study in Detroit, Michigan. Ozone concentrations were
9 measured for about 3 mo at 16 sites in the metropolitan Detroit area and in nearby Ontario,
10 Canada. Values at 15 sites were correlated with those at a site adjacent to the Detroit
11 Science Center, about 3 km north of the central business district in Detroit. In general, the
12 correlation decreased as distance from the Science Center site increased; and, in general, the
13 actual concentrations increased with distance from that site toward the north-northeast. The
14 highest O₃ concentrations were recorded at sites about 10 to 70 km north-northeast of the
15 urban core. At greater distances or in other directions, O₃ maxima decreased.

16 Concentrations of O₃ vary with altitude and with latitude. While a number of reports
17 contain data on O₃ concentrations at high altitudes (e.g., Coffey et al., 1977; Reiter, 1977b;
18 Singh et al., 1977; Evans et al., 1985; Lefohn and Jones, 1986), fewer reports are available
19 that present data for different elevations at the same locality. There appears to be no
20 consistent conclusion concerning the relationship between O₃ exposure and elevation.

21 Wolff et al. (1987) have reported, for a short-term study at High Point Mountain in
22 northwestern New Jersey, that both the daily maximum and mid-day O₃ concentrations were
23 similar at different altitudes, but that the O₃ exposures increased with elevation. Wolff et al.
24 (1987) conducted a study of the effects of altitude on O₃ concentrations at three sites located
25 at three separate elevations on High Point Mountain in northwestern New Jersey. Data for
26 several days indicate that in mid-May, when atmospheric mixing was good, vertical profiles
27 were nearly constant, with concentrations increasing only slightly with elevation. Likewise,
28 the daily O₃ maxima were similar at different elevations. At night, however,
29 O₃ concentrations were nearly zero in the valley (i.e., the lowest-elevation site) and increased
30 with elevation. Comparison of the O₃ exposures at the three sites (number of hours
31 >0.08 ppm) showed that greater cumulative exposures were sustained at the higher

1 elevations. Comparable data from an urban area (Bayonne, NJ) about 80 km southeast of
2 High Point Mountain showed that the cumulative exposures were higher at all three of the
3 mountain sites than in the urban area (Wolff et al., 1987). The investigators concluded from
4 their concentration and meteorological data that elevated, mountainous sites in the eastern
5 United States may be expected to be exposed to higher O₃ exposures than valley sites
6 throughout the year.

7 Winner et al. (1989) have reported that for three Shenandoah National Park sites (i.e.,
8 Big Meadows, Dickey Ridge, and Sawmill Run), the 24-h monthly mean O₃ concentrations
9 tended to increase with elevation, but that the number of elevated hourly occurrences equal to
10 or above selected thresholds did not. The authors reported that the highest elevation site (Big
11 Meadows) experienced a smaller number of concentrations at or below the minimum
12 detectable level than did the other two sites. The larger number of hourly average
13 concentrations that occurred at or below the minimum detectable level at both Dickey Ridge
14 and Sawmill Run resulted in lower 24-h averages at these sites.

15 Lefohn et al. (1990c), characterizing the O₃ exposures at several high-elevation sites,
16 reported that based on cumulative indices, the Whiteface Mountain summit site (WF1)
17 experienced a slightly higher exposure than the lower elevation Whiteface Mountain (WF3)
18 site. The site at the base of Whiteface Mountain (WF4) experienced the lowest exposure of
19 the three O₃ sites at Whiteface Mountain. Among the MCCC Shenandoah National Park
20 sites, the SH2 site experienced higher O₃ exposures than the high-elevation site (SH1). The
21 "total dose" (the sum of all hourly average concentrations) and sigmoidal (W126) indices
22 were slightly higher at the SH2 than the SH1 site. The data capture at the two sites for the
23 5-mo period was similar. However, the sum of the concentrations ≥ 0.07 ppm and number
24 of hourly concentrations ≥ 0.07 ppm were slightly higher at the SH1 than at the SH2 site.
25 For the Whiteface Mountain sites, both the sum of the concentrations ≥ 0.07 ppm (SUM07)
26 and the number of hourly concentrations ≥ 0.07 ppm were higher at the WF1 site than at the
27 WF3 site.

28 When the Big Meadows, Dickey Ridge, and Sawmill Run Shenandoah National Park
29 data for 1983 to 1987 were compared, a higher resolution of the differences among the
30 regimes was observed when the cumulative indices were used. No specific trend could be
31 identified that showed the higher elevation, Big Meadows, site had consistently experienced

1 higher O₃ exposures than the lower elevation sites. In 2 of the 5 years, the higher elevation
2 site experienced lower exposures than the Dickey Ridge and Sawmill Run sites, based on
3 "total dose" or sigmoidal indices. For 4 of the 5 years, the SUM07 index yielded the same
4 result.

5 An important issue for assessing possible impacts of O₃ at high-elevation sites that
6 requires further attention is the use of mixing ratios (e.g., ppm) instead of absolute
7 concentration (e.g., in units of micrograms per cubic meter) to describe O₃ concentration.
8 In most cases, mixing ratios (e.g., ppm) or mole fractions are used to describe
9 O₃ concentrations. Lefohn et al. (1990c) have pointed out that the manner in which
10 concentration is reported may be important when assessing the potential impacts of air
11 pollution on high-elevation forests. Concentration (in units of micrograms per cubic meter)
12 varies as a function of altitude. Although the change in concentration is small when the
13 elevational difference between sea level and the monitoring site is small, it becomes
14 substantial at high-elevation sites. Given the same part-per-million value experienced at both
15 a high- and low-elevation site, the absolute concentrations (i.e., micrograms per cubic meter)
16 at the two elevations will be different. Since both O₃ and ambient air are gases, changes in
17 pressure directly affect their volume. According to Boyle's law, if the temperature of a gas
18 is held constant, the volume occupied by the gas varies inversely with the pressure (i.e., as
19 pressure decreases, volume increases). This pressure effect must be considered when
20 measuring absolute pollutant concentrations. At any given sampling location, normal
21 atmospheric pressure variations have very little effect on air pollutant measurements.
22 However, when mass/volume units of concentration are used and pollutant concentrations
23 measured at significantly different altitudes are compared, pressure (and hence volume)
24 adjustments are necessary.

25 These exposure considerations are trivial at low-elevation sites. However, when one
26 compares exposure-effects results obtained at high-elevation sites with those from low-
27 elevation sites, the differences may become significant (Lefohn et al., 1990c). In particular,
28 assuming that the sensitivity of the biological target is identical at both low and high
29 elevations, some adjustment will be necessary when attempting to link experimental data
30 obtained at low-elevation sites with air quality data monitored at the high-elevation stations.
31

4.7 INDOOR OZONE CONCENTRATIONS

Most people in the United States spend a large proportion of their time indoors. A knowledge of actual exposures of populations to indoor levels of O₃ is essential for the interpretation and use of results associated with epidemiological studies. However, essentially all routine air pollution monitoring is done on outdoor air. Until the early 1970s, very little was known about the O₃ concentrations experienced inside buildings. The ratio of the indoor/outdoor O₃ concentrations (I/O) is a parameter that has been widely used for studying the indoor and outdoor relationships, sources, and exposure patterns of O₃. However, the data base on this subject is not large and a wide range of I/O O₃ concentration relationships can be found in the literature. The only significant source of O₃ in indoor residential air is infiltration of outdoor O₃, with ventilation rates affecting the flow of air between indoor and outdoor (Zhang and Liou, in press).

Reported I/O values for O₃ are highly variable (U.S. Environmental Protection Agency, 1986a) and range from <0.1 to 0.80±0.10 for various indoor environments and ventilation rates (Weschler et al., 1989). Unfortunately, the number of experiments and kinds of structures examined to date provide only limited data for use in modeling indoor exposures. Data were summarized by Yocom (1982) describing studies of indoor-outdoor gradients in buildings and residences for either O₃ or photochemical oxidant. This information was presented in the previous document (U.S. Environmental Protection Agency, 1986a). The results were highly variable. A relatively large number of factors can affect the difference in O₃ concentrations between the inside of a structure and the outside air. In general, outside air infiltration or exchange rates, interior air circulation rates, and interior surface composition (e.g., rugs, draperies, furniture, walls) affect the balance between replenishment and decomposition of O₃ within buildings (U.S. Environmental Protection Agency, 1986a). Although indoor concentrations of O₃ will almost invariably be less than outdoors, the fact that people spend more time indoors than outdoors may result in greater overall indoor exposures.

Cass et al. (1991) have discussed the importance of protecting works of art from damage due to O₃. Based on experiments that show that the fading of artists' pigments in the presence of O₃ is directly related to the product of concentration x duration of exposure, it appears that museum personnel face unusual challenges because indoor O₃ exposure must

1 be reduced to very low levels in order to protect the collections from accumulated damage
2 over periods of 100 years or more. Druzik et al. (1990) reported that in a survey of
3 11 museums, galleries, historical houses and libraries in southern California, facilities with a
4 high air exchange with the outdoors and no pollutant removal system have indoor
5 O₃ concentrations greater than two-thirds as high as outdoor concentrations. The author
6 reported that museums with conventional air conditioning systems showed indoor
7 O₃ concentrations about 30 to 40% of those outside, while museums with no forced
8 ventilation system, where slow air infiltration provides the only means of air exchange, have
9 indoor O₃ levels typically 10 to 20% of those outdoors. Several other studies have been
10 reported in the literature and Table 4-18 lists the I/O ratios reported from these efforts as
11 well as those from earlier years.

12 Automobiles and other vehicles constitute another indoor environment in which people
13 may spend appreciable amounts of time. As with buildings, the mode of ventilation and
14 cooling helps determine the inside concentrations. The U.S. EPA (1986a) describes studies
15 for the I/O ratios. In one study reported by Contant et al. (1985), the I/O ratios from
16 49 measurements inside vehicles were 0.44 for the mean, 0.33 for the median, and 0.56 for
17 maximum concentrations measured. Chan et al. (1991) reported an I/O ratio of 0.20 for
18 median in-vehicle concentrations (0.011 ppm) and time-matched fixed-site measurements
19 (0.051 ppm).

20 At present, there are no long-term monitoring data on indoor air pollutant
21 concentrations comparable to the concentration data available for outdoor locations. Thus,
22 for estimates of the exposure of building or vehicle occupants to O₃ and other photochemical
23 oxidants, it is necessary to rely on extrapolations of very limited I/O data.

26 4.8 ESTIMATING EXPOSURE TO OZONE

27 4.8.1 Introduction

28 It is important that accurate estimates of both human and vegetation exposure to O₃ are
29 available for assessing the risks posed by the pollutant. In the Introduction of this chapter,
30 the differences between concentration, exposure, and dose were discussed. In this section,
31 examples are provided on how both fixed-site monitoring information, as well as human

TABLE 4-18. SUMMARY OF REPORTED INDOOR-OUTDOOR OZONE RATIOS

Structure	Indoor-Outdoor Ratio	Reference
Hospital	0.67 ^a	Thompson et al. (1971)
Residence (with evaporative cooler)	0.60 ^a	Thompson et al. (1973)
Office (air conditioned; 100% outside air intake)	0.80±0.10	Sabersky et al. (1973)
(air conditioned; 70% outside air intake)	0.65±0.10	Sabersky et al. (1973)
Office	0.66 0.54	Shair and Heitner (1974) Shair and Heitner (1974)
Office/Lab	0.62	Hales et al. (1974)
Residence	0.70	Sabersky et al. (1973)
Residence	0.50-0.70	Sabersky et al. (1973)
Two offices	0.3	Moschandreas et al. (1978)
Residence (gas stoves) (all electric)	0.19 0.20	Moschandreas et al. (1981)
Office	0.29	Moschandreas et al. (1978)
School Room	0.19 (max. conc.)	Berk et al. (1980)
Residence	0.10-0.25	Berk et al. (1981)
Residences (1 each) (air conditioned) (100% outside air; no air conditioning)	0.00-0.09 1.0	Stock et al. (1983)
Residences (12) (air conditioned)	0.21 (mean conc.) 0.12 (med. conc.) 0.59 (max. conc.)	Contant et al. (1985)
Residences (41)	0.3	Lebowitz et al. (1984)
Residences (6) (window open) (window closed) (air conditioning)	0.59±0.16 0.26±0.12 0.28±0.12	Zhang and Liroy (In press)
Art Gallery	0.5	Shaver et al. (1983)

**TABLE 4-18 (cont'd). SUMMARY OF REPORTED INDOOR-OUTDOOR
OZONE RATIOS**

Structure	Indoor-Outdoor Ratio	Reference
Art Gallery (three modes of ventilation in each 24-h period: recirculation, mixture of recirculated and outside air, and 100% outside air)	0.70 ± 0.10 (mean conc.)	Davies et al. (1984)
Museums	<0.1	Shaver et al. (1983)
Museum	0.45	Nazaroff and Cass (1986)
Museums (with high air exchange, but no air conditioning)	0.69-0.84 (1-h) 0.50-0.87 (8-h)	Druzik et al. (1990)
(with no air conditioning and with low air exchange rate)	0.10-0.59 (1-h) 0.10-0.58 (8-h)	
(with natural convection-induced air exchange system)	0.33-0.49 (1-h) 0.28-0.40 (8-h)	
(with conventional air conditioning system but with no activated carbon air filtration)	0.24-0.40 (1-h) 0.25-0.41 (8-h)	
(with activated carbon air filtration system)	0.03-0.37 (1-h) 0.03-0.31 (8-h)	

^aMeasured as total oxidants.

exposure models, are used to estimate risks associated with O₃ exposure. A short discussion is provided on the importance of hourly average concentrations, used in the human health and vegetation experiments, mimicking as closely as possible "real world" exposures.

Human exposure represents the joint occurrence of an individual being located at point (x,y,z) during time *t*, with the simultaneous presence of an air pollutant at concentration C_{x,y,z} (t) (U.S. Environmental Protection Agency, 1991). Consequently, an individual's exposure to an air pollutant is a function of location as well as time. If a volume at a location can be defined such that air pollutant concentrations within it are homogeneous yet potentially different from other locations, the volume may be considered a "microenvironment" (Duan, 1982). Microenvironments may be aggregated by location (i.e.,

1 indoor or outdoor) or activity performed at a location (i.e., residential, commercial) to form
2 microenvironment types.

3 The Air Quality Criteria for Carbon Monoxide (U.S. Environmental Protection Agency,
4 1991) discusses the difference between individual and population exposures. The report
5 notes that Sexton and Ryan (1988) define the pollutant concentrations experienced by a
6 specific individual during normal daily activities as "personal" or "individual" exposures.
7 A personal exposure depends on the air pollutant concentrations that are present in the
8 location through which the person moves, as well as on the time spent at each location.
9 Because time-activity patterns can vary substantially from person to person, individual
10 exposures exhibit wide variability (U.S. Environmental Protection Agency, 1991). Thus,
11 although it is a relatively straightforward procedure to measure any one person's exposure,
12 many such measurements may be needed to quantify exposures for a defined group. The
13 daily activities of a person in time and space define his or her activity pattern. Accurate
14 estimates of air pollution exposure generally require that an exposure model account for the
15 activity patterns of the population of interest.

16 From a public health perspective, it is important to determine the "population
17 exposure," which is the aggregate exposure for a specified group of people (e.g., a
18 community or an identified occupational cohort). Because exposures are likely to vary
19 substantially between individuals, specification of the distribution of personal exposures
20 within a population, including the average value and the associated variance, is often the
21 focus of exposure assessment studies.

22 In many cases, the upper tail of the distribution, which represents those individuals
23 exposed to the highest concentrations, is frequently of special interest because the
24 determination of the number of individuals who experience elevated pollutant levels can be
25 critical for health risk assessments. This is especially true for pollutants for which the
26 relationship between dose and response is highly nonlinear. Runeckles and Bates (1991)
27 have pointed out the importance of peak concentrations in eliciting adverse human effects.
28 As indicated in the Introduction, results using controlled human exposures have shown the
29 possible importance of concentration in relation to duration of exposure and inhalation rate.
30 The implication of the importance of concentration can be translated into the conclusion that

1 the simple definition of exposure as equal to concentration multiplied by time may be too
2 simplified.

3 Because, for most cases, it is not possible to estimate population exposure solely from
4 fixed-station data, several human exposure models have been developed. Some of these
5 models include information on human activity patterns (i.e., the microenvironments people
6 visit and the times they spend there). These models also contain submodels depicting the
7 sources and concentrations likely to be found in each microenvironment, including indoor,
8 outdoor, and in-transit settings.

9 10 **4.8.2 Fixed-Site Monitoring Information Used To Estimate Population** 11 **and Vegetation Exposure**

12 For most cases, from the information provided in earlier sections in this chapter, fixed-
13 site monitors alone cannot accurately depict population exposures because (1) indoor and
14 in-transit concentrations of O_3 may be significantly different from ambient O_3 concentrations,
15 and (2) ambient outdoor concentrations of O_3 that people come in contact with may vary
16 significantly from O_3 concentrations measured at fixed-site monitors. Fixed-site monitors
17 measure concentrations of pollutants in ambient air. Ambient air as noted by the EPA (1991)
18 is defined in the Code of Federal Regulations (1991) as air that is "external to buildings, to
19 which the general public has access." But the nature of modern urban lifestyles in many
20 countries, including the United States, is that people spend an average of over 20 h per day
21 indoors (Meyer, 1983). Reviews of studies summarized in Section 4.7 show that indoor
22 O_3 concentration measurements vary significantly from simultaneous measurements in
23 ambient air. The difference between indoor and outdoor air quality and the amount of time
24 people spend indoors reinforces the conclusion that, for most cases, using ambient air quality
25 measurements alone do not provide accurate estimates of population exposure.

26 For vegetation, in most cases, it is assumed that exposure is the same as the
27 concentration information provided at fixed monitors in the field (see Sections 5.5 and 5.6).
28 In some cases, because of (a) foliar scavenging and (b) height differences between the
29 vegetation canopy and pollutant monitor, the measured concentration is not equivalent to the
30 vegetation exposure.

1 A subgroup that has been studied by several investigators to assess the influence of
2 ambient air pollution on their respiratory health and function is children attending summer
3 camp. Because children are predominantly outdoors and relatively active while at camp,
4 they provide a unique opportunity to assess the relationships between respiratory health and
5 function and concurrent air pollution levels. Children may be at potentially increased risk
6 from air pollution by virtue of their lifestyle patterns, which often involve several hours of
7 outdoor exercise, regardless of air quality, during daylight hours.

8 For campers, attempts have been made to estimate human exposure to O₃ using types
9 of activity patterns (Mage et al., 1985); Paul et al., 1987). Mage et al. (1985) developed an
10 objective approach to estimate the dose delivered to the lung of a 12-year-old camper by
11 using: pulmonary minute volume associated with a specific activity, the fractional
12 penetration beyond the trachea, and infiltration of ozone indoors. Lioy and Dyba (1989)
13 have applied the parameters used by Mage et al. (1985) to predict the delivered O₃ dose over
14 a four-day episode period. The schedule of a hypothetical camper was matched to the actual
15 O₃ concentrations, and the predicted doses were estimated.

16 Several studies involving children attending summer camp have been summarized in
17 Chapter 7. In one study, Avol et al. (1990) reported that O₃ levels at a southern California
18 summer camp, located 190 km southeast of Los Angeles, rose gradually throughout each
19 day, displaying a "broad peak" between 1000 and 2000 h each day. Daily maxima typically
20 occurred in late afternoon (1500 to 1700 h); subsequently, concentrations gradually declined
21 to non-zero overnight O₃ levels of 0.025 to 0.050 ppm. Spektor et al. (1991) investigated
22 the pulmonary function of 46 healthy children on at least 7 days for each child during a
23 4-week period at a northwestern New Jersey residential summer camp in 1988. The daily
24 levels of 1-h peak O₃ and the 12-h average H⁺ concentrations are shown in Figure 4-24.
25 On 5 of these days, the current NAAQS of 0.12 ppm was exceeded. The maximum hourly
26 concentration attained during the study was 0.150 ppm. The year 1984 was a milder
27 O₃ exposure year and Figure 4-25 summarizes the maximal 1-h O₃ concentrations at
28 Fairview Lake during a 1984 study period (Spektor et al., 1988).

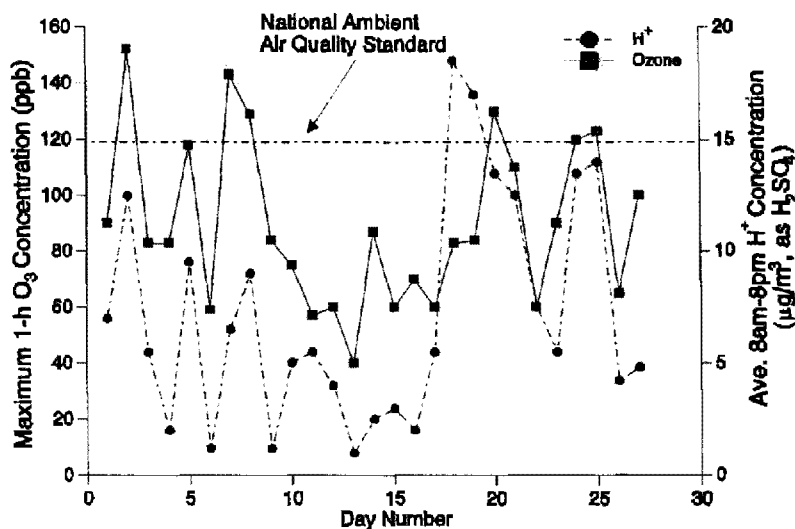


Figure 4-24. Maximum 1-h ozone concentrations (in parts per billion) and average 8:00 a.m. through 8:00 p.m. strong acid concentrations (expressed as micrograms per cubic meter of sulfuric acid) for each day that pulmonary function data were collected at Fairview Lake camp in 1988. The correlation coefficient (r) between O_3 and H^+ was 0.56.

Source: Spektor et al. (1991).

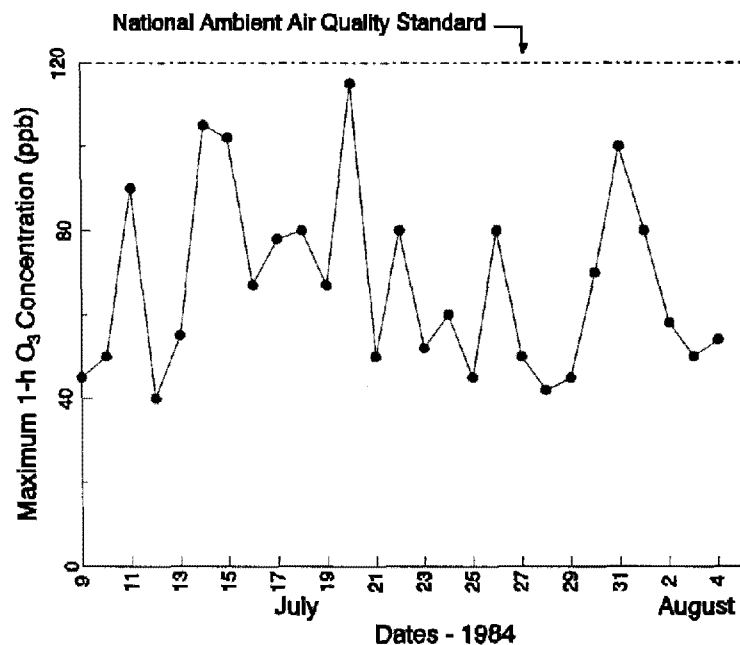


Figure 4-25. Maximal 1-h ozone concentrations at Fairview Lake during the study period.

Source: Spektor et al. (1988).

4.8.3 Personal Monitors

A personal exposure profile can be identified by using a personal exposure monitor. McCurdy (1994) has described the development of personal exposure monitors by several companies. However, little data are available describing personal exposures for individuals using these monitors. An example of a pilot study using a personal exposure monitor was described for assessing O₃ exposure to 23 children by Liu et al. (1993). The authors collected indoor, outdoor, and personal O₃ concentration data as well as time-activity data in State College, Pennsylvania. Results from the pilot study demonstrated that fixed-site ambient measurements may not adequately represent individual exposures. Outdoor O₃ concentrations showed substantial spatial variation between rural and residential regions. The authors reported that the use of fixed-site measurements could result in an error as high as 127%. In addition, Liu et al. (1993) reported that models based on time-weighted indoor and outdoor concentrations explained only 40% of the variability in personal exposures. When the model used included observations for only those participants who spent the majority of their day in or near their homes, an R² of 0.76 resulted when estimates were regressed on measured personal exposures. The authors concluded that contributions from diverse indoor and outdoor microenvironments should be considered to estimate personal O₃ exposure accurately. From these results, it is clear that additional data are needed to better quantify the O₃ exposures to which populations are exposed.

4.8.4 Population Exposure Models

The availability of personal exposure monitors has facilitated the use of the direct and indirect approaches to assessing personal exposure. Whether the direct or indirect approach is followed, the estimation of population exposure requires a model. Sexton and Ryan (1988) suggest that most exposure models can be classified as one of three types: statistical, physical, or physical-stochastic.

In the U.S. EPA (1991), all three types are discussed. The statistical approach requires the collection of data on human exposures and the factors thought to be determinants of exposure. These data are combined in a statistical model, normally a regression equation or an analysis of variance, to investigate the relationship between air pollution exposure (dependent variable) and the factors contributing to the measured exposure (independent

variables). If the study group constitutes a representative sample, the derived statistical model may be extrapolated to the population defined by the sampling frame. In the physical modeling approach, the investigator makes an a priori assumption about the underlying physical processes that determine air pollution exposure and then attempts to approximate these processes through a mathematical formulation. Because the model is chosen by the investigator, it may produce biased results because of the inadvertent inclusion of inappropriate parameters or the improper exclusion of critical components. The physical-stochastic approach combined elements of both the physical and statistical modeling approaches. The investigator begins by constructing a mathematical model that describes the physical basis for air pollution exposure. Then a random or stochastic component (that takes into account the imperfect knowledge of the physical parameters that determine exposure) is introduced into the model. The physical-stochastic approach limits the effect of investigator-induced bias by the inclusion of the random component, and allows for estimates of population distributions for air pollution exposure. Misleading results still may be produced, however, because of poor selection of model parameters. In addition, the required knowledge about distributional characteristics may be difficult to determine.

McCurdy (1994) has reviewed the current status of human exposure modeling. The author describes two distinct types of O₃ exposure models: those that focus narrowly on predicting indoor O₃ levels and those that focus on predicting O₃ exposures on a community-wide basis. The models that predict indoor O₃ levels have been described by Sabersky et al. (1973), Shair and Heitner (1974), Nazaroff and Cass (1986), and Hayes (1989, 1991). McCurdy (1994) discusses four distinct models that predict O₃ exposure on a community-wide basis. These models are:

1. pNEM/O₃ based on the NEM series of models (Paul et al., 1986; Johnson et al., 1990; McCurdy et al., 1991).
2. SAI/NEM (Hayes et al., 1984; Hayes and Lundberg, 1985; Austin et al., 1986; Hayes et al., 1988; Hayes and Rosenbaum, 1988).
3. REHEX (Lurmann and Colome, 1991; Winer et al., 1989; Lurmann et al., 1989; Lurmann et al., 1990).
4. Event probability exposure model (EPEM) (Johnson et al., 1992).

1 McCurdy (1994) points out that all four models are related to the NEM (National
2 Ambient Air Quality Standards Exposure Model approach). The NEM is an EPA exposure
3 model developed in the 1980s (Biller et al., 1981). Outdoor air quality data are obtained
4 from monitoring or modeling data. In most applications of NEM, fixed-site monitoring data
5 are used. The hourly average values are transformed by a suitable relationship so that they
6 better represent air quality outside of the various microenvironments of interest. McCurdy
7 (1994) points out that the important point of the NEM spatial dimension is that people can be
8 assigned to a monitor using United States Census data. In addition, community trips can be
9 assigned among the districts, grid cells, or neighborhood types using Census data. Thus, the
10 NEM model simulates the movement of people through space for work-trip purposes.
11 Interested readers are referred to McCurdy (1994) for further discussion of the pNEM
12 model.

13 The SAI/NEM is based on an earlier version of NEM. The SAI version has more
14 districts, more monitoring input data, and a more detailed mass-balance model to predict
15 indoor O₃ concentrations that pNEM/O₃ or earlier versions. The REHEX model adopted
16 some of the NEM computer code but uses a more detailed geographic resolution. Similar to
17 the NEM models and SAI/NEM, REHEX explicitly uses home/work trip data to "move"
18 people through the region during their day. The REHEX calculates O₃ exposure and dose
19 using discrete distributions of hourly averaged air quality. The model contains an exposure-
20 response relationship that allows analysts to directly estimate discrete, hourly averaged
21 O₃ dose levels in exposed individuals (McCurdy, 1994). The author points out that the
22 Event Probability Model (EPEM) does not provide distributions of O₃ exposure for any
23 specified population group. The model estimates the probability that a person selected at
24 random will experience a particular exposure situation. The estimate is based on an
25 individual being outdoors for an entire hour. McCurdy (1994) notes that if a person were
26 outdoors for a shorter period, he or she would not be counted. Vostal and Johnson (1993)
27 have described the use of the EPEM for the Houston, Texas area for the 1982 O₃ season.

29 **4.8.5 Concentration and Exposures Used in Research Experiments**

30 It is important to adequately characterize the exposure patterns that result in vegetation
31 and human health effects. In Chapter 5 (see Section 5.5), it has been pointed out that the

1 hourly average concentrations used in many of the high treatment experimental studies did
2 not necessarily mimic those concentrations observed under ambient conditions. Although the
3 ramifications of this observation on the effects observed is not clear, it was pointed out that
4 the highest treatments used in many of the open-top chamber experiments were bimodal in
5 the distribution of the hourly average concentrations. In other experiments designed to assess
6 the effects of O₃ on vegetation, constant concentration (i.e., square wave) exposures were
7 implemented. As has been discussed in earlier sections of this Chapter, hourly average
8 concentrations change by the hour and "square wave" exposure regimes do not normally
9 occur under ambient conditions. In addition to the exposures used at the highest treatment
10 levels, there is concern that the hourly average concentrations used in the control treatments
11 may be lower than those experienced at isolated sites in the United States or in other parts of
12 the world. Although the ramifications of using such exposure regimes is unclear, there is
13 some concern that the use of such levels may result in an overestimation of vegetation yield
14 losses when compared to treatments greater than the control treatment (see Section 5.5 and
15 Lefohn and Foley, 1992).

16 For assessing the human health effects of O₃ exposure, a series of studies has explored
17 prolonged 6.6 h O₃ exposures at low levels (i.e., 0.08 to 0.12 ppm) (Horstman, 1990).
18 McDonnell et al. (1991), using similar hourly average concentration regimes, have confirmed
19 the findings reported by Horstman et al. (1990). All the research investigations using 6.6-h
20 durations have applied constant concentrations during the exposure period. If, as indicated in
21 the Introduction of this chapter, concentration is more important than duration and ventilation
22 rate, different human health effects may occur as a result of different exposure regimes that
23 have identical 6.6-h average concentrations. Because of this, it is important to explore the
24 different types of exposure regimes that occur under ambient conditions during an 8-h
25 episode.

26 Lefohn and Foley (1993) reported on an analysis of hourly average data for
27 O₃ monitoring sites that (1) never experienced an exceedance of an hourly average
28 concentration equal to or greater than 0.12 ppm and (2) experienced 8-h daily maximum
29 average concentrations greater than 0.08 ppm. For those monitoring sites that met the above
30 two criteria, they identified the number of times the 8-h daily maximum average
31 concentration exceeded 0.08 ppm during the monitoring year. For the period 1987 to 1989,

1 there were 925 exposure regimes identified from 166 site-years of data that met the above
2 criteria. The data were then organized into the following seven categories:

- 3
4 I. The occurrence of 8-h daily maximum averages greater than 0.08 ppm
5 and less than 0.09 ppm;
- 6
7 II. The occurrence of 8-h daily maximum averages greater than
8 0.08 ppm but less than or equal to 0.082 ppm, which contained
9 only hourly average concentrations greater than 0.08 ppm but less
10 than or equal to 0.082 ppm;
- 11
12 III. 8-h daily maximum averages greater than 0.08 ppm, which
13 contained hourly average concentrations less than 0.09 ppm;
- 14
15 IV. 8-h daily maximum averages greater than 0.08 ppm and less than
16 0.09 ppm, which contained at least 1 hourly average concentration
17 greater than or equal to 0.09 ppm but less than 0.10 ppm;
- 18
19 V. 8-h daily maximum averages greater than 0.08 ppm and less than
20 0.09 ppm, which contained at least 1 hourly average concentration
21 greater than or equal to 0.10 ppm;
- 22
23 VI. 8-h daily maximum averages less than 0.08 ppm, which contained
24 at least 1 hourly average concentration greater than or equal to
25 0.09 ppm but less than 0.10 ppm; and
- 26
27 VII. 8-h daily maximum averages less than 0.08 ppm, which contained
28 at least 1 hourly average concentration greater than or equal to
29 0.10 ppm.

30
31 Figure 4-26 summarizes the results of the analysis. The results indicated that there was a
32 poor relationship between the value of the 8-h daily maximum average concentration and the
33 frequency of occurrence of hourly average concentrations within specific ranges (e.g.,
34 between 0.09 and 0.10 ppm). In no case could the authors identify a monitoring site that
35 experienced the "square-wave" type of exposure that was described in Category II (i.e., the
36 occurrence of 8-h daily maximum averages greater than 0.08 ppm but less than or equal to
37 0.082 ppm, which contained only hourly average concentrations greater than 0.08 ppm but
38 less than or equal to 0.082 ppm). Lefohn and Foley (1993) concluded that the "square
39 wave" exposures used in the 6.6-h duration human health effects experiments were not found
40 under ambient conditions. The authors identified 453 additional exposure regimes, where the

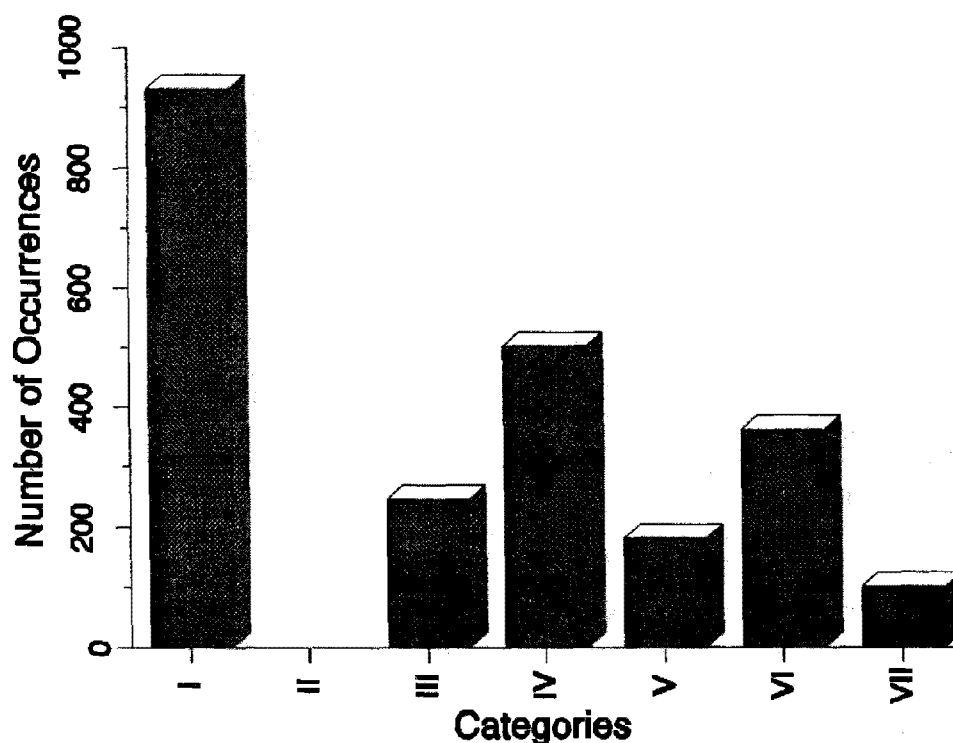


Figure 4-26. The number of occurrences for each of the seven categories described in text.

Source: Lefohn and Foley (1993).

1 8-h daily maximum average was less than 0.08 ppm but experienced maximum hourly
 2 average concentrations greater than or equal to 0.09 ppm. Thus, if hourly average
 3 concentrations ≥ 0.08 ppm are of concern for affecting human health, there will be instances
 4 where occurrences above this threshold are evident, but the 8-h average value is below
 5 0.08 ppm.

4.9 CONCENTRATIONS OF PEROXYACETYL NITRATES IN AMBIENT ATMOSPHERES

4.9.1 Introduction

The biological effects of PAN in human exposures, toxicological studies of animals, and plant response and yield have been considered previously (U.S. Environmental Protection Agency, 1986). Controlled human exposure studies involving O_3 and $O_3 + PAN$

1 are discussed elsewhere in this document (Section 7.2.6.3). Some effects on respiratory
2 parameters have been reported in one study, but not in others. However, the PAN
3 concentrations used in these studies have been well above the maximum ambient
4 concentrations usually experienced within the Los Angeles Basin many years ago (U.S.
5 Environmental Protection Agency, 1986) and, most especially, above the maximum ambient
6 concentrations in the more recent measurements considered in this section.

7 The PANs are of importance as reservoirs for NO_2 as NO_x is depleted relative to
8 VOCs in plumes moving downwind into less polluted areas (Section 3.2.4). In performance
9 evaluation of ozone air quality models, measured concentrations of PANs are useful in model
10 evaluation (Section 3.6.4.2).

11 In the previous air quality criteria for O_3 and other photochemical oxidants (U.S.
12 Environmental Protection Agency, 1986), extensive tabulations of PAN and peroxypropionyl
13 nitrate (PPN), $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OONO}_2$, concentrations were given based on measurements
14 made between 1965 and 1981 based on references up to 1983. In the present work,
15 references starting in 1983 up to the present are used for measurements of PANs in urban
16 and rural locations. The urban area measurements are from the United States, Canada,
17 France, Greece, and Brazil. The use of measurements from abroad serve to illustrate or
18 support certain U.S. results as well as to demonstrate the widespread presence of PANs in
19 the atmosphere.

21 **4.9.2 Urban Area Peroxyacetyl Nitrate Concentrations**

22 The prior criteria document for ozone and other photochemical oxidants contains for
23 urban sites a number of tables tabulating measurements of PAN, peroxypropionyl nitrate
24 (PPN), the PPN to PAN ratios, and the PAN to O_3 ratios (Altshuller, 1983; U.S.
25 Environmental Protection Agency, 1986). Based on comparisons of PAN measurements in
26 Los Angeles in 1980 with those made in the 1960s, it was uncertain whether PAN
27 concentrations had decreased. In the Los Angeles area, the average and maximum PAN
28 concentrations reported ranged from 1.6 to 31 ppb and from 6 to 214 ppb. The wide
29 variations at least in part was associated with the range of years, different seasons, and
30 differing average times among studies. The PPN to PAN ratios in Los Angeles on average
31 ranged among studies from 0.15 to 0.2, whereas the PAN to O_3 ratios on average ranged

1 among studies from 0.04 to 0.2. In the earlier PAN measurement results, studies conducted
2 in the South Coast Air Basin of California predominated.

3 The average PAN concentrations measured in other cities usually were lower than in
4 the Los Angeles area, whereas the maximum PAN concentrations overlapped with the lower
5 end of range in Los Angeles. The PPN and PAN ratios in other cities ranged from 0.1 to
6 0.4, while the PAN to O₃ ratios were in the 0.01 to 0.05 range.

7 Seasonally, PAN to O₃ ratios tended to be somewhat higher in the winter. The diurnal
8 characteristics of O₃ and of PAN were similar, but not identical.

9 The recent urban area measurement results are tabulated in Table 4-19. The earlier
10 maximum PAN concentrations reported usually were substantially higher than those given in
11 Table 4-19. A possible exception occurs for the Claremont, CA, results. Measurements of
12 PAN and PPN were made in 1989 and 1990 at sites downwind of Los Angeles: Perrin,
13 90 km east-southeast, and Palm Springs, 120 km east of Los Angeles (Grosjean and
14 Williams, 1992). The concentrations of PAN and PPN were high, and the concentration
15 maxima occurred during the evening hours consistent with downwind transport from the
16 Los Angeles area rather than local sources.

17 In Southern California, the maximum PAN concentrations appear to be more evenly
18 distributed spatially during the fall than during the summer (Williams and Grosjean, 1990).
19 At coastal and central locations, the PAN maxima during the fall were comparable to those
20 observed at inland locations during the summer.

21 As observed previously, PAN concentrations in other U.S. cities as well as cities in
22 other countries tend to be substantially lower than in Los Angeles and its surrounding urban
23 areas (Table 4-19). An exception occurs for the measurements from Paris (Tsalkoni et al.,
24 1991). Maximum PAN concentrations in the 20 to 35 ppb range were observed.

25 In recent measurements in Atlanta, GA, at the Georgia Institute of Technology (GIT)
26 campus site made in 1992, not only were PAN and PPN measured, but very occasionally
27 peroxyacetylnitrate (MPAN) $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OONO}_2$ was observed (Williams
28 et al., 1993). Maximum diurnal concentrations of PANs and O₃ occur in late afternoon and
29 early evening. The average MPAN concentration was 0.3 ppb, and the maximum value was
30 0.5 ppb and constituted about 15% of the concurrent PAN concentrations. MPAN is a
31 product of the atmospheric photooxidation of local biogenic sources of isoprene.

**TABLE 4-19. SUMMARY OF MEASUREMENTS OF PEROXYACETYL NITRATE
AND PEROXYPROPIONYL NITRATE IN URBAN AREAS**

Site	Months/ Year	Number of Days Sampled	PAN Concentration (ppb)		PPN Concentration (ppb)		Reference
			Average/Mean	Maximum	Average/Mean	Maximum	
Long Beach, CA	6-12/1987	16	NA ^a	16	NA ^a	NA ^a	Williams and Grosjean (1990)
Anaheim, CA	6-12/1987	14	NA ^a	19	NA ^a	NA ^a	Williams and Grosjean (1990)
Los Angeles, CA	6-12/1987	16	NA ^a	13	NA ^a	NA ^a	Williams and Grosjean (1990)
Burbank, CA	6-12/1987	16	NA ^a	19	NA ^a	NA ^a	Williams and Grosjean (1990)
Azusa, CA	6-9/1987	11	NA ^a	13	NA ^a	NA ^a	Williams and Grosjean (1990)
Claremont, CA	6-9/1987	10	NA ^a	30	NA ^a	NA ^a	Williams and Grosjean (1990)
Perrin, CA	6/1989 to 6/1990	NA ^a	1.6	9.1	NA ^a	0.73	Grosjean and Williams (1992)
Palm Springs, CA	6/1989 to 6/1990	NA ^a	1.6	7.6	NA ^a	0.42	Grosjean and Williams (1992)
Downey, CA	2/1984	10	1.2	6.7	0.06	0.40	Singh and Salas (1989)
Boulder, CO	5-6 and	12	0.63	2.0	0.08	0.3	Ridley et al. (1990)
	8-9/1987	45	0.59	3.8	0.07	0.6	
Denver, CO	3/1984	9	0.64	2.0	0.02	0.09	Singh and Salas (1989)
Houston, TX	3/1984	9	0.75	7.9	0.045	0.54	Singh and Salas (1989)
Philadelphia, PA	4/1983	19	1.1	3.7	0.14	0.50	Singh and Salas (1989)
Staten Island, NY	4/1983	7	1.6	5.5	0.21	0.90	Singh and Salas (1989)
Atlanta, GA	7-8/1992	36	0.71	2.9	0.14	0.37	Williams et al. (1993)
Edmonton, Alberta, Canada	12/1983 to 4/1984	66		7.5	NA ^a	NA ^a	Peake et al. (1988)
Calgary, Alberta, Canada	7/1981 to 2/1982	213	0.14	6.6	NA ^a	NA ^a	Peake and Sandhu (1983)
University of Calgary, Alberta, Canada	10/1980 to 8/1981	175	0.22	2.4	NA ^a	NA ^a	Peake and Sandhu (1983)
Simcoe, Ontario, Canada	6/1980 to 3/1981	191	1.3	5.6	NA ^a	NA ^a	Corkum et al. (1986)

**TABLE 4-19 (cont'd). SUMMARY OF MEASUREMENTS OF PEROXYACETYL NITRATE
AND PEROXYPROPIONYL NITRATE IN URBAN AREAS**

Site	Months/ Year	Number of Days Sampled	PAN Concentration (ppb)	Maximum	PPN Concentration (ppb)	Maximum	Reference
			Average/Mean		Average/Mean		
Rio de Janeiro							
Vila Isabel	7/1985	8	NA ^a	5.4	NA ^a	1.0	Tanner et al. (1988)
PUC/RJ	7/1985	4	NA ^a	3.3	NA ^a	0.6	Tanner et al. (1988)
Athens, Greece	2-11/85	113	NA ^a	3.7	NA ^a	NA ^a	Tsani-Bazaca et al. (1988)
Paris, France	11/85-11/86	NA ^a	1.1	20.5	NA ^a	NA ^a	Tsalkani et al. (1991)

^aNA = Not available.

1 In a study in Rio de Janeiro made to investigate the effects of the use of ethanol or
2 ethanol-containing fuel on PAN concentrations, the maximum PAN concentration reached
3 5.4 ppb (Tanner et al., 1988). However, this maximum concentration is well below the
4 maximum concentrations reported in and around Los Angeles, and it falls within the
5 maximum PAN values reported for a number of other cities in Table 4-19.

6 1 **4.9.3 Concentration of Peroxyacetyl Nitrate and Peroxypropionyl Nitrate** 2 **in Rural Areas**

3 Prior measurements of nonurban PAN and PPN concentrations and PAN to O₃ ratios
4 are available (Altshuller, 1983; U.S. Environmental Protection Agency, 1986). At nonurban
5 sites, not impacted by urban plumes, PAN and PPN concentrations are much lower than in
6 urban areas. Average PAN concentrations ranged between 0.1 and 1 ppb, while the PAN to
7 O₃ ratios were at or below 1%.

8 Concentrations of PAN, PPN, and other PANs have been reported (Table 4-20) at
9 Tanbark Flat, CA, 35 km northeast of Los Angeles, during 1989, 1990, and 1991 and at
10 Franklin Canyon, CA, 25 km west of Los Angeles, during 1991 (Grosjean and Williams,
11 1992; Grosjean et al., 1993). As indicated by the results tabulated in Table 4-20, the
12 concentrations were high at these mountain sites, the PPN to PAN ratios were relatively
13 high, and the concentration maxima occurred during the afternoon hours. These
14 concentration levels of PAN and PPN are attributed to downwind transport from the
15 Los Angeles urban area. The MPAN, $\text{CH}_2 = \text{C}(\text{CH}_3)\text{C}(\text{O})\text{OONO}_2$, was very occasionally
16 detected with average concentrations of 1.2 ppb at Tanbark Flat and 1.0 ppb at Franklin
17 Canyon in 1991.

18 At Tanbark Flat, the O₃ and PAN diurnal concentration patterns were similar to those
19 in upwind urban areas. The PAN to O₃ ratios at the O₃ maximum were as follows: 1989,
20 0.05; 1990, 0.08; 1991, 0.05—all the ratios are within the same range as at sites in urban
21 areas in and around Los Angeles.

22 Other measurements of PAN and PPN or PAN are available over a period of years at
23 Niwot Ridge, CO, just west of the Denver-Boulder area, at Point Arena, CA, and at a forest
24 site, Scotia, PA (Ridley et al., 1990). The concentrations reported at all of these sites are
25 much lower than the mountain sites in California. The Niwot Ridge site, which does show

**TABLE 4-20. SUMMARY OF MEASUREMENTS OF PEROXYACETYL NITRATE
AND PEROXYPROPIONYL NITRATE IN RURAL AREAS**

Site	Months/ Year	Number of Days Sampled	PAN Concentration (ppb)	Maximum	PPN Concentration (ppb)	Maximum	Reference
			Average/Mean		Average/Mean		
Tanbark Flat, CA	8-10/1989	69	2.9	> 16.1	0.75	5.1	Williams and Grosjean (1991)
Tanbark Flat, CA	8,9/1990	34	4.8	22.0	0.76	4.3	Grosjean et al. (1993)
Tanbark Flat, CA	8/1991	22	2.8	12.8	0.43	2.66	Grosjean et al. (1993)
Franklin Canyon, CA	9/1991	9	1.6	7.0	0.18	1.15	Grosjean et al. (1993)
Niwot Ridge, CO	7/1984	16	0.28	2.3	0.016	0.17	Singh and Salas (1989)
Niwot Ridge, CO	6-7/1984	23	≈0.25	NA ^a	NA ^a	NA ^a	Fahey et al. (1986)
Niwot Ridge, CO	8-9/1984	21	≈0.25	NA ^a	NA ^a	NA ^a	Fahey et al. (1986)
Niwot Ridge, CO	6-7/1987	46	0.81 (E) 0.21 (W)	3.2	0.08 (E) 0.01 (W)	0.45	Ridley et al. (1990)
Point Arena, CA	1/1984	14	0.12	1.1	0.005	0.07	Singh and Salas (1989)
Point Arena, CA	Spring/1985	NA ^a	0.05	NA ^a	NA ^a	NA ^a	Ridley (1991)
Scotia, PA	Summer/1986	NA ^a	≈0.6	NA ^a	NA ^a	NA ^a	Ridley (1991)
Scotia, PA	6-8/1988	47	1.0	NA ^a	NA ^a	NA ^a	Buhr et al. (1990)
Kananaskis Valley, Alberta, Canada	9/1979, 4/1982, 6-8/1982	NA ^a	≈0.5	2.3	NA ^a	NA ^a	Paske et al. (1983)
Frijoles Mesa, NM	10/1987- 1/1989	NA ^a	0.26	1.9	NA ^a	NA ^a	Gaffney et al. (1993)

^aNA = Not available.

1 the effects of easterly upslope flow of air parcels from Denver-Boulder, are still low
2 compared to the sites downwind of the urban Los Angeles area (Table 4-20).

3 The PAN concentrations at the Scotia, PA, rural site in the eastern United States tend
4 to be somewhat higher than the Niwot Ridge or Point Arena sites (Table 4-20). This
5 difference may relate to higher regional precursor concentration levels.
6
7

8 **4.10 CONCENTRATION AND PATTERNS OF HYDROGEN PEROXIDE** 9 **IN THE AMBIENT ATMOSPHERE**

10 Efforts to measure hydrogen peroxide (H_2O_2) began in the 1970s, but the early reports
11 of H_2O_2 concentrations above 10 ppb and even 100 ppb appear to be in error because of the
12 artifact H_2O_2 generated within the presence of O_3 (Section 3.5.1.3). Subsequent
13 measurements of H_2O_2 in the 1980s resulted in maximum H_2O_2 concentrations at or below
14 5 ppb and mean concentrations at or below 1 ppb (Sakugawa et al., 1990).

15 Studies comparing more recent methods for measuring H_2O_2 , which were conducted in
16 North Carolina, indicated differences among measurement methods in synthetic mixtures of
17 H_2O_2 , including possible interferences, and in the ambient atmosphere of up to about $\pm 25\%$
18 (Kleindienst et al., 1988). However, results from the same study from mixtures irradiated in
19 a smog chamber produced larger differences among methods, especially with the luminol
20 technique compared with the fluorescence techniques and with tunable-diode laser absorption
21 spectroscopy. Another comparison study was conducted in California, resulting in
22 differences in methods for measuring H_2O_2 varying by a factor or two (Lawson et al., 1988).
23 In the measurements of H_2O_2 discussed below, the cryogenic fluorescence method or the
24 scrubber-coil fluorescence methods were generally used.

25 Based on interpretation of a compilation of H_2O_2 measurements made between
26 1984 and 1988 at a number of urban locations, at rural/remote locations, and on aircraft
27 flights, it was concluded that the higher H_2O_2 concentrations were associated with the
28 following measurement conditions: (1) in the afternoon hours, (2) during summer months,
29 (3) at rural locations, and (4) at lower latitudes (Sakugawa et al., 1990; Van Valin et al.,
30 1987). The H_2O_2 concentrations increase from the surface to the top of the boundary layer
31 (Daum et al., 1990). Available values for mean H_2O_2 concentrations at U.S. locations were

(1) summit of Whitetop Mountain, VA: summer, 0.80 ppb; winter, 0.15 ppb (Olszyna et al., 1988); (2) summit of Whiteface Mountain, NY: 1986, 0.6 ppb; 1987; 0.8 ppb (Mohnen and Kadlecek, 1989); and (3) Westwood, CA: summer, \approx 1.0 ppb; winter, 0.2 ppb (Sakugawa and Kaplan, 1989). At Westwood, the highest correlation with various parameters was found for solar radiation consistent with the higher H_2O_2 concentrations being observed in the afternoon during the late spring and early summer months (Sakugawa and Kaplan, 1989). In the same study, the average H_2O_2 concentrations were observed to increase from Westwood, near the coast in the Los Angeles Basin, to Duarte (inland) and at Daggett in the Mohave Desert and at Sky Mountain and Lake Gregory in the San Bernadino Mountains. The ratios of O_3 to H_2O_2 concentrations at these sites were ≥ 100 . In subsequent measurements, the same relationship in H_2O_2 concentrations between Westwood and the other California sites listed above was observed (Sakugawa and Kaplan, 1993). Unlike the results at several urban sites and other mountain sites, it was reported that the highest diurnal H_2O_2 concentrations at Lake Gregory in the San Bernadino Mountains were observed during the nighttime hours (Sakugawa and Kaplan, 1993).

4.11 CO-OCCURRENCE OF OZONE

4.11.1 Introduction

There have been several attempts to characterize air pollutant mixtures (Lefohn and Tingey, 1984; Lefohn et al., 1987b). Pollutant combinations can occur at or above a threshold concentration either together or temporally separated from one another. For example, for characterizing the different types of cooccurrence patterns, Lefohn et al. (1987b) grouped air quality data within a 24-h period starting at 0000 h and ending at 2359 h. Patterns that showed air pollutant pairs appearing at the same hour of the day at concentrations equal to or greater than a minimum hourly mean value were defined as *simultaneous-only* daily cooccurrences. When pollutant pairs occurred at or above a minimum concentration during the 24-h period, without occurring during the same hour, a *sequential-only* cooccurrence was defined. During a 24-h period, if the pollutant pair occurred at or above the minimum level at the same hour of the day *and* at different hours during the period, the cooccurrence pattern was defined as *complex-sequential*.

1 A cooccurrence was not indicated if one pollutant exceeded the minimum concentration just
2 before midnight and the other pollutant exceeded the minimum concentration just after
3 midnight. As will be discussed below, studies of the joint occurrence of gaseous NO_2/O_3
4 and SO_2/O_3 have concluded that (a) the cooccurrence of two-pollutant mixtures lasted only a
5 few hours per episode, where an episode was defined by the threshold concentration used,
6 and (b) the time between episodes is generally long (i.e., weeks, sometimes months) (Lefohn
7 and Tingey, 1984; Lefohn et al., 1987b).

8 For exploring the cooccurrence of O_3 and other pollutants (e.g., acid precipitation,
9 acidic cloudwater, and acidic sulfate aerosols), there are limited data available. In most
10 cases, routine monitoring data are not available from which to draw general conclusions.
11 However, published results are reviewed and summarized for the purpose of assessing an
12 estimate of the possible importance of cooccurrence patterns of exposure.

13 14 **4.11.2 Nitrogen Oxides**

15 Ozone occurs frequently at concentrations equal to or greater than 0.03 ppm at many
16 rural and remote monitoring sites in the United States (Evans et al., 1983; Lefohn, 1984;
17 Lefohn and Jones, 1986). Therefore, for many rural locations in the United States, the
18 cooccurrence patterns observed by Lefohn and Tingey (1984) for O_3 and NO_2 were defined
19 by the presence or absence of NO_2 . As anticipated, Lefohn and Tingey (1984) reported that
20 most of the sites analyzed experienced fewer than 10 cooccurrences (when both pollutants
21 were present at an hourly average concentration ≥ 0.05 ppm). However, the authors did
22 note that several urban monitoring sites in the southern California South Coast Air Basin
23 experienced more than 450 cooccurrences. The rural sites of Riverside, Fontana, and
24 Rubidoux, California had more than 100 cooccurrences. Denver, Colorado and San Jose,
25 California, also experienced more than 100 cooccurrences of O_3/NO_2 . Lefohn and Tingey
26 (1984) reported that for Rubidoux, because NO_2 concentration maxima tended to peak in the
27 evenings or early morning, the cooccurrences were present at these times. For more
28 moderate areas of the country, Lefohn et al. (1987b) reported that even with a threshold of
29 0.03 ppm O_3 , the number of cooccurrences with NO_2 was small.

4.11.3 Sulfur Dioxide

Because elevated SO₂ concentrations are mostly associated with industrial activities (U.S. Environmental Protection Agency, 1992a), cooccurrence observations are usually associated with monitors located near these types of sources. Lefohn and Tingey (1984) reported that for the rural and nonrural monitoring sites investigated, most sites experienced fewer than 10 cooccurrences of SO₂ and O₃. Only Rockport, Indiana and Paradise No. 21 (Kentucky) had more than 40 cooccurrences during the monitoring period (48 and 45, respectively). The monitors at these two sites were influenced by the local sources. The authors noted that at Fontana, California, there were numerous O₃ episodes above 0.05 ppm and there was a high probability that when the SO₂ hourly average concentrations rose above 0.05 ppm, both pollutants would be present at levels equal to or greater than 0.05 ppm.

Meagher et al. (1987) reported that several documented O₃ episodes at specific rural locations appeared to be associated with elevated SO₂ levels. The investigators defined the cooccurrence of O₃ and SO₂ to be when hourly mean concentrations were equal to or greater than 0.10 ppm and 0.01 ppm, respectively. Upon reviewing the hourly mean O₃ and SO₂ data used by Lefohn et al. (1987b), in 1980 (using a threshold of 0.05 ppm for both pollutants) the Paradise No. 23 (KY), Giles County (TN), Murphy Hill (reported as Marshall Co. by Meagher et al., 1987) (AL), and Saltillo (reported as Hardin Co. by Meagher et al., 1987) (TN) sites experienced fewer than 7 days over a 153-day period for a cooccurrence of any form (i.e., simultaneous-only, sequential, and complex-cooccurrence). Thus, as reported by Lefohn et al. (1987b), the cooccurrence pattern of O₃ and SO₂ was infrequent.

The above discussion was based on the cooccurrence patterns associated with the presence or absence of hourly average concentrations of pollutant pairs. Taylor et al. (1992) have discussed the joint occurrence of O₃, nitrogen, and sulfur in forested areas using cumulative exposures of O₃ with data on dry deposition of sulfur and nitrogen. The authors concluded in their study that the forest landscapes with the highest loadings of sulfur and nitrogen via dry deposition tended to be the same forests with the highest average O₃ concentrations and largest cumulative exposure. Although the authors concluded that the joint occurrences of multiple pollutants in forest landscapes were important, nothing was mentioned about the hourly cooccurrences of O₃ and SO₂ or O₃ and NO₂.

4.11.4 Acidic Sulfate Aerosols

Acid sulfates, which are usually composed of sulfuric acid, ammonium bisulfate, and ammonium sulfate, have been measured at a number of locations in North America. Acidic sulfate and neutralized species can accumulate and range in concentration from 0 to 50 $\mu\text{g}/\text{m}^3$ at a specific location or a number of locations simultaneously (Lioy, 1989). For many summertime studies, peaks of H_2SO_4 and/or H^+ appear to be associated with the presence of a slow-moving high pressure system (Lioy and Waldman (1989). Acid sulfates are found primarily in the fine particle size range ($<2.5 \mu\text{m}$ in diameter). Lioy (1989) reports that the acidic sulfate concentrations measured in the summertime can be found at 20 $\mu\text{g}/\text{m}^3$ for over an hour and can be found at high concentrations of 10 to 20 $\mu\text{g}/\text{m}^3$ for 6 to 24 h at one or more sites (Lioy, 1989). Acidic sulfate aerosol concentrations can occur at concentrations in the summertime above 10 $\mu\text{g}/\text{m}^3$ for periods greater than 5 h (Lioy, 1989). As has been discussed earlier in this chapter, the highest O_3 exposures for sites affected by anthropogenically derived photooxidant precursors are expected to occur during the late spring and summer months. Thus, the potential for O_3 and acidic sulfate aerosols to cooccur at some locations in some form (i.e., simultaneously, sequentially, or complex-sequentially) is real. Our knowledge of the potential exposure of the cooccurrence of acidic sulfate aerosols and O_3 is limited because routine monitoring data for acidic aerosols are not available. Information on the cooccurrence patterns is limited to research studies and some of the results of these studies is provided in this section.

Spektor et al. (1991) investigated the effects of single- and multiday O_3 exposures on respiratory function in active normal children aged 8 to 14 years at a northwestern New Jersey residential summer camp in 1988. During the investigation, the authors measured daily levels of 1-h peak O_3 and the 12-h average H^+ concentrations. On 7 days the acid aerosol concentrations (reported as H_2SO_4) were higher than 10 $\mu\text{g}/\text{m}^3$, reaching a 12-h maximum of 18.6 $\mu\text{g}/\text{m}^3$. Figure 4-24 shows the relationship between daily maximum O_3 and daily 12-h average H^+ concentrations. Thurston et al. (1992) have reported occurrences in 1988 of maximum 24-h average concentrations of H^+ as high as 18.7 $\mu\text{g}/\text{m}^3$ (Buffalo, New York) and a maximum daily hourly average concentration of 0.164 ppm. Although lower than Buffalo, high O_3 or H^+ values were reported by the investigators for Albany and White Plains, New York. It is unclear whether the O_3 or H^+ maximum

concentrations occurred simultaneously; however, it is clear that high concentrations could occur either sequentially, complex-sequentially, or simultaneously. Evidence exists in the literature indicating that hourly cooccurrences are experienced. Raizenne and Spengler (1989) have described an episodic cooccurrence pattern in 1986 of high hourly averaged concentrations of O_3 and H_2SO_4 that occurred at a residential summer camp located on the north shore of Lake Erie, Ontario, Canada (Figure 4-27). Thurston et al. (1994) have conducted a study of ambient acidic aerosols in the Toronto, Ontario metropolitan area in July and August of 1986, 1987, and 1988, and have reported on the fine particle ($d_a < 2.5 \mu m$) samples collected twice per day. The authors reported that their results indicated that acidic aerosol episodes (i.e., $H^+ \geq 100 \text{ nmol/m}^3$) occurred routinely during the summer months and that H^+ peaks were correlated with sulfate episodes. Figure 4-28 illustrates the relationship among SO_4^{2-} , H^+ , and O_3 .

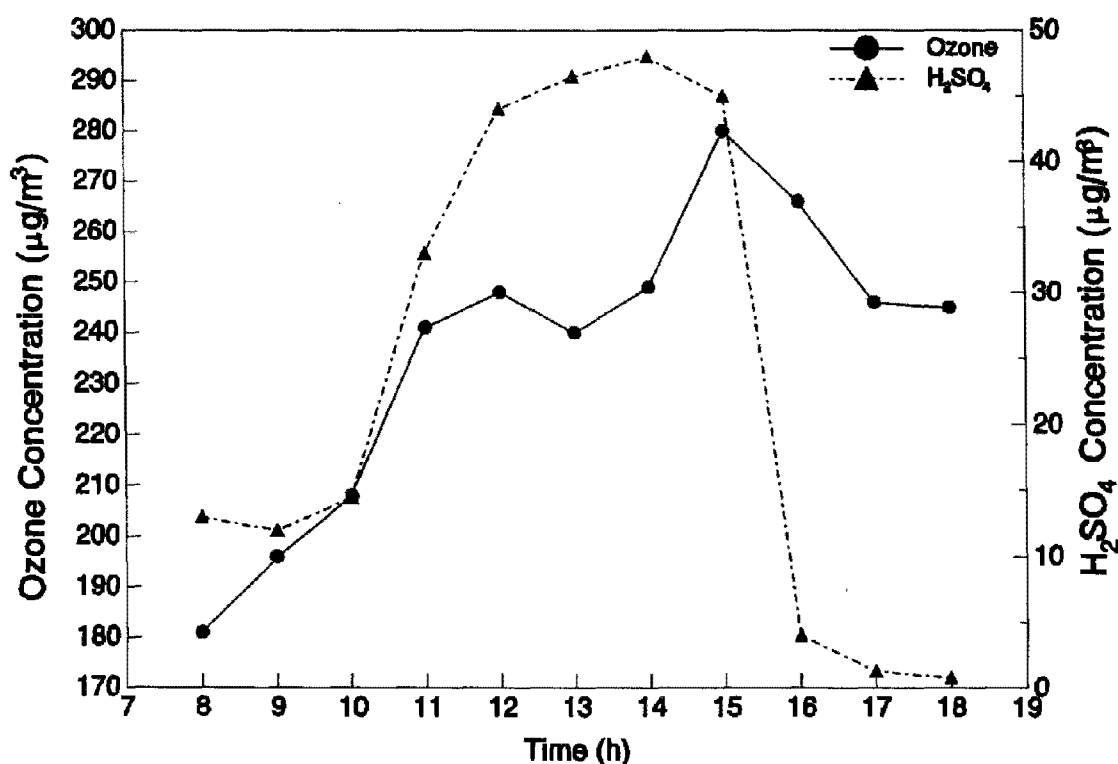


Figure 4-27. The co-occurrence pattern of O_3 and H_2SO_4 for July 25, 1986.

Source: Raizenne and Spengler (1989).

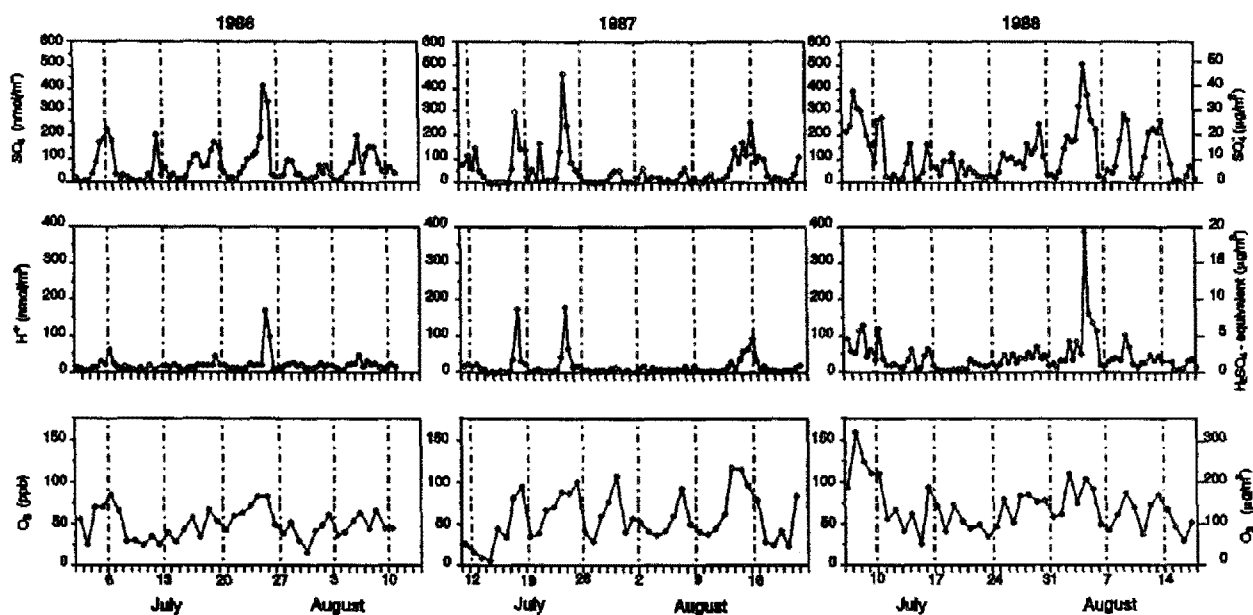


Figure 4-28. Sulfate, hydrogen ion, and ozone measured at Breadalbane St. (Site 3) during July and August, 1986, 1987, and 1988.

Source: Thurston et al. (1994).

4.11.5 Acid Precipitation

Concern has been expressed about the possible effects on vegetation from cooccurring exposures of O_3 and acid precipitation (Prinz et al., 1985; National Acid Precipitation Assessment Program, 1987; Prinz and Krause, 1988). Little information has been published concerning the cooccurrence patterns associated with the joint distribution of O_3 and acidic deposition (i.e., H^+). In a nonpeer-reviewed paper, Lefohn and Benedict (1983) reviewed the EPA's SAROAD monitoring data for 1977 through 1980 and, using National Atmospheric Deposition Program (NADP) and Electric Power Research Institute (EPRI) wet deposition data, evaluated the frequency distribution of pH events for 34 NADP and 8 EPRI chemistry monitoring sites located across the United States. Unfortunately, there were few sites where O_3 and acidic deposition were comonitored.

As a result, Lefohn and Benedict (1983) focused their attention on O_3 and acidic deposition monitoring sites that were closest to one another. In some cases, the sites were as far apart as 144 km. Using hourly O_3 monitoring data, and weekly and event acidic

deposition data from the NADP and EPRI databases, the authors identified specific locations where the hourly mean O₃ exposures were ≥ 0.10 ppm and 20% of the wetfall daily or weekly samples were below pH 4.0. Elevated levels of O₃ were defined as hourly mean concentrations equal to or greater than 0.10 ppm. Although for many cases, experimental research results of acidic deposition on agricultural crops show few effects at pH levels above 3.5 (NAPAP, 1987), it was decided to use a pH threshold of 4.0 to take into consideration the possibility of synergistic effects of O₃ and acidic deposition.

Based on their analysis, Lefohn and Benedict (1983) reported five sites where there may be the potential for agricultural crops to experience additive, less than additive, or synergistic (i.e., greater than additive) effects from elevated O₃ and hydrogen ion exposures. The authors stated that they believed, based on the available data, the greatest potential for interaction between acid rain and O₃ exposures in the United States, with possible effects on crop yields, may be in the most industrial areas (e.g., Ohio and Pennsylvania). However, they cautioned that, because no documented evidence existed to show that pollutant interaction had occurred under field growth conditions and ambient exposures, their conclusions should only be used as a guide for further research.

In their analysis, Lefohn and Benedict (1983) found no colocated sites. The authors rationalized that data from non-co-monitoring sites (i.e., O₃ and acidic deposition) could be used because O₃ exposures are regional in nature. However, work by Lefohn et al. (1988a) has shown that hourly mean O₃ exposures vary from location to location within a region and that cumulative indices, such as the percent of hourly mean concentrations equal to or greater than 0.07 ppm, do not form a uniform pattern over a region. Thus, extrapolating hourly mean O₃ concentrations from known locations to other areas within a region may provide only qualitative indications of actual O₃ exposure patterns.

In the late 1970s and the 1980s, both the private sector and the government funded research efforts to better characterize gaseous air pollutant concentrations and wet deposition. The event-oriented wet deposition network, EPRI/Utility Acid Precipitation Study Program, and the weekly oriented sampling network (NADP) provided information that can be compared with hourly mean concentrations of O₃ collected at several comonitored locations. No attempt was made to include hydrogen ion cloud deposition information. In some cases, for mountaintop locations (e.g., Clingman's Peak, Shenandoah, Whiteface Mountain, and

Whitetop), the hydrogen ion cloud water deposition is greater than the hydrogen ion deposition in precipitation (Mohnen, 1988) and the cooccurrence patterns associated with O_3 and cloud deposition will be different than those patterns associated with O_3 and deposition in precipitation.

Smith and Lefohn (1991) explored the relationship between O_3 and hydrogen ion in precipitation, using data from sites which monitored both O_3 and wet deposition simultaneously and within one minute latitude and longitude of each other. The authors reported that individual sites experienced years in which both hydrogen ion deposition and total O_3 exposure were at least moderately high (i.e., annual H^+ deposition $\geq 0.5 \text{ kg ha}^{-1}$ and an annual O_3 cumulative sigmoidally-weighted exposure (W126) value $\geq 50 \text{ ppm-h}$). With data compiled from all sites, it was found that relatively acidic precipitation ($\text{pH} \leq 4.31$ on a weekly basis or $\text{pH} \leq 4.23$ on a daily basis) occurred together with relatively high O_3 levels (i.e., W126 values $\geq 0.66 \text{ ppm-h}$ for the same week or W126 values $\geq 0.18 \text{ ppm-h}$ immediately before or after a rainfall event) approximately 20% of the time, and highly acidic precipitation (i.e., $\text{pH} \leq 4.10$ on a weekly basis or $\text{pH} \leq 4.01$ on a daily basis) occurred together with a high O_3 level (i.e., W126 values $\geq 1.46 \text{ ppm-h}$ for the same week or W126 values $\geq 0.90 \text{ ppm-h}$ immediately before or after the rainfall event) approximately 6% of the time. Whether during the same week or before, during, or after a precipitation event, correlations between O_3 level and pH (or H^+ deposition) were weak to nonexistent. Sites most subject to relatively high levels of both hydrogen ion and O_3 were located in the eastern portion of the United States, often in mountainous areas.

4.11.6 Acid Cloudwater

In addition to the cooccurrence of O_3 and acid precipitation, results have been reported on the cooccurrence of O_3 and acidic cloudwater in high-elevation forests. Vong and Guttorp (1991) characterized the frequent O_3 -only and pH -only single-pollutant episodes, as well as the simultaneous and sequential cooccurrences of O_3 and acidic cloudwater. The authors reported that both simultaneous and sequential cooccurrences were observed a few times each month above cloud base. Episodes were classified by considering hourly O_3 average concentrations $\geq 0.07 \text{ ppm}$ and cloudwater events with $\text{pH} \leq 3.2$. The authors reported that simultaneous occurrences of O_3 and pH episodes occurred 2-3 times per month

1 at two southern sites (Mitchell, NC and Whitetop, VA) and the two northern sites (Whiteface
2 Mountain, NY and Moosilauke, NH) averaged 1 episode/month. No cooccurrences were
3 observed at the central Appalachian site (Shenandoah, VA), due to a much lower cloud
4 frequency. Vong and Guttorp (1991) reported that the simultaneous occurrences were
5 usually of short duration (mean 1.5 h/episode) and were followed by an O₃-only episode.
6 As would be expected, O₃-only episodes were longer than cooccurrences and pH episodes,
7 averaging an 8-h duration.

10 4.12 SUMMARY

11 Ozone is an omnipresent compound that is measured at levels above the minimum
12 detectable level at all monitoring locations in the world. Although all O₃ and other
13 photochemical oxidant-induced effects on vegetation and ecosystems, as well as human
14 health, rely on an accurate determination of exposure through knowledge of O₃ and other
15 photochemical oxidant concentrations, most of the human and welfare effects research is
16 focused on O₃ exposures (e.g., hourly average concentration and duration of exposure).
17 To obtain a better understanding of the potential for ambient O₃ exposures affecting human
18 health and vegetation, hourly average concentration information was summarized for urban,
19 rural forested, and rural agricultural areas in the United States.

20 The distribution of O₃ or its precursors at a rural site near an urban source is affected
21 by wind direction (i.e., whether the rural site is located up- or down-wind from the source).
22 It is difficult to apply land-use designations to the generalization of exposure regimes that
23 may be experienced in urban versus rural areas, because the land use characterization of
24 "rural" does not imply that a specific location is isolated from anthropogenic influences.
25 Rather, the characterization only implies the existing use of the land. Because it is possible
26 for urban emissions, as well as O₃ produced from urban area emissions, to be transported to
27 more rural downwind locations, elevated O₃ concentrations can occur at considerable
28 distances from urban centers. Urban O₃ concentration values are often depressed because of
29 titration by nitric oxide. Because of the absence of chemical scavenging, O₃ tends to persist
30 longer in nonurban than in urban areas and exposures may be higher than in urban locations.

1 For purposes of using air quality data for assessing human health and vegetation effects,
2 it is important to distinguish among concentration, exposure, and dose. For human health
3 considerations, the following definitions are used:

- 4
5 1. The "concentration" of a specific air pollutant is the amount of that
6 material per unit volume of air. Air pollution monitors measure pollutant
7 concentrations, which may or may not provide accurate exposure estimates.
8
- 9 2. The term "exposure" is defined as any contact between an air contaminant
10 of a specific concentration and the outer (e.g., skin) or inner (e.g.,
11 respiratory tract epithelium) surface of the human body. Exposure implies
12 the simultaneous occurrence of the two events.
13

14 Similar to human health considerations for vegetation, concentrations of airborne
15 contaminants are considered to be exposure when they are experienced by a plant. For the
16 purposes of vegetation, this chapter has adopted the concept that dose is the amount of
17 pollutant absorbed by the plant. Because most of the data presented in this chapter are from
18 fixed monitors, dose is not addressed.

19 For vegetation, as indicated in Chapter 5 (Section 5.5), extensive research has focused
20 on identifying exposure indices with a firm foundation on biological principles. Many of
21 these exposure indices have been based on research results indicating that the magnitude of
22 vegetation responses to air pollution is more an effect of the magnitude of the concentration
23 than the length of the exposure. For O₃, the short-term, high concentration exposures have
24 been identified by many researchers as being more important than long-term, low
25 concentration exposures (see Chapter 5 for further discussion). Similarly, for human health
26 considerations, results using controlled human exposures have shown the possible importance
27 of concentration in relation to duration of exposure and inhalation rate.

28 In summarizing the hourly average concentrations in this chapter, specific attention is
29 given to the relevance of the exposure indices used. For example, for human health
30 considerations, concentration (or exposure) indices such as the daily maximum 1-h average
31 concentrations, as well as the number of daily maximum 4-h or 8-h average concentrations
32 above a specified threshold, are used to characterize information in the population-oriented
33 locations. For vegetation, several different types of exposure indices are used. Because
34 much of the NCLAN exposure information is summarized in terms of 7-h average

1 concentrations, this exposure index is used. However, because peak-weighted, cumulative
2 indices (i.e., exposure parameters that sum the products of hourly average concentrations
3 multiplied by time over an exposure period have shown considerable promise in relating
4 exposure and vegetation response (see Section 5.5), several exposure indices that use either a
5 threshold or a sigmoidally weighted scheme are used in this chapter to provide insight
6 concerning the O₃ exposures that are experienced at a select number of rural monitoring sites
7 in the United States. The peak-weighted cumulative exposure indices such as the SUM06
8 (the sum of all hourly average concentrations equal to or greater than 0.06 ppm), SUM08
9 (the sum of all hourly average concentrations equal to or greater than 0.08 ppm), and W126
10 (the sum of the hourly average concentrations that have been weighted according to a
11 sigmoid function that is theoretically based on a hypothetical vegetation response) are used.

12 Ozone hourly average concentrations have been recorded for many years by the State
13 and local air pollution agencies who report their data to the U.S. Environmental Protection
14 Agency. The 10-year (1983 to 1992) composite average trend for the second highest daily
15 maximum hourly average concentration during the O₃ season for 509 trend sites and a subset
16 of 196 NAMS sites, shows that the 1992 composite average for the trend sites is 21 % lower
17 than the 1983 average and 20% lower for the subset of NAMS sites. The 1992 value is the
18 lowest composite average of the past ten years. The 1992 composite average is significantly
19 less than all the previous nine years, 1983 to 1991. The relatively high O₃ concentrations in
20 1983 and 1988 were likely attributable in part to hot, dry stagnant conditions in some areas
21 of the country that were especially conducive to O₃ formation.

22 Between 1991 and 1992, the composite mean of the second highest daily maximum 1-h
23 O₃ concentrations decreased 7% at the 672 sites and 6% at the subset of 222 NAMS sites.
24 Between 1991 and 1992, the composite average of the number of estimated exceedances of
25 the O₃ standard decreased by 23% at the 672 sites, and 19% at the 222 NAMS sites.
26 Nationwide VOC emissions decreased 3% between 1991 and 1992 (U.S. Environmental
27 Protection Agency, 1993). The composite average of the second daily maximum
28 concentrations decreased in eight of the ten EPA Regions between 1991 and 1992, and
29 remained unchanged in Region VII. Except for Region VII, the 1992 regional composite
30 means are lower than the corresponding 1990 levels.

1 Information is provided in the Chapter on methods used for investigating techniques for
2 adjusting O₃ trends for meteorological influences. Historically, the long-term O₃ trends in
3 the United States characterized by the U.S. Environmental Protection Agency have
4 emphasized air quality statistics that are closely related to the NAAQS. Information is
5 provided on the use of alternative indices. Besides the U.S. Environmental Protection
6 Agency, additional investigators have assessed trends at several locations in the United States
7 and information is provided for both urban and rural areas.

8 Interest has been expressed in characterizing O₃ exposure regimes for sites experiencing
9 daily maximum 8-h concentrations above specific thresholds (e.g., 0.08 or 0.10 ppm).
10 Documented evidence has been published showing the occurrence, at some sites, of
11 multihour periods within a day of O₃ at levels of potential health effects. While most of
12 these analyses were made using monitoring data collected from sites in or near nonattainment
13 areas, one analysis showed that at five sites, two in New York state, two in rural California,
14 and one in rural Oklahoma, an alternative O₃ standard of an 8-h average of 0.10 ppm would
15 be exceeded even though the existing 1-h standard would not be. The study indicated the
16 occurrence at these five sites, none of which was in or near a nonattainment area, of
17 O₃ concentrations showing only moderate peaks but showing multihour levels above
18 0.10 ppm.

19 An important question is whether an improvement in O₃ levels would produce
20 distributions of 1-h O₃ that result in a broader diurnal profile than those seen in high-oxidant
21 urban areas where O₃ regimes contain hourly average concentrations with sharper peaks.
22 The result would be an increase in the number of exceedances of daily maximum 8-h average
23 concentrations ≥ 0.08 ppm, when compared to those sites experiencing sharper peaks. One
24 research effort observed, using aerometric data at specific sites, how O₃ concentrations
25 change when the sites change compliance status. One of the parameters examined was 4-h
26 daily maxima. The number of exceedances for a specific daily maximum average
27 concentration tended to decrease as fewer exceedances of the current 1-h standard were
28 observed at a given site. The number of occurrences of the daily maximum 4-h average
29 concentration ≥ 0.08 ppm and the number of exceedances of the current form of the standard
30 had a positive, weak correlation ($r = 0.51$). The investigators reported few changes in the
31 shape of the average diurnal patterns as sites changed attainment status. The lack of a

1 change in shape may have explained why the investigators could not find evidence that the
2 number of occurrences of the daily maximum 4-h average concentration ≥ 0.08 ppm
3 increased when the sites experienced few high hourly average concentrations.

4 There has been considerable interest in possibly substituting one index for another when
5 attempting to relate O_3 exposure with an effect. For example, using O_3 ambient air quality
6 data, the number of exceedances of 0.125 ppm and the number of occurrences of the daily
7 maximum 8-h average concentrations ≥ 0.08 ppm have been compared with the result that a
8 positive correlation ($r = 0.79$) existed between the second-highest 1-h daily maximum in a
9 year and the expected number of days with an 8-h daily maximum average concentration
10 > 0.08 ppm O_3 . However, there was not much predictive strength in using one O_3 exposure
11 index to predict another was not strong. Similarly, the maximum 3-mo SUM06, second
12 highest daily maximum hourly average concentration, and second highest daily maximum 8-h
13 average concentration exposure indices were compared. For the rural agricultural and forest
14 sites, the relationships among the indices were not strong.

15 One of the difficulties in attempting to use correlation analysis between indices for
16 rationalizing the substitution of one exposure index for another for predicting an effect (e.g.,
17 SUM06 versus the second highest daily maximum hourly average concentration) is the
18 introduction of the error associated with estimating levels of one index from another.
19 Evidence has been presented in the literature for recommending that if a different exposure
20 index (e.g., second highest daily maximum hourly average concentration) is to be compared
21 to, for example, the SUM06 for adequacy in predicting crop loss, then the focus should be
22 on how well the two exposure indices predict crop loss using the effects model that is a
23 function of the most relevant index and not on how well the indices predict one another.
24 Less error would be introduced if either of the two indices were used directly in the
25 development of an exposure-response model.

26 The U.S. EPA has indicated that a reasonable estimate of natural O_3 background
27 concentration near sea-level in the United States today, for an annual average, is from
28 0.020 to 0.035 ppm. This estimate included a 0.010 to 0.015 ppm contribution from the
29 stratosphere and a 0.01 ppm contribution from photochemically-affected biogenic non-
30 methane hydrocarbons. In addition, the U.S. EPA estimated that an additional 0.010 ppm is
31 possible from the photochemical reaction of biogenic methane. The U.S. EPA concluded

1 that a reasonable estimate of natural O₃ background concentration for a 1-h daily maximum
2 at sea-level in the United States during the summer is on the order of 0.03 to 0.05 ppm.
3 Reviewing data from sites that appear to be isolated from anthropogenic sources, it has been
4 reported that in almost all cases, (1) none of the sites experienced hourly average
5 concentrations ≥ 0.08 ppm and (2) the maximum hourly average concentrations were in the
6 range from 0.060 to 0.075 ppm. Using data from these sites, in the continental United States
7 and southern Canada, the 7-mo (April to October) average of the 7-h daily average
8 concentrations range from approximately 0.028 to 0.050 ppm. At an O₃ monitoring site at
9 the Theodore Roosevelt National Park in North Dakota, 7-mo (April to October) averages of
10 the 7-h daily average concentrations of 0.038, 0.039, and 0.039 ppm, respectively, were
11 experienced in 1984, 1985, and 1986. These 7-mo seasonal averages (i.e., 0.038 and
12 0.039 ppm) appear to be representative of values that may occur at other fairly clean sites in
13 the United States and other locations in the Northern Hemisphere.

14 Diurnal variations are those that occur during a 24-h period. Diurnal patterns of
15 O₃ may be expected to vary with location, depending on the balance among the many factors
16 affecting O₃ formation, transport, and destruction. Although they vary with locality, diurnal
17 patterns for O₃ typically show a rise in concentration from low or levels near minimum
18 detectable amounts to an early afternoon peak. The diurnal pattern of concentrations can be
19 ascribed to three simultaneous processes: (1) downward transport of O₃ from layers aloft;
20 (2) destruction of O₃ through contact with surfaces and through reaction with nitric oxide
21 (NO) at ground level; and (3) in situ photochemical production of O₃.

22 Although it might appear that composite diurnal pattern diagrams could be used to
23 quantify the differences of O₃ exposures between sites, caution has been expressed in their
24 use for this purpose. The average diurnal patterns are derived from long-term calculations of
25 the hourly average concentrations, and the resulting diagram cannot adequately identify, at
26 most sites, the presence of high hourly average concentrations and thus may not adequately
27 be able to distinguish O₃ exposure differences among sites. Unique families of diurnal
28 average profiles exist and it is possible to distinguish between two types of O₃ monitoring
29 sites. A seasonal diurnal diagram provides the investigator with the opportunity to identify
30 whether a specific O₃ monitoring site has more scavenging than any other site. For low-
31 elevation sites, intra-day variability is most significant due to the pronounced daily amplitude

1 in O₃ concentration between the pre-dawn minimum and mid-afternoon-to-early-evening
2 maximum, while inter-day variation is more significant in the high-elevation sites.

3 Seasonal variations in O₃ concentrations in urban areas usually show the pattern of high
4 O₃ in late spring or in summer and low levels in the winter. Because of temperature,
5 relative humidity, and seasonal changes in storm tracks from year to year, the general
6 weather conditions in a given year may be more favorable for the formation of O₃ and other
7 oxidants than during the prior or following year. For example, 1988 was a hot and dry year
8 in which some of the highest O₃ concentrations of the last decade occurred, while 1989 was
9 a cold and wet year in which some of the lowest concentrations occurred.

10 Several investigators have reported on the tendency for average O₃ concentrations to be
11 higher in the second versus the third quarter of the year for many isolated rural sites. This
12 observation has been attributed to either stratospheric intrusions or an increasing frequency of
13 slow-moving, high-pressure systems that promote the formation of O₃. However, for several
14 clean rural sites, the highest exposures have occurred in the third quarter rather than in the
15 second. For rural O₃ sites in the southeastern United States, the daily maximum 1-h average
16 concentration was found to peak during the summer months. For sites located in rural areas,
17 but not isolated from anthropogenic sources of pollution, the different patterns may be
18 associated with anthropogenic emissions of NO_x and hydrocarbons.

19 Concentrations of O₃ vary with altitude and with latitude. There appears to be no
20 consistent conclusion concerning the relationship between O₃ exposure and elevation.
21 An important issue for assessing possible impacts of O₃ at high-elevation sites that requires
22 further attention is the use of mixing ratios (e.g., ppm) instead of absolute concentration
23 (e.g., in units of micrograms per cubic meter) to describe O₃ concentration. In most cases,
24 mixing ratios (e.g., ppm) or mole fractions are used to describe O₃ concentrations. The
25 manner in which concentration is reported may be important when assessing the potential
26 impacts of air pollution on high-elevation forests. Concentration (in units of micrograms per
27 cubic meter) varies as a function of altitude. Although the change in concentration is small
28 when the elevational difference between sea level and the monitoring site is small, it becomes
29 substantial at high-elevation sites. Given the same part-per-million value experienced at both
30 a high- and low-elevation site, the absolute concentrations (i.e., micrograms per cubic meter)
31 at the two elevations will be different. Since both pollutants and ambient air are gases,

1 changes in pressure directly affect their volume. This pressure effect must be considered
2 when measuring absolute pollutant concentrations. Although these exposure considerations
3 are trivial at low-elevation sites, when one compares exposure-effects results obtained at
4 high-elevation sites with those from low-elevation sites, the differences may become
5 significant.

6 Most people in the United States spend a large proportion of their time indoors. Until
7 the early 1970s, very little was known about the O₃ concentrations experienced inside
8 buildings. Even to date, the data base on this subject is not large and a wide range of
9 indoor/outdoor O₃ concentration relationships can be found in the literature. Reported I/O
10 values for O₃ are highly variable. A relatively large number of factors can affect the
11 difference in O₃ concentrations between the inside of a structure and the outside air.
12 In general, outside air infiltration or exchange rates, interior air circulation rates, and interior
13 surface composition (e.g., rugs, draperies, furniture, walls) affect the balance between
14 replenishment and decomposition of O₃ within buildings. Indoor/outdoor O₃ concentration
15 ratios generally fall in the range from 0.1 to 0.7 and indoor concentrations of O₃ will almost
16 invariably be less than outdoors.

17 It is important that accurate estimates of both human and vegetation exposure to O₃ are
18 available for assessing the risks posed by the pollutant. Examples are provided on how both
19 fixed-site monitoring information and human exposure models are used to estimate risks
20 associated with O₃ exposure. A short discussion is provided on the importance of hourly
21 average concentrations, used in the human health and vegetation experiments, mimicking as
22 closely as possible the "real world" exposures.

23 In many cases, the upper tail of the distribution, which represents those individuals
24 exposed to the highest concentrations, is frequently of special interest because the
25 determination of the number of individuals who experience elevated pollutant levels can be
26 critical for health risk assessments. This is especially true for pollutants for which the
27 relationship between dose and response is highly nonlinear.

28 Because, for most cases, it is not possible to estimate population exposure solely from
29 fixed-station data, several human exposure models have been developed. Some of these
30 models include information on human activity patterns (i.e., the microenvironments people
31 visit and the times they spend there). These models also contain submodels depicting the

1 sources and concentrations likely to be found in each microenvironment, including indoor,
2 outdoor, and in-transit settings.

3 A subgroup that has been studied by several investigators to assess the influence of
4 ambient air pollution on their respiratory health and function is children attending summer
5 camp. Because children are predominantly outdoors and relatively active while at camp,
6 they provide a unique opportunity to assess the relationships between respiratory health and
7 function and concurrent air pollution levels. Examples are provided on the type of exposure
8 patterns that children experience.

9 A personal exposure profile can be identified by using a personal exposure monitor.
10 Little data are available for individuals using personal exposure monitors. Results from a
11 pilot study demonstrated that fixed-site ambient measurements may not adequately represent
12 individual exposures. Outdoor O₃ concentrations showed substantial spatial variation
13 between rural and residential regions. The study showed that the use of fixed-site
14 measurements could result in an error as high as 127%. In addition, the study showed that
15 models based on time-weighted indoor and outdoor concentrations explained only 40% of the
16 variability in personal exposures. The investigators concluded that contributions from
17 diverse indoor and outdoor microenvironments could estimate personal O₃ exposure
18 accurately.

19 The field of human exposure modeling is relatively young, with the first rigorous
20 exposure modeling analyses appearing in the mid-1970s and the theoretical constructs
21 regarding human exposure to environmental pollution being published in the early 1980s.
22 Two distinct types of O₃ exposure models exist: those that focus narrowly on predicting
23 indoor O₃ levels and those that focus on predicting O₃ exposures on a community-wide basis.
24 The following four distinct models address the prediction of O₃ exposures on a community-
25 wide basis:

- 26 1. pNEM/O₃ (based on the NEM series of models)
- 27
- 28 2. SAI/NEM
- 29
- 30 3. REHEX
- 31
- 32 4. Event probability exposure model (EPEM)
- 33

1 It is important to adequately characterize the exposure patterns that result in vegetation
2 and human health effects. In Chapter 5 (see Section 5.5), it has been pointed out that the
3 hourly average concentrations used in many of the high treatment experimental studies did
4 not necessarily mimic those concentrations observed under ambient conditions. Although the
5 ramifications of this observation on the effects observed is not clear, it was pointed out that
6 the highest treatments used in many of the vegetation open-top chamber experiments were
7 bimodal in the distribution of the hourly average concentrations. In other experiments
8 designed to assess the effects of O₃ on vegetation, constant concentration (i.e., square wave)
9 exposures were implemented. As has been discussed in earlier sections of this Chapter,
10 "square wave" exposure regimes do not normally occur under ambient conditions. Similar
11 "square wave" exposures have been used in human health effects studies. In addition to the
12 exposures used at the highest treatment levels for vegetation experiments, there is concern
13 that the hourly average concentrations used in the charcoal-filtered control treatments may be
14 lower than those experienced at isolated sites in the United States or in other parts of the
15 world. Although the ramifications of using such exposure regimes is unclear, there is some
16 concern that the use of such levels may result in an overestimation of vegetation yield losses
17 when compared to treatments greater than the control treatment.

18 Published data on the concentrations of photochemical oxidants other than O₃ in
19 ambient air are neither comprehensive nor abundant. A review of the data shows that PAN
20 and peroxypropionyl nitrate (PPN) are the most abundant of the non-O₃ oxidants in ambient
21 air in the United States, other than the inorganic nitrogenous oxidants such as nitrogen
22 dioxide (NO₂), and possibly nitric acid (HNO₃). At least one study has reported that a
23 higher homologue of the series, peroxybenzoyl nitrate (PBzN), like PAN, is a lachrymator.
24 No unambiguous identification of PBzN in the ambient air of the United States has been
25 made.

26 Given the information available on PAN, the concentrations of PAN that are of most
27 concern are those to which vegetation could potentially be exposed, especially during
28 daylight hours in agricultural areas. These are followed in importance by concentrations
29 both indoors and outdoors, in urban and nonurban areas, to which human populations could
30 potentially be exposed. Most of the available data on concentrations of PAN and PPN in
31 ambient air are from urban areas. The levels to be found in nonurban areas will be highly

1 dependent upon the transport of PAN and PPN or their precursors from urban areas, since
2 the concentrations of the NO_x precursors to these compounds are considerably lower in
3 nonurban than in urban areas.

4 There have been several attempts to characterize air pollutant mixtures. Pollutant
5 combinations can occur at or above a threshold concentration either together or temporally
6 separated from one another. Studies of the joint occurrence of gaseous NO₂/O₃ and SO₂/O₃
7 have concluded that (a) the cooccurrence of two-pollutant mixtures lasted only a few hours
8 per episode, and (b) the time between episodes is generally long (i.e, weeks, sometimes
9 months). Using hourly averaged data collected at rural sites for vegetation considerations,
10 the periods of cooccurrence represent a small portion of the potential plant growing period.
11 For human ambient exposure considerations, in most cases, the simultaneous cooccurrence of
12 NO₂/O₃ was infrequent. However, for several sites located in the southern California South
13 Coast Air Basin, more than 450 simultaneous cooccurrences of each pollutant, at hourly
14 average concentrations equal to or greater than 0.05 ppm, were present. Although the focus
15 of cooccurrence research has been on patterns associated with the presence or absence of
16 hourly average concentrations of pollutant pairs, some researchers have discussed the joint
17 occurrence of O₃, nitrogen, and sulfur in forested areas, combining cumulative exposures of
18 O₃ with data on dry deposition of sulfur and nitrogen. One study reported that several forest
19 landscapes with the highest dry deposition loadings of sulfur and nitrogen tended to
20 experience the highest average O₃ concentrations and largest cumulative exposure. Although
21 the investigators concluded that the joint occurrences of multiple pollutants in forest
22 landscapes were important, nothing was mentioned about hourly cooccurrences of O₃ and
23 SO₂ or O₃ and NO₂.

24 Our knowledge of the potential exposure of the cooccurrence of acidic sulfate aerosols
25 and O₃ is limited because routine monitoring data for acidic aerosols are not available.
26 Information on the cooccurrence patterns is limited to research studies and some of the
27 results are provided in this chapter. Acid sulfates, which are usually composed of sulfuric
28 acid, ammonium bisulfate, and ammonium sulfate, have been measured at a number of
29 locations in North America. Acidic sulfate and neutralized species can accumulate and range
30 in concentration from 0 to 50 μg/m³ at a specific location or a number of locations
31 simultaneously. For many summertime studies, peaks of H₂SO₄ and/or H⁺ appear to be

1 associated with the presence of a slow-moving high pressure system. Acid sulfates are found
2 primarily in the fine particle size range ($<2.5\ \mu\text{m}$ in diameter). The acidic sulfate
3 concentrations measured in the summertime can be found at $20\ \mu\text{g}/\text{m}^3$ for over an hour and
4 can be found at high concentrations of 10 to $20\ \mu\text{g}/\text{m}^3$ for 6 to 24 h at one or more sites.
5 Acidic sulfate aerosol concentrations can occur at concentrations in the summertime above
6 $10\ \mu\text{g}/\text{m}^3$ for periods greater than 5 h. The highest O_3 exposures for sites affected by
7 anthropogenically derived photooxidant precursors are expected to occur during the late spring
8 and summer months. Thus, the potential for O_3 and acidic sulfate aerosols to cooccur at
9 some locations in some form (i.e., simultaneously, sequentially, or complex-sequentially) is
10 real and requires further characterization.

11 Concern has been expressed about the possible effects on vegetation from cooccurring
12 exposures of O_3 and acid precipitation. One study explored the relationship between O_3 and
13 hydrogen ion in precipitation, using data from sites which monitored both O_3 and wet
14 deposition simultaneously and within one minute latitude and longitude of each other. The
15 investigators reported that individual sites experienced years in which both hydrogen ion
16 deposition and total O_3 exposure were at least moderately high (i.e., annual H^+ deposition
17 $\geq 0.5\ \text{kg ha}^{-1}$ and an annual O_3 cumulative sigmoidally-weighted exposure (W126) value
18 $\geq 50\ \text{ppm-h}$). With data compiled from all sites, it was found that relatively acidic
19 precipitation ($\text{pH} \leq 4.31$ on a weekly basis or $\text{pH} \leq 4.23$ on a daily basis) occurred together
20 with relatively high O_3 levels (i.e., W126 values $\geq 0.66\ \text{ppm-h}$ for the same week or W126
21 values $\geq 0.18\ \text{ppm-h}$ immediately before or after a rainfall event) approximately 20% of the
22 time, and highly acidic precipitation (i.e., $\text{pH} \leq 4.10$ on a weekly basis or $\text{pH} \leq 4.01$ on a
23 daily basis) occurred together with a high O_3 level (i.e., W126 values $\geq 1.46\ \text{ppm-h}$ for the
24 same week or W126 values $\geq 0.90\ \text{ppm-h}$ immediately before or after the rainfall event)
25 approximately 6% of the time. Whether during the same week or before, during, or after a
26 precipitation event, correlations between O_3 level and pH (or H^+ deposition) were weak to
27 nonexistent. Sites most subject to relatively high levels of both hydrogen ion and O_3 were
28 located in the eastern portion of the United States, often in mountainous areas.

29 The cooccurrence of O_3 and acidic cloudwater in high-elevation forests has been
30 characterized. The frequent O_3 -only and pH -only single-pollutant episodes, as well as the

1 simultaneous and sequential cooccurrences of O₃ and acidic cloudwater, have been reported.
2 Both simultaneous and sequential cooccurrences were observed a few times each month
3 above cloud base.
4
5

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